Optoelectronic Properties of CuInSe_2 Grown by Traveling Heater Method Using Cu-In Alloy Solvent

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The CuInSe_2 (CIS) crystals were grown by traveling heater method (THM) using Cu-40 at%In alloy as the solvent metal. The composition mapping by electron probe microscopic analysis was stoichiometric and homogeneous throughout the crystal. The conduction was p-type with the carrier concentration and hole mobility in the order of magnitude of 10^{20} - 10^{22} m^{-3} and $10^{-3} \text{ m}^2 \text{Vs}^{-1}$ at 300 K, respectively. The emission peaks in the photoluminescence spectra were identified as the free exciton and the defects of Se vacancy (V_{Se}) and Cu antisite (Cu on In site, Cu_{In}). From the emission intensity measurement, it was found that the nonradiative recombination centers decreased in the direction from the bottom to the top end of the crystal, while the defects of V_{Se} and Cu_{In} remained almost uniform. The results indicate that the quality of the CIS crystal enhanced by the THM growth in comparison to that of the crystal by the Bridgman method in which non-radiative recombination centers were predominant.

Keywords : chalcopyrite-type compound, copper indium diselenide, crystal growth, traveling heater method, alloy solvent, p-type conduction, Hall effect, photoluminescence, excitonic emission, lattice defect

I. Introduction

The I-III-VI₂ chalcopyrite-type semiconductor of CuInSe_2 (CIS) is a material for photovoltaic application of thin film solar cell. For such practical application, most studies of CIS have been developed with thin films. In spite of achievement of high efficiencies⁽¹⁾⁽²⁾, the approach to explore the thin film quality is not completed.

The growth and characterization of the bulk crystals will give us a useful information for understanding the quality of the thin films as well as bulk crystals. The bulk single crystals have been prepared by the normal freezing and the Bridgman method⁽³⁾⁻⁽⁸⁾. In those cases, the chalcopyrite-type crystals were grown through a solid state phase transition ($T_t=1083 \text{ K}$)⁽⁹⁾⁻⁽¹¹⁾ from the zincblende-type crystal in the Cu-In-Se system, which may cause defects leading to poor quality of the single crystal. In order to perform the crystal growth under T_t , the growth by traveling heater method (THM) was firstly applied to CIS by using In solvent and the large crystal was obtained with excellent composition uniformity⁽¹²⁾⁽¹³⁾.

The present study concerns the THM growth of CIS using

Cu-In alloy as the solvent metal. Since the high efficiency of the CIS solar cells has been limited to the Cu-rich side⁽¹⁾⁽²⁾ in the wide nonstoichiometric composition range of CIS, the composition analysis and the optoelectronic measurements for the grown crystals will be helpful to elucidate the thin film quality and the defect states.

II. Experimental

The CIS polycrystals as the feed material were synthesized with the stoichiometric composition by the direct reaction of the constituent elements; Cu (nominal purity, 99.99 %), In (99.9999 %) and Se (99.9999 %). The total amount of the elements were weighed at 10-15 g. The amount of Cu-40at%In alloy as the solvent was necessary to be limited to 1-3 g in order to keep the solvent zone at about 10 mm. The growth conditions of the feed polycrystal were the maximum temperature kept at 1290 K and pulling rate at 7 mm/h. The THM was performed in the conventional heating system with a main heating zone and two adjacent subheating zones as shown in Fig. 1. The maximum temperature of the main heating zone was kept at 1043 K, where the width was 15 mm at 1023 K with the temperature gradient of about 6 K/mm at 1023 K. The subheating zones were kept at about

Fig. 1. Schematic diagram of THM apparatus. (a) Growth ampule and (b) temperature profile.

630 K. The solvent metal, a feed polycrystal and a quartz rod were placed subsequently and vacuum sealed in a pointed carbon-coated quartz ampule of 10 mm ID and 140 mm length after repeated evacuations and argon introductions. The quartz rod was fixed at the top of the feed to plug the upper vacant space in the ampule. The growth was performed by passing the ampule through the high temperature zone at a rate of 4 mm/d for 10 d. As the comparison to the THM growth, the Bridgman growth was made in a quartz ampule under the condition; the maximum heating temperature of 1050 K and the pulling rate of 3 mm/d.

The morphology of the as-grown boule was investigated by the visual viewing and optical microscope. The boule was cut along or across the growth direction. The composition was investigated by electron probe microscopic analysis (EPMA), where pure Cu, InP and ZnSe were used as standard materials and ZAF (atomic number, absorption and fluorescence) correction was made. The resistivity and Hall effect were measured at 300 K by the van der Pauw's method using Pt pressure contacts after confirmation of Ohmic contacts. Photoluminescence (PL) was measured at 77 K by using Ar laser (514.5 nm, 180 mW) for excitation, 500 mm-monochromator and a germanium detector, where the sample was etched for 10 s by brome methanol ($1\text{Br}_2:10\text{CH}_3\text{OH}$) prior to the measurement.

III. Results and discussion

(1) THM growth and composition

After the growth, the zone solution metal resulted at the upper end of the boule. The metallic Cu was found to have deposited on the whole surface of the boule with thickness of less than 0.2 mm. The boule was a polycrystalline aggregate

Fig. 2. Microscopic structures showing precipitations at the end portion of the CIS crystals grown by THM using Cu-40 at% In alloy solvent.

