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Phase diagram of the Sb_2Se_3-$CuInSe_2$ pseudobinary system and flux growth of $CuInSe_2$ single crystals

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The phase diagram of the Sb_2Se_3-$CuInSe_2$ pseudobinary system is constructed by using differential thermal analysis and X-ray diffraction. Based on the constructed phase diagram, solution growth of $CuInSe_2$ crystals is investigated. The grown crystals are evaluated by X-ray diffraction, electron probe microanalysis, Hall effect and inductively coupled plasma measurements. The results indicate that the crystals are not contaminated by the constituent of the flux, i.e., Sb. Hence, Sb_2Se_3 is promising as a solvent for the growth of $CuInSe_2$ crystals at temperatures lower than 800°C.

1. Introduction

Recently, $CuInSe_2$ has been received considerable attention as adsorber material for solar cell applications. However, little is known about the effects of defects and impurities on the physical properties. In order to carry out successful studies, the growth of $CuInSe_2$ single crystals with larger size and higher perfection is required. Crystal growth by the flux method is a significant approach for the purpose. Many efforts have aimed at the selection of a suitable solvent, CuSe [1, 2], In [3] and Cu-In [4] are proposed as solvents for $CuInSe_2$.

For the purpose of obtaining higher-quality crystals, we have attempted to grow at lower temperatures using Sb_2Se_3 as a solvent. Sb_2Se_3 has a melting point of 610°C, and does not decompose. Furthermore, it is expected that Sb_2Se_3 is not incorporated in $CuInSe_2$ crystals, which is supposed from the results on the liquid phase epitaxial growth of $AgGaS_2$ using a Sb_2S_3 solvent [5]. In this paper, the phase diagram of the Sb_2Se_3-$CuInSe_2$ pseudobinary system is constructed by differential thermal analysis (DTA) and X-ray diffraction (XRD). Then, the vertical Bridgman flux growth of $CuInSe_2$ is performed and the grown crystals are characterized.

2. Experimental procedure

A mixture of $CuInSe_2$ and Sb_2Se_3, weighed to about 1 g in total, was sealed in a quartz ampoule with a dimension of 9 mm^{ϕ} (ID)×35 mm in length under a vacuum of $\sim 10^{-5}$ Torr, and synthesized by heating over 1000°C. Then, the DTA curves were observed by raising the temperature at constant rate of 2 K/min. The phase transition points except for the liquidus points were determined from the extrapolated onset of DTA peaks in the heating and cooling processes. The liquidus points were difficult to determine in the heating process, since the $CuInSe_2$ solid was slowly dissolved into the solvent, leading to a broad DTA hump from which a DTA onset could not be well recognized. Thus, the liquidus points were determined only in the cooling process, where DTA onsets were clearly observed.

The samples were identified by X-ray powder diffraction (XRD) using the Cu-K_α characteristic line (1.5405 Å) at room temperature. The XRD patterns of the products after DTA measurements were compared with the patterns of the $CuInSe_2$ and Sb_2Se_3 starting materials to determine the contained phases.

The starting materials for flux growth were polycrystalline $CuInSe_2$ synthesized from Cu, In and Se elements (6 N grades) and the powder of Sb_2Se_3 (6 N grade) in the prescribed mole ratio. Both materials were weighted to about 25 g in total, and filled in a quartz ampoule. The ampoule with a dimension of 15 mm^{ϕ}(ID)×80 mm in length, was sealed under a vacuum of $\sim 10^{-6}$ Torr. The ampoule was mounted in a vertical 3-zone furnace having a temperature gradient of 40°C/cm and heated to 100°C higher than the liquidus point. After homogenization for 3 h, the ampoule was cooled down to 500°C at a rate of 35°C/day. During crystal growth, the ampoule was rotated at a speed of 3 rpm.

