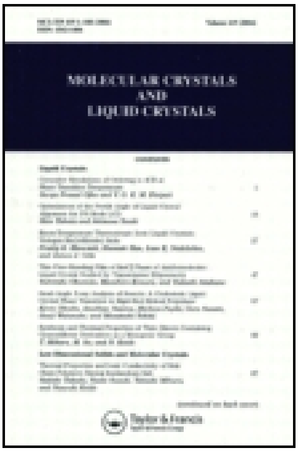

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Effect of Thermal Treatment on Physical Properties of CdTe Thin Films Deposited by a Solution-Based Method

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The influence of substrate and post-annealing temperature steps on the unique physical, structural, morphology and optical properties of CdTe thin films deposited by a non-vacuum spray process were investigated for solar cells. Scanning electron microscopy (SEM) and X-ray diffraction spectrometer (XRD) were employed to study surface morphologies and structural changes, respectively. It was observed that CdTe films produced at substrate temperature of 130°C had substantially larger grain size and showed denser morphology. Annealing at 130°C–330°C in air caused small grains throughout the surface at random. Annealing at 430°C, however, initiated fusing between grains and produced uniform morphology with an average grain size of about 60 nm. XRD analyses showed that CdTe films deposited at 130°C and then post-annealed at 430°C behaved in the originally strong (111) direction without the formation of secondary $CdTeO_3$ phase. Optical band gap measurements indicated that the values of CdTe films grown at 130°C and post-annealed at 430°C in ambient condition were about 1.45 eV. All results exhibit 130°C and 400°C to be critical deposition temperature and heat treatment temperature at which physical, optical and structural properties of CdTe thin films start to change.

Keywords Thin film; solar cell; solution-based method; CdTe

Introduction

Crystalline solar cells, particularly those made with silicon and gallium arsenide, have achieved energy conversion efficiencies approaching the theoretical limits for their respective band gaps. Furthermore, the small remaining losses are reasonably well understood. However, during the last years the photovoltaic world has been enriched with other interesting materials. Among them, CdTe is considered as one of the most suitable polycrystalline in the family of II–VI binary compounds for the photovoltaic applications because of its unique physical, optical, and electronic properties. Its direct band gap is around 1.45 eV and its value is ideal to be used as a light absorber in solar cells [1]. Absorption coefficient

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*Address correspondence to Prof. Tae Jin Lee, School of Chemical Engineering, Yeungnam University, 214-1 Dae-dong, Gyeongsan 712-749, Republic of Korea. Tel: (+82)53-810-2519; Fax: (+82)53-810-4631. E-mail: tjlee@ynu.ac.kr of CdTe is over 10^4 cm^{-1} and it is high enough to fabricate the thin film photovoltaic devices [2]. The absorption edge is very sharp and thus, more than 90% of the incident light is absorbed in a few micrometers of the material [3]. Up to now, the CdTe films have been deposited using a variety of techniques like closed-spaced-sublimation, physical vapor deposition and magnetron sputtering. Those technologies cause the high production costs because of their requirements of an expensive vacuum system and a high temperature condition. Solution-based chemical deposition processes, however, have a number of important advantages due to their low cost and low temperature processing conditions. Those processes are also able to be used to fabricate the thin film solar cell devices over large area on various substrates.

The purpose of this study is to investigate the effect of the heating temperature of substrates and annealing temperature of CdTe thin films grown by a modified spray method in low cost. The prepared CdTe films were characterized with X-ray diffraction (XRD), 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

