

## FABRICATION OF $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) FILMS BY ONE-STEP ELECTROCHEMICAL DEPOSITION AND ANNEALING

YIH-MIN YEH, HSIANG CHEN<sup>a\*</sup>, SUNG-MIN LIU, SHAUNG-LINTSAI<sup>a</sup>  
*Graduate School of Optomechatronics and Materials, Wu Feng University,  
Chia-yi, Taiwan, ROC*

<sup>a</sup>*Department of Applied Materials and Optoelectronic Engineering, National  
ChiNan University, Puli, Taiwan, ROC*

In this study, we fabricated  $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films by one-step electrochemical deposition and annealing. In the deposition process, additives including trisodium citrate and triethanolamine were included to improve the film quality. In addition, various deposition voltages were adjusted to vary the film composition. Then, to investigate the annealing effect, heat treatment with different annealing time was examined. To study the structural, morphological and compositional properties of CZTS thin films, the as-deposited and annealed CZTS thin films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and Hall Effect Analyzer.

(Received October 11, 2013; Accepted December 13, 2013)

*Keywords:*  $\text{Cu}_2\text{ZnSnS}_4$ ; electrodeposition; annealing; trisodium citrate; triethanolamine

### 1. Introduction

With increasing demand of energy, environmental pollution, and global warming, clean and renewable energy sources have been regarded as the ultimate solution to future energy crisis. Among all the renewable energy sources, solar power solar cells have been intensively investigated as one of the alternative energy sources. Currently, silicon-based solar cell is the popular mainstream in solar cell technologies. However, the indirect bandgap of silicon material with low optical absorption coefficient has a very thick absorber layer of film of  $100\mu\text{m}$  order [1]. To replace the traditional silicon-based photovoltaic technology,  $\text{CuInGaSe}_2$  (CIGS) and  $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) have been proposed as thin and effective absorber materials to fabricate solar cells. Compared with CIGS absorber consisting of rare elements of In and Ga, CZTS is made up of rich elements on earth. Similar to CIGS films quaternary compounds CZTS thin film has an energy gap of 1.4-1.5 eV and  $10^4\text{ cm}^{-1}$  absorption coefficient [2].

To synthesize CZTS films, various vacuum fabrication methods including hybrid sputtering method [3], RF magnetron sputtering [4], thermal evaporation [5], pulsed laser deposition [6,7], electron beam evaporation sulfide precursor [8,9] have been proposed. Recently, the conversion efficiency of the CZTS-based solar cell has reached 11.1% [10]. CZTS films deposited in vacuum conditions. Therefore, non-vacuum fabrication processes including spraying techniques [11,12], photochemical deposition [13], sol-gel method [14-15], spin-coating method [16] and electrodeposition [17-21] have been reported to produce CZTS film.

---

\* Corresponding author: hchen@ncnu.edu.tw

## 2. Experiment

### 2.1 Experimental parameters and electrodeposition conditions

To carry out one-step CZTS film electrodeposition, various electrolytes including were included in the plating solution. The plating solution composition is shown in Table 1. To electrodeposit the CZTS film, multifunction constant voltage and current meter (PotentiostatGalvanostat) were applied with three electrodes at room temperature without stirring. Pt was used as the counter electrode, the Mo conductive glass was used as the working electrode, and silver / silver chloride (Ag/AgCl) as reference electrode.

### 2.2 Electrodeposition CZTS pre-treatment steps

The main recipes of CZTS plating solution and the operating conditions are shown in Table 1. First, acetone, methanol, isopropanol, and DI water was applied to cleanse the Mo substrate. Then, aqueous ammonia (25%) was used to remove molybdenum oxide.

### 2.3 CZTS annealing process

The deposited CZTS film was placed in a vacuum furnace for annealing. The final annealing temperature was 550°C [24]. The temperature elevation profile for annealing is shown in Fig. 1.

