

## Research Article

# Effect of Ga/Cu Ratio on Polycrystalline CuGaSe<sub>2</sub> Thin Film Solar Cell

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Structural and electrical properties of polycrystalline CuGaSe<sub>2</sub> thin films have been studied by changing the Ga/Cu ratio in the films. CuGaSe<sub>2</sub> thin films with various Ga/Cu ratio were grown over Mo-coated soda-lime glass substrates. With the increase of Ga content in CuGaSe<sub>2</sub>, morphology of the films was found to deteriorate which is associated with the smaller grain size and the appearance of impurity phases presumably due to the phase transition from the chalcopyrite structure to the defect-related phase on the surface of the films. Properties of the Ga poor films were affected by the Cu rich secondary phases. Electrical properties of the films were strongly influenced by the structural properties and degraded with increasing the Ga/Cu ratio in the film. Device performances, fabricated with the corresponding CuGaSe<sub>2</sub> films, were found to be correlated with the Ga/Cu ratio in the films and consistent with the observed structural and electrical properties.

## 1. Introduction

Chalcopyrite Cu(In,Ga)Se<sub>2</sub>, abbreviated as CIGS, is one of the most promising materials to realize high-efficiency, low-cost thin film solar cell. Efficiency of 19.9% has already been achieved for the CIGS-based solar cell [1]. As the ideal CIGS bandgap for highest conversion efficiency is speculated theoretically to be around 1.4 eV [2], CuGaSe<sub>2</sub> ( $x = \text{Ga}/\text{In} + \text{Ga} = 1.0$ ) with a bandgap of 1.68 eV [3] can be considered as a leading material to enable the highest possible efficiency. Moreover, the large band gap makes the CuGaSe<sub>2</sub>, an ideal absorber material for the top cell in a photovoltaic tandem device together with CuInSe<sub>2</sub> as the bottom cell absorber [4]. However, so far, CuGaSe<sub>2</sub> solar cells with a CdS buffer have achieved efficiency of around 9.3% for thin film [5] and 9.7% for single crystal solar cells [6]. Therefore, a better understanding of the material properties of CuGaSe<sub>2</sub> is needed to realize efficiency beyond the current level. The electrical, optical, and microstructural

properties of CIGS films are dominated by the various intrinsic defects originated from the off stoichiometry of the film composition [7–9]. Moreover, deviation from the ideal stoichiometry during growth of this material is reported to contain some secondary phases preferably segregated on the surface of the film. Particularly, formation of the Cu(In,Ga)<sub>3</sub>Se<sub>5</sub>, Cu(In,Ga)<sub>2</sub>Se<sub>3.5</sub>, and so forth phases on the surface of the slightly Cu-poor film (Ga/Cu-rich) and Cu-Se related secondary phase in the Cu-rich film is a commonly observed phenomenon in CIGS material grown by various methods [10, 11] and reported to have significant impact on the material properties as well as fabricated device performances [12, 13]. Therefore, to achieve the optimized material quality of CuGaSe<sub>2</sub> material which is compatible for highest possible efficiency, an extensive study of this material with various compositions is indispensable. Although there have been various studies reported regarding the effect of composition over the properties of CIGS thin film, in case of CuGaSe<sub>2</sub>, study of the film properties as well as solar

cell performances in connection with the above mentioned secondary phases are scarce specially due to the relatively high defect formation energy of this defect in standard grown CuGaSe<sub>2</sub> films. In this paper, we have systematically varied the Ga/Cu ratio in the CuGaSe<sub>2</sub> absorber layer to study the effect of Ga content on the electrical and structural properties of the film. Also correlation between the performances of the fabricated solar cells and various Ga/Cu ratios in the absorber layer has been investigated.

