O U R N A L O F

Ceramic Processing Research

The preparation of CIGS (Cu(In,Ga)Se₂) by a solution route method

Theeranun Siritanon^{a,*}, Thapanee Sarakonsri^{a,*} and Chanchana Thanachayanont^b

^aDepartment of Chemistry, Faculty of Science, NANOTEC Center of Excellence, Chiang Mai University, Chiang Mai, 50200 Thailand. ^bNational metal and materials technology center, Klong Luang, Pathumthani, 12120 Thailand.

Cu(In,Ga)Se₂ (CIGS) nanoparticles which are used as a precursor material for a CIGS absorber layer for CIGS-based solar cells were successfully synthesized by a simple solution route. The dispersed metal ions were reduced simultaneously in the solutions using zinc particles. The types of solvent, size of zinc particle, and reaction temperature were studied as the parameters of synthesis. The products were characterized by powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Energy dispersive X-ray spectroscopy (EDS). It was found that suitable conditions to synthesize CIGS particles were ethylene glycol as a solvent, zinc powder (45 micrometers) as a reducing agent and 60 degree Celsius as a reaction temperature.

Key words: CIGS, Solution route, Synthesis, Solar cell, Electron microscope.

Introduction

Nowadays, there are significant concerns on environmental problems and the rapid increase in energy consumption. Scientists all over the world are trying to find alternative clean energy sources. Solar cells are one of the most interesting choices because of the cleanness and no limitation in sun power. Solar cells can be divided into two types based on the substances used as semiconductors, which are silicon-based solar cells and solar cells base on other compounds. CIGS {Cu(In,Ga)Se₂} is a p-type semiconductor that has been used as an absorbing layer for a high efficiency solar cell. CIGS has a tetragonal crystal structure with a space group I-42d as shown in Fig 1. Cu atoms are in 0,0,0 positions. Ga/In atoms are in 0,0,1/2 positions. Se atoms are in 0.2574, 1/4,1/8 positions.

Due to the advantages of CIGS-based solar cells which are a cheaper price, more flexibility and lighter weight [1], several methods for preparing the CIGS absorber layer have been developed. Nanoparticle-based spray deposition which is a non-vacuum method used to prepare the absorber layer has some advantages over vacuum coevaporation methods [2]. In nanoparticle-based spray deposition, in which CIGS nanoparticles were used as a precursor, the nanosize-effect lowers the melting temperature of the material so that less energy is required. In addition, it is a less complicated method with a lower processing cost because no vacuum system is needed, and is flexible to scaling up [3].

However, the CIGS nanoparticles precursor material used in nanoparticle-based spray deposition can be prepared



Fig. 1. CIGS compound structure.

by several procedures. For example, a solvothermal route in which Cu, In, Se, and Ga powder were allowed to react at high temperature and pressure [4] and a colloidal process in which CuI, InCl₃, GaI₃ and NaSe₂ were reacted at low temperature [2].

In this study, we introduce a solution process for preparing CIGS nanoparticles. A solution route method has been used for preparing a variety of alloy nanoparticles [5]. With this simple process, ions of metals will be reduced by a suitable reducing agent under suitable conditions. The major benefit of the solution route method is its simplicity because no pressure, vacuum or large amount of heat are needed. The possibility of forming particles and their morphology depend on the condition of synthesis, which are the solvent, type, and size of the reducing agent, reaction temperature, and reaction time.

Therefore, in this research, CIGS were synthesized under different conditions. In order to find a suitable condition, the temperature was varied from 0 °C, to room temperature

^{*}Corresponding author:

Tel : 6653-941907 Fax: 6653-892277

E-mail: theeranun_s@hotmail.com, scchi017@chiangmai.ac.kr

and 60 °C, the reducing agents were zinc powder (45 micrometers) and zinc dust (10 micrometers), and the solvents were ethylene glycol, dimethylsulfoxide, and dimethylformamide.