Table 1. Composition of the plating solution and the deposition condition

Composition of plating solution	
CuSO <sub>4</sub>	0.02M
ZnSO <sub>4</sub>	0.01M
SnSO <sub>4</sub>	0.02M
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.02M
Trisodium Citrate	0.2M
Tartaric Acid	0.1M
pH	4.5~5.0
voltage	-1.3~-1.6 V

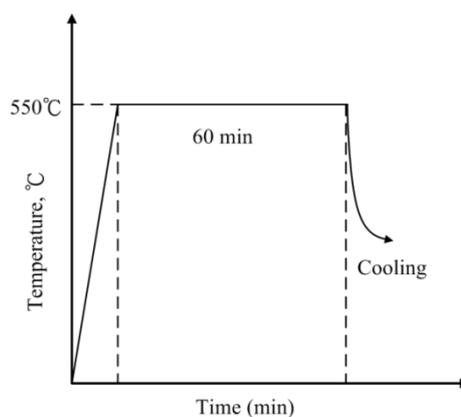
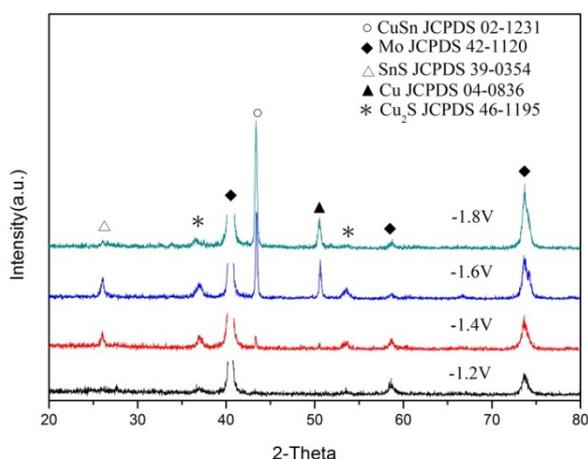


Fig. 1 The temperature elevation profile for annealing

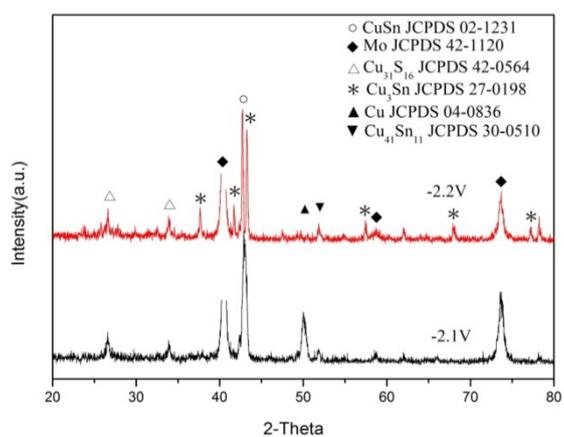
### 3. Results and discussion

#### 3.1 The influence of deposition voltage

To examine the influence of the deposition voltage, the deposited CZTS film was investigated by XRD patterns as shown in Fig. 2(a) and (b). The CZTS films deposited with different voltages ranging from -1.2V to -2.2V were annealed with rapid thermal annealing (RTA) at 550 °C for 1 hour. Figure 2 (a) shows that the diffraction peaks of molybdenum substrate could be observed but nothing else could be observed for the film deposited at -1.2V. As the deposition voltage increased to -1.3V and -1.4V, the CuSn, SnS, and Cu<sub>2</sub>SnS<sub>3</sub> diffraction peaks appeared as shown in Fig. 2(a). In addition, Cu phase emerged at the deposition voltage of -1.6 V. As the deposition voltage further increased to -1.8V, the CuSn, Cu, SnS, and Cu<sub>2</sub>SnS<sub>3</sub> phase diffraction peaks became strongest as shown in Fig. 2(a). As the deposition voltage increased to -2.1 V, the diffraction peaks of CuSn, SnS, Cu<sub>2</sub>SnS<sub>3</sub> and Cu phase became weaker but the diffraction peaks of molybdenum became stronger. At the deposition voltage of -2.2V, the molybdenum substrate began to dissociate and the diffraction peak of Mo decrease drastically and many impurity peaks emerged as shown in Fig. 2(b). Since CZTS deposition with a negative voltage around 2 V might cause dissociation and produce impurities, we chose deposition voltages below 1.7 V. In addition to XRD analyses, SEM images of the film deposited with deposition voltages of -1.1, -1.3, -1.5, and -1.7V are shown in Fig. 3 (a), (b), (c), and (d). Consistent with XRD analyses, the most compact film with high material quality was deposited at -1.7 V as shown in Fig. 3 (d).