## 2. Experimental

Polycrystalline CuGaSe<sub>2</sub> thin films with the typical thickness of 2 μm were grown over Mo-coated soda-lime glass (SLG) substrates through a three-stage coevaporation process using molecular beam epitaxy system [14]. Evaporation was done at a base pressure of approximately  $1 \times 10^{-6}$  Pa from three Knudsen cells (K-cells) that were the respective Cu, Ga, and Se sources. Growth temperature of the first stage was kept at 400°C during coevaporation of Ga and Se. Temperature was increased to 520°C at the 2nd and 3rd stage when Cu, Se and Ga, Se coevaporation was done, respectively. To get the uniform composition of the films, substrate was kept in constant rotation of 10 rpm during deposition. All the samples were grown at the constant flux rate of Cu, Ga, and Se. Typical deposition time for the 1st and 2nd stage was 60 minutes and 25 minutes, respectively. The duration of the 2nd stage was determined by the target Cu/Ga ratio of 1.3 at the end of the 2nd stage. Finally 3rd stage growth time determines the final Cu/Ga ratio in the growth CuGaSe<sub>2</sub> film. By lengthening the duration of 3rd stage, we can reduce the Cu/Ga ratio and vice versa. Thus, several CuGaSe<sub>2</sub> films with various Ga/Cu ratio have been fabricated by changing the third stage growth time. After 3rd stage of the growth, during the cooling of the substrate, Cu and Ga cell shutters were closed; however Se cell remained open for 30 minutes to irradiate Se flux to avoid reevaporation of Se from the surface of the film. Thus all the films were considered to be grown in sufficient Se environment.

Device fabrication was completed by chemical bath deposition of CdS buffer layer and successive deposition of RF-sputtered highly resistive *i*-ZnO, conductive *n*-type Al:ZnO layers, and finally Al grids as front electrode by thermal evaporation. The film thickness of the Mo, CdS, *i*-ZnO, and Al:ZnO layers were typically 0.8 μm, 50 nm, 70 nm, and 400 nm, respectively. For the electrical characterization, CuGaSe<sub>2</sub> was grown on SLG directly.

The composition of the grown CuGaSe<sub>2</sub> films was measured by electron probe microanalysis (EPMA) at 15 kV of acceleration voltage. The structural properties of the films were examined by scanning electron microscopy (SEM). Electrical properties were studied by the van der Pauw Hall measurement method at room temperature. The photovoltaic properties of the fabricated solar cells were analyzed by ESS-1000 solar simulator at room temperature. Xe lamp was used as light source to illuminate AM 1.5 sun light which corresponds to the intensity of 100 mW/cm<sup>2</sup>.

## 3. Results and Discussions

**3.1. Structural Properties.** Microstructural properties of the CuGaSe<sub>2</sub> thin films were studied by scanning electron microscope (SEM). Sample structure for this experiment was considered as CuGaSe<sub>2</sub>/Mo/SLG. Figures 1(a)–1(d) show the SEM images of the surface view of several CuGaSe<sub>2</sub> thin films grown with various Ga/Ca in the films. The amount of the Ga/Cu ratio in the film strongly influences the morphology and structure of the film including the grain size and shape [15]. Films with near stoichiometric composition having Ga/Cu = 1.05 show the best morphology with large uniform grains as seen from Figure 1(c). No void or impurity phase was seen on the surface of the film. With increasing the Ga content in the film (Figure 1(b)), no apparent reduction in grain size was observed. However, overall morphology deteriorates. Some minor phase precipitates were observed at grain boundary locations of the facet-like grains. For further increase of the Ga content (e.g., Ga/Cu = 2.03), film was found to be associated with smaller grains covered with melted-like impurity phases as seen in Figure 1(a). With an increase in the bulk Ga/Cu ratio (i.e., with a decrease of Cu content) in the film above the stoichiometry, structural modification occurs which starts from the surface of the film directing along the depth of the film towards the substrates [16]. Therefore, we believe impurity phases covering the surface region of the Ga-rich films might originate from the ordered defect compounds (e.g., CuGa<sub>3</sub>Se<sub>5</sub>) which is also known as defect chalcopyrite.

General tendency of the grain size in the film being smaller with increasing Ga/Cu ratio in our study is consistent with the observation of various authors where they reported that Cu-rich films usually are associated with larger grains than that of Cu-poor films [17, 18]. Schlenker et al. [19] calculated the activation energy for grain boundary motion as a function of Cu content in the CIGS thin films. Higher Cu contents lead to the lower activation energies and therefore to the formation of larger grains. This calculation explains our observation of smaller grains in Ga-rich films as seen from the surface view of the films. On the contrary, relatively smaller grain in the Cu-rich film with Ga/Cu = 0.89 can be explained by the formation of Cu<sub>2-x</sub>Se phases between CuGaSe<sub>2</sub> grains, that hinder the lateral growth of the CuGaSe<sub>2</sub> grains resulting in smaller grains [20]. Void appeared in the Cu-rich film can be attributed to the difference of the growth rate between inherent CuGaSe<sub>2</sub> grains and converting grains during the final stage of the film growth.