Materials and Methods

CIGS nanoparticles were synthesized by a solution route using Ga₂(SO₄)₂(99.995%; Aldrich), CuCl₂.2H₂O (99%; Ajax Finechem), InCl₃.nH₂O(39% Indium; Fluka) and SeO₂(97%; Fluka) as sources of ions. Heat and acid treatment (HCl) were used to initiate $Ga_2(SO_4)_2$ dissolution in the solvent. Then CuCl₂,2H₂O, InCl₃.nH₂O, and SeO₂ were dissolved in the solvent which was stirred by a magnetic stirrer. Ethylene glycol (EG) (purity 100.0%, J.T.baker), dimethylsulfoxide (DMSO), (purity 99.5%, AR grade, Sigma-Aldrich), and dimethyformamide (DMF) (purity 99.8%, Carlo Erba) were used as solvents in the conditions as given in Table 1. The reducing agents which were zinc powder (Zn, MW 65.37, purity 99.9%, Ajax chemical), and zinc dust(purity 98+%, Aldrich) were gradually added to reduce the metal ions at controlled temperature before the mixture was ultrasonically agitated for 1 hour. The reaction temperature was held for 12 hours and stirring maintained. After that, the reaction mixture was stirred over night at room temperature. The precipitates were filtered, washed with methanol (purity 100.0%, J.T.Baker) and dried at 60 °C in an oven. The size and morphology of products were investigated by a powder X-ray diffractometer (XRD)(siemenD500/D501, CuKa (\lambda1.54) Ni filter), a scanning electron microscope equipped with an

Results and Discussion Fig. 2, 3 and 4 show powder XRD patterns of synthesized

(TEM) (JEM-2010).

products using ethylene glycol, dimethyl formamide, and dimethyl sulfoxide as solvents respectively. From Fig. 2-4, the characteristic peaks of CIGS particles according to JCPDS No. 40-1488 are found as a major component with only one condition, HEGZ45 which used ethylene glycol as solvent, 45 micrometer zinc particles as reducing

energy dispersive X-ray spectroscope (EDS) (SEM) (JOEL

JSM-5910FE), and a transmission electron microscope



Fig. 2. The XRD patterns of all synthesized products using ethylene glycol as a solvent.

order	CODE —	conditions					
		solvent	Reducing agent; Zinc (μ m)	Temperature (°C)			
1	REGZ45	Ethylene glycol	45	Room			
2	REGZ10	Ethylene glycol	10	Room			
3	RDSZ45	Dimethylsulfoxide	45	Room			
4	RDSZ10	Dimethylsulfoxide	10	Room			
5	RDFZ45	Dimethylformamide	45	Room			
6	RDFZ10	Dimethylformamide	10	Room			
7	HEGZ45	Ethylene glycol	45	60			
8	HEGZ10	Ethylene glycol	10	60			
9	HDSZ45	Dimethylsulfoxide	45	60			
10	HDSZ10	Dimethylsulfoxide	10	60			
11	HDFZ45	Dimethylformamide	45	60			
12	HDFZ10	Dimethylformamide	10	60			
13	CEGZ45	Ethylene glycol	45	0			
14	CEGZ10	Ethylene glycol	10	0			
15	CDSZ45	Dimethylsulfoxide	45	0			
16	CDSZ10	Dimethylsulfoxide	10	0			
17	CDFZ45	Dimethylformamide	45	0			
18	CDFZ10	Dimethylformamide	10	0			

 Table 1. Processing parameters for the synthesis of CIGS nanoparticles.



Fig. 3. The XRD patterns of all synthesized products using dimethyl formamide as a solvent.



Fig. 4. The XRD patterns of synthesized products using dimethyl sulfoxide as a solvent.

agent and 60 °C as the reaction temperature. The three main peaks of CIGS phase appear at 28.017, 46.1194, and 55.7463 degree (2 θ) corresponding to the (112), (220), and (312) planes, respectively. The broadening and shift of the main peaks indicate the product obtained from this synthesis condition is small particles and consists of a mixture of Cu(In,Ga)Se₂ with different ratios of elements. Selenium metal is found as a major component with some other compounds and a small amount of CIGS in all the other conditions.

The EDS results shown in Table 2-4, agree well with the XRD results, indicating that the products obtained from all conditions except HEGZ45 had selenium as the major component. There were different morphologies of selenium, which are hexagonal prisms, rods, and an uncertain morphology, found in different conditions as can be seen from SEM images in Fig. 5-7.

