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

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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 $I\bar{4}$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 $P\bar{4}2m$ and Se with the space group $P3_121$. Result from the resistivity measurement shows the resistivity is between (1,596 – 9,666) x $10^{-3}\Omega$m, 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

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semiconductor material wich 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 optoelectic 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 metod for cultivate this material.Thegrowth of polycrystalline semiconductor ternary compound $CuInSe_2$ materials can be used by a vertical furnace temperature single zone, that must be modificated 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.

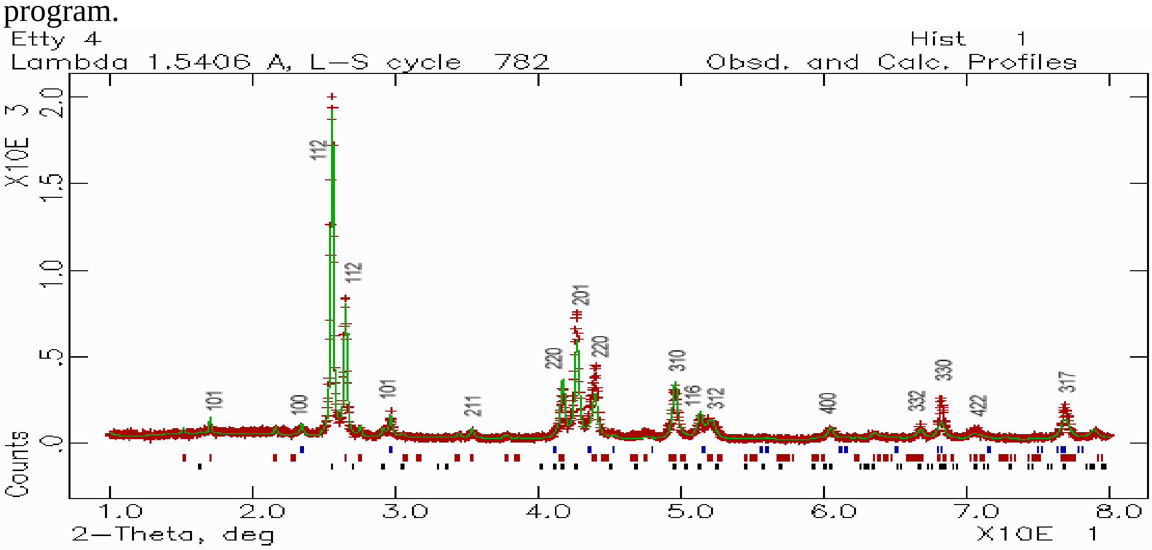

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Figure 1.The pattern of $CuInSe_2$ ternary alloy X-ray diffractogram at top side. The (+) curve showed observation data and the (-) full line showed calculation.

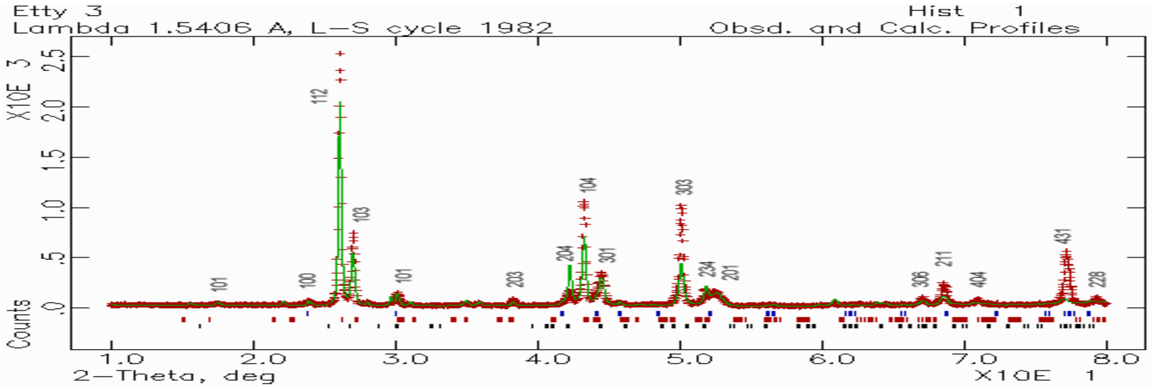

Figure 2. The pattern of $CuInSe_2$ ternary alloy X-ray diffractogram at middle side. The (+) curve showed observation data and the (-) full line showed calculation.

