Characterization Study of Band Gap, Resistivity, Crystal Structure, and Phase Identification of CuInSe_2 Ternary Alloy

Bungaran Saing^1, and Budi Arto^2
^1) Departement of Chemical Engineering, Faculty of Engineering, University of Bhayangkara Jaya, Jakarta, Indonesia
Email: bungaran.saing@yahoo.com
^2) Departement of Mechanical Engineering, Faculty of Engineering, University of Indonesia Christian University, Jakarta, Indonesia
Email: damaz581102@gmail.com

Abstract. Characterization study of band gap, resistivity, crystal structure, and phase identification of CuInSe_2 ternary alloy which is the synthesis result of Bridgman method by using modified simple single zone temperature, have been carried out. The phase identification and crystal structure of obtained polycrystal were characterized by X-ray diffraction. Then the X-ray diffractograms were analyzed by using crystallographic software package GSAS. Electrical resistivity and bandgap were measured by using Van der Pauw method. Identification and analysis of diffractogram show that ternary alloy of CuInSe_2 has main phase of space group I4_ad and lattice parameters a and c of 6.1173 Å and 11.7144 Å respectively. The other coexisting phases were identified as CuIn_5Se_8 with the space group P4_2m and Se with the space group P3_21. Result from the resistivity measurement shows the resistivity is between (1.596 – 9.666) x 10^-3 Ωm, and Bandgap is around 1.03 – 1.61 eV.

Keywords: crystal structure, phase identification, bandgap, CuInSe_2

1. Introduction
Indonesia is a tropics that have big enough of solar energy. Based on collected data of solar radiation from seven locations in Indonesia, the solar radiation in Indonesia can be clarified respectively - were as follows: for the western region and eastern Indonesia by irradiating distribution in the Western Region of Indonesia, around 4.3 kWh / m^2 / day with a monthly variation of approximately 10% and Eastern Region of Indonesia about 4.7 kWh / m^2 / day with a monthly variation of approximately 9%, thus the potential of the average solar irradiation in Indonesia around 4.5 kWh / m^2 / day with variations monthly about 9%.[1]

Non-silicon semiconductor material is intensively developed for thin film solar cell’s coating, are CuInSe_2 (and its alloys such as CuInS_2, Cu (InGa) Se_2, or CuInSe), CdTe, and silicon amorph. CuInSe_2 is the most promising material for solar cells[2] for many reason.

The commonly techniques used to deposited of semiconductor are Bridgman method, Czockralski method, and sputtering (dc and rf). Basically, all these techniques have each advantages and disadvantages. The advantage of Bridgman technique is produced massive...
semiconductor material which very homogeneous, but this technique worked at a very high temperature, and it took the material (quartz tube) so it may expensive. [3]

Now on the center of attention from researchers around the world is CuInSe$_2$ alloy and other materials of ternary compounds. It can be potential to be base material optoelective devices such as solar cells and photo-detectors. Partial substitution of indium (In) and gallium (Ga) in the compound material added the optical absorption of this material are suited for solar cell applications. [4,5] The research importance of compound ingredient was to research the properties of materials such as in the form of a single crystal. However, we can also examine the properties of the material that formed of polycrystalline, in fact the single crystal and polycrystalline have similar properties except in this case of the grain boundary.

CuInSe$_2$ is a direct band gap semiconductor material. It causes very strong material absorbs a photon. [6,7] Alloy material was made by polycrystalline and growth of CuInSe$_2$ generally performed by melted these materials in an ampoule vacuum pressure of $10^{-4}$Torr and it put in a vertical furnace with dual zone temperature method. The Bridgman method was the suitable method for cultivate this material. The growth of polycrystalline semiconductor ternary compound CuInSe$_2$ materials can be used by a vertical furnace temperature single zone, that must be modified previously to furnace that can produced similar conditions with dual zone temperature vertical furnace.

The research just only characterized ternary alloy CuInSe$_2$, which has grown by a modified Bridgman method. Domination an high quality semiconductor manufacturing technology was need an high precision and accurate crystal growing equipment which able to process automatically and stable.

This research purposed for characterized of ternary alloy CuInSe$_2$ synthesize by Bridgman method which can be expected a specifications of diesel basic ingredient. The results of this research was also expected as a reference to the next research, especially the made of thin layer of solar cell application. Besides the series of these researches were expected to provide a new hope and information of applications development that ever been.

