

OPTIC AND ELECTRIC PROPERTIES OF $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ INGOT

A. Harsono Soepardjo¹, Muhammad Nurdin² & Arya Rezavidi³

¹Department of Physics, Faculty of Mathematics and Natural Science University of Indonesia

²Postgraduate Student of Material Science, Department of Physics, Faculty of Mathematics and Natural Science University of Indonesia

³Agency for the Assessment and Application of Technology

¹Email: cms_ui@yahoo.com

ABSTRACT

Fabrication of ingot is first step to produce device solar cell and the second step is fabrication of thin film. This research will be explain only the optic and electric properties of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ ingot solar cell. A solar cell material has been produced from $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ using the Bridgman method. At the Bridgman Method, solar cell material was heated at maximum temperature 1050°C and re-cooled until ambience temperature. Heating and cooling process of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ material took 71 hours. The result is an ingot which was then optically and electrically characterized. Optic characterization utilized XRD (X-ray Diffraction) and XRF (X-ray Fluorescent), whereas electric characterization utilized the four-point and two-point probe. The result of XRD characterization showed that the crystal orientation was [101], [112], [103], [211], [213], [301], [312], [008], and [424]. This crystal orientation was the principal crystal orientation of solar cell material I-III-VI₂. By using the XRD result, the crystal lattice parameter a, c, and c/a can be measured. The structure of this material was chalcopyrite with a c/a ≈ 2 value, whereas other optic characterizations used XRF to measure the material's % weight composition. Measurement using XRF resulted in the % best weight composition of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ as follows: Cu: 20.7233%, Ga: 9.1403%, In: 28.8963%, and Se: 41.2401%. Result of electric characterization showed that this material is a type p semiconductor and its resistivity is 6.280 Ωm.

Key words: *Crystal orientation, crystal structure, Bridgman method, chalcopyrite, solar cell, ingot.*

1. INTRODUCTION

$\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is a solar cell material, which is a derivative of group I-III-VI₂. This is a solar cell material, which physically has the same properties, optically as well as electrically, as CuInSe_2 and CuGaSe_2 . In general, $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is a material with a chemical composition of $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ where $x = 0.5$; for $x = 0$ the material has a chemical composition of CuInSe_2 and with the value of $x = 1$ the material composition becomes CuGaSe_2 . Numerous researches on the optic and electric properties of this material group has been conducted and there are many other phenomena which should be further investigated [1-5]. In the last few years, the solar cell device $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ which has been joined with CdS has often been investigated and produced an efficiency of over 16% [6-9]. The research steps in this paper are as follows: first, $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ was made using the Bridgman method; the produced $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ ingot were cut into several pieces/parts and these pieces/parts were then characterized. Production of solar cell polycrystal ingot group I-III-VI₂ using the Bridgman method has often been conducted as this method is relatively easy and simple [10,11]. The first optic characterization used XRD to discover its crystal orientation. The XRD result can be used to measure crystal lattice parameter a, b, and c. Further, from the resulting value of these crystals we can determine the crystal structure of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$. The crystal structure of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is the same as the crystal structure of CuInSe_2 and CuGaSe_2 , which is a chalcopyrite structure. The crystal structure of chalcopyrite has the following parameters: lattice crystal a is equal to b and c is two times a. The second optic characterization utilizes XRF and from the result the % weight composition of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ can be determined, whereas electric characterization using the four-point and two-point probe results to determining the resistivity and type of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$. In the end of this research, mainly the expected results are the structure of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is chalcopyrite and the type of material is p type semiconductor.

2. MATERIALS AND METHODS

The production of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ polycrystal ingot utilizes the Bridgman method [12]. The elements of Cu, Ga, In, and Se utilizes elements with a purity level of 5N (99.999%) until 7N (99.99999%). After these elements have been weighed, they are then put in a quartz tube and this tube is vacuumed with a vacuum level reaching 5 Torr. The quartz tube is a tube in which one of its end is made into a sharp cone; in the heating and cooling process it is expected that the initial formation of polycrystals will begin in this area. The heating and cooling process can follow like this; the heating process started low speed with increase the temperature up to 200°C during 8 hours. After this

step the temperature keep constant during 24 hours and continue to increase up to 400°C during 3 hours and the temperature again keep constant during 1 hour and the last increase temperature up to 1050°C during 6 hours. With this temperature keep constant and rocking by swung an angle 360° during 2 hours. The next step is cooling process, started to decrease temperature during 1 hour up to boiling temperature that is 1000°C . During 2 hours this temperature keep constant and finally the last process is decrease temperature with the low speed up to room temperature during 24 hours. The heating and cooling process of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ within the Bridgman furnace will last almost three (3) days, as shown in Figure 1. Figure 2 shows the Bridgman furnace.

