한국표면공학회지
J. Kor. Inst. Surf. Eng.
Vol. 37, No. 4, 2004.
<연구논문>

Effect of Ga, S Additions in CuInSe$_2$ for Solar Cell Applications

Kyoo-Ho Kim*

School of Metallurgical and Materials Engineering, Yeungnam University
Gyongsan, Republic of Korea 712-749

(Received 7 June 2004 ; accepted 10 August 2004)

Abstract

Gallium or sulphur additions in CuInSe$_2$ were prepared using RF magnetron sputtering and pulsed laser deposition respectively. All of the observed thin films shows a chalcopyrite structure with the S and Ga addition increases the favourable (112) peak. The optical absorption coefficients were slightly decreased. The energy band gap of films could be shifted from 1.04 to 1.68 eV by adjusting the mole ratio of S/(S+Se) and Ga/(In+Ga). It is possible to obtain the optimum energy band gap by adding S or Ga solute at a certain ratio in favour of Se and In respectively. It is also necessary to control the ratio of Ga and S additions and to retain a certain portion of In and Se to provide better properties of thin films.

Keywords : Ga, S addition, CuInSe$_2$, Solar cell

1. INTRODUCTION

Demand for renewable energies has been increased during the last two decades. One of the potential resources is solar energy. CuInSe$_2$ (CIS) semiconductor of chalcopyrite structure has been considered as one of the promising absorber materials for solar cell applications with reported efficiency exceeded 15%[1]. It has a band gap energy E_g of 1.04 eV, which is lower than the optimum band gap energy of solar cells corresponds with solar spectra. The compound of Cu(In$_x$Ga$_{1-x}$)(S$_y$Se$_{1-y}$)$_2$ can have an energy band gap between 1.0 eV to 1.7 eV, which is very interesting for aiming higher conversion efficiency[2,3]. In addition, large attention also has been given to employ a low cost and high efficient deposition process for better performance.

It is of great interest to study the effect of alloying in CIS because different chemical composition can possess a significant difference in the properties. This paper deals with the effect of Ga and S addition in CIS. Properties of the thin film solar cell absorbers were observed. Gradual substitution of Ga and S for In and Se is mainly expected to provide a more suitable band gap and thus more efficient conversion efficiency. In addition, this study is also aimed to reduce fabrication cost and film toxicity because of the In and Se employment.

2. EXPERIMENT

The addition of S in CIS thin films was prepared using RF magnetron sputtering from binary powder target compounds of high purity Cu$_2$Se, In$_2$Se$_3$, Cu$_2$S and In$_2$ S$_3$ (99.999%), while the addition of Ga was done using pulsed laser deposition (PLD) from high purity powder element of Cu, In, Ga and Se (99.999%). The ratios of S/(S+Se) target were x = 0, 0.25, 0.5, 0.75 and 1, obtained from the following equation:

$$x = \frac{a(Cu_2S + In_2S_3)}{a(Cu_2S + In_2S_3) + b(Cu_2Se + In_2Se_3)}$$

The In/(In+Ga) ratio were x = 0, 0.2, 0.4, 0.6, 0.8 and 1. They were obtained by the changes of the composition ratio of the targets. Both of the thin films deposited on 7059 corning glass substrates at a working pressure of 10^{-2} Torr. The deposition conditions are given in Table 1.

The surface morphologies of the deposited thin films were studied by scanning electron microscopy

---

*Corresponding author. E-mail : khokim@yu.ac.kr

Table 1. Deposition conditions

	Pulsed Laser Deposition	RF Magnetron Sputtering
Laser source, Pulse width	ArF (λ = 193 nm), 25 ns	-
Laser/RF power	140 mJ/pulse, Rep rate 8Hz	100 W
Substrate temperature	450°C	400°C
Deposition time	60 min	120 min

(SEM), and the bulk compositions were determined with Energy Dispersive X-ray Spectroscopy (EDX) Fisons KEVEX Superdry at 20 kV. The phases and the crystallographic structure of the compound films were determined by X-ray Diffractometer (XRD) Rigaku-RINT 2200, using Cu $K\alpha_1$ radiation 1.5406Å, Ni-filter. Optical absorption coefficients and band gap energy of the thin films were observed by UV-Visible NIR spectrophotometer Hitachi 330 in the λ range of 2500~400 nm.