(a)



(b)

Fig. 2 XRD patterns of the film deposited at (a) -1.2, -1.4, -1.6 and, -1.8V (a) -2.1 and -2.2 V.

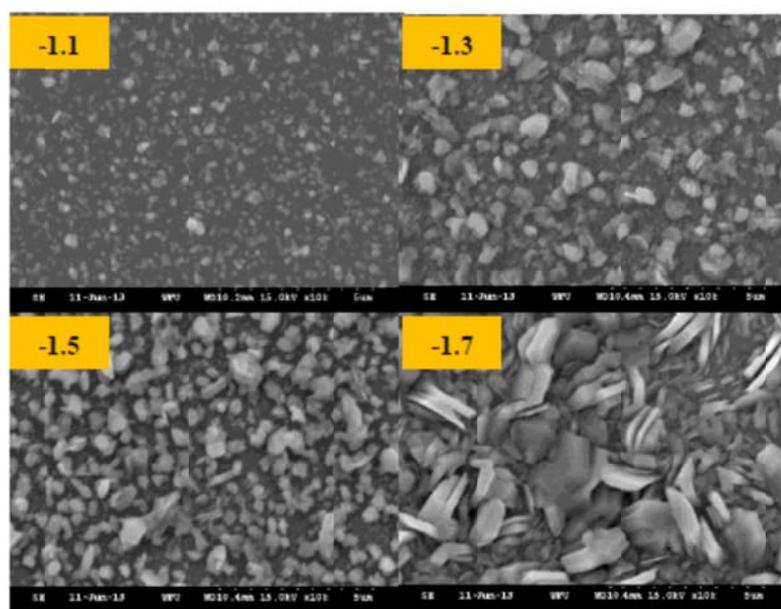


Fig. 3 SEM images of the film deposited at -1.1, -1.3, -1.5 and, -1.7V

### 3.2 The effect of additives to CZTS

To understand the influence of additives, trisodium citrate as complexing agent was incorporated into the plating solution. The concentration of trisodium citrate varied from 0.1M, via 0.15M to 0.25M. Figure 4 is the XRD patterns for the deposited film in solutions containing trisodium citrate. After deposition, the films were annealed with vulcanization. In the XRD patterns of copper sulfide phase, when the concentration of sodium citrate to continue to increase to 0.25 M, the diffraction peak intensity might decrease slightly. Furthermore, different concentrations of triethanolamine (TEA) might also influence the crystalline structures of the CZTS film. In our experiment, we added TEA with concentrations between 50 mM and 150 mM for comparison as shown in Fig. 5. The results indicate that TEA might have negative influences on the quality of the CZTS film because the CuZn phase was always smaller than the Mo phase, especially when TEA with 100 mM was included.

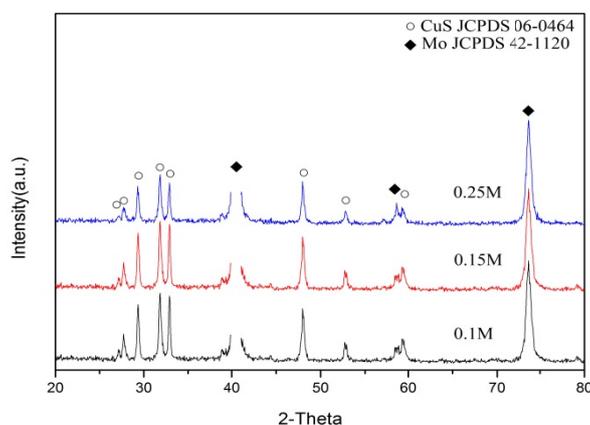


Fig. 4 XRD patterns for the deposited film in solutions containing trisodium citrate

