Fabrication of $CuInSe_2$ Single Crystals From Melt Growth by Directional Freezing Method

Ng. Gaewdang and T. Gaewdang
Photonic Materials Research Laboratory, Department of Applied Physics, Faculty of Science
King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Road
Ladkrabang, Bangkok 10520

Abstract

Single crystals of the semiconducting compound $CuInSe_2$ prepared from the melt by directional freezing method using the horizontal Bridgman-Stockbarger traveling furnace and the temperature gradient freezing 45 degree tilt-furnace techniques. The experimental details and crystal morphology of the as-grown ingots obtained by both techniques were reported. X-ray powder diffraction patterns of the crushed crystals were carried out to determine the lattice parameters. The energy gap being 1.03 eV was evaluated, at room temperature, from the optical transmission spectrum. The conductivity types of the samples were either p-type or n-type with low resistivity values in the range 1.4 - 6.1 Ω-cm. The change in the electrical resistivity values of $CuInSe_2$ was investigated by annealing at 100-600 °C in vacuum and in a slowly flow of pure nitrogen gas. At annealing temperature lower than 500 °C, the resistivity values of all samples were slightly changed. However, at annealing temperature higher than 500°C, the p-type samples were changed to n-type ones except the n-type samples which remained the same conductivity type with slightly lower resistivity values.

Keywords : $CuInSe_2$, directional freezing method, electrical resistivity

1. INTRODUCTION

$CuInSe_2$ is a semiconducting I-III-VI_2 compound with chalcopyrite structure and is of great interest for solar cell applications as its band gap is close to the ideal for solar photovoltaic conversion and it posseses a very high absorption coefficient [1]. It has a direct band gap at 1.04 eV and can be obtained both n and p type. Small deviations from stoichiometry can greatly alter the carrier concentration and hence the conductivity value by several orders of magnitude [2].

$CuInSe_2$ possesses some exceptional charac-teristics for heterojunction application with CdS. The lattice match between $CuInSe_2$ and hexagonal CdS is exceptionally good ; the difference in the relevant lattice parameters of 0.07 Å , or a mismatch of approximately 1.2 % , introduces only a small amount of interfacial states [3]. The electron affinities of $CuInSe_2$ and CdS are close enough to minimize any potential barriers to the photoinduced carriers. An important demonstra-tion of the feasibility of the heterojunction cosisting of p-$CuInSe_2$ single crystals and a chemical bath deposited CdS thin films had a measured efficiency in excess of 12% [4].

Several methods have been employed to produce $CuInSe_2$ single crystals such as vertical Bridgman, zone leveling , directional freezing , chemical vapour deposition. In this paper , We report the comparison of $CuInSe_2$ single crystal grown by Bridgman- Stockbarger traveling furnace and by the programmed temperature gradient freezing with 45 degree tilt-furnace techniques. Crystal structure of the as-grown $CuInSe_2$ single crystal was checked by X-ray diffraction technique.

Energy gap was determined by the optical transmission measurements. Finally, the electrical resistivity of as-grown and annealed samples was also investigated by the Van de Pauw method at room temperature.

2. EXPERIMENTAL DETAILS

2.1 Crystal growth

For the crystal growth, a fused quartz tube of 10 mm inner diameter and 150 mm in length sealed at one end as a conical shape with cone angle about 30 ° was used as the ampoule. The ampoule was degreased with aceton, etched in HF+ HNO_3 in a ratio 1:1. This was followed by rinsing with deionized water and cleaning in and ultrasonic bath of deionized water. Next, after washing with deionized water , the ampoule was dried in N_2 flow and baked at 100 °C for several hours in an oven. High purity (5N) elements of Cu, In and Se , in weighted stoichiometric proportions, with total 10 g of charge were introduced into the ampoule , which was then evacuated and sealed in vacuum with a pressure $5x10^{-6}$ Torr. In order to prevent oxidation of the compound which can occur by fracture of the internal ampoule during cooling, the ampoule was introduced into the other ampoule which have a higher diameter and then evacuated and sealed in vacuum.