To get the structural properties of the bulk of the films, we have examined SEM images of the cross-sectional view of the similar sets of the samples, as shown in Figures 2(a)–2(d). Unlike the surface morphology and grain size, the cross-sectional view was not significantly influenced by the variation of Ga/Cu ratio in the films. Ordered columnar grains, orientated with respect to Mo back contact, were observed for the near stoichiometric film with Ga/Cu = 1.05. No significant change in grain size and orientation was observed when Ga content in the film was increased. However, some smaller grains were accumulated at the

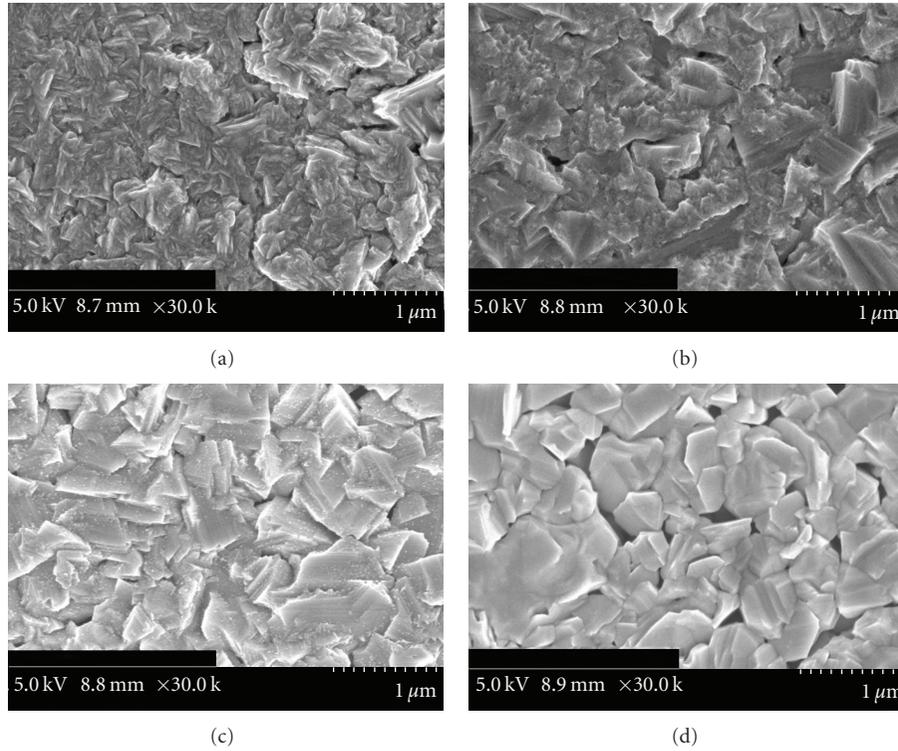


FIGURE 1: SEM images of the surface view of the as-grown  $\text{CuGaSe}_2$  thin films. Various  $\text{CuGaSe}_2$  layers were grown with changing Ga/Cu ratio in the film (a) Ga/Cu = 2.04, (b) Ga/Cu = 1.45, (c) Ga/Cu = 1.05, and (d) Ga/Cu = 0.89.