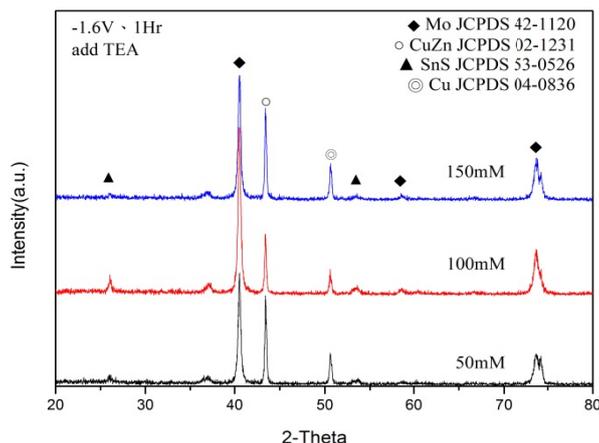


Fig. 5 XRD patterns for the deposited film in solutions containing TEA

### 3.3 The influence of deposition time on the film surface morphology

Moreover, the deposition time was also investigated with SEM. In our experiment, the films were deposited at  $-1.4$  V for 30, 40, 60, 120 min treated with rapid annealing temperature (RTA) at  $550$  °C after one hour. The SEM images for the film deposited for 30, 40, 60, 120 min are shown in Fig. 6 (a), (b), (c), and (d). The results show formation of large particles at the deposition time of 30 min. After the film was deposited for 40 minutes, the grain boundaries began to merge with lots of microporosity. The results reveal film deposition for 60 minutes could form a dense and uniform film plane. After deposition for 120 minutes, the film became more roughness, resulting in uneven particle that caused some pores.

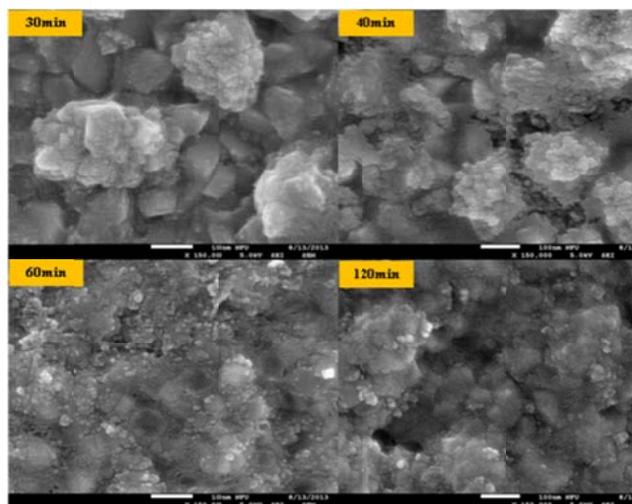


Fig. 6 The films deposited at  $-1.4$  V for 30, 40, 60, 120 min

### 3.4 The annealing effects on the CZTS film

To investigate the annealing effects on the film, the CZTS films deposited at  $-1.3$  V,  $-1.4$  V,  $-1.5$  V, and  $-1.6$  V were annealed at with RTA at  $550$  °C for various time. The XRD patterns are shown in Fig. 7 (a), (b), (c), and (d). The results indicate that the strongest CuSn and  $\text{Cu}_2\text{SnS}_3$  phases occurred around the annealing time of 10 minutes as shown in Fig. 7(b). As the annealing time increased to 20 minutes or longer, the CuSn and  $\text{Cu}_2\text{SnS}_3$  phases became weaker as shown in Fig. 7(c) and (d). Furthermore, to study the influence of electrical characteristics of the

films, the CZTS films were analyzed by a Hall effect analyzer. Table 2 shows the carrier concentration and the sheet resistance of the CZTS films deposited at -1.3V, -1.4V, -1.5V, and -1.6V were annealed at with RTA at 550 °C for various time. The experimental results indicate that low sheet resistances could be obtained for the CZTS films annealed for 10 minutes. In addition, the as-deposited film belonged to N-type but most of the CZTS film belonged to P-type after annealing treatment.