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

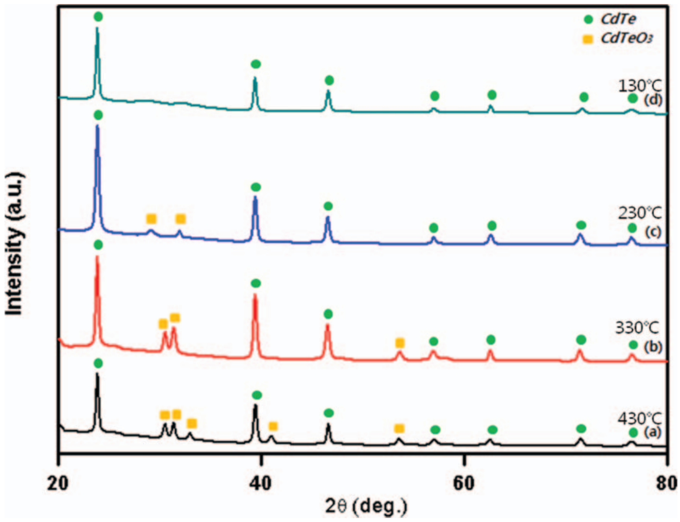

Figure 1. XRD diffraction patterns of CdTe thin films grown on the glass substrate heated at 130°C and annealed at (a) 130°C, (b) 230°C, (c) 330°C and (d) 430°C.

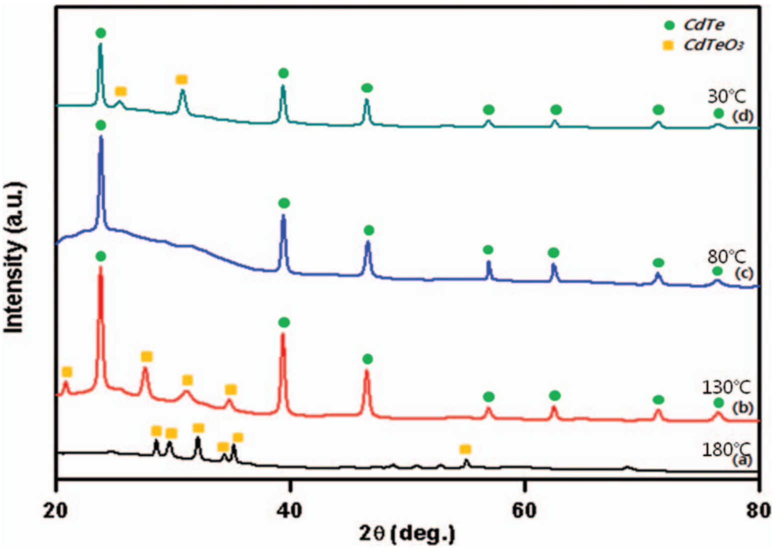

Figure 2. XRD diffraction patterns of CdTe thin films grown at (a) 30°C, (b) 80°C, (c) 130°C and (d) 180°C with fixed annealing temperature at 430°C.

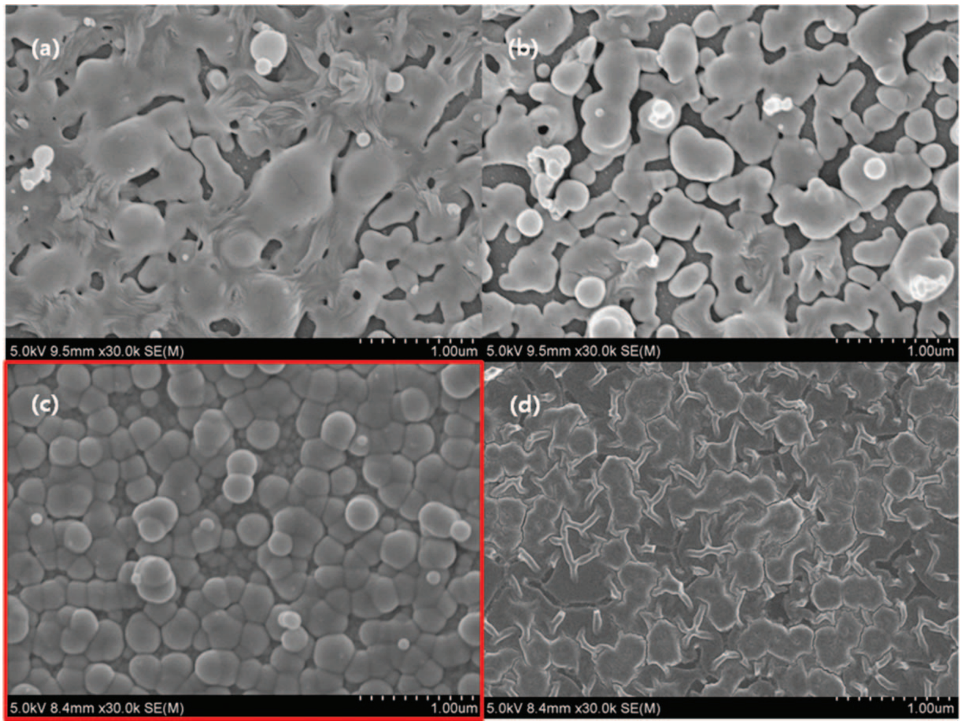

Figure 3. SEM micrographs of CdTe films grown at (a) 30°C, (b) 80°C, (c) 130°C and (d) 180°C and then annealed at 430°C.