The structural and compositional properties of the grown crystals were determined by XRD and electron probe microanalysis (EPMA). Hall concentrations and mobilities were measured at room temperature by the Van der Pauw method using a HL5500PC from Nippon Bio-Rad Laboratories. In the measurements, electrodes were made by Ni plating, where we ascertained the ohmic contacts.

3. Results and discussion

Fig. 1 shows XRD patterns of the samples having compositions from 10 to 70 mol% $CuInSe_2$ after DTA measurements, where the peaks of $CuInSe_2$ and Sb_2Se_3 are indicated by the symbol "▼" and "●", respectively. Only the diffraction peaks of Sb_2Se_3 and $CuInSe_2$ phases are seen in all XRD patterns and no other phases are observed. The phase diagram of Sb_2Se_3-$CuInSe_2$ pseudobinary system determined from the XRD and DTA results of measurements is shown in Fig. 2. The eutectic temperature is deduced to be at 520°C between 5–90 mol% $CuInSe_2$. The eutectic composition is evaluated to be 10 mol% $CuInSe_2$. The transition temperature from sphalerite to chalcopyrite phase [6–9] was determined to be at about 800°C in 50–100 mol% $CuInSe_2$. The liquidus temperature decreases with decreasing concentration of $CuInSe_2$. Hence, it is expected that $CuInSe_2$ firstly crystallizes in chalcopyrite structure in 10–50 mol% $CuInSe_2$. It should be emphasized that this phase diagram offers the possibility to grow $CuInSe_2$ crystals at low temperatures of 520–800°C.

The crystal growth of $CuInSe_2$ was performed, based on the phase diagram. The bulk single crystals were grown from a solution of 50 mol% $CuInSe_2$, which has almost the liquidus line below the phase transition temperature of $CuInSe_2$. A photograph of a typical grown boule is shown in Fig. 3. A crack-free single crystal of about 11 mm in length grew from the bottom of the boule towards the growth direction as shown in this figure.

Fig. 4 shows the XRD patterns measured at powder samples which were taken in the three regions labelled

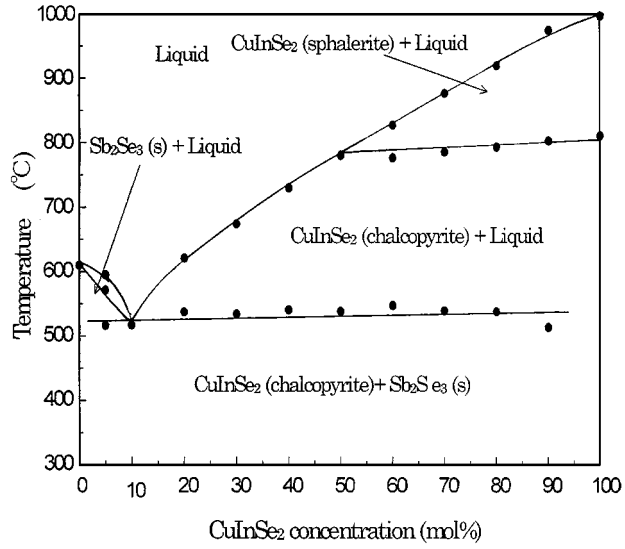

Figure 2 Phase diagram of the Sb_2Se_3-$CuInSe_2$ pseudobinary system as determined from DTA and XRD measurements.