The probable reason for these different forms of selenium is that selenium has many allotropes and hexagonal selenium is the most thermodynamically-stable form which

 Table 2. The EDS results of synthesized products using ethylene glycol as a solvent

order	CODE			%weight		
oruer	CODE -	Cu	In	Ga	Se	0
1	CEGZ45	17.70	0.42	0.0	79.68	2.14
2	CEGZ10	18.81	0.38	0.23	80.58	0.00
3	REGZ45	11.58	0.60	0.00	81.91	1.55
4	REGZ10	16.26	0.87	0.14	82.73	0.00
5	HEGZ45	19.50	8.64	6.01	43.29	17.90
6	HEGZ10	6.77	1.28	3.78	76.50	11.66

Table 3. The EDS results of synthesized products using dimethyl formamide as a solvent

order	CODE			%weight		
order	CODL	Cu	In	Ga	Se	0
1	CDFZ45	18.09	1.00	0.62	71.78	8.50
2	CDFZ10	22.21	2.90	10.58	47.45	16.86
3	RDFZ45	13.85	2.84	3.30	68.05	11.96
4	RDFZ10	23.42	0.00	13.90	49.38	13.29
5	HDFZ45	8.26	2.00	3.67	75.69	10.39
6	HDFZ10	14.29	0.15	9.07	57.20	19.29

 Table 4. The EDS results of synthesized products using dimethyl sulfoxide as a solvent

order	CODE			%weight		
order	CODE	Cu	In	Ga	Se	0
1	CDSZ45	0.26	0.13	0.00	99.61	0.00
2	CDSZ10	3.28	0.76	0.00	95.97	0.00
3	RDSZ45	46.27	0.00	1.42	52.32	0.00
4	RDSZ10	32.27	0.00	3.20	64.54	0.00
5	HDSZ45	9.81	0.85	0.24	89.10	0.00
6	HDSZ10	4.63	0.30	2.65	92.41	0.00

can be formed by heating other allotropes [6] Therefore, selenium formed in the reaction should be favorably turned into the hexagonal structure at higher temperature. There may be, however, many other factors rather than temperature that affects the allotropic form of selenium.

As can be seen in Table 2, the ratio of elements in the HEGZ45 condition was significantly different from all other conditions where more indium and gallium were found and less selenium was detected. Fig. 8 shows high magnification SEM images of the HEGZ45 product. From Fig. 8, the products obtained from the HEGZ45 condition had two different morphologies. The first one was submicrometer plate-like particles whose ratio of elemental components; Cu : In : Ga : Se obtained from the EDS study was 1 : 0.43 : 0.20 : 1.45 which may be written as $CuIn_{0.43}Ga_{0.20}Se_{1.45}$. The other was a group of small particles with a 1 : 0.17 : 0.16 : 1.70 ratio of Cu : In : Ga : Se or $CuIn_{0.17}Ga_{0.16}Se_{1.70}$. The EDS results show several compositions in the CIGS phase which agreed well with the XRD peak broadening (Fig. 2).



Fig. 5. The SEM images of synthesized products using ethylene glycol as a solvent in conditions, (a) CEGZ45, (b) CEGZ10, (c) REGZ45, (d) REGZ10, (e) HEGZ45, (f) HEGZ10.



Fig. 6. The SEM images of synthesized products using dimethyl formamide as a solvent in condition, (a) CDFZ45, (b) CDFZ10, (c) RDFZ45, (d) RDFZ10, (e) HDFZ45, (f) HDFZ10.

The product from the HEGZ45 condition was also studied by TEM as shown in Fig. 9. Fig. 9 shows that the HEGZ45 product particle size was on average 100 nm. The SAD pattern confirmed that the precipitate obtained was CIGS. Fig. 9(b) indicated that the product was well crystallized. The d-spacing measured directly from Fig. 9(b)



Fig. 7. The SEM images of synthesized products using dimethyl sulfoxide as a solvent in condition, (a) CDSZ45, (b) CDSZ10, (c) RDSZ45, (d) RDSZ10, (e) HDSZ45, (f) HDSZ10.



Fig. 8. SEM images of the product synthesized by the HEGZ45 condition, (a) plate-like structure, (b) group of small particles.



Fig. 9. TEM images of products from the HEGZ45 condition.

was 3.17 Å refering to plane (112) of the CIGS compound.

The probable mechanism of product formation via the reduction reaction in solution can be explained by two processes which are the nucleation and the particle growth as shown in Fig. 10. In the nucleation step, metal ions which form complexes with solvent molecules, received electrons from the reducing agent and produced nucleation cores. This process is the coupling between ligand exchange and a charge transfer reaction. After that, the nucleation core acted as a



Fig. 10. Probable mechanism of particle formation [7], (a) nucleation core, (b) growth process.

mixed electrode where two half redox reactions occurred. At one side, the oxidation reaction took place when the reducing agent gave electrons to the surface of the core and at the other side; another metal ion left in the solution received electrons from the core in the reduction reaction [7].