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} [4]. Solution pH value was maintained to ~10 by the addition of ammonium hydroxide (NH_4OH). The flow rate of the solution was ~1.0 ml/min for the deposition on the substrates during the spray. The films were deposited on the substrate heated at 30°C, 80°C, 130°C, and 180°C using non-vacuum spray system. 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 films, the as-deposited CdTe thin films were thermally treated at various temperatures ranged from 130°C to 430°C for 30 min in the ambient 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.

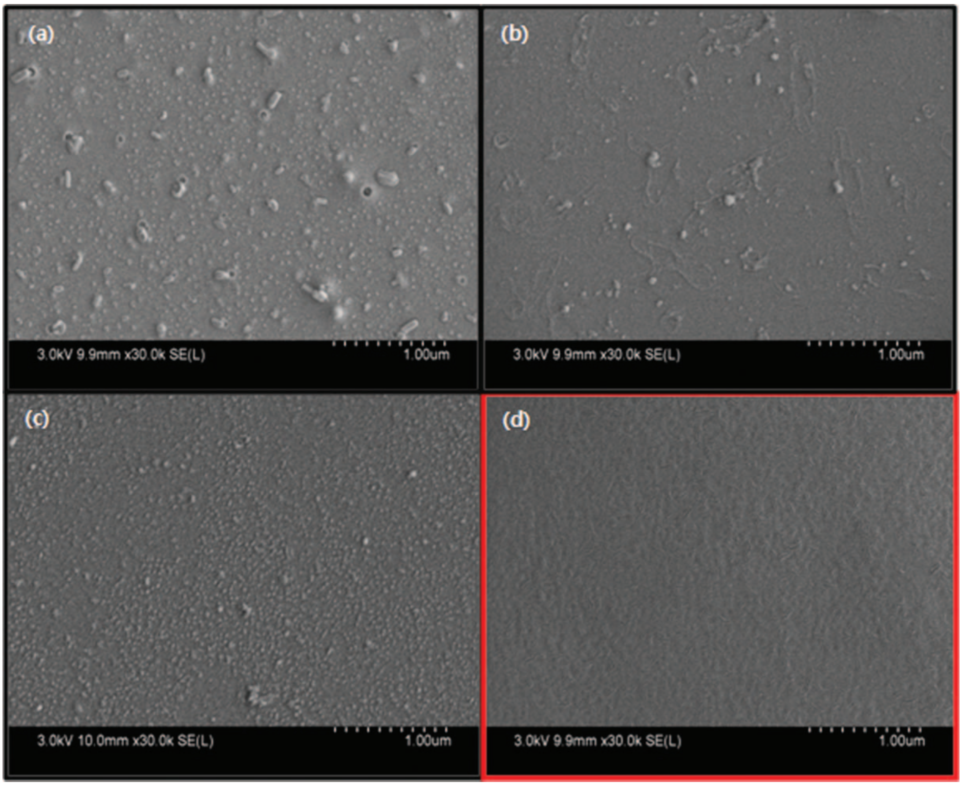

Figure 4. SEM micrographs of CdTe films deposited at 130°C. The as-deposited films were annealed at (a) 130°C (b) 230°C, (c) 330°C and (d) 430°C.

Results and Discussion

The CdTe thin films were deposited on the glass substrates by the modified chemical spray method at low temperature in low cost. In order to confirm the effects of the heating temperature of substrate and the annealing temperature on the physical properties of CdTe thin films, the prepared CdTe films were investigated.

