CHAPTER 2

EXPERIMENTAL

In this section will explain about materials, chemicals, instruments and apparatus that were used for the $Cu_{0.5}Ag_{1.5}InSe_3$ preparation. Moreover, the procedure of preparation will be described as follow.

2.1 Materials, Chemicals and Instruments

2.1.1 Materials and Chemicals

1) Acetic acid, CH_3COOH, 99.9 %, Carlo Erba
2) Copper (II) acetate, $Cu(CH_3COO)_2.nH_2O$ (98.5%), Carlo Erba
3) Diethanolamine, $[CH_2OHCH_2]_2NH$), 99.9%, Aldrich
4) Hydrogen peroxide, H_2O_2, (90%), Aldrich
5) Indium(III)nitrate hydrate, $In(NO_3)_3$, 99.9%, Aldrich
6) Propan-2-ol, $CH_3CH(OH)CH_3$, 99.5%, Lab-Scan
7) Selenium dioxide, SeO_2, 99.8%, Aldrich
8) Silver nitrate, $AgNO_3$, 99.8%, Lab-Scan
9) Sulfuric acid, H_2SO_4, 96.3%, J.T. Baker

2.1.2 Apparatus and Instruments

1) Sonicator; Bandelin Sonorex, Germany
2) Heidolph MR 3001, ITS(Thailand) Co.,LTD , Thailand
3) Power Sonic 405, Microprocess controlled Bemch-top Ultralsonic Cleaner, Labtech
4) Glove Box, Febix
5) Nitrogen furnace, Febix

6) Four Point Probe Instrument, Febix

7) Seebeck analyzer, Febix

8) Scanning electron microscope:SEM, JEOL JSM-5910LV

9) X-ray diffractometer (CuKa, Ni filter, l=1.54), **Siemen D500/D501**, Germany

10) Transmission electron microscope: TEM, JEM 2010

2.2 Simulation of $Cu_{0.5}Ag_{1.5}InSe_3$ structure

The basic data of Cu_2GeSe_3 was filled In CaRIne 3.1 program. The data showed in figure 2.1. In addition, the unit cell constant was showed as follow.

a = 5.7810 nm c = 11.6090 nm

α = 90 ° β = 90 ° γ = 90 °

Space group = 142d Atomic position of structure was showed in appendix [1]

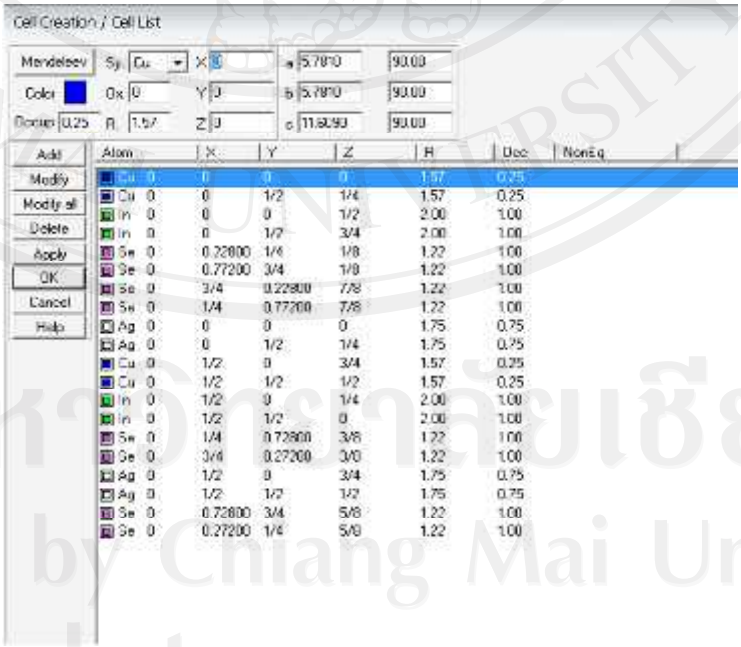

Figure 2.1 The process of cell creation of $Cu_{0.5}Ag_{1.5}InSe_3$ structure.

2.3 Preparation of $Cu_{0.5}Ag_{1.5}InSe_3$ (CAIS) gel

The $Cu_{0.5}Ag_{1.5}InSe_3$ (CAIS) preparation method required 4 metal sources as precursors; Copper acetate [$Cu(CH_3COO)_2$], Silver nitrate [$AgNO_3$], Indium nitrate [$In(NO_3)_3$] and Selenium dioxide [SeO_2]. The flow chart of gel preparation was showed in Figure 2.2 Each metal precursor was dissolved in 2-propanol and stirred at the control temperature for 2 hours in control atmosphere. Stabilizer (Diethanolamine: $[CH_2OHCH_2]_2NH$) and DI water were added and stirred for 2 hours.

Various parameters were studied, which were preparing temperature, pH, preparing atmosphere, annealing atmosphere, mole ratio of metal precursor: solvent: stabilizer: water, drying and annealing time. Finally, all metal gels, prepared by using appropriate mole ratio, were combined together to form CAIS gel.