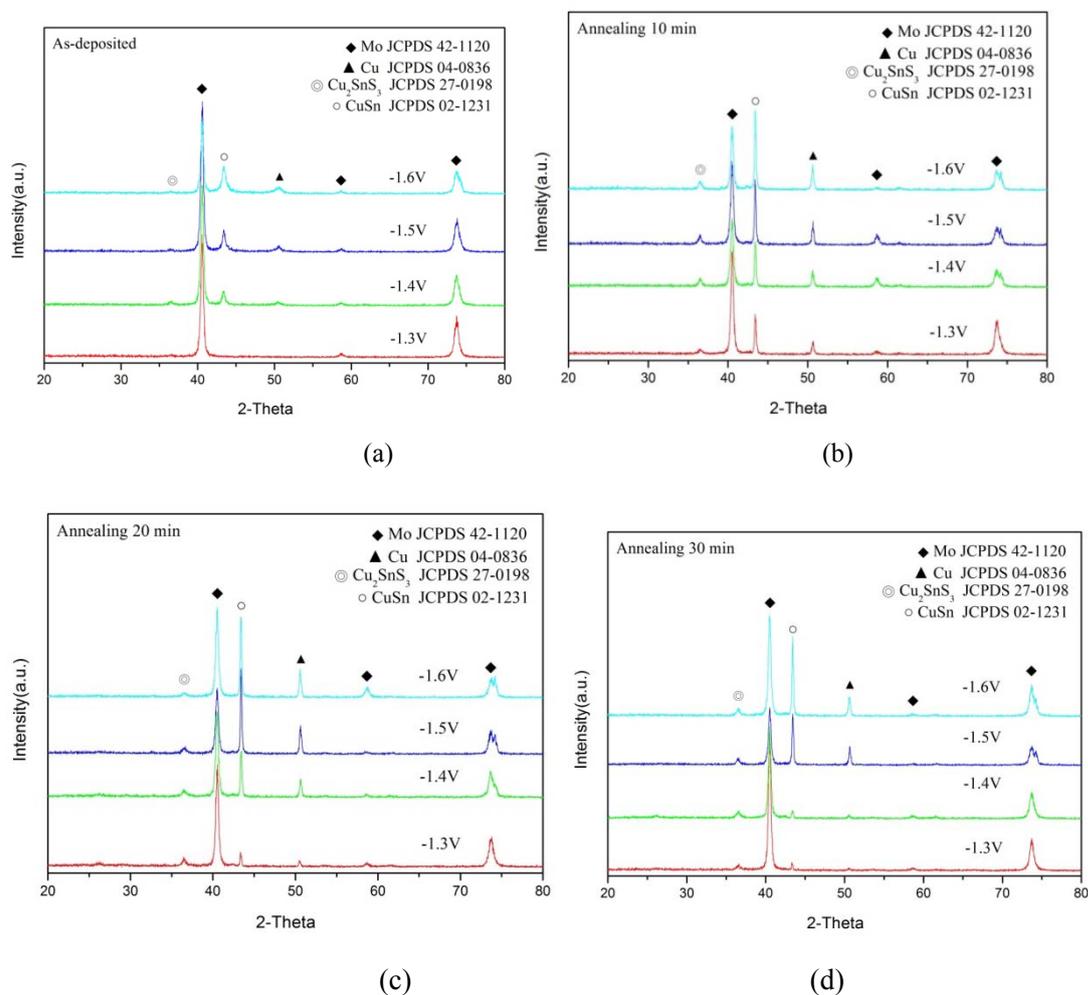


Fig.7 The XRD pattern of the CZTS films deposited at -1.3V, -1.4V, -1.5V, and -1.6V were annealed at with RTA at 550 °C for (a) the as-deposited (b) 10 min (c) 20 min (d) 30 min.