Figure 1 display the typical XRD spectra obtained from CdTe films deposited on a substrate heated at 130°C and annealed at four different temperatures, which are 130°C, 230°C, 330°C and 430°C, in air for 30 min. The diffraction patterns show that the as-deposited CdTe thin films annealed at a certain temperature have zinc-blend structure with a strong preferred orientation along (111) direction. As shown in Fig. 1, additional peaks other than CdTe were observed in the spectra of Fig. 1(a), (b) and (c) while there was no peak for $CdTeO_3$ in Fig. 1(d). Additional peaks are attributed to the peak of $CdTeO_3$. We presumed that the deposition processing under ambient conditions could likely lead to the formation of secondary $CdTeO_3$ phase along with CdTe. Figure 1 shows that CdTe thin films deposited by the solution-based chemical spray method should be annealed at higher than 330°C in order to prevent the formation of $CdTeO_3$.

Often the deposition conditions may affect the final thin film quality. In order to investigate the dependence of the heating temperature of the substrate on the crystalline phase, we deposited the CdTe films at the different substrate temperatures. Figure 2(a), (b), (c) and (d) show the XRD spectra of CdTe films deposited at four different heating temperatures, which are 30°C, 80°C, 130°C and 180°C, respectively. The annealing temperature of the as-deposited films was fixed to 430°C. The major peaks observed in the XRD patterns of Fig. 2(c) were corresponding to (111), (220), (311), (400), (331), (422), and (511) planes, which coincided with those in the standard JCPDS data (03-62-0890). The major peak detected at 23.80^o showed zinc-blend structure with preferred orientation along the intensity of (111) peak. However, as shown in Figure. 2(a), (b), and (d), additional peaks were clearly presented, which corresponded to $CdTeO_3$. Since the non-vacuum spray deposition method was carried out under the ambient environment, it is considered that oxygen in the air led to the formation of $CdTeO_3$ during the process. An oxide phase is possibly formed during the film growth. Cd and Te ions in the spray solution form complexes such as $Cd(OH)_2$, TeO_2, and $TeO_3{}^{2+}$ [5]. If these complexes dissociate slowly or suddenly, it can lead to the formation of secondary $CdTeO_3$ phase along with CdTe. This dissociation will occur if the substrate temperature is too low or too high. Comparing with Fig. 2(a), (b), and (d), there was a significant reduction of $CdTeO_3$ peak intensity in the XRD spectra at 130°C as shown in Fig. 2(c). From these results, it is confirmed that the crystal growth of the as-deposited CdTe films are significantly affected by the heating temperature of the substrates during the solution-based chemical spray process.

Effects of not only the heating temperature of substrate but also the annealing temperature on the morphology of the CdTe films were investigated by SEM. Figure 3 shows the surface morphologies of the films grown at substrate temperatures of 30°C, 80°C, 130°C and 180°C. As can be seen from the Figure, the CdTe films grown at 130°C was well formed with uniformity, large grain size and dense. It was clearly observed that the granular structure becomes more compact. The grain would be grown through four stages. In the first stage, the grain reaches a maximum size and it slowly decreases in the size in the second phase. In the third stage, the coalescence of grains leading to a larger grain growth occurs and then a densely packed film is formed to reduce the porosity in the last stage. It is a clear evident that the surface morphology is strongly dependent on the substrate temperature. The size of the grains was distributed in the range of 200–250 nm as presented in the Fig. 3(c).

