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EFFECT OF DEPOSITION METHODS ON PHYSICAL PROPERTIES OF POLYCRYSTALLINE CdS

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ABSTRACT

Cadmium sulfide is commonly used as the window material for thin film solar cells, and can be prepared by several techniques such as sputtering, spray pyrolysis, close spaced sublimation (CSS), thermal evaporation, solution growth methods, etc. In this study, CdS films were deposited by thermal evaporation, close spaced sublimation, and solution growth methods, respectively, and the effects of the methods on physical properties of polycrystalline CdS deposited on ITO/glass were investigated. Also, the effects of variously prepared CdS thin films on the physical properties of CdTe deposited on the CdS were investigated. The thickness of polycrystalline CdS films was maintained at 0.3μm except for the solution grown CdS when 0.2μm thick CdS was deposited. After the deposition, all the samples were annealed at 400℃ or 500℃ in H2 atmosphere. To investigate physical properties of the deposited and annealed CdS thin films, UV-VIS spectro-photometry, X-ray diffractometry (XRD), and Auger electron spectroscopy (AES), and cross sectional transmission electron microscopy(XTEM) were used to analyze grain size, crystal structure, preferred orientation, optical properties, etc. The annealed CdS showed the bandedge transition at 510nm and the optical transmittance high than 80% for all of the variously deposited films. XRD results showed that CdS thin films variously deposited and annealed had the same hexagonal structures, however, showed different preferred orientations. CSS grown CdS had [103] preferred orientation, thermally evaporated CdS had [002], and CdS grown by the solution growth had no preferred orientation. The largest grain size was obtained for the CSS grown CdS while the least grain size was obtained for the solution grown CdS. Some of the physical properties of CdTe deposited on the CdS thin film such as grain size at the junction and grain orientation were affected by the physical properties of CdS thin films.

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 for the n-type material for p-n junction of the solar cells. To fabricate CdS for the solar

cells, sputtering[1], spray pyrolysis, close spaced sublimation[1], thermal evaporation, and solution growth, etc. have been used and, after the deposition, annealings are generally followed to remove the defects formed during the deposition and to improve the crystallinity through the recrystallization process[1-7].

Currently, CdS grown by the solution growth method is the most widely used for the fabrication of high efficiency CdTe solar cells, however, the effects of CdS growth methods on the physical and electrical properties of CdTe deposited on the CdS are not well understood. In this study, the effects of CdS growth methods on the physical properties of the deposited CdS on ITO glass and the effects of the various CdS/ITO glass on the physical properties of CdTe were investigated to understand the effects of physical and electrical properties of the deposited CdTe/CdS on the CdTe solar cell efficiency. As CdS deposition methods, CSS method which is widely used for CdTe deposition[4], thermal evaporation method used for thin film fabrication in general, and solution growth method widely used for CdS deposition were used to vary the physical properties of CdS.

EXPERIMENT

As substrates, ITO/sodalime glass(that is, ITO glass) was used after ultrasonic cleaning in alcohol and deionized water rinse followed by N_2 blow drying. To deposit different types of CdS, thermal evaporation, solution growth, and close spaced sublimation techniques have been used. Thermal evaporation was conducted in vacuum less than 10^{-5}Torr while the substrate temperature was maintained at 100, 200, or 300℃, respectively and the thickness of the evaporated CdS was kept at 3000Å. In case of solution growth methods, a solution made of 0.025M $Cd(AC)_2$, $(NH_3)CS$, 0.6M NH_4OH, 0.1M $NH_4(AC)$, and 0.025M $(NH_2)_2CS$ was used at 75℃ for 1hour to deposit 0.3μm thick CdS. Solution growth CdS and thermally evaporated CdS were annealed in hydrogen for 20min at 400℃ after the dipping in a $CdCl_2+CH_3OH$ solution. Close spaced sublimated CdS was deposited in Ar or H_2 while source temperature was maintained at 700℃ and the substrate temperature at 500℃. The spacing between source and the substrate was 5mm. The CSS grown CdS was also annealed in hydrogen for 20min at 500℃ after the treatment in the $CdCl_2+CH_3OH$ solution.

To study the effects of the variously prepared (that is, deposited using different methods and annealed in H_2) CdS on the physical properties of CdTe, CdTe was deposited on the variously prepared CdS after the hydrazine hydrate treatment(H_6N_2O) for 2min to improve the junction properties between CdS and CdTe by removing oxides on the annealed CdS. CdTe was deposited by thermal evaporation[8] while the substrate temperature was maintained at 280℃. The evaporation rate was in the range from 0.8 to 1.2μm/min and the thickness of CdTe was 3-4μm. The deposited CdTe thin films were annealed using rapid thermal annealing instead of the conventional furnace annealing to reduce the interdiffusion between CdS and CdTe.

