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저온 용액 공정을 이용한 태양전지용 CdTe 박막 합성

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Synthesis of CdTe Thin Films for Solar Cell using Solution-based Deposition Method at Low Temperature

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Abstract : CdTe thin films for photovoltaic cell devices were deposited on the glass substrates by solution-based deposition methods, at low temperature processing conditions. In order to characterize physical, optical, and electronic properties of CdTe light absorbing polycrystalline material, a series of analysis was carried out in this study.

Key words : CdTe(카드뮴텔룰라이드), Solution method(용액공정), Solar cell(태양전지)

1. Introduction

In contrast to crystalline silicon-based solar cells, the thin film photovoltaics have the great advantages of performing in stable mode, processing in low cost [1], and depositing on large area with various substrates[2]. Cadmiumtelluride (CdTe) thin film is one of the most promising candidates in the family of II-VI type binary compounds for the photovoltaic application. CdTe is considered as a good light absorbing polycrystalline semiconductor material because of its unique physical, optical, and electronic properties. The direct band gap of CdTe in the range of 1.4-1.5 eV is near to the theoretical optimum conversion efficiency (~31%) of solar cells[3]. The cell efficiencies as high as 16.5% have been reported [4]. Absorption coefficient of CdTe is about 10-5 cm-1in the terrestrial solar spectrum range and it is high enough to fabricate the thin film photovoltaic devices[5]. Due to the high absorption coefficient, only 1-2 m thickness of CdTe film is required to absorb most of the photonsin the solar spectrum on the earth. In general, CdS, of which direct band gap is 2.4 eV, is used for an n-type window layer to form a heterojunction with CdTe[6]. Up to now, a variety of methods such as evaporation[7], close spaced sublimation (CSS)[8], electro-deposition[5], Sputtering[9], metal-organic chemical vapor deposition (MOCVD) [10], screen printing[11], and spray pyrolysis[12] have been reported for the formation of polycrystalline CdTe thin films[13]. Those technologies, however, causes the high production costs due to their requirements of an expensive vacuum system and a high temperature condition. Solution-based chemical deposition processes have many significant advantages due to their low cost and low temperature processing natures. Those processes can be used to fabricate large area thin films on various substrates including glasses, semiconductors, metals, and plastics.

The purpose of this work was to investigate the feasibility of the solution-based processes to deposit CdTe thin films for solar cells in low cost. The purpose of this work was to investigate the feasibility of the solution-based processes to deposit CdTe thin films for solar cells in low cost. In this study, we deposited polycrystalline CdTe films using a continuous flow reaction (CFR) process at low temperatures. CFR processes do not require sophisticated vacuum system as well as expensive equipment. The prepared CdTe films were characterized with the aid of XRD, SEM, and TEM. We also fabricated a heterojunction structure of CdTe solar cell devices.

2. Experiment

The commercial microscope glasses (Fisher Scientific) were used as substrates. The substrates were ultrasonically cleaned by 1 M of sodium hydroxide (NaOH, Aldrich Inc) aqueous solution for 15minutes and then rinsed by DI water. Finally, they were dried under a stream of nitrogen gas before being used for fabrication. CdTe thin films were deposited on the substrates using the CFR process in our experiment. Stream A consisted of 0.005 M sodium tellurite (Na_2TeO_3, ALDRICH) and 0.005M hydrazine hydrate (H4N2XH2O, ALDRICH). Stream B consisted of 0.005 M cadmium chloride hemi pentahydrate ($CdCl_2$2.5H_2O, A.C.S Reagent) and 0.025 M ammonium chloride (NH_4Cl, YAKURI PURE CHEMICAL). The reactant streams A and B were mixed in the T-mixer and were then impinged on the glass/ITO substrates, which were heated at 180 ℃. The flow rate of the mixed solution was about 9.5 ml/sec and the time for

impinging was fixed in 3 min. In order to improve the crystallization of films and to avoid their oxidation, the deposited CdTe thin films were annealed at 400? for 1 hour under a nitrogen atmospheric condition. The details of the CFR deposition procedure have been described in our previous papers[14]. A scanning electron microscope (SEM; Hitachi Ltd., S-4800) was employed to examine the surface morphology of the polycrystalline CdTe thin films. The optical properties were measured using a UV-visible spectrophotometer (Ocean Optics Inc, USB 2000 optic spectrometer). An X-ray diffraction spectrometer (XRD; Panalytical, MPD for thin film) were used for the structural analysis of CdTe films. Their particle sizes and crystalline structures were investigated by a transmission electron microscope (TEM; Hitachi H-7600). The chemical composition of the CdTe thin film was studied with the aid of X-ray photoelectron spectroscope (XPS; VG ESCALAB, 200-IXL instrument with Mg K radiation).

