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

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Polycrystalline CdTe thin films for solar cells were deposited on glass substrates using a continuous flow microreactor (CFM) and a modified spray process at low temperature. Their cubic structures were identified by X-ray diffraction (XRD) measurements. Their chemical binding information was investigated with the aid of X-ray photoelectron spectroscope. Scanning electron microscopy (SEM) was employed to examine the films' surface morphologies. Average particle sizes were found by transmission electron microscopy (TEM) to be larger in the spray-deposited film than the microreactor-deposited film. The estimated optical band gap values in UV-vis spectrophotometer were ∼1.57 eV for both films prepared by CFM and spray methods.

Keywords solar cell; photovoltaic cell; CdTe; thin film; absorber layer; chalcopyrite

Introduction

Unlike crystalline silicon-based solar cells, thin film photovoltaic devices have the advantages of stable performance, low cost processing,[1] and being able to be deposited on large areas of various substrates.[2] Cadmium telluride(CdTe) thin film is one of the most promising candidates in the family of II-VI type binary compounds for photovoltaic application. Its unique physical, optical, and electronic properties make it a good light absorbing polycrystalline semiconductor. Its direct band gap of 1.4–1.5 eV allows conversion efficiency close to the theoretical optimum (*ca.* 31%) of solar cells.[3] CdTe solar cells' energy conversion efficiency have been reported as high as 16.5%.[4] The absorption coefficient of CdTe is about 10^{-5} cm^{-1} in the terrestrial solar spectrum range and it is sufficient for its use in thin film photovoltaic devices.[5] This high absorption coefficient allows a CdTe film thickness of only 1–2 μm to absorb most photons in the solar spectrum on the earth.[6] CdS with a direct band gap of 2.4 eV can be used as an n-type window layer forming a heterojunction with CdTe.[7] Up to now, various methods, such as evaporation,[8] close spaced sublimation (CSS),[9] electro-deposition,[10] sputtering,[11] metal-organic chemical vapor deposition (MOCVD),[12]

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screen printing,[13] and spray pyrolysis[14] have been reported for the formation of polycrystalline CdTe thin films.[15] These technologies, however, cause high production costs due to their expensive vacuum systems and high temperature conditions. Solution-based chemical deposition processes have advantages due to their low cost and low temperature processing natures. They can be used to fabricate large area thin films on various substrates including glasses, semiconductors, metals, and plastics.

This work investigates the feasibility of low-cost solution-based deposition of CdTe thin films for solar cells. Polycrystalline CdTe films were deposited using both a continuous flow microreactor (CFM) process at low temperature and a modified chemical spray process under atmospheric conditions. Neither of them required sophisticated and expensive vacuum systems. The prepared CdTe films were characterized with the aid of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and UV-visible spectrophotometer.

Experimental

Preparation of Substrates

Commercial microscope glasses (Fisher Scientific) were used as substrates. They were ultrasonically cleaned in 1 M aqueous sodium hydroxide (NaOH, Aldrich Inc) for 15 minutes and then rinsed with DI water. They were dried under a stream of nitrogen gas before being used for deposition.

Deposition of CdTe thin films

A. Continuous Flow Microreactor Process

CdTe thin films were deposited on the substrates using a CFM process. One reactant stream consisted of 0.02 M tellurium oxide (TeO_2, ALDRICH) and 0.005M hydrazine hydrate ($H_4N_2{\cdot}XH_2O$, ALDRICH). The other was composed of 0.02 M cadmium chloride hemi pentahydrate ($CdCl_2{\cdot}2.5H_2O$, A.C.S Reagent) and 0.1 M ammonium chloride (NH_4Cl, YAKURI PURE CHEMICAL). The solution's pH was adjusted to *ca*. 11 by ammonium hydroxide (NH_4OH, ALDRICH). The reactant streams were mixed in a micro-mixer and were then impinged on the substrates, which were heated at 320°C. The flow rate of the mixed solution was about 9.5 ml/sec and the time for impinging solution was fixed in 3 minutes. To improve film's crystallization and to remove their by-products, the deposited CdTe thin films were annealed at 400°C under a nitrogen atmospheric condition. A detailed description of CFM deposition procedure is reported in our previous papers.[16]