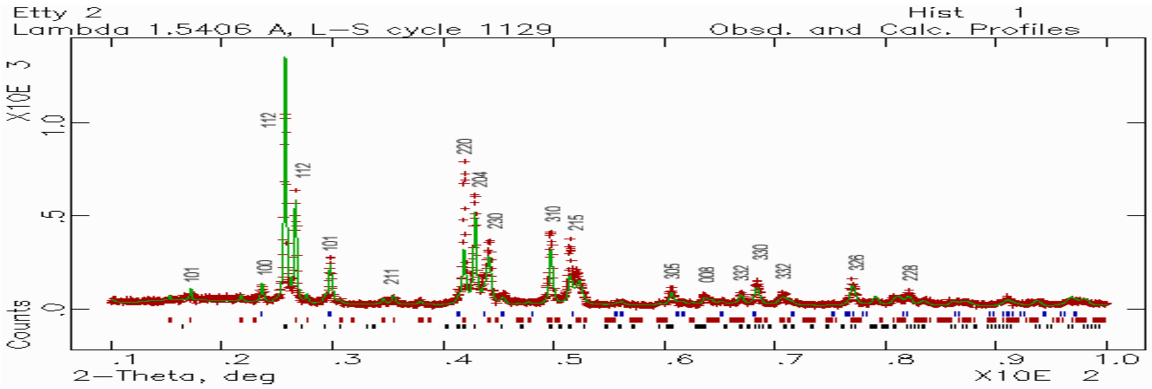

Figure 3. The pattern of $CuInSe_2$ ternary alloy X-ray diffractogram at bottom side. The (+) curve showed observation data and the (-) full line showed calculation.

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 %
	$CuInSe_2$	$I\bar{4}ad$	6.11730	6.11730	11.71449	53.372
1	$CuIn_5Se_8$	$P\bar{4}2m$	5.80816	5.80816	11.68055	27.222
	Se	$P3_121$	4.38144	4.38144	4.96396	19.406
	$CuInSe_2$	$I\bar{4}ad$	6.24718	6.24718	11.94947	66.054
2	$CuIn_5Se_8$	$P\bar{4}2m$	5.90939	5.90939	11.90826	27.325
	Se	$P3_121$	4.35568	4.35568	4.92260	6.621
	$CuInSe_2$	$I\bar{4}ad$	6.12337	6.12337	11.75300	53.502
3	$CuIn_5Se_8$	$P\bar{4}2m$	5.81046	5.81046	11.69003	38.224
	Se	$P3_121$	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 $CuIn_5Se_8$ 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).

Table2. Element composition (wt%) taken from XRF $CuInSe_2$ ternary alloy ingot

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.

Table 3.Resistivity measurement $CuInSe_2$ ternary alloy

Sample	Resistivity (Ωm)
Top	(1,685 - 8,674) x 10^{-3}
Middle	(1,735 - 4,642) x 10^{-3}
Bottom	(1,596 - 9,666) x 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).

Table 4. Band gap measurement Data of $CuInSe_2$ ternary alloy

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 patterms 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 refences by reference were a = b = 6.104 Å, c = 11.714Å and c / a = 1.919. Form phases were $CuInSe_2$ as main phase, $CuIn_5Se_8$ as phas, and Se phase.
c. Electrical resistivity analysis showed uneven i.e. (1.6 to 8.6) x $10^{-3}\Omega$m,(1.7 to 4.6) x $10^{-3}\Omega$m, and (1.5 to 9, 6) x $10^{-3}\Omega$m.
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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