2.3.1 The study of preparing temperature, atmosphere and annealing atmosphere.

The temperature effect was studied by controlled a preparing temperature in to 2 conditions, which were 25^{o}C and 60 ^{o}C in gel preparing process.

The atmosphere of preparing and annealing process were studied. There are 2 conditions of atmosphere; *Air atmosphere*, preparing and annealing process produced in air atmosphere and *Nitrogen atmosphere*, preparing process produced in nitrogen atmosphere (Glove box) and annealing process performed in nitrogen atmosphere (Flow nitrogen gas in furnace).

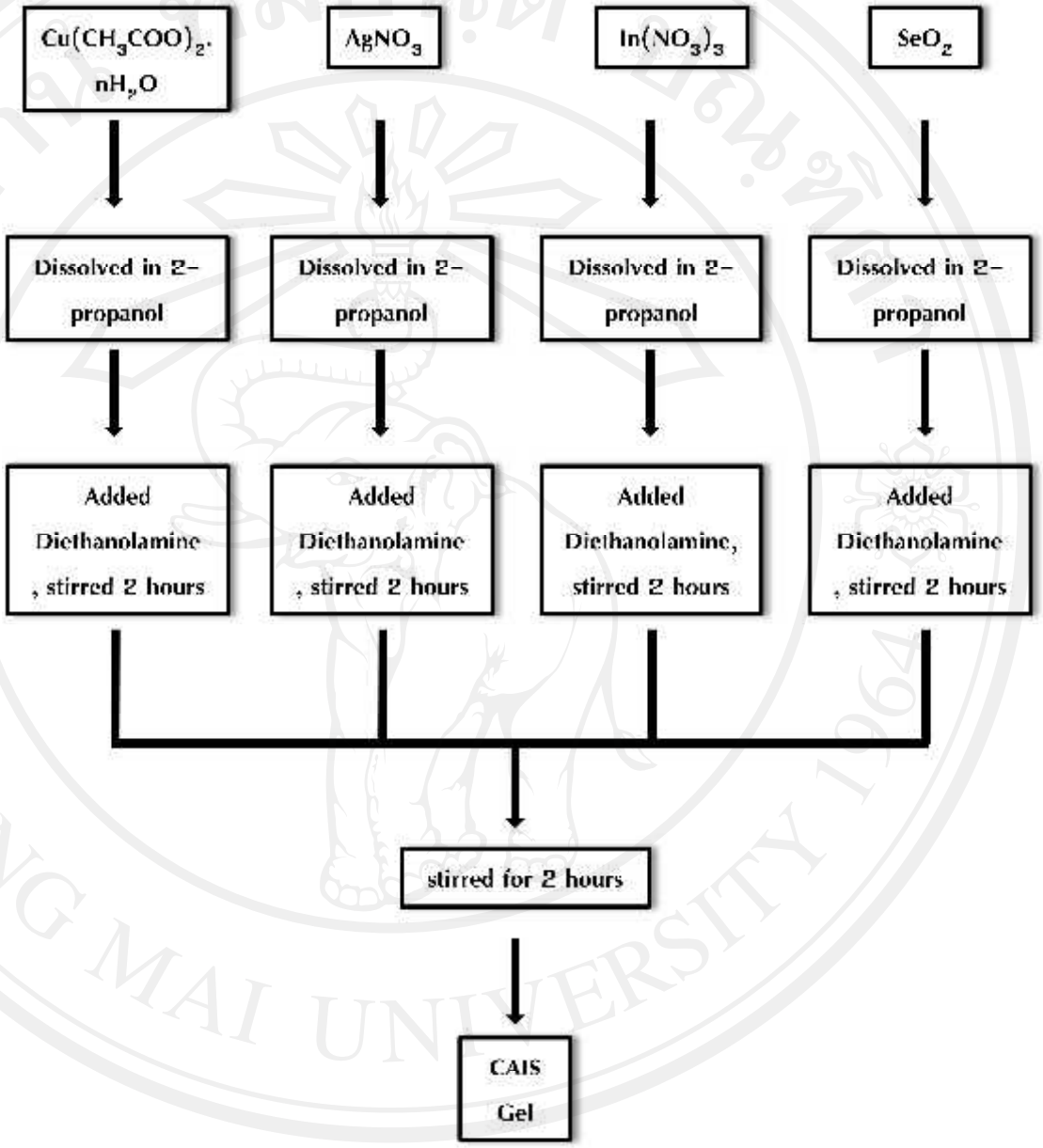

Figure 2.2 The flow chart of $Cu_{0.5}Ag_{1.5}InSe_3$ (CAIS) gel preparation.

2.3.2 The study of pH effect.

The pH effect was studied in gel preparing process. Sulfuric acid was added after the stabilizer adding step to adjust pH value to 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11.

2.3.3 The study of mole ratio.

The mole ratio of metal precursor, solvent, stabilizer and water were studied. The Conditions of mole ratio studied showed in table 2.1

Table 2.1 The mole ratio of metal precursor with solvent, stabilizer and water.