B. Modified Spray Process

For the polycrystalline CdTe thin film deposition by the modified spray process, the precursor solution was prepared by mixing 0.02 M tellurium oxide (TeO_2, Aldrich), 0.02 M cadmium chloride ($CdCl_2$, A.C.S reagent), and 0.48 M hydrazine hydrate ($H_4N_2{\cdot}XH_2O$, Aldrich). The hydrazine hydrate was a reducing agent used to obtain Te^{2-} from Te^{+4}.[17] Ammonium hydroxide (NH_4OH, ALDRICH) added to the precursor solutions was used to control pH. Nitrogen was used as the carrier gas. Deposition was performed at the optimum

substrate temperature of 350°C. All experiments we carried out under atmospheric conditions. In order to improve the crystallization of films and to eliminate the residual porosity and structural free volume in the film, the as-deposited CdTe thin films were annealed at 400°C under a nitrogen atmospheric condition.

Measurements

Scanning electron microscopy (SEM; Hitachi Ltd., S-4800) was used to examine the surface morphology of the polycrystalline CdTe thin films. Films' optical properties were measured using a UV-visible spectrophotometer (Ocean Optics Inc, USB 4000 optic spectrometer). X-ray diffraction (XRD; Panalytical, MPD for thin film) was used for the structural characteristics of CdTe films. Chemical binding information of the CdTe thin film was obtained by X-ray photoelectron spectroscopy (XPS; VG ESCALAB, 200-IXL) with Mg K radiation.

Results and Discussion

A. CdTe Thin Films by the CFM Process

Figure 1 shows an SEM image of the surface morphology, after annealing 400°C, of the CdTe thin film deposited by CFM method. The CdTe thin film appeared uniform and smooth.

The structure and crystalline orientation of the polycrystalline CdTe thin films were determined by the XRD analysis. The as-deposited film was annealed at 400°C for 30 minutes under nitrogen in order to improve the crystallization of films and to avoid their oxidation. The XRD patterns of the thin film thermally treated after the CFM deposition are presented in Figure 2. The major peaks at $2\theta = 23.68°$, $27.57°$, $39.27°$, $46.40°$, $56.84°$, $62.48°$, $71.26°$, and $76.52°$ correspond to the (111), (200), (220), (311), (400), (331), (422), and (511) crystal planes of the CdTe structure, respectively. These diffraction peaks were consistent with the values of the standard (JCPDS 03-065-8879) and could be indexed to CdTe with a cubic structure. Additional peaks in the spectrum corresponded to $CdTeO_3$ (JCPDS 049-1757), which was formed by the oxidation of precursors during the deposition under atmospheric conditions.

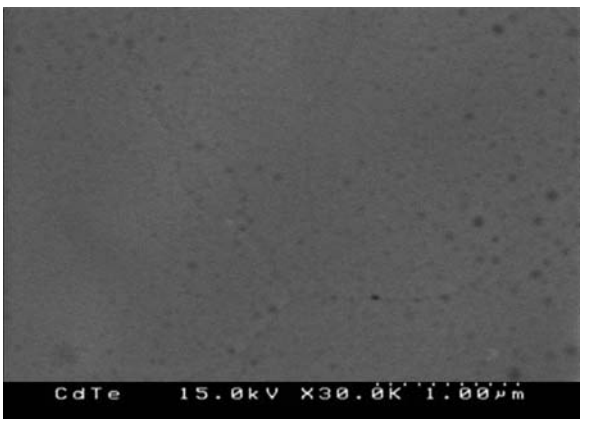

Figure 1. SEM image of CdTe thin film deposited using CFM process.