The physical properties of CdS thin films variously deposited on ITO/glass substrate

and the physical properties of CdTe deposited on the variously prepared CdS were investigated using X-ray diffraction to study the preferred orientation and the crystal structure, AES depth profiling to study the surface and bulk composition of the annealed CdS, UV-VIS spectrophotometer to study the optical transmission property of CdS, and cross-sectional TEM to study the grain size, grain structure, defect, etc. of the variously prepared CdTe/CdS thin films.

RESULTS AND DISCUSSION

Figure 1 shows XRD results of CdS variously deposited on ITO glass before and after the annealing. The deposited and annealed CdS thin films showed the same hexagonal structure for all of the various deposition methods. In Figure 1(a), the effects of deposition pressure of Ar on the preferred orientation of the deposited CdS are also shown and, as the deposition pressure is increased, the preferred orientation of the deposited CdS changed from [002] hexagonal to [103] hexagonal. Figure 1(b) shows the effects of the deposition methods on the preferred orientation of the deposited CdS. The CSS grown CdS had the preferred orientation of [103] hexagonal, the evaporated CdS had [002] hexagonal, and the solution grown CdS had random orientation. The large peak located at 25°(2θ) for the solution grown CdS is related to the crystal peak from ITO glass substrate used in the experiment. Figure 1(c) shows the XRD results of CdS annealed in hydrogen after the various deposition used in the experiment. As shown in the figure, the annealing of the deposited CdS did not change the crystal structure or preferred orientation for all of the deposition methods.

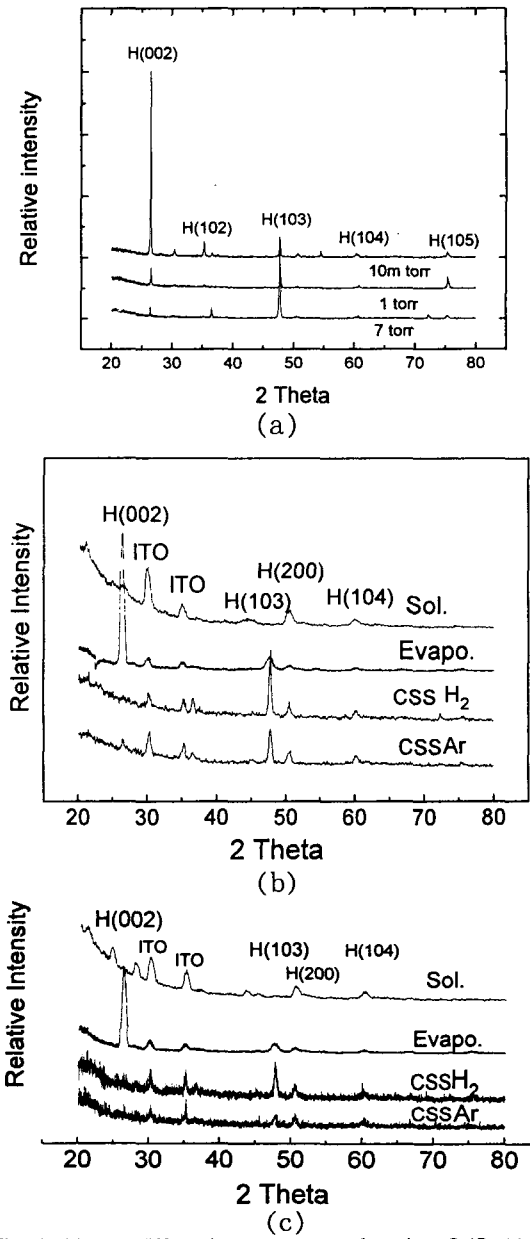


Fig. 1. X-ray diffraction patterns of variou CdS thin films before and after annealing.(a) as-deposited as a function of pressure for CSS grown CdS in Ar environment, (b) as-deposited CdS using various deposition methods, and (c) after annealing for.(b)

The composition ratios of Cd : S for the

variously deposited CdS after the annealings were investigated using AES depth profiling. Figure 2 shows the result of AES depth profiling for the thermally evaporated CdS after the annealing. The surface of the annealed CdS was significantly Cd-rich, however, the bulk of the annealed CdS was near stoichiometric Cd-rich CdS as it is required for the n-type CdS. Table 1 summarized the the results of AES depth profiling for the annealed CdS thin films. As shown in the table, all of the CdS surfaces annealed in H_2 showed significant Cd-rich surfaces, however, bulk CdS thin films were near stiochiometric Cd-rich CdS except for the CSS grown CdS in Ar. In this case, a little sulfur-rich CdS compound was formed which is not desirable for the n-type solar cell.