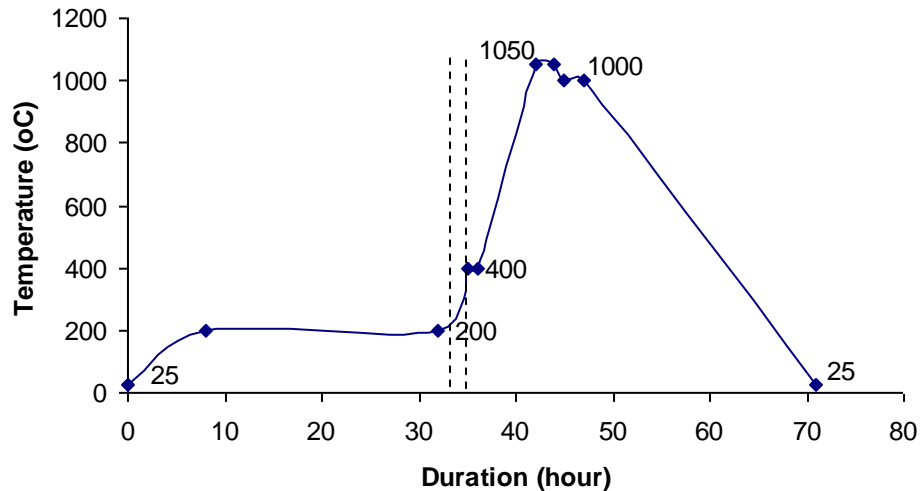


Fig. 1. Heating and cooling process within the Bridgman furnace

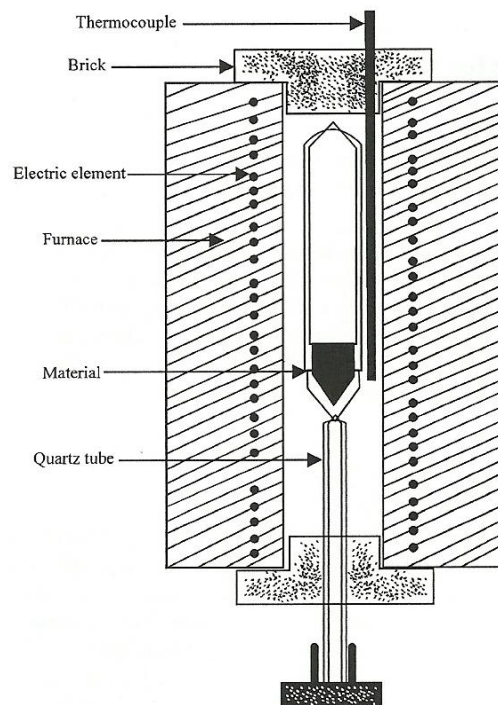


Fig. 2. The Bridgman Furnace

The produced $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ ingot is then sliced into four parts: the upper part (1), the upper middle part (2), the lower middle part (3), and the lower part (4). The lower part is the part with a sharp end. Each of these respective

parts are then characterized optically and electrically. Optic characterization uses XRD, the product is crystal orientation peaks with diffraction angles of 2θ . With this diffraction angle pattern the crystal lattice a , c , and c/a can be measured. If the value of $c/a = 2$, then the crystal structure is chalcopyrite. Measuring $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ sample using XRF will result in a % of weight composition. The % weight stoichiometric composition is $\text{Cu} = 25\%$, $\text{Ga} = 12.5\%$, $\text{In} = 12.5\%$, and $\text{Se} = 50\%$. Electric characterization uses the two point and four-point probe and the result is material resistivity and type. The $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ material is a semi-conductor material with a certain resistivity and this material type can be a type p semi-conductor or type n semi-conductor.

3. RESULTS AND DISCUSSION

Ingot

The ingot produced from the production of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ with the Bridgman method has a diameter of 13 mm and length of 4 cm; this shows that the ingot is not equally massive, several parts are porous, especially the upper-middle and lower-middle parts. The ingot is divided into four parts: the upper part (1), the upper-middle part (2), the lower-middle part (3), and the lower part (4). The lower part has a sharp end, and this part is the part that indicates that the ingot is not porous. This research has contradiction with Soepardjo, 2009 [12], on which the fabrication of I-III-VI₂ has already been successfully by using the Bridgman furnace method. Soepardjo's research is focused on material fabrication in polycrystalline and all parts of the ingot are relatively non porous. The mainly difference from both researches is during rocking process, Soepardjo use rocking process with low spinning speed and this research use rocking process by swinging with an angle 360° .

