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# THM growth of $CuGaSe_2$ using In solutions with non-stoichiometric solute

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Phase relations in (Cu-Ga-Se)-In system have been investigated in order to prepare $CuGaSe_2$ single crystals at relatively low temperatures. The compositions of Cu-Ga-Se solutes in the In solutions, which are single-phase liquids and from which chalcopyrite crystals can be grown, were determined at temperatures over 700°C. On the basis of the results, THM growth of $CuGaSe_2$ was performed at 800°C using zones of In solutions containing $CuGaSe_{2.4}$ non-stoichiometric solute. The obtained single crystals were $CuGa_xIn_{1-x}Se_2$ (1-x=0.07-0.08) solid solutions having a uniform composition.

## 1. INTRODUCTION

The chalcopyrite semiconductors $CuGaSe_2$ and $CuGa_xIn_{1-x}Se_2$ have received considerable interest due to their potential for photovoltaic applications. Recently, thin film solar cells with heterostructures of $ZnO/CdS/CuGa_xIn_{1-x}Se_2$ have achieved conversion efficiencies exceeding 17%[1]. Although most of the studies on $CuGaSe_2$ and $CuGa_xIn_{1-x}Se_2$ have been concerned with polycrystalline thin films, studies on bulk single crystals will be helpful for better understanding of the properties of the semiconductors and provide useful information for improvement of the thin film solar cells.

The nominal $CuGaSe_2$ single crystals have been grown by the traveling heater method (THM) using In solvent [2,3]. However, the growth temperatures were above 850°C, because the In solutions saturated with stoichiometric $CuGaSe_2$ solute at temperatures below 850°C are separated into two phases [2]. For growth of high quality single crystals having low concentrations of defects and less strains, it is desired that the THM growth is performed at lower temperatures. In this study, we investigated the phase relations in (Cu-Ga-Se)-In system at 600-900°C. In particular, the compositions of solutes in single-phase In solutions, from which chalcopyrite crystals can be grown, were examined. On the basis of the results, THM growth of $CuGaSe_2$ was performed at 800°C using zones of In solutions with non-stoichiometric solute.

## 2. PHASE RELATIONS IN (Cu-Ga-Se)-In SYSTEM

As the first step of investigation of the phase relations, ingots of Cu-Ga-Se mixtures, having compositions of Cu:Ga:Se=13-32:13-31:46-61 mol%, were prepared as solutes for In solutions. The prescribed amounts of elemental Cu, Ga and Se were charged in a quartz ampoule and vacuum-sealed. Total weights of the mixtures were 7-13 g. The ampoule was heated up to 1100°C, and was kept at the temperature for 24h for homogenization. Then, it was rapidly cooled by pulling out from the furnace. The prepared Cu-Ga-Se ingots were 9.5 mm in diameter and 25-40 mm in length.

In order to examine the properties of In solutions saturated with the solute at temperature T (T=600-900°C), elemental In of 1-2 g and the Cu-Ga-Se solute ingot were inserted and vacuum-sealed in an a single phase. At T=800°C In solutions saturated with stoichiometric $CuGaSe_2$ solute are separated into two phases, but those with Se-excess solutes (Cu:Ga:Se=1:1:2.4-3.1) become a single phase. Fig. 2 shows examples of XRD patterns of the crystals grown from the In solutions at 800°C. The pattern (a), which was obtained for the crystals grown from an In solution with $CuGaSe_{2.4}$ solute, shows a chalcopyrite structure. But the crystals grown with $CuGaSe_{\alpha}$ ($\alpha$=2.7-3.1) solutes have a zincblende structure as shown in Fig. 2 (b). The compositions of the grown crystals from the In solutions at 800°C are listed in Table 1. The crystals grown from In solutions having $CuGaSe_{\alpha}$ ($\alpha$=2.7-3.1) solutes seem to be $(Ga_yIn_{1-y})_2Se_3$-based solid solutions [4]. The phase relations at 700°C are similar to those at 800°C, but chalcopyrite crystals can not be obtained from single-phase In solutions at 600°C.