For the single crystals grown by the horizontal Bridgman-Stockbarger traveling furnace technique , the ampoule was placed in the middle position of a tubular single zone furnace which was mounted on a parallel rail to allow horizontal translation with the ampoule fixed in position. The furnace was heated rapidly to 200 °C and maintained at this temperature for at least 4 h. This procedure was followed in order to suppress the exothermic and potentially explosive reaction which occurs between indium and selenium at temperature excess of 217 °C [5]. The ampoule was then raised to a temperature of 1150 °C with rate 50 ° C/h and held at this temperature for 24 h, during this time the ampoule was rolled clockwise and counterclockwise alternately by using long ceramic tube, about 5 min in every six hours. After soaking at 1150 °C for 24 h , the furnace with temperature gradient around 20 °C/cm at this temperature, was then pulled by low speed motor with average rate of 0.7 mm/h as previous used for crystal growth of $CuInTe_2$ [6].

A furnace time of approximately 8 days is required. For the single crystals grown by the temperature gradient freezing 45 degree tilt-urnace technique, a mixture of the elements sealed in an evacuated fused quartz ampoule was heated to 1150 °C as described above. The temperature of furnace was controlled by PID temperature controller Shimaden model FP21s. Subsequently, the growth furnace was set in the position 45 degree tilt. The ampoule was tied by a kanthal wire and placed in the middle zone of furnace. The ampoule was slowly cooled with rate 1 °C/h. This cooling rate provided the temperature profile traveling across the ampoule from one side to the other side with a calcutated growth rate about 0.5mm/h. This growth rate is comparable to the cooling rated employed in the horizontal Bridgman-Stockbarger traveling furnace. After two weeks, the furnace was switched off. The as-grown ingot was cut by string saw in the form thin slices of about 2 mm thickness and with irregular or circular shape. The slices were mechanically polished , by sandpaper and by alumina powder with grain size 5 μm, and successively etched in $HCl : HNO_3 : H_2O$ (2:1:1).

2.2 Characterization

The samples were annealed in a slowly flow of pure nitrogen gas at normal atmospheric pressure at the temperature ranging 100-600 °C. The crystallo-graphic structure of crushed crystal was checked by X-ray diffraction with a Philips diffractometer using CuK_α radiation. The optical absorption coefficient was calculated

from the optical transmission measurements made by means of Perkin-Elmer spectrophotometer model 112. Electrical conductivity type was tested by thermal probe technique. Electrical resistivity with In-Sn-Cd alloy (44:42:14) contact were measured by the Van der Pauw configuration at room temperature. The current and voltage drop were measured by Keithley 614 electrometer and by Fluke 8842 A digital multimeter respectively.

3. RESULTS AND DISCUSSION

The black as-grown $CuInSe_2$ ingot with crack-free, void-free and stick-free crystals obtained from the horizontal Bridgman-Stockbarger traveling furnace was shown in Figure 1. The absence of void and sticking in the ingot was presumed to be due to good cleaning process of the ampoule, good mechanical mixing, good initial pumping and sealing. The as-grown ingot shows showes the free surface which is normally the (112) plane [5]. $CuInSe_2$ ingot with 10 mm diameter and 4 cm in length was obtained by the temperature gradient freezing 45 degree tilt-furnace technique (Figure 2). By the latter technique, no preferential growth plane was observed but some small cracks on the surface of ingot were appeared. It is probably due to the strain in the bulk during solidification stage. In contrast, the as-grown crystals obtained from the former technique were free from crack and sticking because this technique provided larger free surface than the latter one.

In order to determine the crystal structure and lattice parameters, X-ray diffraction measurements were made on crushed crystals (Figure 3) and compared to the file JCPDS 23-209. They were found to have single phase chalcopyrite structure. Lattice parameters calculated by the least square method, by using Si as the internal standard, are a = 5.788 Å , c = 11.598 Å and c/a = 2.004. The absorption coefficient (α) depending on the photon energy ($h\nu$) was obtained from the optical transmission measurements which performed on the 70 μ m thickness sample. The energy gap, calculated by extrapolating the $(\alpha h\nu)2$ values to $h\nu = 0$ from $(\alpha h\nu)2$ versus $h\nu$ plots, equals 1.03 eV at room temperature. This energy gap value corresponds to the value reported earlier [5,7].