3. RESULTS AND DISCUSSION

3.1 Composition Ratio of Films

Composition ratio of the targets and the deposited thin films is given in Fig. 1. The deviation can be seen clearly when using RF magnetron sputtering for S/(S+Se) compare to only slightly deviation when using PLD for In/(In+Ga).

The above results show that PLD is a more effective process to obtain a film with less deviation from the target, but RF sputtering offers more simple and economic process. Generally, it is possible to control the composition of deposited films using both methods by controlling of the target compositions.

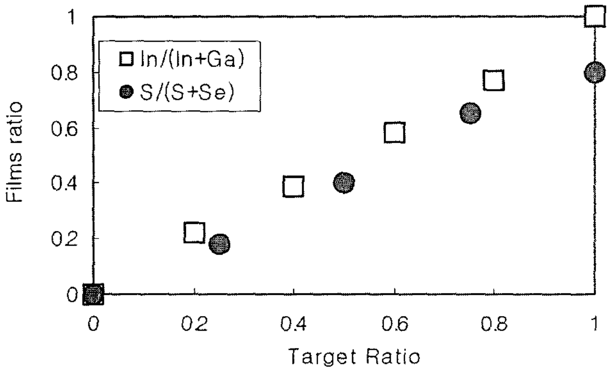


Fig. 1. Composition ratio of target and deposited thin films.

3.2 Structure of Films

The XRD patterns, as given in Fig. 2, show the thin films are strongly oriented on the (112) plane with the increase of S/(S+Se) mole ratio. It can be expected to exhibit higher optical conversion efficiency as resulted from (112) plane, which is the preferred orientation in the CIS thin films[4]. On the other hand, the (112) peak decreases with the addition of Ga, while the (204)(220) peak increase. The latter peak correspond to the formation of $CuGaSe_2$ structure, which shows the highest intensity at x = 0. To some extent, the addition of S and Ga behaves oppositely in this way. According to all of the above XRD patterns, regardless the mole ratios (0 < x < 1) of Ga and S with respect to In and Se, it was found that all

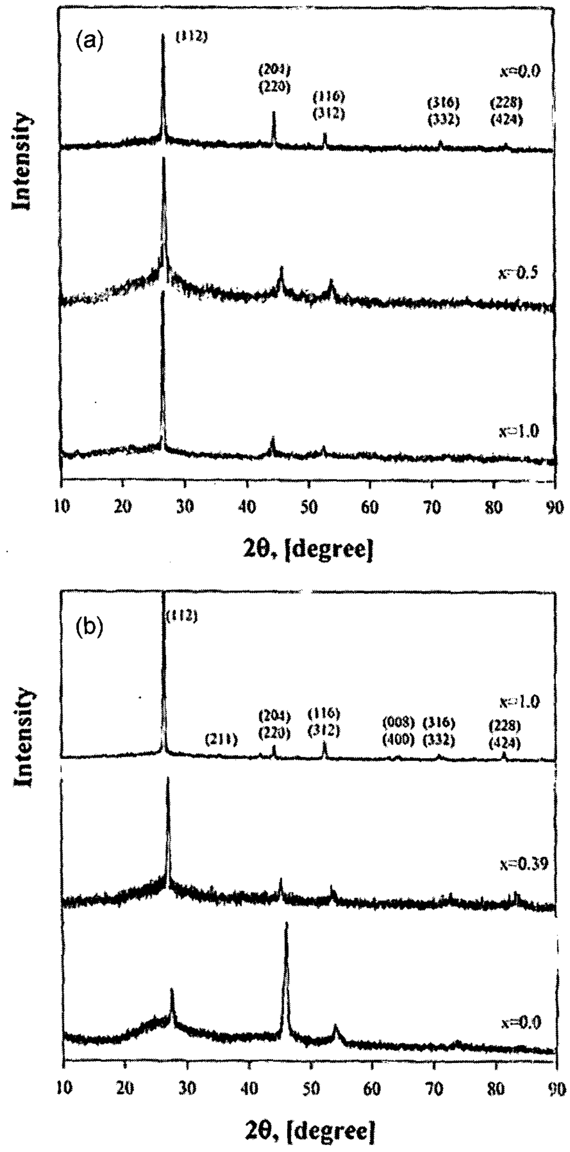


Fig. 2. XRD pattern for different ratio (a) x = S/(S+Se), (b) x = In/(In+Ga).