Optical characterization

The typical measurement result of the ingot can be seen in Figure 3. By using the GSAS (General Structure Analysis System) method the miller index and crystal orientation of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ can be discovered. The Figure shows that the crystal orientation is [101], [112], [102], [211], [213], [220], [301], [312], [008], and [424]. These crystal orientations show that crystals of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ also possess the principal crystal orientation of solar cell material CuInSe_2 and CuGaSe_2 , these are similar with Liao and Rockett, 2002 ; Dale *et al*, 2008 ; and Terasako *et al* 2006 [10, 3, 5] researches, Table 1 shows the relation between diffraction 2θ angle, miller index h, k, l , and the distance inter-crystal d space.

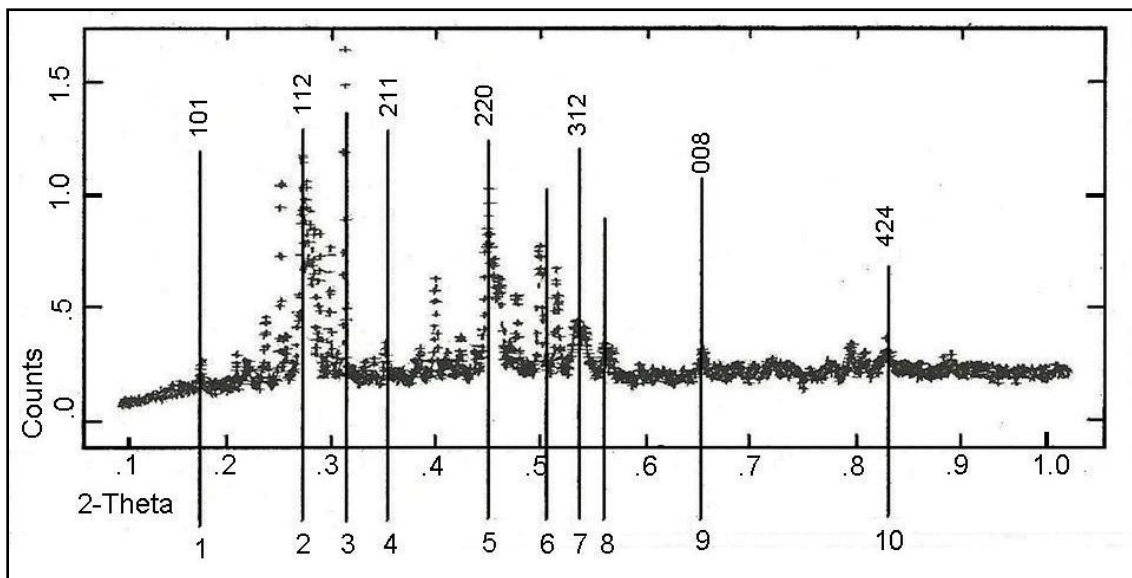


Fig. 3. Typical XRD result of one of the samples

Table 1. Lattice Parameter of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ a, c and miller index

| d | l. miller | | | 2 θ |
|------------------------|-----------|---|---|------------|
| distance inter-crystal | h | k | l | |
| 5.060 | 1 | 0 | 1 | 17.5194 |
| 3.279 | 1 | 1 | 2 | 27.1843 |
| 3.143 | 1 | 0 | 3 | 28.3848 |
| 2.487 | 2 | 1 | 1 | 36.1005 |
| 2.107 | 2 | 1 | 3 | 42.9057 |
| 2.010 | 2 | 2 | 0 | 45.0872 |
| 1.870 | 3 | 0 | 1 | 48.6724 |
| 1.711 | 3 | 1 | 2 | 53.5371 |
| 1.417 | 0 | 0 | 8 | 65.8912 |
| 1.305 | 3 | 3 | 2 | 72.3882 |
| 1.161 | 4 | 2 | 4 | 83.1773 |

By using data in Table 1, the lattice parameter of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ a and c can be determined with the following formula:

$$1/d^2_{hkl} = \{ [(h^2 + k^2) / a^2] + l^2 / c^2 \}$$

The result of a, c, and c/a can be seen in Table 2. It is determine that the result of c/a's value, is that $c/a \approx 2$, and this indicates that the crystal structure of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is a chalcopyrite structure.