2. Materials and Methods
The material are cylindrical ingots with conical ends which length 40 mm and diameter 10 mm that made of ternary compound CuInSe$_2$ by Bridgman method in Puspiptek Laboratory Serpong, Tangerang, Banten.

The equipment: Diffractometer X-ray, electrical resistivity test used four-point probe Van der Pauw method, chemical composition test by XRF instrument, band gap measurement tools.

Procedure: Put material Cu, In, and Se with each purity 99.999% to ampoules, then vacuum the ampoules till $10^{-4}$ Torr by vacuum Veeco 300, 220 V / AC, 1 vacuum pump. In vacuum condition, sealed off the ampoules by the welding. After complete the process, tied the ampoules on a stick then put into furnace cavity properly till the ampoules located in symmetrical position in center. Monitoried the temperature by couple thermo, next programmed the process depend on data which got from each melting point of Cu, In and Se also alloy data. Controlled system done by PID (proportional - integral - differential)
technique that one of controller with closed feedback where the feedback get from installed thermo couples in the furnace. Temperature controller used panel with temperature risen can be set according to characteristic of the process element, as well as the temperature decreased. Besides PID constants from temperarure controller must be searched and determined so that furnace temperarure can be stable.

In sixth phase, shook the furnace by the motor around 15 minutes to get an homogeneous mixture then put the furnace to vertical position. The alloy material wrapped with quartz, so it need an opened process after that cut it transversely. Cut it to be some parts with every parts have 2 mm thickness and numbered them from top till the pointed end.

Test the crystal structure and identified phase by using X-ray diffractometer. Analysis the X-ray diffractogram by using GSAS crystallographic program that developed by AC Larson from Los Alamos National Laboratory, USA. The electrical resistivity was measured by four points probes Van der Pauw method, and composed chemical element by XRF.

3. Results and Discussion

a. Crystal Structure Analysis and Phase Identification

Picture 1, 2 and 3 showed analysed X-ray diffractogram by using GSAS crystallographic program.

![X-ray diffractogram](image)

**Figure 1.** The pattern of CuInSe₂ ternary alloy X-ray diffractogram at top side. The (+) curve showed observation data and the (-) full line showed calculation.
Figure 2. The pattern of CuInSe$_2$ ternary alloy X-ray diffractogram at middle side. The (+) curve showed observation data and the (-) full line showed calculation.

Figure 3. The pattern of CuInSe$_2$ ternary alloy X-ray diffractogram at bottom side. The (+) curve showed observation data and the (-) full line showed calculation.

Table 1. Refine results’ parameter of CuInSe$_2$ ternary alloy ingot samples which has a tetragonal crystal structure used the GSAS

| Sample | Phase   | Space Group | a (Å)    | b (Å)    | c (Å)    | Wt %   |
|--------|---------|-------------|----------|----------|----------|--------|
| CuInSe$_2$ | I$_4$ad | 6.11730     | 6.11730  | 11.71449 | 53.372   |
| 1      | CuIn$_5$Se$_3$ | P$_4$2m   | 5.80816  | 5.80816  | 11.68055 | 27.222 |
|        | Se      | P$_3$121   | 4.38144  | 4.38144  | 4.96396  | 19.406 |
|        | CuInSe$_2$ | I$_4$ad   | 6.24718  | 6.24718  | 11.94947 | 66.054 |
| 2      | CuIn$_5$Se$_3$ | P$_4$2m | 5.90939  | 5.90939  | 11.90826 | 27.325 |
|        | Se      | P$_3$121   | 4.35568  | 4.35568  | 4.92260  | 6.621  |
|        | CuInSe$_2$ | I$_4$ad   | 6.12337  | 6.12337  | 11.75300 | 53.502 |
| 3      | CuIn$_5$Se$_3$ | P$_4$2m | 5.81046  | 5.81046  | 11.69003 | 38.224 |
|        | Se      | P$_3$121   | 4.37664  | 4.37664  | 4.78800  | 8.274  |
X-ray diffractogram analysis used GSAS crystallography program package, showed that CuInSe$_2$ ternary alloy which has tetragonal crystal structure and three phases. The phases were the main phase called CuInSe$_2$ phase with space group $I\bar{4}$ad the lattice parameters $a$ and $c$ for each 6.1173 Å and 11.7144 Å, the 2 other phases called CuIn$_5$Se$_8$ phase with space group $P\bar{4}2m$ and Se phase with space group $P3_121$. It showed that CuInSe$_2$ ternary alloy was polycrystalline, and its crystal structure form was tetragonal with average lattice parameter which got from CuInSe$_2$ ternary alloy is $a = b = 6.11730$ Å and $c = 11.71449$ Å, $c/a = 1.899$. Therefore this value has the difference around 0.140 with $c/a$ constant depend on Rockett and Birmire.\[^3\]

b. Element Composition Analysis
Table 2 showed the measurement of element composition by XRF from CuInSe$_2$ ternary alloy. The sample was taken from CuInSe$_2$ ternary alloy incisions that numbered 1 (top), 2 (middle), 3 (bottom).