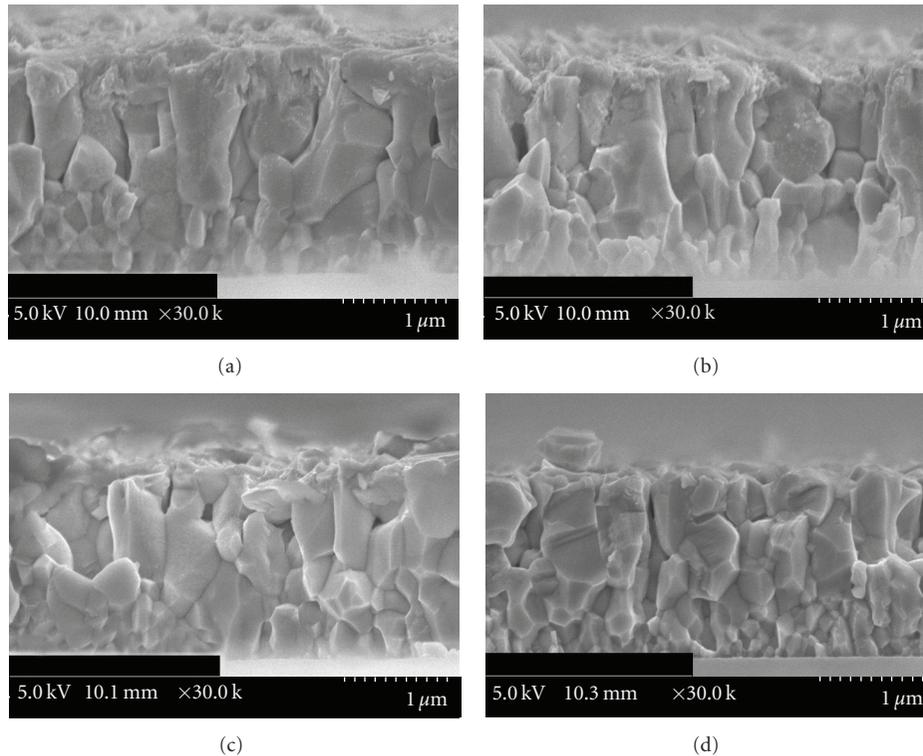


FIGURE 2: Cross-sectional SEM images of the as-grown  $\text{CuGaSe}_2$  thin films. Various  $\text{CuGaSe}_2$  layers were grown with changing Ga/Cu ratio in the film (a) Ga/Cu = 2.04, (b) Ga/Cu = 1.45, (c) Ga/Cu = 1.05, and (d) Ga/Cu = 0.89.

interface of Mo substrate and CuGaSe<sub>2</sub> absorber. Again, highly Cu-rich (Ga/Cu = 0.89) sample exhibits relative smaller columnar grains associated with smaller grains on the side of the Mo back contact.

We explain the above phenomenon as follows: in our three-stage growth system, Cu and Se material were coevaporated at the 2nd stage of growth process. To get overall improved electrical properties with larger grain size, Cu flux was irradiated until Cu/Ga in the film becomes 1.3 at the end of the 2nd stage [21]. Therefore, the columnar-grain orientation and size along the depth towards the substrate should be nominally similar up to second stage of the growth process. However, according to the phase diagram, under this Cu-rich condition, excess Cu can only be in form of Cu-Se phase in Cu-Ga-Se system [22] that preferably segregates on the surface of the film along the growth direction. According to the Cu-Se binary phase diagram [22], Cu-Se can exist as quasiliquid form at the growth temperature of ~520°C at the 2nd stage. Therefore, finally, at the 3rd stage of the growth procedure, when this quasiliquid phase is exposed to the Ga and Se fluxes under the environment of sufficient Se vapor pressure, it contributes to form the CuGaSe<sub>2</sub> film via several vapor-liquid-solid mechanisms [21, 23]. The duration of the Ga and Se flux irradiation finally decides overall Ga/Cu ratio in the film. For Ga-rich samples in our study, the longer duration of Ga and Se flux assists excess Ga and Se to incorporate into the solid system through the formation of V<sub>Cu</sub> and Ga<sub>Cu</sub> antisites defect which eventually initiate structural transition at the near surface region. This structural reformation produces defect chalcopyrite phase, for example, CuGa<sub>3</sub>Se<sub>5</sub> and so forth, starting from the surface along the depth of the film. Therefore, surface of the film should exhibit primarily the characteristic change in grain size and morphology, while bulk of the film may remain nearly identical as observed from the cross-sectional view of the samples in this study. Then, relatively smaller columnar grains, observed at the film with Ga/Cu = 0.89 (Cu/Ga ~ 1.12), can be explained by the variation of growth procedure where composition at the end of the 2nd stage may exceed the threshold value of Cu/Ga = 1.3.

**3.2. Electrical Properties.** For the Hall effect measurement, CuGaSe<sub>2</sub> films were grown directly over SLG and cut into 5 × 5 mm<sup>2</sup> of sizes. Indium was used as ohmic contact electrode. Table 1 lists the majority carrier concentration and the electrical resistivity of several CuGaSe<sub>2</sub> films grown with various Ga/Cu ratio in the film. The film with lower Ga/Cu ratio (Cu at. % = 26.15) has the resistivity of 16.1 Ω-cm which increased up to value of 99.4 Ω-cm when increasing the Ga/Cu ratio to 2.04 (i.e., reducing the Cu content to 15 at. %). The resistivity thus depends on the Ga/Cu ratio in the film. Similarly the hole carrier concentration generally decreases with increasing Ga/Cu ratio in the film.

The general tendency of the increasing of resistivity and decreasing of hole carrier concentration with increasing Ga/Cu ratio in our films can be explained by the structural

TABLE 1: Electrical properties of various CuGaSe<sub>2</sub> thin films having different Ga/Cu ratio in the film. Electrical properties were determined by van der Pauw Hall measurement method at room temperature. CuGaSe<sub>2</sub> films were grown directly over SLG and cut into 5 × 5 mm<sup>2</sup> of sizes, for the measurement.