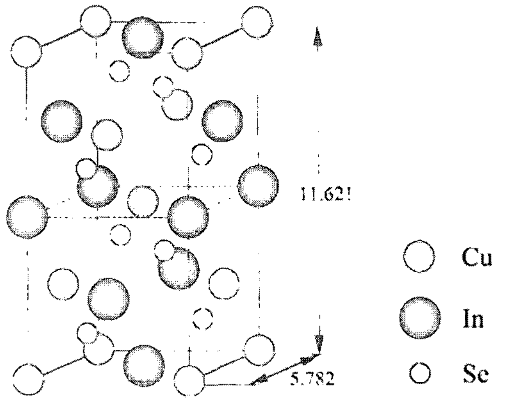


Fig. 3. Chalcopyrite structure of CIS.

of the deposited thin films show a chalcopyrite structure as confirmed by the majority of (112) and (204)(220) peaks. However, considering the beneficial effect of the (112) peak, it is necessary to retain the presence of In in the compound.

Lattice parameters (*a* and *c*) of the chalcopyrite structure (given in Fig. 3) can be calculated from the XRD spectra using the following equation:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

Upon S addition, the values of *a* and *c* are 5.74~5.51 and 11.49~11.12, while Ga addition gives the value of 5.76~5.61 and 11.58~11.09 respectively. From the calculation of change in lattice parameters ratio (*c/a*) it can be concluded the S addition increases the *c/a* ratio from 2.00 to 2.02 while upon the Ga addition the ratio decreases from 2.01 to 1.98 respectively. Yamaguchi[4] reported that the suitable ratio of a chalcopyrite structure for solar cell applications is around 2.0.

3.3 Optical Properties and Band Gap Energy

Optical absorption coefficient, α of the thin films observed by UV-Visible NIR spectrophotometer is given in Fig. 4. The optical absorption coefficient, α, slightly decreases with the addition of S and Ga. All the thin films have the α value at the range 10^3 to 10^5 cm^{-1}, which is a suitable value for solar cell absorber materials. The absorption band shifts to higher photon energy as increasing of the S/(S+Se) and Ga/(Ga+In) ratio.

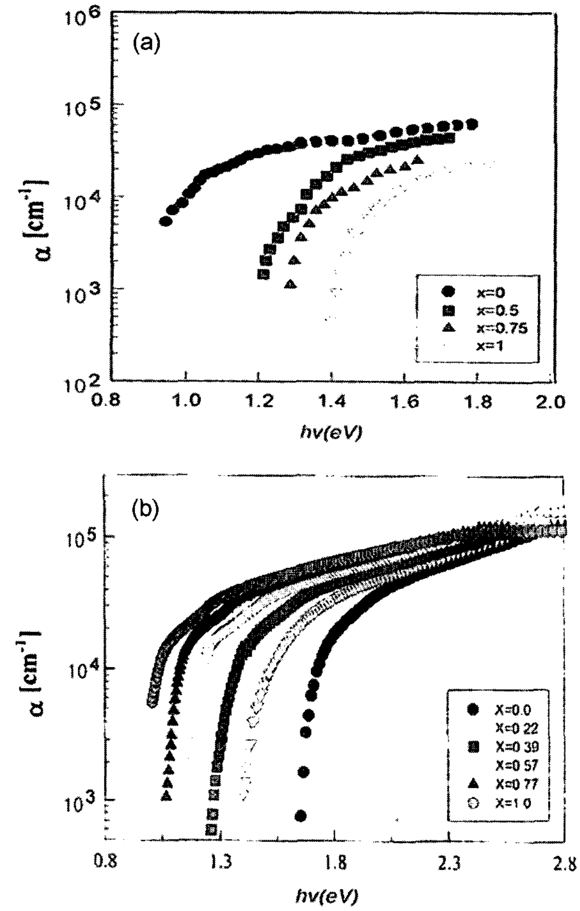


Fig. 4. Optical absorption coefficient of thin films for x = (a) S/(S+Se) ratio and (b) In/(In+Ga) ratio.