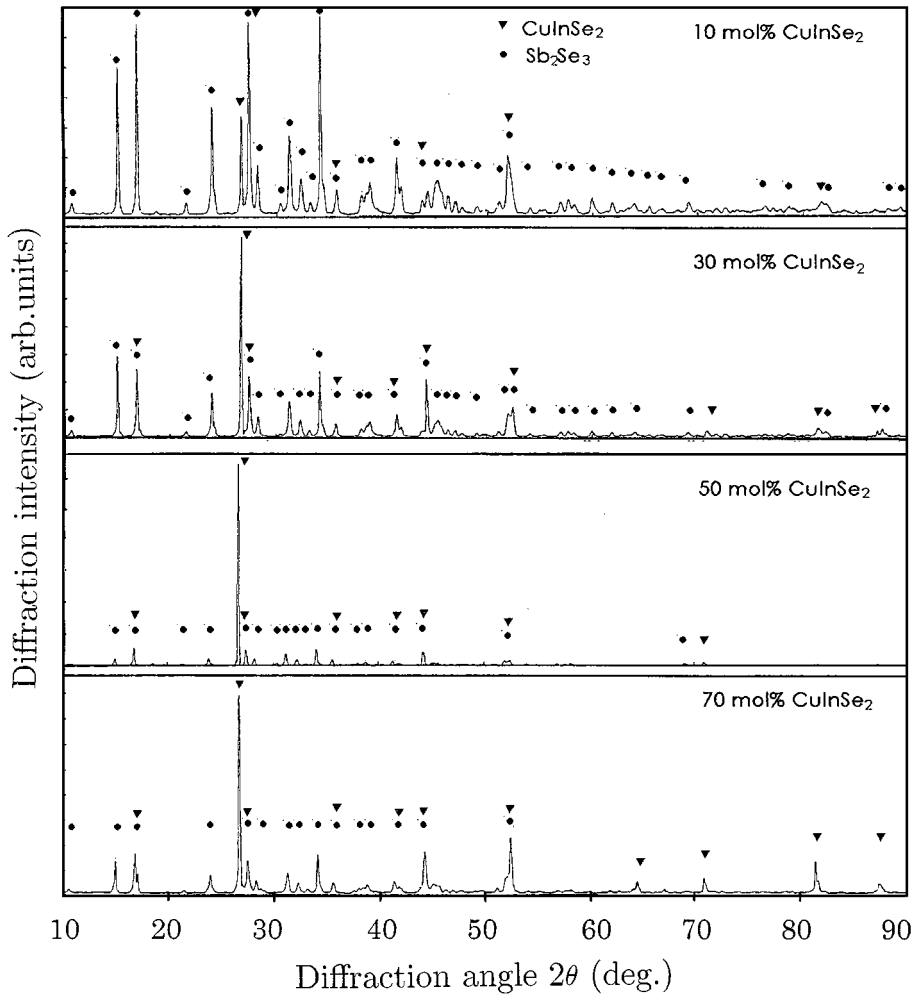

Figure 1 XRD patterns of Sb_2Se_3-$CuInSe_2$ samples having compositions of 10, 30, 50 and 70 mol% $CuInSe_2$ after DTA measurements. (▼: $CuInSe_2$; ●: Sb_2Se_3.)

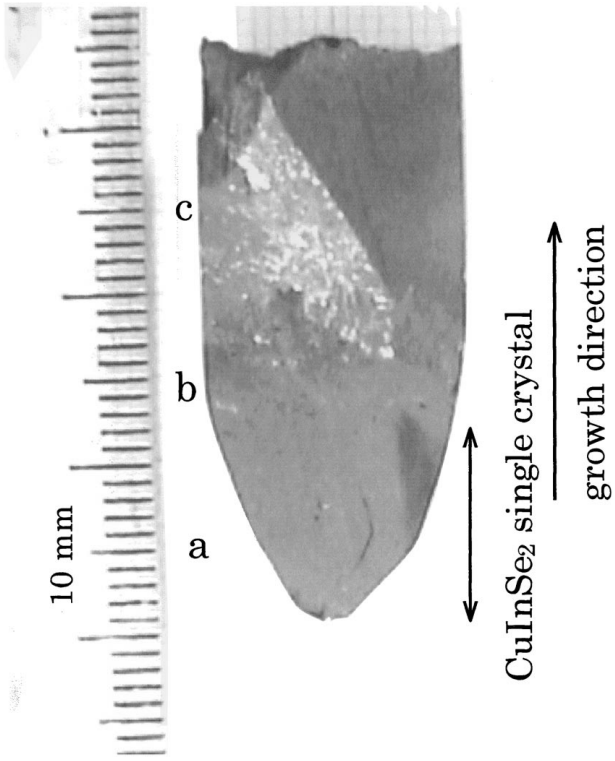

Figure 3 Photograph of a grown boule, region "a" corresponds to the $CuInSe_2$ single crystal in the bottom.