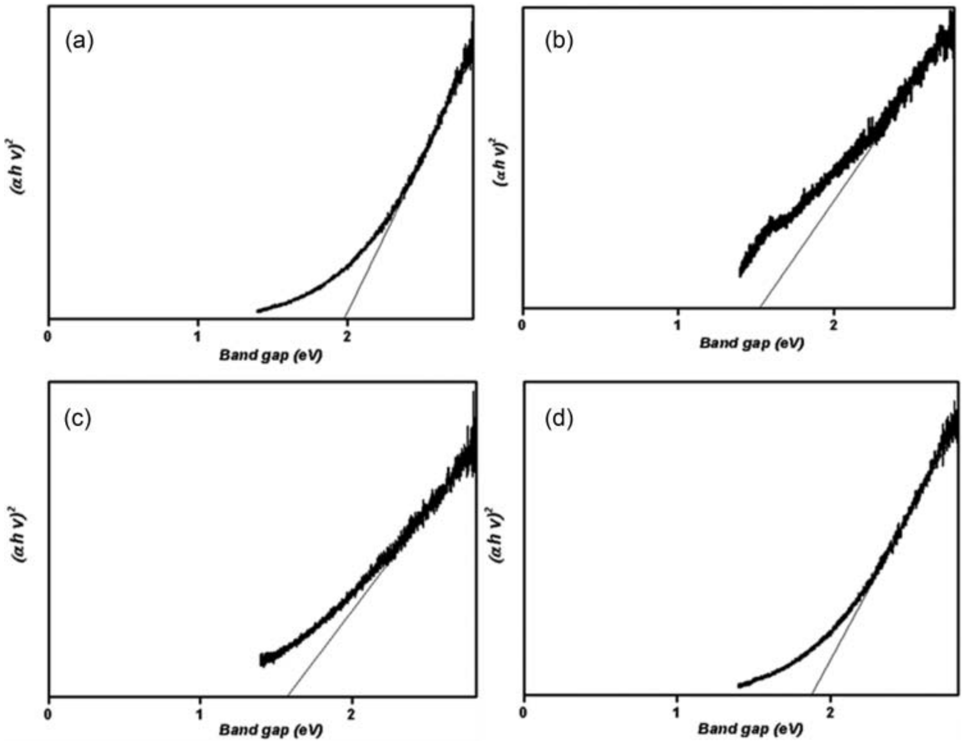

Figure 5. Optical absorption spectra of CdTe films deposited at (a) 30°C, (b) 80°C, (c) 130°C and (d) 180°C. Their annealing temperatures were fixed at 430°C.

Figure 4(a), (b), (c) and (d) show the surface morphology of the films deposited on the substrate heated at 130°C and then annealed at 130°C, 230°C, 330°C and 430°C, respectively, for 30 min. As presented in Fig. 4(a), (b) and (c), the prepared CdTe films not only show lots of irregular pinholes but also exhibit rougher and less dense surface morphologies throughout the surface. When the temperature for the post thermal treatment increased to 430°C, however, CdTe films showed totally different morphology with uniformity. The film had a smooth morphology with an average grain size of about 60 nm. This significant difference in the film morphologies suggests that there is an optimum annealing temperature near 430°C at which allows coalescence of small grains.

Figure 5 indicates the optical band gap measurements of CdTe films. Those were obtained by extrapolating the slope of curves to the x-axis in a plot of $(ahv)^2$ against hv on the basis of UV–visible absorption measurement. The extrapolated values of the optical energy band gap, E_g, are 1.82 eV, 1.56 eV, 1.45 eV and 1.85 eV for the films deposited at substrate temperatures of 30°C, 80°C, 130°C and 180°C, respectively. From Fig. 5, there is a tendency to move the absorption edge towards lower energies for CdTe as the heating temperature of the substrate increases.

The effect of temperature for the post thermal treatment on the band gap of the CdTe thin films deposited at the substrate temperature of 130°C is shown in Fig. 6. While the estimated band gap values for the films annealed at 130°C, 230°C, and 330°C for 30 min in the ambient environment are 1.97 eV, 1.87 eV, and 1.58 eV, respectively, the estimated value from Fig. 6(d) is about 1.45 eV. Since there was no noticeable grain growth in the