The conductivity types of the samples are either p or n-type with low resistivity values in the range 1.4 - 6.1 Ω-cm. Figure 4 shows a plot of ρ/ρ_0 versus annealing temperature for the samples prepared by the horizontal Bridgman-Stockbarger traveling furnace technique. Here ρ and ρ_0 are the pre-heat and post-heat treatments respectively. Annealing carried out with continuous pumping on the heated sample in the middle of the furnace for 24 h shows that a peak is apparent around 500 °C. Samples heat treated above the peak were found to be n-type. Thus, heating in vacuum created donors, presumably due to the loss of selenium from the compound [5,8]. The maximum in resistivity therefore arises from a condition of compensation of donors and acceptors [7]. Our results well agree with those earlier reported by Shih et al. [9].

The annealing experiments were next carried out in a slowly flow of pure nitrogen gas at normal atmospheric pressure. In this case, annealing at 500 °C for 24 h was not sufficient for type-conversion. The samples cut from p-type $CuInSe_2$ ingot grown by both techniques were annealed at 500 °C. It is noted , for these samples which are independent on the growth technique, a change to n-type took place for 50 h or more of heating. Examination of the type-converted samples show that the n-type character in them existed only on the surface, with the interior still p-type. This was found by abrasive removal of an outer layer of material from each sample and by testing with a thermal probe method. It is important to note that in order to attain type-conversion by annealing in a slowly flow of nitrogen gas consumed less time than annealing in an argon gas [13]. These results

suggest that annealing in a nitrogen gas provides more the oxygen trace which causes the existence of In_2O_3 and SeO_2 on the sample surface [8] besides the selenium loss.

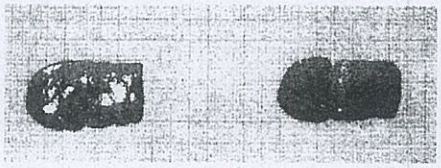

Figure1 Photograph of the as-grown ingot of $CuInSe_2$ prepared by the horizontal Bridgman-Stockbarger technique.

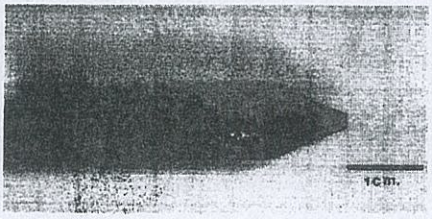

Figure2 Photograph of the as-grown ingot of $CuInSe_2$ prepared by the temperature gradient freezing 45° tilt-furnace technique.

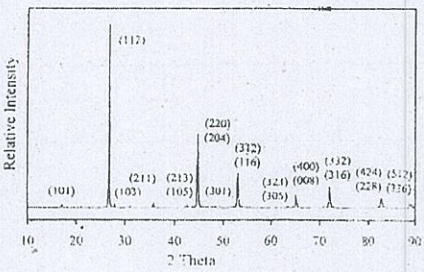

Figure 3 Powder X-ray diffraction patterns for the crushed $CuInSe_2$ crystals.

For n-type samples the conductivity type was not changed by annealing in vacuum or in a nitrogen gas. However, the resistivity value monotonically decreases as the annealing temperature increases. This suggests that the selenium vacancy plays the important role under these annealing conditions. Moreover, some theoretical calculations predict that the formation energy of selenium vacancy is lower than the copper or indium vacancies [10].

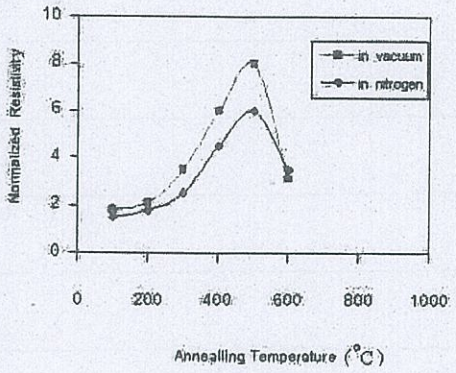

Figure 4 Normalized resistivity of $CuInSe_2$ samples versus annealing temperature.