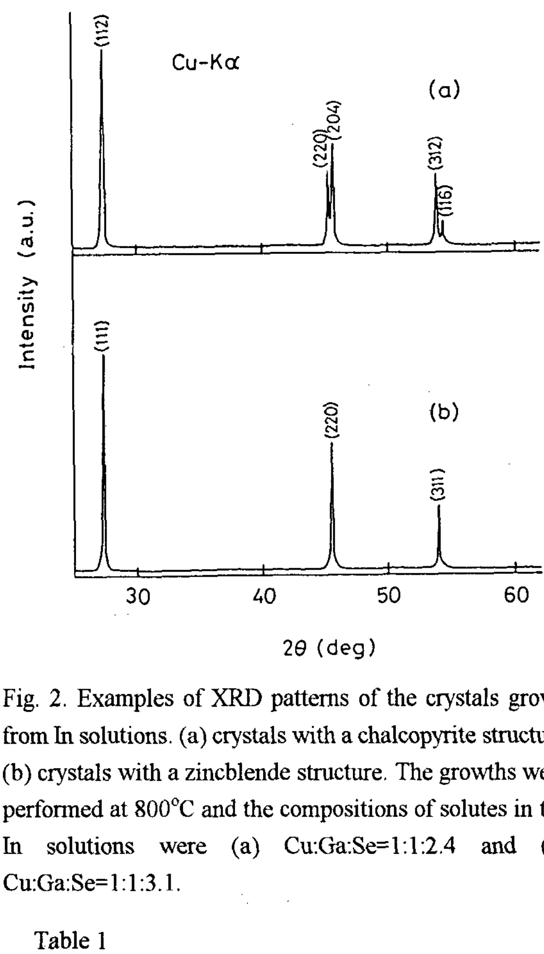


Fig. 2. Examples of XRD patterns of the crystals grown from In solutions. (a) crystals with a chalcopyrite structure. (b) crystals with a zincblende structure. The growths were performed at 800°C and the compositions of solutes in the In solutions were (a) Cu:Ga:Se=1:1:2.4 and (b) Cu:Ga:Se=1:1:3.1.

## 3. THM GROWTH OF $CuGaSe_2$ AT 800°C

The THM growth of $CuGaSe_2$ was carried out at a zone temperature of 800°C. On the basis of the above experimental results, we chose In solutions with a solute composition of Cu:Ga:Se=1:1:2.4, which correspond to a single-phase liquid and from which chalcopyrite crystals can be grown. A pointed carbon-coated quartz ampoule of 10 mm ID was used. Indium ingots of 1.5 g and Se shots of 0.45 g were charged at the bottom of the ampoule as initial zone material, and a $CuGaSe_2$ polycrystal ingot of 13 g was inserted on them as a feed. After the ampoule was vacuum-sealed, it was placed in a vertical THM furnace, and heated up to a zone temperature of 800°C. Thus, an In solution containing $CuGaSe_{2.4}$ non-stoichiometric solute was prepared for the zone by partial dissolution of the feed ingot. The growth was performed by lowering of the ampoule at a speed of 4 mm/day.

Table 1
Structures and compositions of grown crystals from In solutions at 800°C

| Composition of solute (at.ratio) | In solution | Grown crystal | | | | |
|---|---|---|---|---|---|---|
| | | Crystal | Composition (at.%) | | | |
| Cu:Ga:Se | | structure | Cu | Ga | Se | In |
| 1:1:2 | 2 phases | Chalcopyrite | 24.8 | 23.1 | 50.4 | 1.7 |
| 1:1:2.4 | 1 phase | Chalcopyrite | 25.6 | 23.0 | 49.4 | 2.0 |
| 1:1:2.7 | 1 phase | Zincblende | 9.3 | 15.4 | 54.5 | 20.8 |

ampoule. Then, it was heated in a furnace with a flat temperature profile up to T°C, and was kept at the temperature for 24h. A saturated In solution was prepared by dissolving a part of the solute ingot in this procedure. In order to check the existence or non-existence of two liquid phases, the ampoule was rapidly cooled by pulling out from the furnace, and the surface and cross section of the solidified In solution were visually inspected.

For the investigation of features of the solid in equilibrium with the In solution at T°C, solution growth was performed by using Bridgman technique. The lowest portion of the grown crystal, which solidified initially from the In solution, was used for characterization. The crystal structure was examined by X-ray powder diffraction (XRD), and the composition was determined using energy-dispersive X-ray microanalysis (EDX).

Fig. 1 (a-d) shows phase relations in In solutions saturated with Cu-Ga-Se solutes at T=600-900°C. The composition of the solute is represented by the coordinates of a point in the triangular coordinate system, and the conditions of the liquid and structure of the corresponding crystal are described by a symbol (open or filled circle or triangle) for the point. At T=900°C chalcopyrite crystals can be grown from In solutions saturated with stoichiometric $CuGaSe_2$ solute, and the solutions are