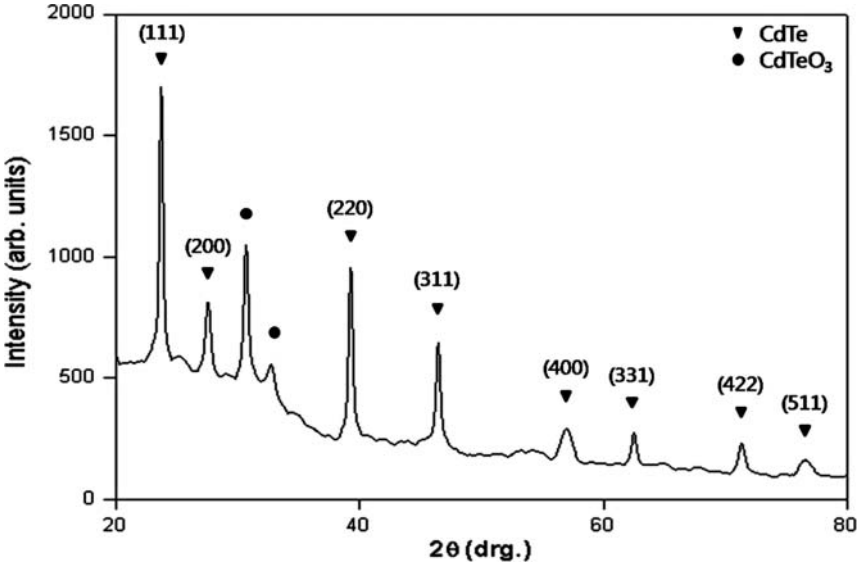

Figure 2. XRD patterns of CdTe thin films deposited using CFM process.

TEM analysis was carried out to determine the particle size distribution of the CdTe thin film deposited by the CFM process. The average particle size of CdTe synthesized in our experiment was about 5.8 nm as shown in Figure 3.

The optical band gap of the CdTe thin film was characterized by UV-Vis spectrophotometer. As shown in Figure 4, the optical band gap value was estimated to be ∼1.57 eV.

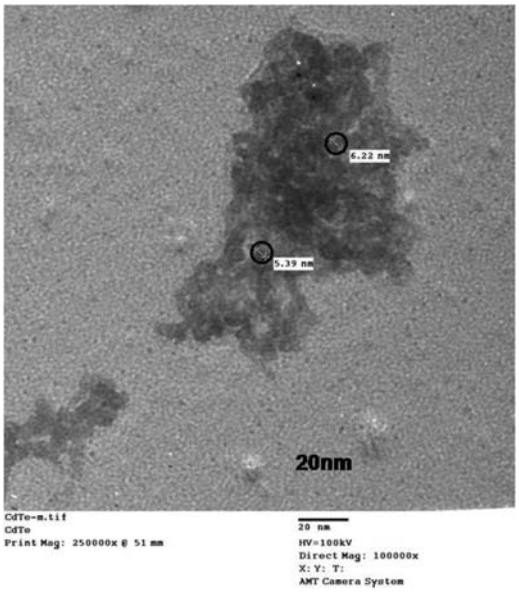

Figure 3. TEM image of CdTe particles prepared using CFM process. Average particle size of CdTe: *ca*. 5.8 nm.

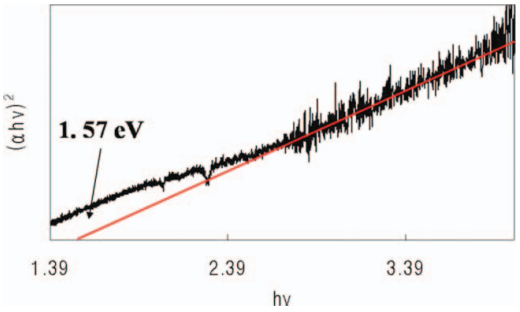

Figure 4. UV-vis absorption spectrum of CdTe film deposited using CFM method on glass substrate and its estimated optical band gap.

It was reported that the band gap of the pure polycrystalline CdTe thin film was 1.5 eV.[18] The difference between our estimated value and the reported value is likely caused by the presence of $CdTeO_3$.

X-ray photoelectron spectroscopy (XPS) was performed to obtain chemical composition and binding information of the CdTe thin films prepared in this study. The XPS spectrum between 0 and 1200 eV is shown in Figure 5. 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 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 the electronic state of $CdTeO_3$ $3d_{3/2}$ and Te $3d_{3/2,}$ respectively.[19]

B. CdTe Thin Films by Modified Chemical Spray Process

Polycrystalline CdTe thin films were also deposited on glass substrate by modified chemical spray method at low temperature. The SEM images of the CdTe thin films deposited on the glass substrate for 3 minutes are shown in Figure 6. Image (a) depicts the surface morphology of the CdTe film and image (b) shows its cross section. The film was well grown with uniform grain sizes. Void spaces were not observed in the CdTe thin films deposited by the solution-based chemical spray method at low temperature. The film thickness was around 10 μm and it was shown to be quite dense by the SEM cross sectional image. The thickness of film could be controlled by the spraying time and volume.