4. CONCLUSIONS

It would appear that good bulk mono-crystalline $CuInSe_2$ ingot can be prepared from the melt by directional freezing method using the horizontal Bridgman-Stockbarger traveling furnace and the temperature gradient freezing 45 degree tilt-furnace techniques. With a thorough ampoule preparation and cleaning prior to charge with the pure starting elements, and good mechanical mixing of the liquid during heating in the furnace, the problems of inhomogeneity, voids and cracks in the ingot can be avoided. Good bulk monocrystalline samples were checked by X-ray diffraction and optical transmission measurements. Irregular shape and circular disk samples were cut from the as-grown ingots prepared by the former technique and by the latter one respectively. The change in the electrical resistivity values and conductivity type-conversion were investigated by annealing in vacuum and in a slowly flow of nitrogen gas. The annealing in a nitrogen gas have demonstrated, for the first time, that type- conversion from p to n can occur at normal atmospheric pressure. The results probably indicated that the n-type was contributed to the selenium vacancy.

5. ACKNOWLEDGEMENTS

The authers thank Asst. Prof. Sompong Chatraporn, Asst. Prof. Dr. Kajornyod Yoodee and Aj Chanwit Chityuttakarn for sealing the ampoules under high vacuum, optical measurements for determining energy gap and for their useful discussion. They are also gratetul Dr. Ekachai Hoonnivathana and Asst. Prof. Noppadon Suttisiri for X-ray diffraction measurements, Asst. Prof. Anupong Srongprapa for electrical resistivity measurements, Miss Ampawon Buabootrara and Miss S. Tippawon Klaiboonmee for crystal growth asistance. This work was partially supported by Department of Applied Physics, Faculty of Science, KMITL.

REFERENCES

[1] J.S. Chen, E. Kolawa, C.M. Garland, and M.A.Nicolet,"Microstructure of Polycrystalline $CuInSe_2$/ (Cd,Zn)S Heterojunction Solar Cells", *Thin Solid Films*, **219**: 183-192, January 1992.

[2] T. Datta, R. Noufi, and S.K. Deb "Electrical conductivity of p-type $CuInSe_2$ Thin Films" *Appl. Lett.*, **47**(10): 1102-1104, November, 1985.

[3] L.L. Kazmerski, F.R. White, and G.K. Morgan, "Thin Films $CuInSe_2$/CdS Heterojunction Solar Cells" *Appl. Phys. Lett.*, **29**(2):268-270, March, 1976.

[4] S. Chatraporn, K. Yoodee, P.Songpong and C. Jityuthakarn, "The $CuInSe_2$ Based Solar Cell Program at Semiconductor Physics Research Laboratory (SPRL)" *Proceeding 2nd Japan-Thailand Joint Seminar on Photovoltaics* :32-36, 1996.

[5] R.D. Tomlinson, "Fabrication of $CuInSe_2$ Single Crystals Using Melt Growth Techniques", *Solar Cell*,**16**:17-26, January/Febuary, 1986.

[6] L. Haworth, R.D. Tomlinson, and I.S. Al-Saffar, "Growth and Characterization of CuInTe2 Single Crystals" *Jap. J. Appl. Phys.* **19** (supl. 19-3):77- 80, 1980.

[7] W.W. Lam, and I. Shih "Crystal Growth of CuGaxIn1-x Se2 by Horizontal Bridgman Method", *Solar Energy Materials and Solar Cells*, **50**:111-117, 1998.

[8] C.H. Champness and G.I. Ahmad, "Annealing of Monocrystalline $CuInSe_2$ Samples", *Thin Solid Films*, 361-362:482-487, 2000.

[9] I. Shih, C.H. Champness, and A.V. Shahidi, " Growth by Directional Freezing of $CuInSe_2$ and Diffused Homojunctions in Bulk Material "*Solar Cells*, **16**:2741,January/Febuary1986, pp. 7-41.

[10] S.M. Wasim, "Transport Properties of $CuInSe_2$" *Solar Cells*, **16**: 289-316, January/Febuary,1986.