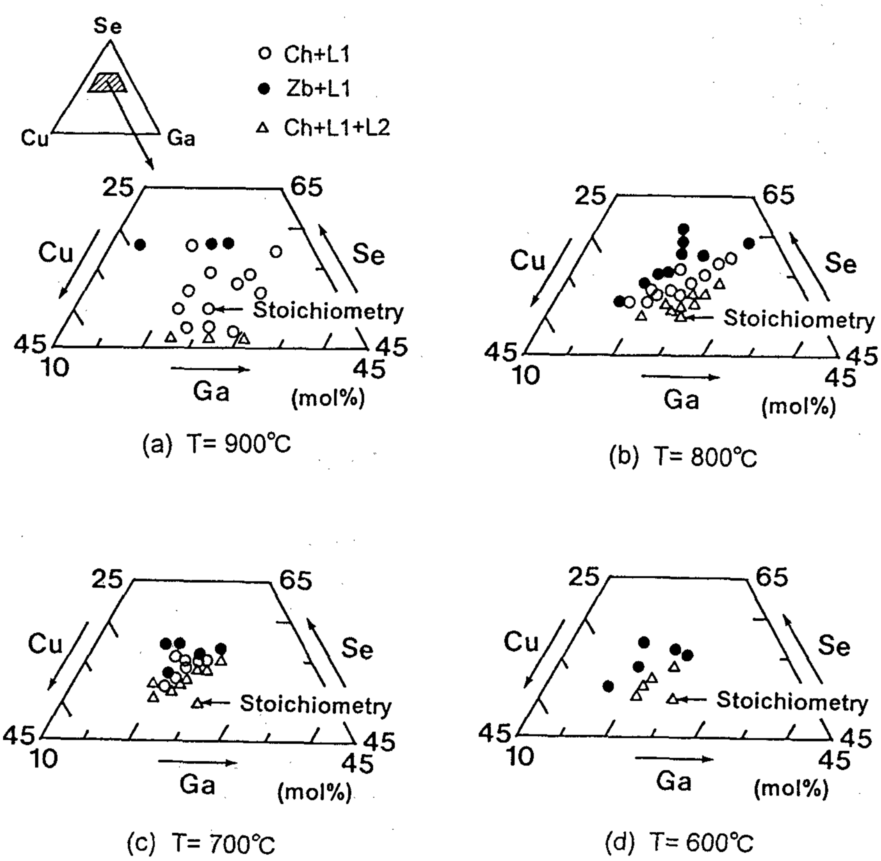


Fig. 1. Phase relations in In solutions saturated with Cu-Ga-Se solute at T=600-900°C. Compositions of the solutes and properties of the In solutions are represented by points in a triangular coordinate system. Ch and Zb represent chalcopyrite and zincblende structures, respectively, for crystals grown from the In solutions. L1 and L1+L2 represent single-phase and two-phase liquids, respectively.

Fig. 3 shows an example of cross sections of the obtained single crystals. The crystal was ascertained to be a $CuGa_xIn_{1-x}Se_2$ solid solution with a chalcopyrite structure from EDX and XRD measurements. The variation of mole fraction 1-x in $CuGa_xIn_{1-x}Se_2$ along the growth direction is shown in Fig. 4. The value of 1-x is 0.07-0.08 and is nearly constant from the tip to near end of the crystal, and the value is larger than that (1-x~0.04) for the THM crystals grown at 950°C.

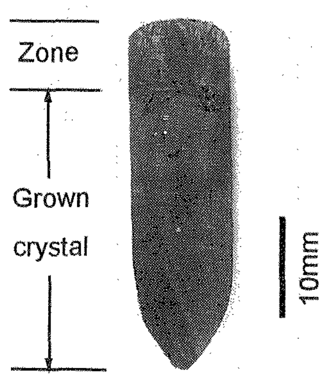


Fig. 3. Cross section of a single crystal grown by THM at 800°C. The zone was an In solution containing $CuGaSe_{2.4}$ non-stoichiometric solute.

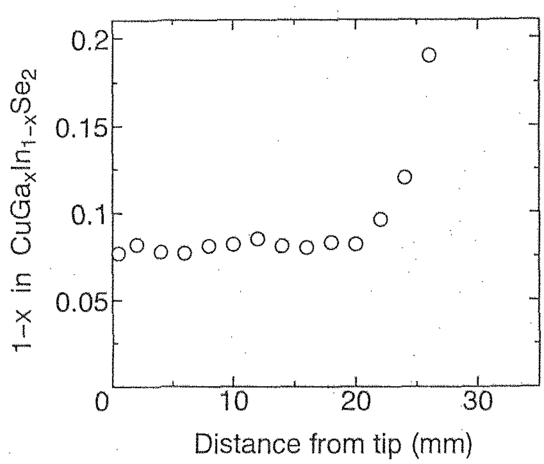


Fig. 4. Variation of 1-x in a THM-grown $CuGa_xIn_{1-x}Se_2$ crystal along the growth direction. The THM growth was performed at 800°C using an In-solution zone containing $CuGaSe_{2.4}$ solute.

## 4. CONCLUSION

The phase relations in (Cu-Ga-Se)-In system at 600-900°C have been investigated. The solute compositions in single-phase In solutions, from which chalcopyrite crystals can be grown, were determined at temperatures over 700°C. On the basis of the results, THM growth of $CuGaSe_2$ was performed at 800°C using an In-solution zone containing $CuGaSe_{2.4}$ non-stoichiometric solute. The obtained single crystals were $CuGa_xIn_{1-x}Se_2$ (1-x=0.07-0.08) solid solutions having a uniform composition.

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