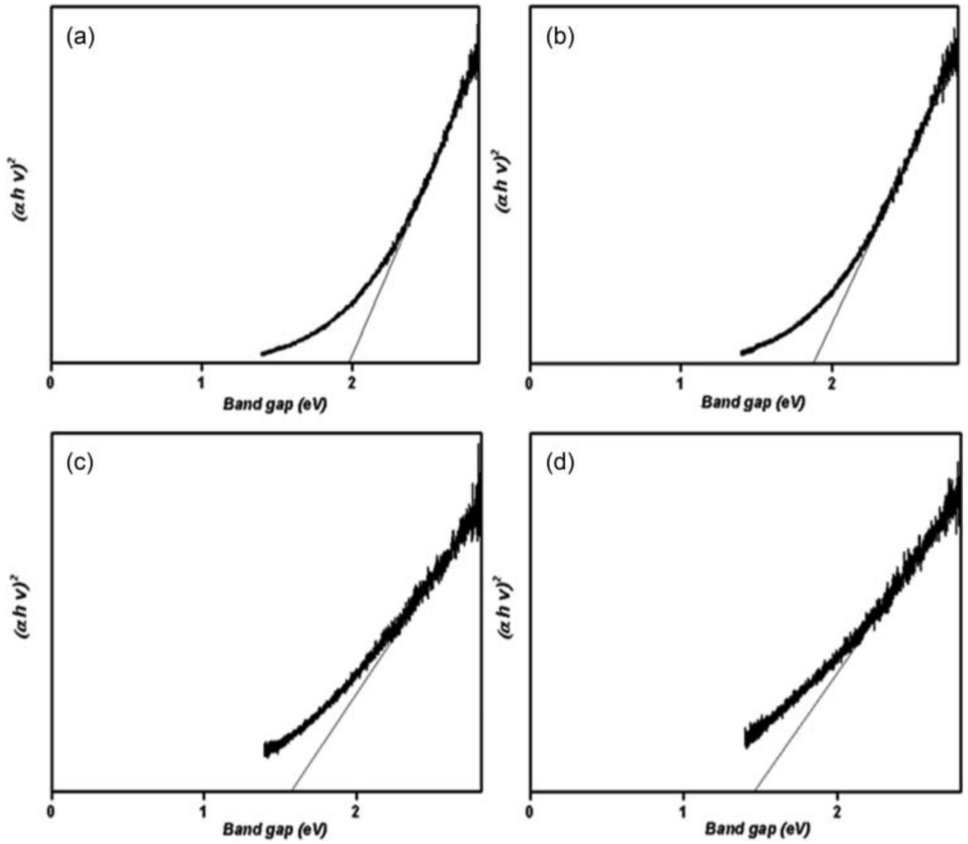

Figure 6. Optical absorption spectra of CdTe thin films deposited at 130°C with various annealing temperatures at (a) 130°C (b) 230°C, (c) 330°C and (d) 430°C.

CdTe thin films at higher than 430°C and the crystal structure remained in cubic, the CdTe thin films annealed at 430°C is close to the optimum band gap of about 1.45 eV [6].

Conclusions

In this work, we studied the changes of the structural, physical and optical properties of CdTe thin films deposited on the glass substrates using a modified spray process in terms of the heating temperature of the substrate and the annealing temperature of the as-deposited CdTe films. From XRD diffraction patterns, it was observed that CdTe thin films deposited at 130°C and annealed at 430°C for 30 min in ambient environment had a zinc-blend structure with a preferred orientation along the (111) direction. In the SEM images, the annealing at 400°C indicated that the grains randomly distributed throughout the surface of CdTe films are fused inter-grain and altered the surface morphology uniformly. Optical band gap of the films became sharper and more approachable optimum band gap (1.45 eV) when substrate and annealing temperature are about 130°C and 430°C, respectively. All these results demonstrate that 430°C is a crucial thermal treatment temperature at which structural, physical and optical properties of CdTe thin films change although substrate temperature plays a more critical role in determining the initial micro-structure of CdTe thin films deposited by solution-based chemical spray method.

Acknowledgment

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References

[1] Romeo, N., Bosio. A., & Romeo, A. (2010). *Sol. Energy Mater. Sol. Cells*, *94*, 2.
[2] Cruz, L. R., Kazmerski, L. L., Moutinho, H. R., Hasoon, F., Dhere, R. G., & de Avilez, R. (1999). *Thin Solid Films*, *350*, 44.
[3] Bosio, A., Romeo, N., Mazzamuto, S., & Canevari, V. (2006). *Prog. Cryst. Growth Charact. Mater. 52*, 247.
[4] Ison, V. V., Rao, A. R., & Dutta, V. (2009). *Sol. Energy Mater. Sol. Cells*, *93*, 1507.
[5] Murase, K., Honda, T., Yamamoto, M., Hirato, T., & Awakura, Y. (2000). *J. Electrochem. Soc.*, *147*, 2210.
[6] Bacaksiz, E., Basol, B. M., Altunbas, M., Novruzov, V., Yanmaz, E., & Nezir, S. (2007). *Thin solid Films*, *515*, 3079.