Equation 1-5 [8] shows the standard reduction potentials of each specie. As can be seen, the E_{cell} of the oxidation-reduction between selenium, copper, indium, gallium, and zinc leads to a negative Gibb free energy and a reaction which is favorable to react spontaneously. It can be said that zinc can reduce all species. However, the results from XRD, SEM, and EDS show that only the HEGZ45 condition gave CIGS particles, all others gave elemental selenium as the major product.

This might be explained by considering the mechanism shown in Fig. 10. All types of species had to receive electrons at the same time to form nucleation cores in the nucleation process. Further, they had to be reduced at the nucleation core surface in the particle growth process. In addition, the ability to receive electrons and the rate of the reduction reaction of each species must not be very different or only the species with a higher ability will be formed. Therefore, the two major factors influencing the formation of products are the difference in the ability to receive electrons represented by the standard reduction potentials of each ion and the distances between each species in the solution.

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad E^\circ = 0.74 \text{ V}$$
 (1)

- $Cu^{2+} + 2e^- \rightarrow Cu$ $E^\circ = 0.34 \text{ V}$ (2)
- $In^{3+} + 3e^{-} \rightarrow In$ $E^{\circ} = -0.34 \text{ V} (3)$

 $Ga^{3+} + 3e^- \rightarrow Ga$ $E^{\circ} = -0.56 \text{ V}$ (4)

 $Zn^{2+} + 2e^{-} \rightarrow Zn$ $E^{\circ} = -0.76 V (5)$

Selenium dioxide, which was used as a selenium source, in an acidic solvent with a small amount of water will be in



Fig. 11. Structures of solvents, (a) Ethylene glycol, (b) Dimethyl sulf, (c) Dimethyl formamide.

the form of selenous acid form (H_2SeO_3) [6]. Selenous acid is a strong oxidizing agent and can be reduced rapidly. The formation of selenium metal is the most thermodynamics favorable reaction due to the highest E°_{cell} achieved and consequently the least Gibb free energy. Moreover, because the intermolecular force between the solvent molecule and selenous acid was only a weak force, the type of solvent did not play an important role. Therefore, selenium metal could be formed most-easily in every condition and consume almost all the electrons provided by zinc. Therefore, no other ions could be reduced.

There are many other factors affecting the particle formation such as chemical properties of the metal ion, ligand, and reducing agent. The parameters which were studied and will be discussed here were the solvent, size of the reducing agent and reaction temperature.

The effect of the solvent in the reaction might be discussed by considering the structures shown in Fig. 11. Besides the selenium source in the form of selenous acid, other metal sources occurred in the ionic species. When metal ions were dissolved, solvent molecules acted as ligands and donate electron pairs. In dimethyl sulfoxide and dimethyl formamide, Cu²⁺, In³⁺, and Ga³⁺ may be solvated by 6 molecules of solvent and form large complexes with a high steric effect [9-14]. This causes the metal ions be less labile and makes them difficult to react or receive electrons. Although ethylene glycol may also solvate the ions and form complexes, the smaller steric effect of ethylene glycol molecule leads to a greater lability of complexes. Moreover, by considering the solvent properties of each solvent, ethylene glycol has the smallest dipole (Table 5) and consequently forms only weak interactions with metal ions which leads to less stable complexes. The less the stabling of the complex, the easier it is for the reduction reaction to occurr. Therefore, among all the solvents used in these reactions, ethylene glycol was probably the best one for the synthesis. Moreover, the difference in solvent properties of each solvent, for example, polarity, and absolute viscosity (Table 5), may affect the ability to receive electrons form ions and further studies should be held to conclude these effects in detail.

According to kinetic chemistry [15], a high temperature causes molecules to collide more frequently with more energy and leads to a faster reaction. Moreover, a reaction which cannot occur at low temperature, may take place at a higher temperature because of the decrease in free energy according to thermodynamics theory as shown in equation 6 [15]:

 Table 5. Some properties of the solvents; ethylene glycol, dimethyl sulfoxide, and dimethyl formamide [16]

Solvent	Ethylene glycol	Dimethyl formamide	Dimethyl sulfoxide
Empirical formulae	$C_2H_6O_2$	HCON(CH ₃) ₂	C_2H_6SO
Molecular weight	62.07	73.09	78.13
Boiling point (°C)	198	153	189
Melting point (°C)	-13	-61	18.5
Dipole (D)	2.31	3.8	3.96
Polarity (water 100)	79.0	40.4	44.4
Absolute viscosity At 25°C	20	0.82	2.0

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

Nevertheless, a higher temperature might weaken the coordinate bonds between metal ions and ligands allowing the metal ions to react easily in the solution.