| Unsure | Wt(%) Sample |
|--------|--------------|
|        | 1            | 2            | 3            |
| Cu     | 29.3239      | 34.3687      | 37.6815      |
| In     | 36.7999      | 37.3043      | 35.2260      |
| Se     | 31.8650      | 26.5839      | 25.1107      |
| Si, Fe | 1.2408       | 1.8933       | 1.3798       |

The composition of CuInSe$_2$ ternary alloy indicated there were other elements, it because there was impurities when sample preparation, for example when vacuum time, welding, or ingot cutting.

c. Resistivity Analysis
Table 3 showed resistivity measurement with four-point probe and Van der Pauw method, from CuInSe$_2$ ternary alloy. The resistivity measurement took few places of CuInSe$_2$ ternary alloy incisions then averaged them. The incisions were taken from number 1 (top side), 2 (middle side), and 3 (bottom side). The measurement of semiconductor type showed that wafer was tipe-p.

| Sample | Resistivity (Ωm) |
|--------|------------------|
| Top    | $(1.685 - 8.674) \times 10^{-3}$ |
| Middle | $(1.735 - 4.642) \times 10^{-3}$ |
| Bottom | $(1.596 - 9.666) \times 10^{-3}$ |
Resistivity measurement of CuInSe$_2$ ternary alloy showed that the resistivity was uneven, although the type of semiconductor was same type-p. The variation of electricity resistivity from CuInSe$_2$ ternary alloy was associated by many factors or possibilities, among other things it influenced of atom dislocated population or other vacancy atomic. Therefore the placement $H^+$ ion in vacancy atomic caused bandgap lessen as theoretically. The lessen caused of the position of these ions to the center of recombination which took place between valence band and conduction band.

Cu was a conductance that has a high conductivity values. Se was a type-p semiconductor that has high conductivity. In was valence 3 conduction that can be used in Silicon. If these 3 materials was joined with special condition (deposition parameter), it could be a p-type of CuInSe$_2$. Commonly Cu made conductivity bigger besides In and Se formed p-type$^{[9]}$.  

d. Band Gap Analysis

Table 4 showed the Band Gap measurement of CuInSe$_2$ ternary alloy. The measurement, were taken from resistivity measurement in many places then averaged them. The places were incisions CuInSe$_2$ ternary alloy at top side (number 1), middles side (number 2), and bottom side (number 3).

| Sample  | Band Gap ( eV) |
|---------|----------------|
| Top     | (1.03 – 1.61 ) |
| Middle  | (1.02 – 1.32)  |
| Bottom  | (1.01 – 1.57)  |

Previously researcher found band gap value of CuInSe$_2$ ternary alloy was 1.02 eV$^{[2]}$. But this research found around 1.01 – 1.59 eV, there was above the average from other researchers.

4. The Conclusion

According to the observation and analysis of CuInSe$_2$ ternary alloy, it can be concluded as follows:

a. CuInSe$_2$ ternary alloy growing used vertical furnace single zone temperature as a modification was quite good.

b. Crystal structure analysis and identified from diffractogram patterns showed lattice parameters of CuInSe$_2$ polycrystall were $a = b = 6.11730$ Å and $c = 11.71449$ Å, $c/a = 1.899$. Besides lattice parameters based on these references by reference were $a = b = 6.104$ Å, $c = 11.714$Å and $c / a = 1.919$. Form phases were CuInSe$_2$ as main phase, CuIn$_5$Se$_8$ as phas, and Se phase.

c. Electrical resistivity analysis showed uneven i.e. (1.6 to 8.6) x $10^{-3}$Ωm,(1.7 to 4.6) x $10^{-3}$Ωm, and (1.5 to 9.6) x $10^{-3}$Ωm.

d. Composition analysis showed that the composition was not the same i.e. Cu (29.3239%), In (36.7999%), Se (31.8650), and Si + Fe (1.24%).

e. Band Gap analysis were (1.03 to 1.61) eV, (1.02 to 1.32) eV, and (1.01 to 1.57) eV.
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