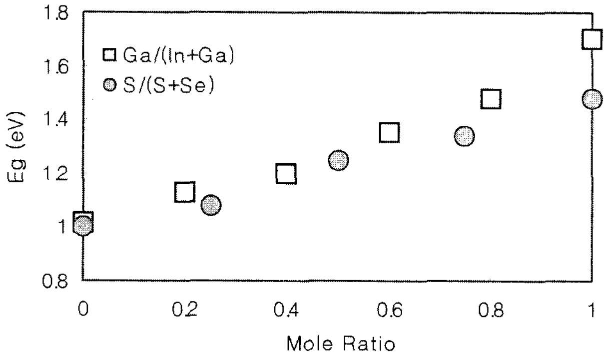


Fig. 5. Energy band gap of deposited films as a function of composition ratio.

Band gap energy (E_g) of the films was calculated using Dubrovski equation[5] derived from α. Basically, in a direct transition semiconductor like CIS, as shown by the shape α transition spectra, band gap energy can be related by,

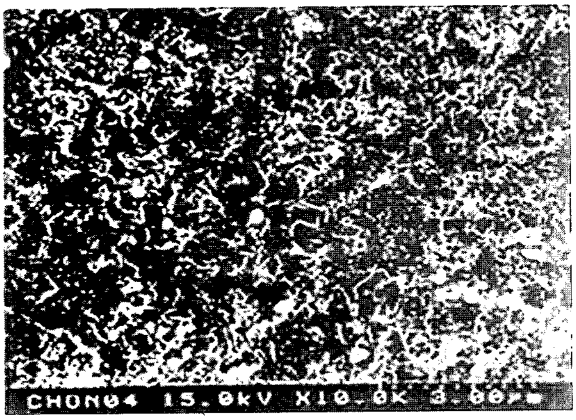
$$\alpha^2 = h\nu - E_g$$

where *h* is Planck's constant and ν is frequency of the incident photon. It shows that the addition of S increases E_g from 1.02 eV to 1.48 eV, while the addition of Ga also increases E_g from 1.00 to 1.64 eV.

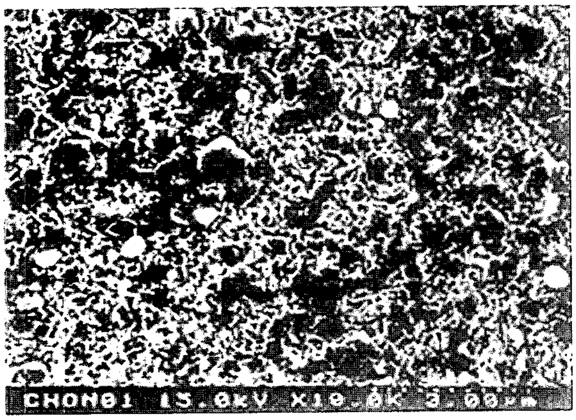
Fig. 5 shows the energy band gap observed by photo-reflectance for CIS and E_g is varied by the composition ratio of CIS thin films. The value of E_g

is increased up to 1.48 eV with the full addition of S and 1.68 eV with Ga. These results are correspond to the result of $CuIn(S_xSe_{1-x})_2$ reported by Schock[6] and the Bowing phenomena of E_g in $Cu(In_xGa_{1-x})Se_2$ reported by Walter[7] and Rincon[8].