"a", "b" and "c" of the boule of Fig. 3, as compared with an XRD spectrum of Sb_2Se_3. The diffraction peaks of $CuInSe_2$ and Sb_2Se_3 are indicated by the symbol "▼" and "●", respectively. Only the diffraction lines of the $CuInSe_2$ chalcopyrite phase are observed in the bottom region "a" of the boule. $CuInSe_2$ and Sb_2Se_3 phases are observed in the upper regions "b" and "c". The concentration of Sb_2Se_3 is shown to increase along the growth direction from the half to the upper of the grown boule. The lattice constants of the single crystal were $a = 5.782$ Å, and $c = 11.602$ Å, which are in good agreement with the values of the starting material used and of the JCPDS files [10]. The results suggest that the grown crystal is not contaminated by Sb_2Se_3 solvent within the detection limit of XRD.

Fig. 5 shows the composition variation along the growth direction of the boule measured by EPMA. The Cu : In : Se ratio is shown to be about 1 : 1 : 2 and is uniform throughout the region "a" of the single crystal. On the other hand, antimony is detected through the boule above 12 mm. The impurity analysis of the single crystals was performed by means of inductively coupled plasma (ICP) spectrometry. The result indicated that the single crystal contained antimony at a level below 0.1 mol%.

The electrical properties of the grown crystals measured by the Van der Pauw method are summarized in