The results showed that although condition HEGZ10 was set at the same reaction temperature and with the same solvent as condition HEGZ45, it did not form the CIGS phase. Thus it can be concluded that the size of the reducing agent particle also plays an important role in phase formation. The possible reason is that the zinc dust was very small in size and consequently had a large surface area for the reaction to take place. Each dust particle was oxidized separately at the same time at a relatively high rate. Therefore, it was consumed rapidly by H^+ and selenous acid and could not provide enough electrons for other species.

Conclusions

Cu(In,Ga)_{0.5}Se₂ or CIGS was successfully synthesized via a simple solution method. The best conditions to synthesize CIGS phase was HEGZ45, used ethylene glycol as a solvent, 45 micrometer sized zinc particles as a reducing agent, and 60 °C as a reaction temperature. The XRD results showed that the product obtained was CIGS particles according to JCPDS No. 40-1488 with the three main peaks at 28.017, 46.1194 and 55.7463 degree(20) corresponding to the (112), (220) and (312) planes, respectively. Two main forms of CIGS phase were found, the first one is plate-like particles and the second is groups of small particles. The EDS results show that the ratio of elemental components Cu : In : Ga : Se of the plate-like particle was 1:0.43:0.20:1.45 and that of the groups of small particles was 1:0.17:0.16:1.70. The TEM observation showed that the product particle size was in the range of 100 nm and was well crystallized. The d-spacing measured directly from a TEM image was 3.17 Å refer to the planes (112) of the CIGS compound. The probable mechanism of formation had 2 processes which were the nucleation and the growth processes. The type of solvent, the reducing agent particle size, and the reaction temperature had significant influences on the reaction.

Acknowledgements

This work was supported by the NANOTEC, NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network and Junior Science Talent Project (JSTP). Chiang Mai University's Electron Microscopy Research and Service Center and Mr. Suwit Chaisupan are thanked for sample testing.

References

- 1. F. Ksesler, D. Herrmann and M. Powalla. 2005. Thin Solid Films 480-481: 491-498.
- Ahn Sejin, KiHyun Kim, YoungGab Chun and KyungHoon Yoon. 2006. Thin Solid Films. 515 :4036-4040.
- 3. J.M. Jacobson, B.N. Hubert, B. Ridley, B. Nivi and S. Fuller. U.S. Patent No. 6294401(2001).
- 4. Y.-G Chun, K.-H. Kim and K.-H. Yoon. 2005. Thin Solid Films 480-481: 46-49.
- 5. T. Sarakonsri, C.S. Johnson, S.A. Hackney and M.M. Thackeray. 2006. Journal of Power Sources. 153:319-327.
- 6. N.N. Greenwood and A. Earnshaw, "Chemistry of the *Elements*", 2nd Ed., Elsevier: Butterworth Heinemann.
- J. Wagner, T.R. Tshikhudo, J.M. Kohler, *Chemical Engineering Journal*, (2008), 135S, S104-S109.
- 8. J.A. Dean, "Lange's Handbook of Chemistry", 13th Ed., McGraw-Hill.
- 9. W.G. Movius, A. Nicholas, *Inorganic Chemistry*, 8[4] (1969) 925-931.
- K. Ishihara, S. Funahashi, M. Tanaka, *Inorganic Chemistry*, 25[16] (1986) 2898-2901.
- 11. K. Ozutsumi, S. Ishiguro and H. Ohtaki. *Bulletin of the Chemical Society of Japan*, 61[3] (1988) 945-951.
- J.J. Habeeb, F.F. Said and D.G. Tuck, *Inorganic and Nuclear Chemistry Letter*, 15[2] (1979) 113-116.
- A.A. Molla, M. Skripkin, M. Kritikos, I. Persson and J. Mink, *Dalton Transaction*, 9 (2003) 1746-1753.
- 14. H.L. Schalefer and H.P. Opitz, *Anorganische and Allgemeine Chemie*, 313 (1961) 178-186.
- P. Atkins and J. Paula, "Physical Chemistry", 7th Ed., 2001, Oxford.
- T.Sarakonsri, "Complete Report: The Study on Dendrite Compound Synthesis by Solution Route Method Project", 2005 (in Thai).