The structural information of the CdTe films was characterized by XRD. The XRD patterns of the film annealed after the spray deposition are given in Figure 7. Major peaks observed in the XRD patterns were attributed to (111), (200), (220), (311), (400), (331), (422), and (511) crystal planes, which corresponded to the CdTe reference (JCPDS 03-65-0890). The major peak detected at $2\theta \approx 23.759^\circ$ indicated cubic phase CdTe with preferred orientation along the (111) direction. Additional peaks other than the CdTe were attributed to the peaks of $CdTeO_3$ and Te. Processing under ambient conditions could likely lead to the formation of secondary $CdTeO_3$ phase along with CdTe. In our experiment, elemental Te was detected in the XRD analysis of the CdTe films prepared by the spray deposition method. The thin film having a Te-rich CdTe film by keeping the constant Cd(II)/Te(VI) concentration ratio was well synthesized by the spray process. As the quality of ohmic contact of the Te-rich film is dependent on the stoichiometry of the CdTe, a Te-rich surface is favorable for good pseudo ohmic contact formation.[20, 21] Comparing the XRD patterns in Figure 7 for the film deposited by the spray process with those in Figure 2 for the film

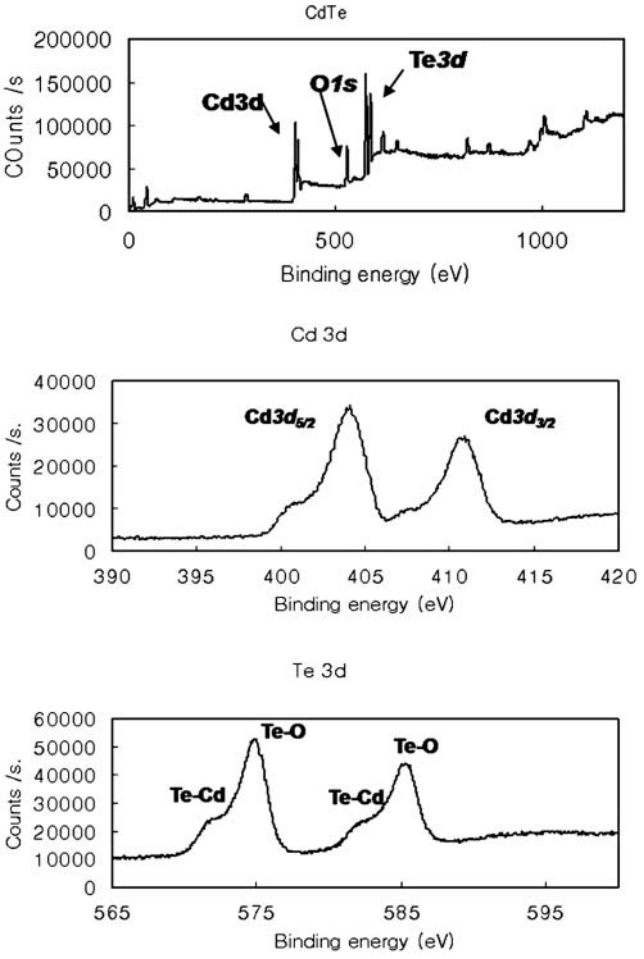

Figure 5. XPS spectra of CdTe thin film deposited using CFM process.

prepared by the CFM process, peaks corresponding to Te are found in the spectrum of the spray-deposited film and not in that of the CFM deposited film. We presumed that the existence of Te in the XRD measurement was caused by a smaller spray nozzle size than the tube size, which was 1.22 cm in diameter, used in the CFM process. Due to the nozzle's smaller size, the droplet size was reduced after striking the heated substrate and therefore caused the solvent to evaporate at a faster rate, completing the pyrolytic chemical reaction. Since this could occur throughout the film growth during film deposition, the CdTe thin film deposited by spray method had a Te-rich CdTe surface, unlike the CdTe thin film deposited using the CFM method.

TEM analysis was performed to determine their grain size distribution. Average particle size of the CdTe synthesized by the spray method was about 20.23 nm as shown in Figure 8. The size of the CdTe particle in the film deposited by the spray method was larger than that of the CdTe particle deposited by CFM process. The estimated optical band gap of the CdTe film prepared by the spray process was $\sim$1.57 eV as shown in Figure 9.