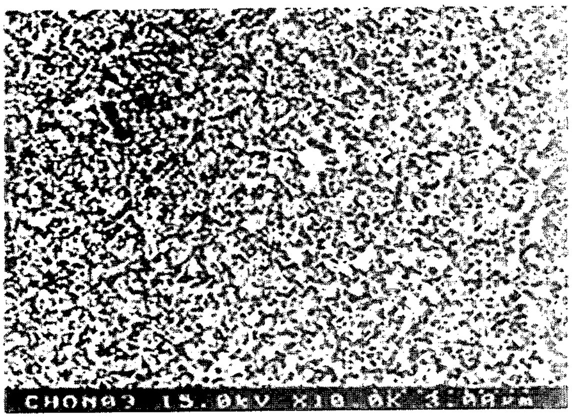
Considering the optimum E_g value for solar cell absorber of 1.4~1.5 eV, one can expect that, in the $Cu(In_xGa_{1-x})(S_ySe_{1-y})_2$ compound system, the composition ratio of S/(S+Se) is suitable in the range of 0.7~0.9 and the Ga/(In+Ga) ratio in the range of 0.6~0.8 in order to achieve a better performance.



(a) x = 0



(b) x = 0.5



(c) x = 1

Fig. 6. SEM micrograph of $CuInSe_2$ thin films (a) with the addition of S solute (b) where x = S/(S+Se) and with the addition of Ga solute (c) where x = Ga/(In+Ga) of Cu(In Ga) Se_2.

3.4 Microstructure

The microstructure of the thin films, as observed by SEM and given in Fig. 6. It shows that the addition of Ga (c) provides finer grain size. This effect is not clearly seen in S addition (b). It is believed that the grain size is affected by the solute addition and deposition method.

Generally, finer grain size exhibits lower absorption coefficient[4], therefore, it is necessary to control the ratio of Ga addition with respect to In. One can also consider of performing extra heat treatment in order to increase the grain size, as reported by Mitchell, *et al.*[9].

4. CONCLUSIONS

CISS and CIGS thin films for solar cell absorber applications were prepared by RF magnetron sputtering and pulsed laser deposition methods. All of the observed thin films show a chalcopyrite structure as confirmed by the majority of (112) and (204)(220) peaks, regardless the change in mole ratio of S/(S+Se) and Ga/(In+Ga). S addition increases the favourable (112) peak, while Ga addition increases the favourable (204)(220) peaks.

The optical absorption coefficients slightly decrease by increasing the mole ratio of S/(S+Se) and Ga/(In+Ga). Addition of Ga provides finer grain size in the microstructure.

The energy band gap of CISS shifts from 1.04 to 1.48 eV by adjusting the S/(S+Se) mole ratio and the energy band gap of CIGS shifts from 1.00 to 1.68 eV by adjusting the Ga/(In+Ga). It is possible to obtain an optimum energy band gap by adding S and Ga solute at a certain ratio instead of toxicity of Se and expense of In.

It is also necessary to control the ratio of Ga and S additions and to retain a certain portion of In to provide better properties of CIGS thin films. It is possible to control the ratio of deposited films by controlling mole ratio of the target materials.

ACKNOWLEDGMENT

This research was supported by the Yeungnam University research grants.

REFERENCE

1. M. A. Contreras *et al.*, Sol. En. Mat. and Sol. Cel., 41-42 (1996) 231-246.
2. J. M. Stewart *et al.*, Proc. ICTMC-7 ed. by S.K. Deb and A. Zunger, (1987) 59.
3. T. Dullweber *et al.*, Thin Solid Films, 361-362 (2000) 478-481.
4. T. Yamaguchi *et al.*, J. Appl. Phys., 69 (1991) 7714.
5. G. B. Dubrovski, Sov. Phys Solid State, 3 (1961) 943.
6. H. W. Schock *et al.*, J. Appl. Phys., 76 (1994) 2904.
7. T. Walter *et al.*, Thin Solid Films, 224 (1993) 74.
8. C. A. D. Rincon *et al.*, Mat. Chem. and Phys., 70 (2001) 300-304.
9. K. Mitchell *et al.*, IEEE Trans. on Electron Devices, 37 (1990) 410.