One of the required properties of deposited CdS thin films for the application to the CdTe solar cell is high optical transmittance for the range of the light absorbed by CdTe.[1] Figure 3 shows the optical transmittance as a function of optical wavelength measured by an UV-VIS Spectrophotometer for the annealed CdS thin films on the ITO glass substrate. CSS grown and thermally evaporated CdS thin films showed a sharp increase in the transmission near 510nm which is the band gap energy of CdS. Solution grown CdS also showed the sharp increase of optical transmission near the 510nm, however, also showed some degree of optical transmission below the wavelength possibly due to the thinner CdS compared to those deposited by other methods. The wavelength of the light absorbed by CdTe is from 800nm, and from the figure, it appears that higher than 80% of the light is transmitted to CdTe for all of the CdS thin films deposited in the experiment. Actually this transmittance includes the optical transmittance of the ITO glass

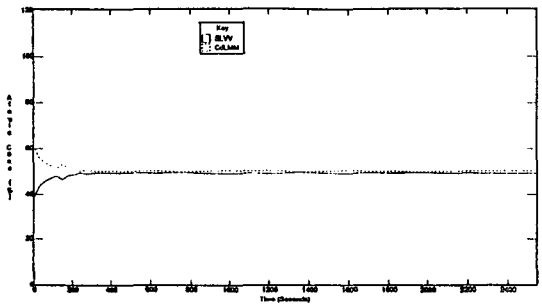


Fig. 2. AES depth profile of CdS film deposited by thermal evaporation followed by the annealing in hydrogen environment.

Table. 1 Results of Auger depth profiling of the CdS thin films annealed after the deposition using various methods.

Deposition Technique	Surface		Bulk	
	Cd	S	Cd	S
Close spaced Ts=550℃ in Ar	58.187	41.183	47.970	52.030
Sublimation Ts=550℃ in H_2	59.418	40.582	50.544	49.456
Themal Evaporation(Ts=200℃)	56.293	43.707	50.390	49.610
Solution growth methods	56.292	43.708	50.466	49.534

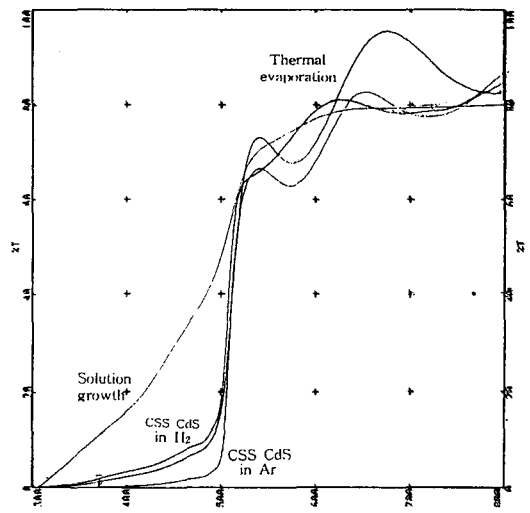


Fig. 3. Optical transmittances of annealed CdS thin films after the deposition by various methods

substrates used in the experiment. Therefore, the optical transmittance of CdS itself will be higher than the measured optical transmittance.

To find out the effects of the various CdS thin films on the physical properties of the CdTe deposited on them, thermally evaporated 3−4㎛ thick CdTe was deposited at 280℃ on the variously prepared CdS thin films. Figure 4 shows the XRD results of the CdTe thin films deposited on the variously prepared CdS. The CdS thin films were cleaned in a chromate solution for 10sec and in a hydrazine solution for 1min before the deposition of CdTe and the deposited CdTe was annealed at 550℃ using rapid thermal annealing for 2min. All of the deposited CdTe thin films had the same cubic zinc blend structure, however, CdTe deposited on the CSS grown CdS showed a little different structure compared to the others.