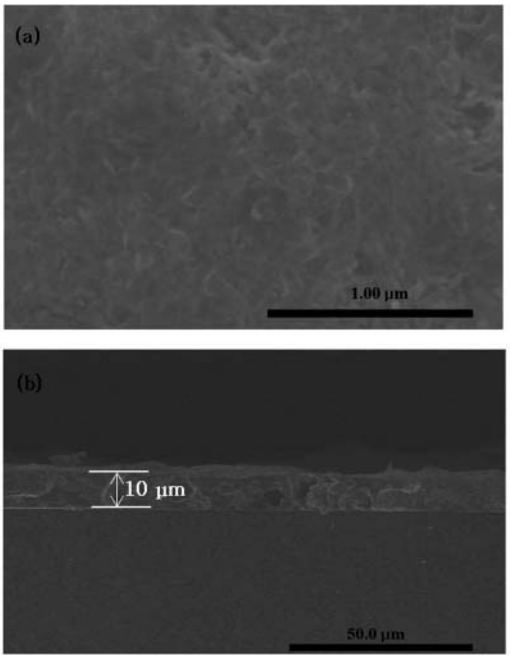

Figure 6. SEM images of CdTe thin film deposited on glass substrate by chemical spray method. (a) surface morphology, and (b) cross sectional image.

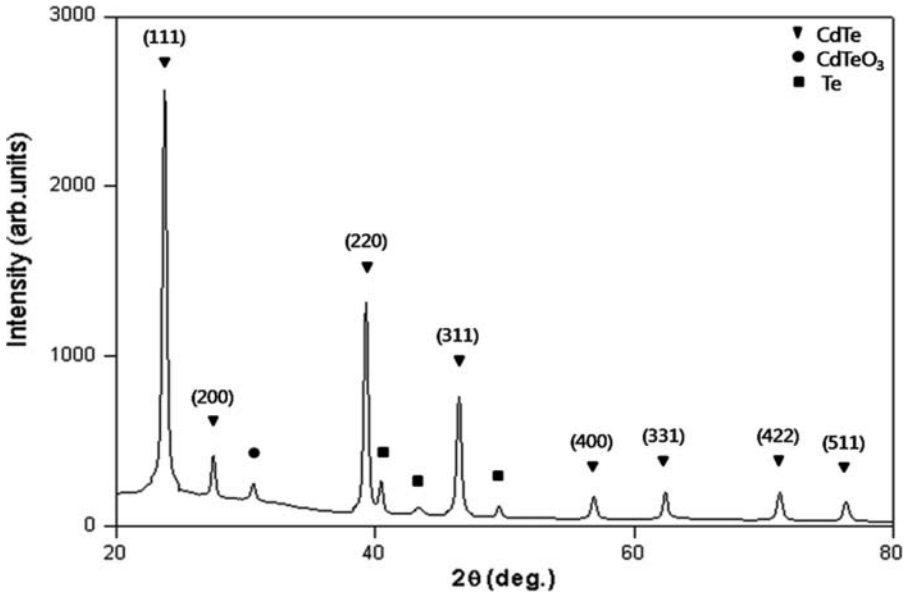

Figure 7. X-ray diffraction (XRD) pattern of CdTe thin film deposited on glass substrate by chemical spray process.

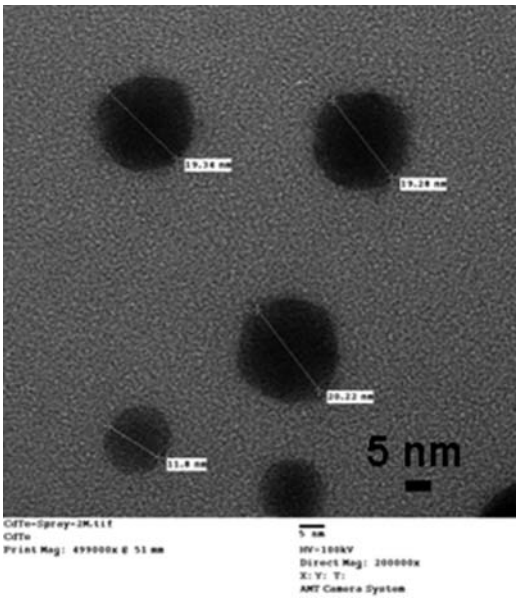

Figure 8. TEM image of CdTe prepared by spray process.