Annealing 550°C	Potential	Conductive Type	Mobility (cm <sup>2</sup> /V sec)	Concentration (cm <sup>-3</sup> )	Sheet resistance (Ω/□)
Annealing 10min	1.3V	P	1.108	1.282E+01	4.393E-06
	1.4V	P	2.051	6.980E+00	4.361E-06
	1.5V	P	2.373	1.309E+01	2.009E-06
	1.6V	P	6.033	6.320E+01	1.637E-06
Annealing 20min	1.3V	P	3.868	8.450E-01	1.910E-05
	1.4V	N	3.912	3.347E-01	4.768E-06
	1.5V	P	1.068	2.204E+01	2.650E-06
	1.6V	P	2.153	1.842E+01	1.574E-06
Annealing 30min	1.3V	P	7.503	4.296E-01	1.936E-05
	1.4V	P	1.387	2.476E-01	1.817E-05
	1.5V	P	7.612	2.281E+01	3.596E-06
	1.6V	P	2.955	8.110E+00	2.605E-06
As-deposited	1.3V	N	3.399	8.214E+00	2.236E-05
	1.4V	N	4.834	1.001E+00	1.291E-05
	1.5V	N	2.136	3.376E+00	8.657E-06
	1.6V	N	9.034	1.177E+01	5.870E-06

Table 2 Carrier concentration and the sheet resistance of the CZTS films deposited at -1.3V, -1.4V, -1.5V, and -1.6V were annealed at with RTA at 550 °C for various time

### 3.5 The composition of the CZTS film

To analyze the film composition, EDS analysis reveal the composition of the CZTS film as shown in Fig. 8. The Cu/Zn/Sn/S compositions were 14.95%, 1.69%, 0.72%, and 82.64%. A previous study shows that the volatilization of tin might cause the loss of tin [25].

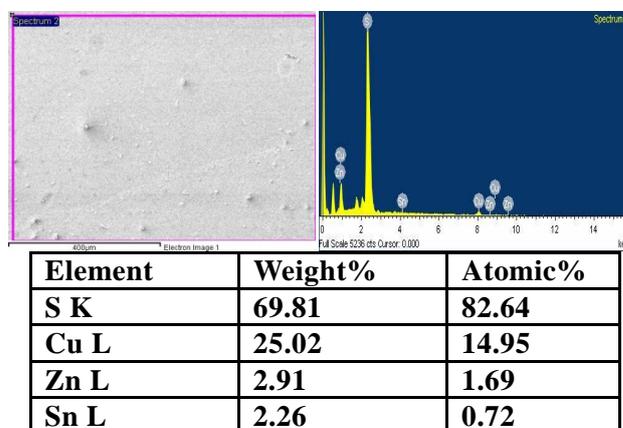


Fig. 8. CZTS film composition

## 4. Conclusion

In this research, CZTS films were grown on the Mo substrate by one-step electrodeposition method and annealing. Multiple material and electrical analyses were used to examine the film quality. To study the effects of the deposition condition, various deposition time, deposition voltage, and additive concentrations were varied to improve the film quality. In addition, we investigated the relation between the annealing time and the film quality. The electrodeposited CZTS films are promising for future development of the CZTS-based solar cell