Ga/Cu	Resistivity (Ω-cm)	Carrier concentration (cm <sup>-3</sup> )
0.89	88.5	5.8 × 10 <sup>15</sup>
0.96	16.1	2.0 × 10 <sup>16</sup>
1.05	16.3	1.5 × 10 <sup>16</sup>
1.45	34.2	6.9 × 10 <sup>15</sup>
2.04	99.4	6.0 × 10 <sup>15</sup>

properties as studied by SEM images in Figures 1(a)–1(d). The lowering of Cu content (i.e., increasing Ga/Cu ratio) in the film resulted in smaller grain size which is responsible for increased grain boundary in the film. The carrier transport properties are greatly influenced by the increased grain boundary in polycrystalline thin films resulting in the increased resistivity and reduced free carrier concentration [24]. These inferior structural properties are primarily responsible for degraded electrical properties in the Ga-rich films. Thus, poor electrical properties in the film with smaller grain can explain the higher resistivity and reduced carrier concentration in our Cu-rich film with Ga/Cu = 0.89.

As we have mentioned earlier that decreasing of Cu content in the film is associated with the V<sub>Cu</sub> and Ga<sub>Cu</sub> antisites type defects which are the building block of ordered defect phase like CuGa<sub>3</sub>Se<sub>5</sub>, CuGa<sub>5</sub>Se<sub>8</sub>, and so forth. It is reported that polycrystalline CuIn<sub>3</sub>Se<sub>5</sub> is *n*-type material and highly resistive with the resistivity of around ~10<sup>7</sup> Ω-cm and with lower carrier concentration [25]. Thus, taking into account that Ga-rich samples in this study could be bilayer structure of chalcopyrite and ordered defect phase, we can consider that this defect phase is one of the reasons for poor electrical properties of CuGaSe<sub>2</sub> thin film when Ga/Cu ratio was increased. Moreover, although we did not make a systematic study of the effect of Na in our grown CuGaSe<sub>2</sub> films, the increased amount of the diffused Na in the Ga-rich film (due to longer deposition time) may segregate on the surface of the film and drive to form Na-induced defect phase which is based on defect-chalcopyrite structure similar to that of CuGa<sub>3</sub>Se<sub>5</sub> as proposed by Nadenau et al. [26]. Therefore, this defect phase may also affect the electrical properties of the Ga-rich film.

**3.3. Solar Cell Performances.** To understand the effect of Ga/Cu variation in the absorber layer, over the solar cell performance, we have fabricated several CuGaSe<sub>2</sub> based solar cell structure using the corresponding absorber layer. The device structure becomes Al/Al:ZnO/*i*-ZnO/CdS/CuGaSe<sub>2</sub>/Mo/SLG. Any segregated Cu-Se phase on the surface of all the CuGaSe<sub>2</sub> films was etched off with KCN solution prior to the fabrication of following buffer layer; therefore, the effect of surface Cu-rich phase can be discarded over the solar cell performances. The resulting illuminated *I*-*V* characteristic curves of the fabricated CuGaSe<sub>2</sub> solar cells

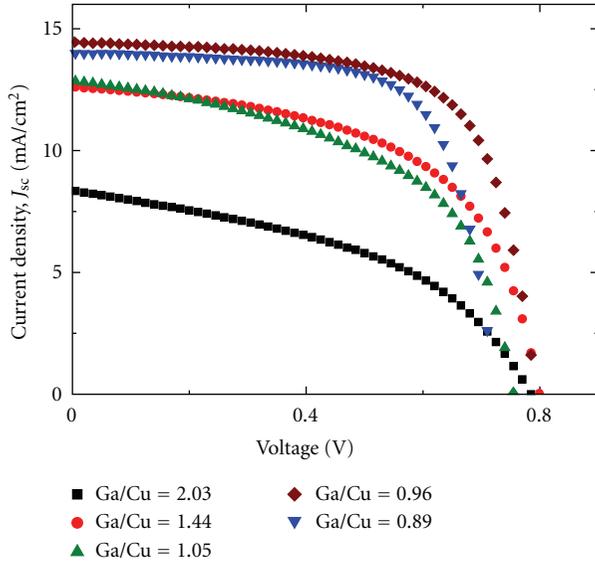


FIGURE 3:  $I$ - $V$  characteristics of various  $\text{CuGaSe}_2$  thin film solar cells measured by solar simulator under the illumination of AM1.5 which corresponds to the light intensity of  $100 \text{ mW/cm}^2$ . The active area of the cell was  $0.465 \text{ cm}^2$ .