In this study, CdTe thin films with good surface morphologies were successfully synthesized for photovoltaic applications using two distinct solution-based processes, which are the CFM and the spray, without any sophisticated and expensive vacuum systems. The experimental parameters and the physical properties of the CdTe films prepared by two deposition methods are summarized in Table 1 for comparison purposes.

In the conventional CBD process, the formation of thin film can take place heterogeneously on the substrate surface or homogeneously in the solution resulting in particle formation. For the formation of thin films, the homogeneous particle formation is highly undesirable since the adsorption of the particles on the substrate surface yields powdery and non-adherent films. We developed the CFM and the modified spray processes as to be capable of decoupling the homogeneous particle formation from the heterogeneous thin film growth and to be able to overcome the drawbacks associated with the conventional CBD

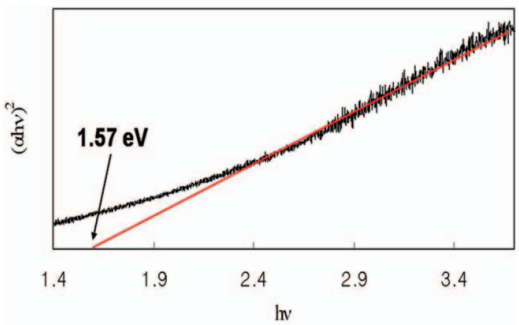

Figure 9. UV-Vis absorption spectrum of the CdTe film deposited by spraying on glass substrate and its estimated optical band gap.

Table 1. Experimental parameters and physical properties of the CdTe films prepared by two deposition methods

Process	CFM	Spray
Experimental conditions		
Chemicals	0.02 M TeO_2 + 0.005 M $H_4N_2{\cdot}XH_2O$ 0.02 M $CdCl_2{\cdot}2.5H_2O$ + 0.1 M NH_4Cl	0.02 M TeO_2 + 0.02 M $CdCl_2$ + 0.48 M $H_4N_2{\cdot}XH_2O$
Deposition time	3 minutes	3 minutes
Substrate temperature	320°C	350°C
Annealing temperature	400°C	400°C
Thin film properties		
Morphology	uniform and dense	uniform and dense
Band gap	~1.57 eV	~1.57 eV
Particle size	5.8 nm	20.23 nm
Crystal structure	Cubic (JCPDS 03-065-8879)	Cubic (JCPDS 03-65-0890)
By-product	$CdTeO_3$	$CdTeO_3$, Te

process. The homogeneous chemistry of the reacting flux could be controlled precisely by the inlet concentrations, temperature, and the residence time. Various substrates including the flexible ones can be used in these two processes for the fabrication of large area thin films at a lower cost.

Both processes were carried out at lower temperature processing conditions than the ones of the gas phase processes. They will contribute lower production costs. The films reaches to the required thickness for the absorber layer of photovoltaic devices only after 3 minutes of deposition time which will provide good throughput for thin film PV manufacturing.

Conclusions

CdTe thin films for photovoltaic cell were deposited on glass substrates by two solution-based deposition methods, which were the CFM process and the modified spray process. Both solution-based deposition methods were carried out at low temperature and under non-vacuum processing conditions. These processes will be easily applied to large area thin films on the various substrates in low costs.

In order to characterize physical and optical properties of the CdTe light absorbing polycrystalline materials, a series of analyses were carried out in this study. From SEM, XRD, and TEM analyses, CdTe thin film prepared by CFM method had a cubic structure. Its average particle size was about 5.8 nm in a few minutes. The additional peaks corresponding to $CdTeO_3$, which were formed by the oxidation of precursors during the process, were observed in X-ray diffraction patterns.

The film deposited by the spray method also had a cubic phase with a preferred orientation along the (111) direction. The formation of $CdTeO_3$ and Te were observed in the CdTe films deposited by the spray method in the XRD analysis. Average grain size of CdTe prepared by the spray method was about 20.23 nm in about 3 minutes. The estimated

optical band gap values in UV-vis spectrophotometer were ∼1.57 eV for both films prepared by CFM and spray methods.

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