Metal precursor (mole)	**Solvent** (mole)	**Stabilizer** (mole)
1	30	0
1	30	2
1	30	3
1	40	0
1	40	2
1	40	3

Metal precursor (mole)	**Water** (mole)
1	0
1	1
1	2

Since the mole ratio effected the viscosity of gel, the studied of mole ratio was conducted. The solvent ratio was selected by the amount of solvent that can dissolve metal precursor. Then, stabilizer ratio and water mole ratio were varied.

2.3.4 The study of annealing time.

After the process of the mole ratio of CAIS gel was completed. Annealing time was studied in the last process of gel preparation. The conditions showed in table 2.2

Table 2.2 The conditions of annealing temperature and annealing times.

Drying times (hour)	**Annealing temperature** (^oC)	**Annealing times** (hour)	**Condition name**
1	-	-	D1C300H0
1	300	1	D1C300H1
1	300	3	D1C300H3
1	300	5	D1C300H5

Code from this table "DxCxxxHx" refer to

Dx : drying for x hour

Cxxx : annealing at xxx degree Celsius

Hx : annealing for x hour

2.4 Preparation of $Cu_{0.5}Ag_{1.5}InSe_3$ Thin films

Thin film of $Cu_{0.5}Ag_{1.5}InSe_3$ (CAIS) was prepared by using Dip-Coating technique. There were 2 kinds of substrate; Glass and Alumina. Both of them were cleaned it with 70:30 of conc. sulfuric acid with hydrogen peroxide for 1 hour at 60^oC. Then cleaned again with deionized water for 3 times and dried in an oven. Then substrates were successfully cleaned.

Each 10 ml. of CAIS gel was added in beaker for dip-coating at speed 15 mm/min. The times of dip-coating were showed in table 2.3.

Table 2.3 The conditions of dip-coating times.

Substrate	Dip-coating times
Glass	5
	10
Alumina	5
	10

2.5 Physical properties characterization

The material structures were analysis by X-ray diffraction technique. The XRD patterns from randomly oriented powder mount using Cu Kα radiation. Diffraction patterns were recorded from 20 to 80^{o} 2θ with a step interval of 0.02 ^{o} 2θ and counting time of 1 s per step. Then the particles size, morphology of CAIS powder and thickness of CAIS thin films were investigated using scanning electron microscopic technique. Next, energy dispersive x-ray spectroscopic technique was used to analyze percent of elements. At last particles size, morphology of CAIS powder was investigated using scanning electron microscopic technique.

2.6 Electrical properties characterization

2.6.1 Electrical conductivity

The electrical conductivity of films was analyzed by Four Point Probe technique. The current 0.05 mA was applied to the films using step current 0.01 mA/S.

Four Point Probe technique was used to measured the resistivity(ρ). To obtain the electrical conductivity was applied to equation (2.1) to calculated the electrical conductivity (σ) from resistivity value.

$$\sigma = 1/\rho \qquad (2.1)$$

2.6.2 Seebeck coefficient

The Seebeck coefficient was analyzed by Seebeck analyzer. It was analyzed form the difference number of voltage divided by the difference number of temperature. The diagram of seebeck analyzer was showed in Figure 2.3. In the diagram the temperature at 2 sides; hot side (T_H) and cold side (T_C) were measured.

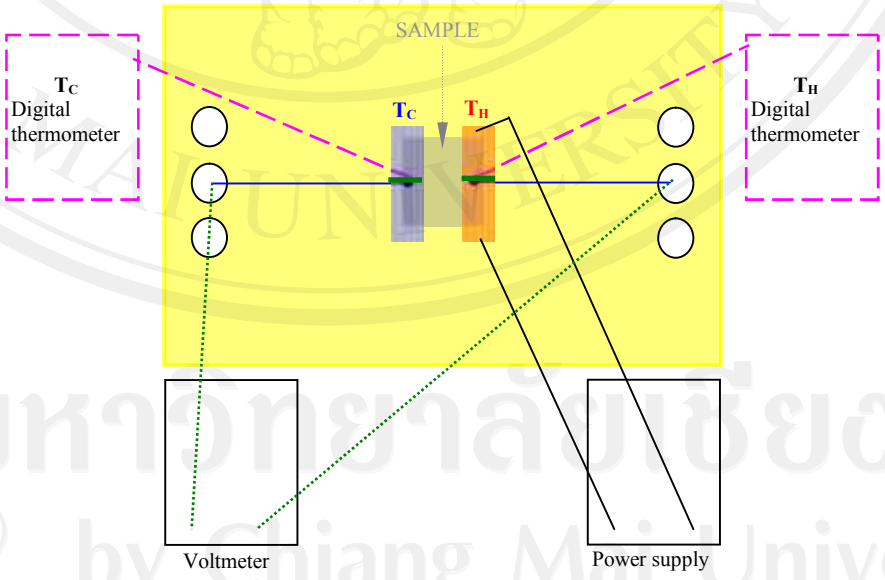

Figure 2.3 The diagram of Seebeck analyzer.

The The Seebeck coefficient (α) was analyzed by using equation (2.2)

$$\alpha = \frac{\Delta V}{\Delta T} \qquad (\text{volt.K}^{-1}) \qquad (2.2)$$

ΔV = difference number of voltage (volt)

ΔT = difference number of temperature (K)