are shown in Figure 3. It is clear from the figure that all the devices suffer from the higher series resistance as evident from the slope of the higher voltage region of the curve. However, the resistivity increases with increasing Ga/Cu ratio in the film. Also the shunt resistance is lower for the device fabricated with the  $\text{CuGaSe}_2$  absorber layer with higher Ga/Cu ratio. The shunt resistance becomes higher with reducing Ga/Cu ratio in the film. The higher series resistance and reduced shunt resistance in the Ga-rich  $\text{CuGaSe}_2$  based solar cell resulted in the lower fill factor in the  $I$ - $V$  curve. The poor junction properties of the Ga-rich solar cell as evident from the illuminated  $I$ - $V$  curve were also reflected in the ideality factor of the junction. An increase in the Ga/Cu ratio in the absorber layer was found to increase the ideality factor of the solar cells as measured from the dark  $I$ - $V$  curve using a one diode model. The increased ideality factor indicates the degradation of the junction properties of the Ga-rich  $\text{CuGaSe}_2$  based solar cell associated with increased recombination centers at the absorber-buffer junction. This may arise from the formation of the junction with defect-rich phase having poor electrical properties and the buffer layer.

The performance parameters of the fabricated solar cell have been plotted in Figure 4. Open circuit voltage,  $V_{oc}$ , seems to be insensitive to the Ga/Cu ratio in the film, while fill factor, FF, and short circuit current density,  $J_{sc}$ , were significantly influenced by the Ga/Cu ratio. Improved FF and  $J_{sc}$  in Cu-rich film can be explained by the improved morphology and structural properties of the absorber layer associated with improved electrical properties with increasing Cu-content. This improved FF and  $J_{sc}$  resulted in the increase of the cell efficiency when Ga/Cu ratio was reduced up to the near stoichiometric composition (in this study Ga/Cu = 0.96). When composition deviates from the stoichiometry to more Cu-rich composition (more reduced

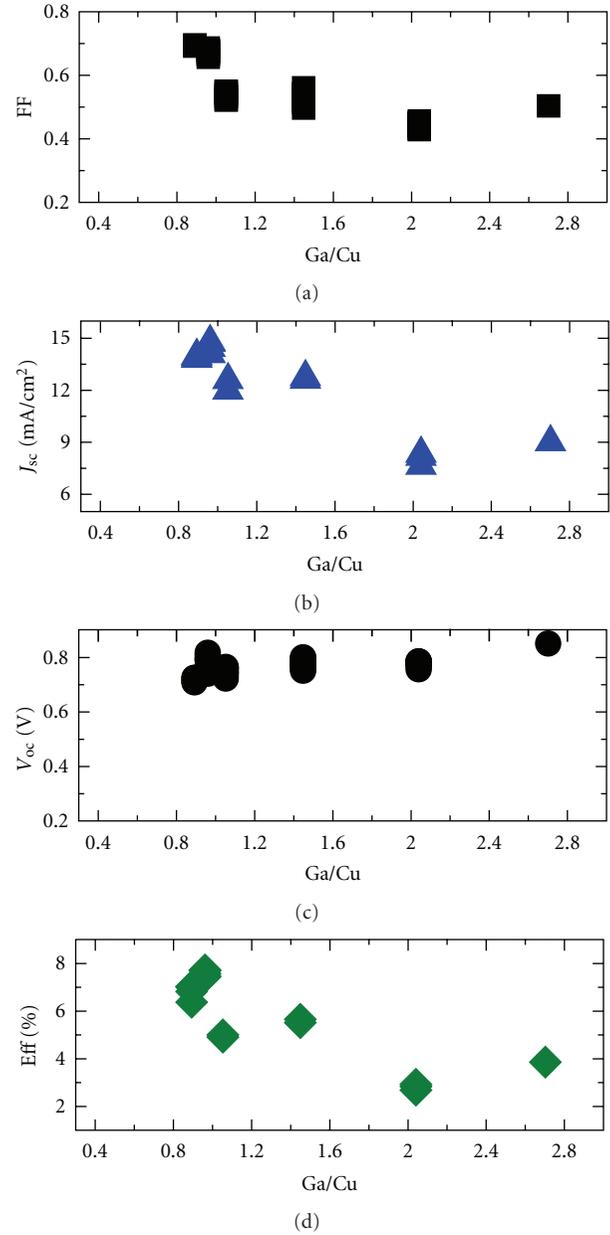


FIGURE 4: Device parameter of various  $\text{CuGaSe}_2$  thin film solar cells as a function of Ga/Cu ratio in the  $\text{CuGaSe}_2$  absorber layer.