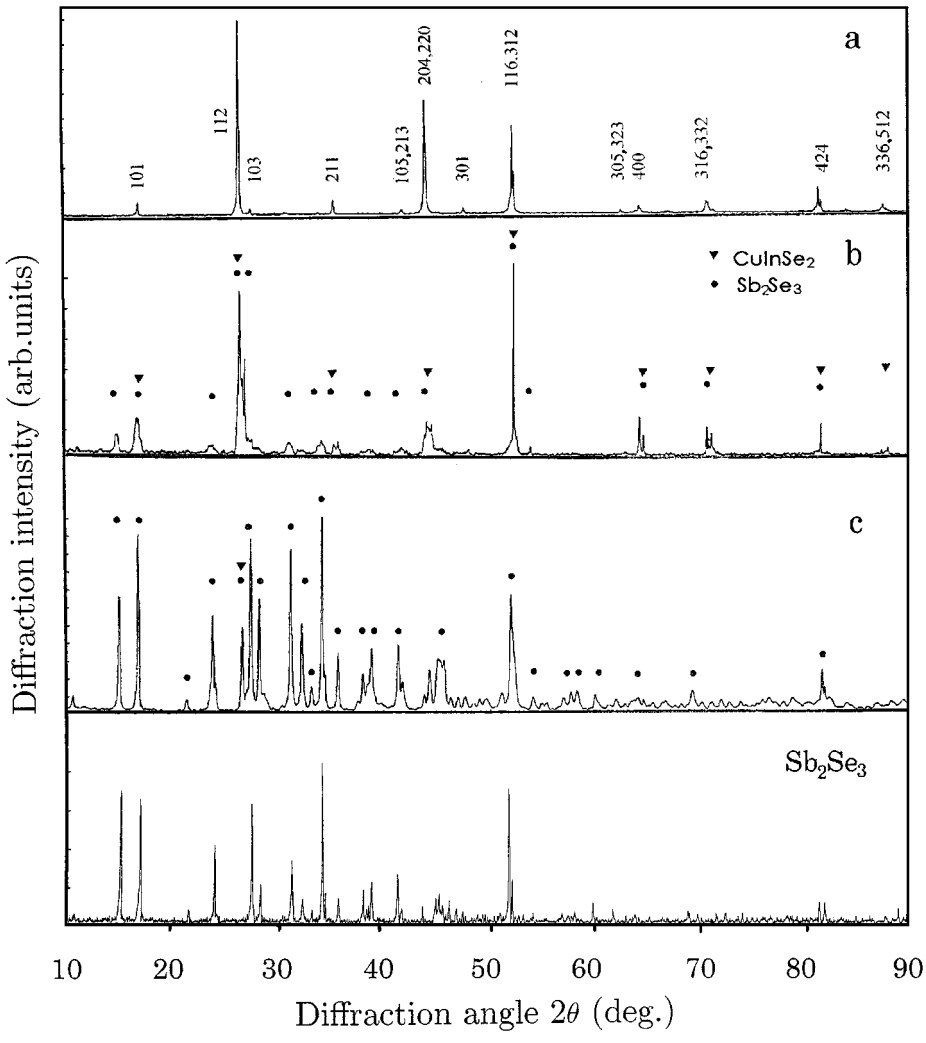

Figure 4 XRD patterns of the three regions of a grown boule, where the regions "a", "b" and "c" are illustrated in Fig. 3. (▼: $CuInSe_2$; ●: Sb_2Se_3.)

TABLE I Electrical properties of the starting material and of the grown crystals of $CuInSe_2$ at 300 K

Sample	Conduction type	Resistivity ρ (Ω cm)	Concentration n or p (cm^{-3})	Mobility μ (cm^2/Vs)
Starting material-1	p	1.1×10^{1}	6.6×10^{17}	<1
Starting material-2	n	5.3×10^{-2}	1.3×10^{18}	8.7×10^{1}
Grown crystal-1	p	1.2×10^{2}	1.2×10^{16}	8.3×10^{0}
Grown crystal-2	p	7.2×10^{0}	9.7×10^{16}	4.8×10^{0}

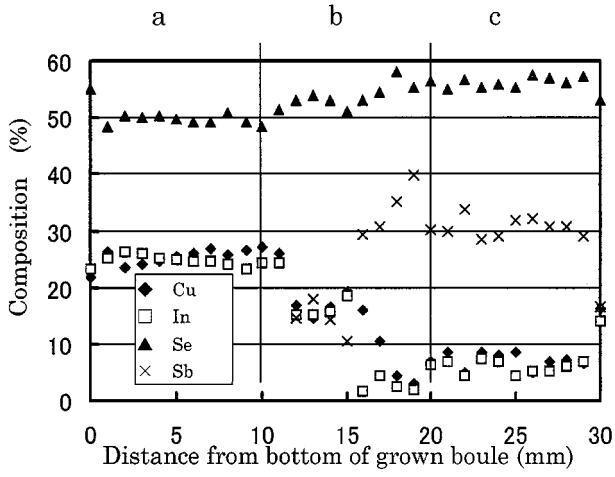

Figure 5 Variations of Cu, In, Se and Sb compositions of a grown boule along the growth direction.

Table I. The grown crystals 1 and 2 were grown by using the starting materials 1 (from bottom part of synthesized polycrystalline ingot) and 2 (from upper part of synthesized polycrystalline ingot), respectively. It can be seen that the crystals are p-type conductivity with lower carrier concentrations and higher Hall mobilities than those of the p-type starting material. This indicates that a Sb_2Se_3 solvent exerts no influence on the purity of the grown crystals.

4. Conclusions

The phase diagram of the Sb_2Se_3-$CuInSe_2$ pseudobinary system was constructed. Based on the determined phase diagram, the flux growth using Sb_2Se_3 as a solvent was investigated. $CuInSe_2$ crack-free single crystals with chalcopyrite structure were grown at a temperature below the chalcopyrite-sphalerite phase transition. The results of XRD, EPMA, Hall effect and ICP measurements indicated that the grown crystals are not contaminated by the flux constituent antimony. In conclusion, a Sb_2Se_3 solvent is suitable for the growth of $CuInSe_2$ crystals at temperatures below the solid-state phase transition.

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