The cross-sections of the deposited CdTe/CdS/ITO glass thin films were observed using

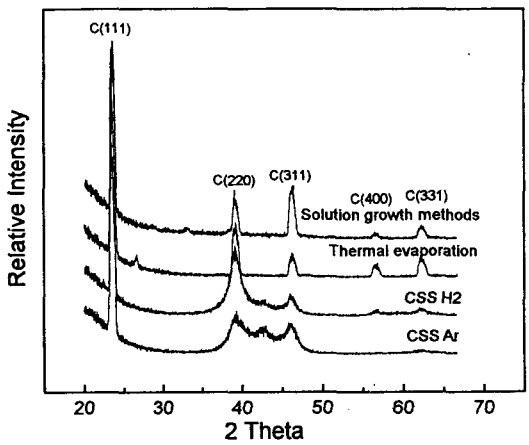


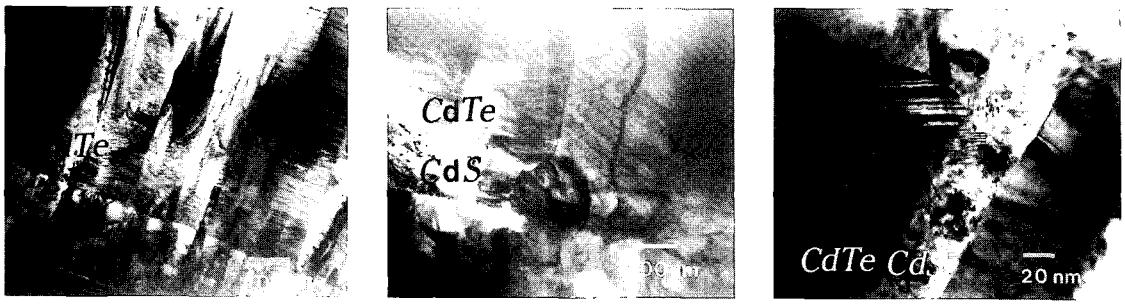
Fig. 4. X-ray diffraction patterns of CdTe thin films deposited on the variously prepared CdS thin films. CdTe thin films were annealed at 550℃ using rapid thermal annealing for 2min.

cross-sectional TEM and are shown in Figure 5. As shown in the TEM micrographs, the grain size of the CdS thin film was the largest for the CSS grown CdS and that of solution grown CdS was the smallest. Cross-sectional TEM micrographs also showed that CdS grown on the ITO glass has columnar structures for thermally evaporated CdS and CSS grown CdS, while solution grown CdS has equiaxed grains. CdTe deposited on the CdS was epitaxially related to the deposited CdS especially for the thermally evaporated CdS. The degree of epitaxial relationship between CdTe and CdS was reduced for the CSS grown CdS and, for the solution grown CdS, the relationship appeared not present due the random orientation of the CdS grains. In case of the CSS grown CdS, the presence of the [103] hexagonal preferred orientation may influence the epitaxial relation between CdTe and CSS grown CdS. However, as the CdTe thin film grows, the CdTe grain size changed and formed columnar structures for all of the cases, therefore, the grain size and preferred orientation of CdTe thin films deposited on variously prepared CdS became similar regardless of the CdS deposition methods used in the experiment.

CONCLUSIONS

The effects of various deposition methods of CdS thin films on the optical and physical properties of CdS were studied and the effects of variously deposited CdS on the physical properties of CdTe were also studied for the CdTe/CdS/ITO glass system.

Deposited and annealed CdS from the vari



(a) (b) (c)

Fig. 5. Cross-sectional TEM micrographs of deposited CdTe/CdS for the variously prepared CdS. (a) for thermally evaporated CdS, (b) CSS grown CdS in hydrogen environment and (c) for solution grown CdS.

ous deposition techniques showed the same hexagonal structure, however, their preferred orientations were different. The CSS grown CdS had [103] hexagonal preferred orientation, the thermally evaporated CdS had [002] hexagonal preferred orientation, and the solution grown CdS had no preferred orientation. Annealed CdS thin films showed different bulk compositions depending on the deposition techniques. After the H_2 annealing, all of the variously prepared CdS surfaces were significantly Cd-rich, however, bulk compositions were near stoichiometric Cd-rich CdS for CSS grown CdS deposited in H_2 environment, thermally evaporated CdS, and solution growth CdS which is suitable for n-type CdS. On the other hand, CSS grown CdS in Ar environment was sulfur-rich after the annealing.

TEM micrographs showed that CSS grown or thermally evaporated CdS has a columnar grain structure but solution grown CdS has a random equiaxed grain structure. Among the variously prepared CdS thin films, the grain size of the CSS grown CdS is the largest. The grain size of the CdS thin film affected the grain size of the CdTe thin film near the junction, but the grain size changed as the CdTe thin film grew, therefore, no significant differences in the grain size between CdS deposition techniques were observed near the CdTe surface. XRD data showed that CdTe thin films deposited on the variously prepared CdS have the same cubic zincblende structure, however, CdTe deposited on the CSS grown CdS has a little different crystal orientation compared to the others.

Based on these results, CdTe/CdS solar cells will be fabricated and the effects of the physical properties of CdS thin films on the CdTe/CdS solar cell efficiencies will be measured and the results will be published in the near future.

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