Ga/Cu ratio), device performance starts to decrease mainly due to the adverse effect of Cu-rich secondary phase in the absorber layer. Thus, Ga/Cu ratio in  $\text{CuGaSe}_2$  film plays an important role over the performance of solar cell.

#### 4. Conclusion

The effects of Ga/Cu ratio on the properties of  $\text{CuGaSe}_2$  thin films as well as on the solar cell performance were examined. For higher Ga/Cu ratio, over all structural properties and electrical properties of the  $\text{CuGaSe}_2$  thin films degraded which deteriorates the solar cell performance fabricated with the corresponding films. Possible origin of the degraded

material properties of the Ga-rich films can be attributed to the formation of the  $V_{Cu}$  and  $Ga_{Cu}$  type defects which eventually forms Cu-poor defect related phase of inferior material properties. On the contrary, material properties of the Ga-poor (i.e., Cu-rich) samples are influenced by the formation of Cu-Se related phase. Performance of the fabricated solar cell based on the corresponding absorber layers was found to be strongly correlated with the Ga/Cu ratio in the films. Within the range of Ga/Cu ratio, examined in this study, optimum Ga/Cu ratio close to the stoichiometry was found to be preferable to get better material properties and device performance as well.

## References

- [1] I. Repins, M. A. Contreras, B. Egaas et al., "19.9%-efficient ZnO/CdS/CuInGaSe<sub>2</sub> solar cell with 81.2% fill factor," *Progress in Photovoltaics*, vol. 16, no. 3, pp. 235–239, 2008.
- [2] W. Shockley and H. Queisser, "Detailed balance limit of efficiency of *p-n* junction solar cells," *Journal of Applied Physics*, vol. 32, no. 3, pp. 510–519, 1961.
- [3] S. Chichibu, T. Mizutani, K. Murakami et al., "Band gap energies of bulk, thin-film, and epitaxial layers of CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>," *Journal of Applied Physics*, vol. 83, no. 7, pp. 3678–3689, 1998.
- [4] S. Nishiwaki, S. Siebentritt, P. Walk, and M. Ch. Lux-Steiner, "A stacked chalcopyrite thin-film tandem solar cell with 1.2 V open-circuit voltage," *Progress in Photovoltaics*, vol. 11, no. 4, pp. 243–248, 2003.
- [5] V. Nadenau, D. Hariskos, and H. W. Schock, "CuGaSe<sub>2</sub> based thin film solar cells with improved performance," in *Proceedings of the 14th European Photovoltaic Solar Energy Conference*, H. S. Stephens, Ed., vol. 85, pp. 1250–1253, Bedford, UK, 1997.
- [6] M. Saad, H. Riazi, E. Bucher, and M. Ch. Lux-Steiner, "CuGaSe<sub>2</sub> solar cells with 9.7% power conversion efficiency," *Applied Physics A*, vol. 62, no. 2, pp. 181–185, 1996.
- [7] M. M. Islam, T. Sakurai, S. Ishizuka et al., "Effect of Se/(Ga+In) ratio on MBE grown Cu(In,Ga)Se<sub>2</sub> thin film solar cell," *Journal of Crystal Growth*, vol. 311, no. 7, pp. 2212–2214, 2009.
- [8] R. Noufi, R. Axton, C. Herrington, and S. K. Deb, "Electronic properties versus composition of thin films of CuInSe<sub>2</sub>," *Applied Physics Letters*, vol. 45, no. 6, pp. 668–670, 1984.
- [9] M. M. Islam, A. Uedono, S. Ishibashi et al., "Impact of Cu/III ratio on the near-surface defects in polycrystalline CuGaSe<sub>2</sub> thin films," *Applied Physics Letters*, vol. 98, no. 11, Article ID 112105, 2011.
- [10] A. J. Nelson, A. B. Swartzlander, J. R. Tuttle, R. Noufi, R. Patel, and H. Hochst, "Photoemission investigation of the electronic structure at polycrystalline CuInSe<sub>2</sub> thin-film interfaces," *Journal of Applied Physics*, vol. 74, no. 9, pp. 5757–5760, 1993.