Fig. 3. EPMA composition profiles of the CIS crystals grown by THM using Cu-40 at% In alloy solvent. In the following figures, the position in a crystal is given by d/d_0 , where d is a distance from the bottom end along the growth direction and d_0 the separation between the bottom end and the precipitation zone.

which consisted of columnar coarse grains elongated along the growth direction with the dimension of $5 \times 5 \times 15 \text{ mm}^3$ at maximum. The increased amount of the solvent resulted the small CIS crystals which may be due to an increased dissolution of the feed polycrystal into the solvent zone. Figure 2 shows the precipitates elongated along the growth direction in the precipitation zone at the end portion of the CIS crystal. These precipitates consisted of Cu-In alloy, although the existing phase was not identified.

Figure 3 shows the EPMA composition profile along the growth direction of the boule by using 1-g solvent, showing that the composition was stoichiometric and homogeneous in the CIS crystal. In the following figures, the position in the crystal is indicated by a normalized distance of d/d_0 , where d is a distance from the bottom end along the growth direction and d_0 the separation between the bottom end and

Fig. 4 EPMA map taken by using SeLa in the CIS crystals grown by THM(solvent; 4-g pure). Dark region elongated in the growth direction; Cu-In precipitate.

the precipitation zone.

Figure 4 shows the elongated precipitates of the Cu-In alloy in the EPMA map of the boule grown by using 4-g solvent. The increased amount of the solvent was ready to dissolve the whole feed polycrystal into the solvent zone. Therefore the precipitates in the whole boule suggests a possibility that the alloy phase with the high melting point(920 K) may have appeared with the CIS during the solidification from the solution.

(2)Electric properties

The measurement of thermoelectric power indicated that the THM grown crystal was p-type. Since the Cu-rich alloy solvent may have caused the deviation from the stoichiometric composition of CIS, selenium vacancy(V_{Se}), Cu anti-site(Cu atom on In site, Cu_{In}) and Cu interstitial atom were possible. Among these defects, the p-type conduction were only attributable to Cu_{In} , which acts as a singly or doubly ionizable acceptor. Figure 5 shows (a)resistivity, (b)carrier concentration and (c)mobility in terms of position in the THM grown CIS crystals, which are comparable to those of the literature data⁽¹²⁾⁽¹⁴⁾⁻⁽¹⁶⁾ reported for the melt grown crystals. The high resistivity and apparent low carrier concentration might be ascribed to the carrier compensation between holes from Cu_{In} and electrons from V_{Se} .

(3)Photoluminescence spectra

Figure 6 shows the PL spectra in terms of the position in the THM crystal. The emission peaks at 1190, 1270 and 1350-1450 nm were identified on the basis of the literature

Fig. 5 Electrical properties of p-type CIS crystals grown by THM using Cu-40 at% In alloy solvent. (a)Resistivity, (b)carrier concentration and (c)carrier mobility plotted against position along the growth direction in the CIS crystals.

data⁽¹⁴⁾⁽¹⁷⁾⁻⁽²⁰⁾. The origin of the emission peak at 1190 nm was due to the free exciton. The emission peak in the vicinity of 1350-1450 nm was not accurately defined because of an intense absorption by water vapor, the origin was ascribed to the transition between V_{Se} and Cu_{In} states.

The peak at 1270 nm was not identified whether conduction band- Cu_{In} state or V_{Se} state-valence band. The results were consistent with those in the electric measurements. The dashed line in the figure also shows the PL spectrum measured for the crystal grown by the Bridgman method, where the emission intensity was about 1/10 that of the

Fig. 6 Photoluminescence spectra of p-type CIS crystal grown by THM using Cu-40 at% In alloy solvent. The number indicates the position in the crystals given by d/d_0 . The dashed line indicates that of CIS crystal grown by Bridgman method.

Fig. 7 Plots of emission intensities versus position along the growth direction in p-type CIS crystal grown by THM using Cu-40 at% In alloy solvent. Emissions due to (○) free exciton (peak at 1190 nm), (■) conduction band to Cu_{In} or V_{Se} to valence band (1350–1450 nm), and (●) V_{Se} to Cu_{In} (1270 nm).

THM grown crystal. The weak emission from the crystal grown by the Bridgman method may have caused from the nonradiative recombination centers introduced on the transformation from the zincblend-type to chalcopyrite type compound.

Figure 7 shows plots of the emission intensity (I_{Ex}) due to free exciton and relative intensity I/I_{Ex} due to the defects in terms of position in the THM grown crystal. It is found that I_{Ex} increased as the solvent zone proceeded from the bottom to the top end, while I/I_{Ex} for the defects was almost

constant. This fact indicates that the increase in the emission intensity in the spectra was due to the decrease of nonradiative recombination centers along the growth direction from the bottom to the top end in the CIS crystal, while the defect concentration of V_{Se} and Cu_{In} was almost constant.

IV. Summary

1. The growth of CIS bulk crystal was performed by THM using Cu-40 at% In alloy solvent.
2. The grown crystal was stoichiometric in the EPMA composition, which was a polycrystals of coarse-grains elongated in the growth direction with dimensions of $5 \times 5 \times 15 \text{ mm}^3$ at maximum.
3. The conduction of the crystal was p-type with resistivity of 1 Wm , hole concentration of $10^{20-22} \text{ m}^{-3}$ and Hall mobility of $10^{-3} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$.
4. The PL spectrum indicated the emission due to the free exciton, and the emission intensity increased from bottom to top end in the crystal indicating a decrease of nonradiative recombination centers along the growth direction. The spectrum also showed the emissions due to defects of V_{Se} and Cu_{In} , which were almost uniform in the crystal.

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