3. Results and discussions

In order to examine the surface morphology of the CdTe thin film, SEM image was taken as shown in Fig. 1. The film was well formed with uniform grain sizes. However, the observation of the void spaces in SEM image indicated that the film was not deposited in dense. It was believed that these vacancies in the film would affect the proper operation of the devices.

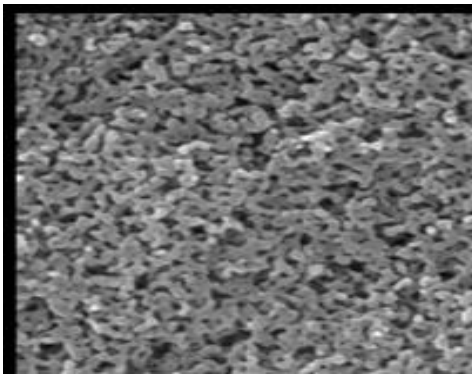


Fig. 1 SEM image of CdTe thin film deposited by CFR process.

The structure and crystalline orientation of the polycrystalline CdTe thin films deposited on the glass substrates was determined by XRD analysis. Fig. 2 (a) presented X-ray diffraction pattern of glass substrate. For the as-deposited films, no diffraction peaks were observed in the XRD spectra as presented in Fig. 2 (b). This result indicated that the crystallinity of the films was very small or the synthesized film was amorphous. The as-deposited films were annealed at 400 ℃ in nitrogen atmosphere in order to improve the crystallization of films and to avoid their oxidation. The XRD patterns of the film thermally treated after the CFR deposition were presented in Fig. 2 (c). Major peaks in Fig. 2 (c) were attributed to (100), (102), (110), (112), (201), and (114). The sediffraction peaks were consistent with the values of the standard (JCPDS 82-0474) and can be indexed as CdTe with hexagonal structure. Additional peaks in the spectrumcorresponded $CdTeO_3$ (JCPDS 49-1757), which was formed by the oxidation of precursors during the process.

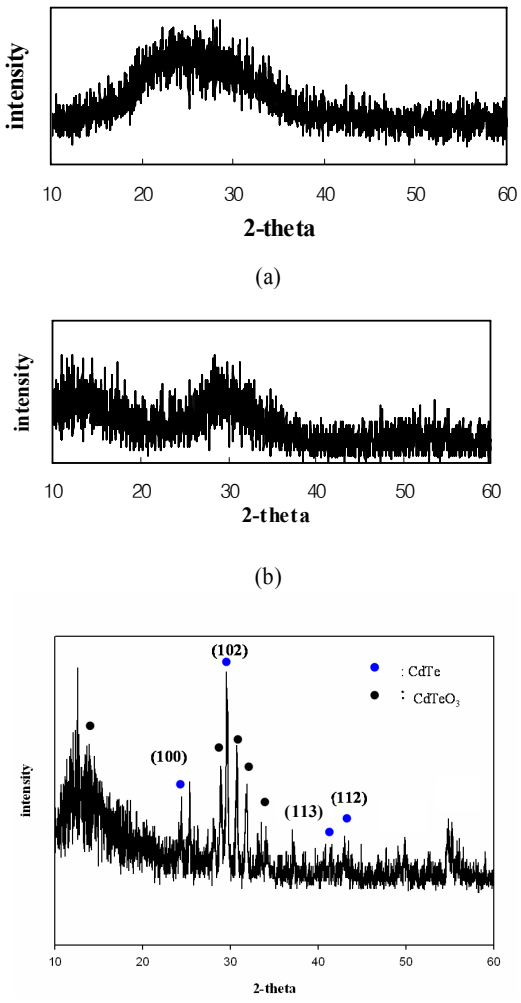
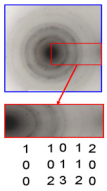


Fig. 2 X-ray diffraction (XRD) pattern of CdTe thin film deposited on the glass substrate using the CFR process; (a) glass substrate, (b) as-deposit (c) post-annealing

TEM analysis was carried out to determine the particle size distribution of the CdTe thin films deposited by CFR process and their crystalline structures. In the high resolution TEM micrograph, the clear crystalline diffraction was observed and the electron patterns indicated the formation of the crystalline structure of CdTe. An electron diffraction pattern along with the d-spacing data obtained from TEM pattern was presented in Fig. 3. The pattern confirms the formation of

polycrystalline thin films that matches the hexagonal CdTe (JCPDS 82-0474) structure. Average particle size of CdTe synthesized in our experiment was about 5.8 nm as shown in Fig. 4.