## References

- [1] DB Mitzi, M Yuan, W Liu, AJ Kellock, SJ Chey, V Deline, AG Schrott, *Advanced Materials*, **20**, 3657 (2008).
- [2] C Steinhagen, M G Panthani, V Akhavan, B Goodfellow, B Koo, Korgel, J. Am. Chem. Soc. **131**, 12554 (2009)
- [3] T Tanaka, T Nagatomo, Kawasaki D, Nishio M, Guo Q, Wakahara A, Yoshida A, Ogawa H, *Journal of Physics and Chemistry of Solids*, **66**, 1978(2005).
- [4] JS Seol, SY Lee, JC Lee, HD Nam, KH Kim, *Solar Energy Materials and Solar Cells*, **75**, 155 (2003).
- [5] K Oishi, G Saito, K Ebina, M, Nagahashi K Jimbo, WS Maw, H Katagiri, M Yamazaki, H Araki, A Takeuchi, *Thin Solid Films*, **517**, 1449(2008).
- [6] K Moriya, K Tanaka, H Uchiki, *Japanese Journal of Applied Physics*, **46**, 5780 (2007).
- [7] SM Pawar, AV Moholkar, IK Kim, SW Shin, JH Moon, JI Rhee, JH Kim, *Current Applied Physics*, **10**, 565 (2010).
- [8] H Katagiri, N Sasaguchi, S Hando, S Hoshino, Ohashi J, Yokota T, *Solar Energy Materials and Solar Cells*, **49**, 407 (1997).
- [9] H Katagiri, K Saitoh, T Washio, H Shinohara, T Kurumadani, S Miyajima, *Solar Energy Materials and Solar Cells*, **65**, 141 (2001).
- [10] K T Teodor, T Jiang, B Santanu, Oki G , Tayfun G , Yu Z ,and David B M. *Advanced Energy Materials*, **3**, 34(2013).
- [11] N Kamoun, H Bouzouita, Rezig B. *Thin Solid Films*, **515**, 5949(2007).
- [12] Kishore Kumar YB, Suresh Babu G, Uday Bhaskar P, Sundara Raja V, *Solar Energy Materials and Solar Cells*, **93**, 1230 (2009).
- [13] K Moriya, K Tanaka, H Uchiki, *Japanese Journal of Applied Physics*, **44**, 715 (2005).
- [14] K Tanaka, N Moritake, H Uchiki, *Solar Energy Materials and Solar Cells*, **91**, 1199 (2007).
- [15] K Tanaka, N Moritake, M Oonuki, H Uchiki, *Japanese Journal of Applied Physics*, **47**, 598 (2008).
- [16] TK Todorov, KB Reuter, DB Mitzi, *Advanced Materials*, **22**, 1 (2010).
- [17] X Zhang, X Shi, W Ye, C Ma, C Wang, *Applied Physics A: Materials Science & Processing*, **94**, 381(2009).
- [18] H Araki, Y Kubo, A Mikaduki, K Jimbo, WS Maw, H Katagiri, M Yamazaki, K Oishi, Takeuchi A, *Solar Energy Materials and Solar Cells*, **93**, 996 (2009).
- [19] JJ Scragg, PJ Dale, LM Peter, *Electrochemistry Communications*, **10**, 639,(2008).
- [20] H Araki, Y Kubo, K Jimbo, WS Maw, HK Katagiri, M Yamazaki, *physica status solidi* **5**, 1266 (2009).
- [21] R Schurr, A Holzling, S Jost, R Hock, VoßT, Schulze J, Kirbs A, Ennaoui A, Lux-Steiner M, Weber A, Kotschau I, Schock HW, *Thin Solid Films*, **517**, 2465,(2009).
- [22] S Cheng, Y He, G Chen, *Materials Chemistry and Physics*, **110**, 449 (2008).
- [23] A Ghazali, Z Zainal, MZ Hussein, A Kassim, *Solar Energy Materials and Solar Cells*, **55**, 237(1998).
- [24] H Araki, Y Kubo, A Mikaduki, K Jimbo, WS Maw, H Katagiri, M Yamazaki, K Oishi, A Takeuchi, *Solar Energy Materials and Solar Cells*, **93**, 996 (2009).
- [25] DB Mitzi, O Gunawan, TK Todorov, K Wang, S Guha, *Solar Energy Materials and Solar Cells*, **95**, 1421 (2011).