- [11] P. Fons, S. Niki, A. Yamada, and H. Oyanagi, "Direct observation of the Cu<sub>2-x</sub>Se phase of Cu-rich epitaxial CuInSe<sub>2</sub> grown on GaAs (001)," *Journal of Applied Physics*, vol. 84, no. 12, pp. 6926–6928, 1998.
- [12] M. M. Islam, T. Sakurai, A. Yamada et al., "Determination of Cu(In<sub>1-x</sub>Ga<sub>x</sub>)<sub>3</sub>Se<sub>5</sub> defect phase in MBE grown Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> thin film by Rietveld analysis," *Solar Energy Materials & Solar Cells*, vol. 95, no. 1, pp. 231–234, 2011.
- [13] D. Schmid, M. Ruckh, F. Grunwald, and H. W. Schock, "Chalcopyrite/defect chalcopyrite heterojunctions on the basis of CuInSe<sub>2</sub>," *Journal of Applied Physics*, vol. 73, no. 6, pp. 2902–2909, 1993.
- [14] K. Sakurai, R. Hunger, N. Tsuchimochi et al., "Properties of CuInGaSe<sub>2</sub> solar cells based upon an improved three-stage process," *Thin Solid Films*, vol. 431–432, pp. 6–10, 2003.
- [15] J. R. Tuttle, D. S. Albin, and R. Noufi, "Thoughts on the microstructure of polycrystalline thin film CuInSe<sub>2</sub> and its impact on material and device performance," *Solar Cells*, vol. 30, no. 1–4, pp. 21–38, 1991.
- [16] M. M. Islam, A. Yamada, T. Sakurai et al., "Cu-dependent phase transition in polycrystalline CuGaSe<sub>2</sub> thin films grown by three-stage process," *Journal of Applied Physics*, vol. 110, Article ID 014903, 5 pages, 2011.
- [17] U. Rau and H. W. Schock, "Electronic properties of Cu(In,Ga)Se<sub>2</sub> heterojunction solar cells-recent achievements, current understanding, and future challenges," *Applied Physics A*, vol. 69, no. 2, pp. 131–147, 1999.
- [18] R. Klenk, T. Walter, H. W. Schock, and D. Cahen, "A model for the successful growth of polycrystalline films of CuInSe<sub>2</sub> by multisource physical vacuum evaporation," *Advanced Materials*, vol. 5, no. 2, pp. 114–119, 1993.
- [19] T. Schlenker, M. Luis Valero, H. W. Schock, and J. H. Werner, "Grain growth studies of thin Cu(In, Ga)Se<sub>2</sub> films," *Journal of Crystal Growth*, vol. 264, no. 1–3, pp. 178–183, 2004.
- [20] R. Caballero, S. Siebentritt, K. Sakurai, C. A. Kaufmann, H. W. Schock, and M. Ch. Lux-Steiner, "Effect of Cu excess on three-stage CuGaSe<sub>2</sub> thin films using in-situ process controls," *Thin Solid Films*, vol. 515, no. 15, pp. 5862–5866, 2007.
- [21] S. Nishiwaki, N. Kohara, T. Negami, H. Miyake, and T. Wada, "Microstructure of Cu(In,Ga)Se<sub>2</sub> films deposited in low Se vapor pressure," *Japanese Journal of Applied Physics*, vol. 38, no. 5, pp. 2888–2892, 1999.
- [22] J. C. Mikkelsen Jr., "Ternary phase relations of the chalcopyrite compound CuGaSe<sub>2</sub>," *Journal of Electronic Materials*, vol. 10, no. 3, pp. 541–558, 1981.
- [23] J. R. Tuttle, M. Contreras, M. H. Bode et al., "Structure, chemistry, and growth mechanisms of photovoltaic quality thin-film Cu(In,Ga)Se<sub>2</sub> grown from a mixed-phase precursor," *Journal of Applied Physics*, vol. 77, no. 1, pp. 153–161, 1995.
- [24] M. Chen, Z. L. Pei, X. Wang et al., "Intrinsic limit of electrical properties of transparent conductive oxide films," *Journal of Physics D*, vol. 33, no. 20, pp. 2538–2548, 2000.
- [25] T. Negami, N. Kohara, M. Nishitani, and T. Wada, "Preparation of ordered vacancy chalcopyrite-type CuIn<sub>3</sub>Se<sub>5</sub> thin films," *Japanese Journal of Applied Physics*, vol. 33, no. 9, pp. L1251–L1253, 1994.
- [26] V. Nadenau, G. Lippold, U. Rau, and H. W. Schock, "Sodium induced secondary phase segregations in CuGaSe<sub>2</sub> thin films," *Journal of Crystal Growth*, vol. 233, no. 1–2, pp. 13–21, 2001.



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