Table 2. Lattice Parameter of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$

| 2 θ | Lattice Parameter (Å) | | |
|------------|-----------------------|---------|--------|
| | a | c | c/a |
| 17.5194 | 5.6595 | 11.2965 | 1.9960 |
| 27.1843 | 5.6804 | 11.3547 | 1.9989 |
| 36.1005 | 5.7005 | 11.3151 | 1.9849 |
| 45.0872 | - | - | - |
| 53.5371 | 5.6768 | 11.3086 | 1.9920 |
| 65.8912 | 5.8444 | 11.6846 | 1.9992 |
| 83.1773 | 5.6809 | 11.3576 | 1.9962 |

The result of characterization using XRF is shown in Table 3. Table 3 shows the % weight composition of several parts of the ingot, whereas Figure 4 shows one of the examples/typical measurement of one of the samples using XRF. Table 3 shows that the % weight composition of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ in every part/area of division does not indicate a stoichiometric composition, only the sample of the second part indicates the best composition which is: Cu = 20.7233%, Ga = 9.1403%, In = 28.8963%, and Se = 41.2401%. This sample shows that there is an overweight of In and insufficient weight of other elements Cu, Ga, and Se. Overall, measurement with XRF is not yet sufficient, and this may be caused by in the ingot producing process where rocking process supposed to be spinning at low speed rather than swung with 360° angle.

Table 3. % Weight Composition of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$

| Samples | Content wt (%) | | | |
|---------|----------------|---------|---------|---------|
| | Cu | Ga | In | Se |
| 1 | 45.7662 | 7.0429 | 9.0601 | 35.7528 |
| 2 | 20.7233 | 9.1403 | 28.8963 | 41.2401 |
| 3 | 8.1672 | 15.0828 | 48.2764 | 24.9801 |
| 4 | 23.5594 | 9.2647 | 27.811 | 29.4451 |

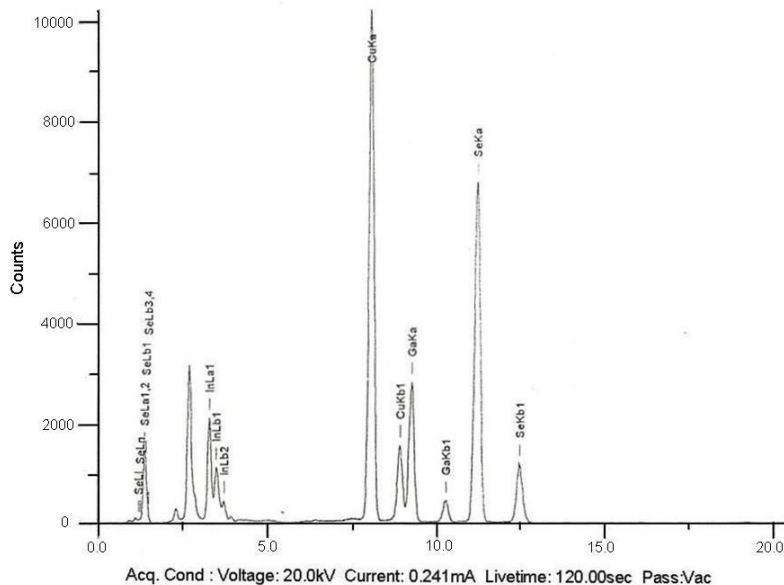


Fig. 4. Typical XRF Result of one of the samples

4. ELECTRICAL CHARACTERIZATION

Electrical characterization utilizes a four-point and two-point probe: the first measurement is to measure resistivity and the second measurement is to determine the type of material. Electric characterization only uses a one-time measurement of resistivity as well as material type measurement. First measurement shows that $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ resistivity is $6.280 \Omega\text{m}$, whereas the second measurement shows that material type is semiconductor p type. The resistivity shows indicates that $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is a semi-conductor material. Recently many device solar cell $\text{Cu}(\text{Ga}_x\text{In}_{1-x})\text{Se}_2$ couple with CdS or ZnS conducted by Pudov et al. 2002, Kannan et al. 2003, and T. Nakada and Mizutani 2002 [7, 9, 11] shown that the material $\text{Cu}(\text{Ga}_x\text{In}_{1-x})\text{Se}_2$ are semiconductor p type.

5. CONCLUSION

This research shows that $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ material is a material that has a chalcopyrite crystal structure as is the case of its derivate CuInSe_2 and CuGaSe_2 which has a lattice parameter of a and $c/a \approx 2$. Crystal orientation and miller index h, k , and l is also the same as its derivate material. The composition of $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$ is still not satisfactory and the ingot form is also not yet perfect as there are still parts which are poreous. A more detailed research is required especially during the production process where rocking should be conducted by spinning the tube with a low velocity spin.

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