	CdTe CFR	CdTe JCPDS-820474	h k l
d-spacing	3.7000	3.7169	1 0 0
	3.0578	3.0074	1 0 2
	2.6428	2.5134	0 1 3
	1.9473	1.9790	1 1 2
	1.8500	1.8584	2 0 0
	1.5745	1.5503	1 0 6

Fig. 3 TEM-electron diffraction pattern of CdTe prepared by CFR process (Index: JCPDS 82-0474, Structure: Hexagonal) and d-spacing data along with the structural orientation.

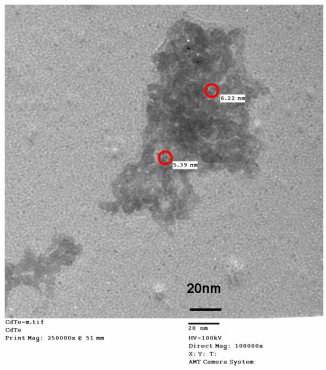


Fig. 4 TEM image of CdTe particles prepared by CFR process. Average particle size of CdTe: ~5.8 nm.

The optical band gap of the CdTe thin film annealed at 400℃ was characterized by a UV-Vis spectrophotometer. As shown in Fig. 5, the optical band gap value was estimated to be ~1.57 eV. It was reported that the band gap of the pure polycrystalline CdTe thin film was 1.5 eV[15]. The existence of $CdTeO_3$ structure should cause higher the energy band gap of the CdTe prepared in this study.

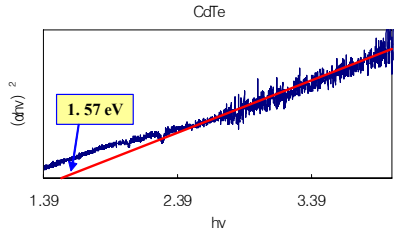


Fig. 5 UV-Vis absorption spectra of the CdTe film deposited by CFR on the glass substrate and its estimated optical band gap

X-ray photoelectron spectroscopy (XPS) was performed to obtain chemical composition and binding information of the CdTe thin film obtained in this study. The XPS spectrum in the range of 0-1200 eV is shown in Fig. 6. The observed binding energy peaks located at 412.0 eV and 404.0 eV correspond to the electronic states of Cd $3d_{5/2}$ and Cd $3d_{3/2}$, respectively. The peaks at 582.5 eV and 572.0 eV match to the electronic state of Te $3d_{3/2}$ and Te $3d_{1/2}$, respectively. The peaks at 586.5 eV and 575.0 eV match to the electronic state of $CdTeO_3$ $3d_{3/2}$ and Te $3d_{3/2}$, respectively[16]. In the XPS analysis, it was confirmed that the formation of $CdTeO_3$ during the CFR process exerted an influence on complicating XRD spectra and higher the band gap.

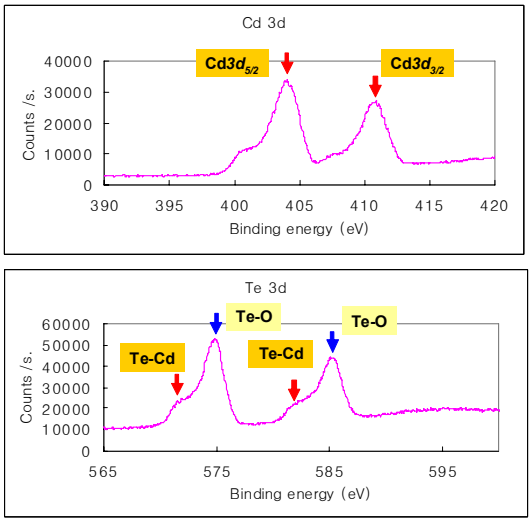


Fig. 6 XPS spectra of CdTe thin filmdeposited by the CFR process

4. Conclusions

CdTe thin films for photovoltaic cell devices were deposited on the glass substrates by solution-based deposition methods, at low temperature processing conditions. In order to characterize physical, optical, and electronic properties of CdTe light absorbing polycrystalline material, a series of analysis was carried out in this study. From XRD and TEM analyses, CdTe thin film prepared by CFR method had a hexagonal structure. Its average particle size was about 5.8 nm. The peaks corresponding to $CdTeO_3$,which was formed by the oxidation of precursors during the process, was observed in X-ray diffraction spectrum. Meanwhile, the film deposited by the spray method has a face-centered cubic phase with preferred orientation along the (200) direction. The estimated optical band gap values in UV-vis spectrophotometer were ~1.57 eV for films prepared by CFR methods. Heterojunction structure of CdTe solar cell device with CdTe thin film deposited in our experiment were successfully fabricated in this study. For the fabrication of the CdTe thin film solar cells having the higher conversion efficiency, further research needs to be done to synthesize the better quality of CdTe thin films and to improve the ohmic contacts between layers. More in-depth investigations are in progress.

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