Microstructure of Splat-Solidified CuInSe₂

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The splat solidification method was applied for making thin platelets of a future solar cell material, CuInSe₂. The microstructure and second phase formation strongly depended on the cooling rate which was decided by the argon gas pressure and specimen thickness. The predominant surface structure was a function of the cooling rate; coarse dendritic and fine equiaxed structures for low and high cooling rate, respectively. The cross-sectional observation indicated that the matrix was chalcopyrite CuInSe₂, but the second phases of InSe and Cu-In compounds were located on the grain boundary. With increasing cooling rate, only the InSe phase was prevented from growth. In this experiment, an appropriate solidification condition was the specimen thickness of 100 μm and the gas pressure of 1.5×10^5 Pa, which enabled the increase in flat surface area and the minimization of second phase precipitation.

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I. Introduction

CuInSe₂ (CIS) is a candidate material for solar cells which has several advantages; high conversion efficiency over 15%⁽¹⁾, the resistance for high energy particle irradiation⁽²⁾, the potential of low cost fabrication⁽³⁾ and so on. However, the Cu-In-Se system is a complex phase diagram, which has a potential to precipitate in many phases, such as Cu₂Se⁽⁴⁾ and Cu-In compounds. It means that the preventing of the second phase should be important for fabricating CIS which has an excellent conversion efficiency.

For preparing films, several methods have been applied; the physical vapor deposition, the selenization of metallic films and the electrodeposition⁽⁵⁾. However, they have not succeeded in controlling the microstructure sufficiently and reducing the cost.

The splat solidification method in which melt is sprayed to some coolant and quenched has the possibility that one can obtain CIS platelets more easily. In this work, the splat cooling was applied as a new solidification method for preparing CIS films. The objective is to clarify the phase separation process in Cu-In-Se system as a function of local cooling rate, which is important for understanding the precipitation of second phases under the splat cooling.

II. Experiments

We used the synthesized CIS for spraying as the starting material. A mixture of Cu (turnings, 99.99%), In (shots, 99.9%) and Se (shots, 99.999%) was weighed to

be about 6 g. The mixture with the stoichiometric composition was put into a quartz ampule after evacuation to pressure of 3×10^{-4} Pa. The synthesizing process was as follows: heating at 1373 K for 1 d followed by cooling from 1373 K to room temperature with -2 K/min. It was identified that the starting material consisted of chalcopyrite and very small amount of zincblende CIS (JCPDS file numbers are 40-1487 and 23-207, respectively.) by X-ray diffraction (XRD). The synthesized CIS was crushed into pieces of about several millimeters, about 0.4 g of which was used for each splat solidification experiment.

Figure 1 shows the outline of splat solidification apparatus, where the inner dimension was 220 mm ϕ and 140 mm in depth. The inside was composed of a quartz jet nozzle, a tungsten heater and a copper block for quenching. After evacuation to 3 Pa, the material was heated up to about 1373 K for 30 s. Then the melt of the material was sprayed at $0.1\text{--}3.0 \times 10^5$ Pa of high-purity argon (99.999%). The sprayed melt collided against the copper block for rapid solidification. The thickness of the samples was controlled by changing the gas pressure which led to different cooling rates.

We analyzed three types of specimens. The first is the sprayed one. The second is standard one. The third is unsprayed one. The latter two specimens were used for reference. The standard sample was deficient in Se by 5.0 at% compared with the stoichiometric composition, that is, Cu:In:Se=27.5:27.5:45.0 at% to make its composition conform to the final one in the sprayed samples. The standard samples were made as follows: heating at 1373 K for 1 d and then cooling down for 2 d. The unsprayed sample was just cooled down in the nozzle in the solidification apparatus.

Analyses and observations were performed by a scan-

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Fig. 1 The outline of the splat cooling system.

ning electron microscope (SEM, JEOL Ltd., JXA-8600), XRD (Rigaku Denki, Geigerflex) and a transmission electron microscope (TEM, Hitachi, Ltd., H-700)). An X-ray micro-analysis (XMA) apparatus attached to the SEM and an energy dispersive spectroscopy (EDS) one (Horiba-2200) attached to the TEM were also used. The XRD patterns were taken from the powder samples. The TEM samples were made by ion milling after embedding in resin and slicing. The grain number density of the sprayed samples was measured after etching with 1% bromine in methanol⁽⁶⁾.

III. Estimation of Cooling Rate

We calculated the cooling rates to study the relation with the microstructure by the finite difference method whose detailed conditions are described below. The cooling rate of the splat solidification has been reported to be the order of 10^4 – 10^5 K/s⁽⁷⁾ and our calculated results were in good agreement with the reference.

1. Constants of CIS

Since the thermal conductivity (λ) has been only measured below 473 K⁽⁸⁾, we extrapolated the data to 1273 K and the value 6.63×10^{-1} J/(m·s·K) was used. The density (ρ) is 5.77×10^3 kg/m³⁽⁹⁾ at the room temperature and this value was used for the whole temperature range because there are no data at higher temperature. The specific heat (C_p) was set to 4.2×10^2 J/(kg·K)⁽⁸⁾ to let it conform to the values studied⁽⁸⁾.

2. Other conditions

The initial temperature of the sample was set to 1273 K. This is lower than the initial temperature of the experiments by 100 K. However, the constants above are of

solid phase of CIS, therefore the calculation should be done below the melting point which is close to 1273 K. The temperature of the copper block was set to 293 K. The adequacy that this temperature is constant is supported by that the mass of the copper block is far larger than that of the specimen. The heat loss from the top of the surface and the heat flow in the horizontal direction were neglected. The sample was divided into nine elements in the vertical direction. The heat transfer coefficient was 8.0×10^6 J/(m²·kg·K) though the sample and the atmosphere were different from the values in the references^{(10)–(14)}. The cooling rate was calculated as the average duration for which the sample was cooled down from 1273 to 1223 K to consider the phenomena around the melting point.

IV. Results

1. Sprayed samples

(1) Overall morphology of the sprayed samples

Figure 2 shows the relationship between the gas pressure and the thickness of samples together with schematic illustrations of the cross-sections. The morphology of the sample sprayed at 0.1×10^5 Pa was a mountain shape. In the case of 0.5×10^5 Pa, the sample had a flat area with the thickness of about 100 μ m, but the area was still small. When the gas pressure was increased to 1.5×10^5 Pa, there were a large thin flat area and a small marginal thick region, where the top view was usually almost circular and the diameter was about 20 mm. In the case of 2.0×10^5 Pa or more, the thickness became thinner, but the sample showed an irregular shape with a small area. It was supposed that some fraction of the melt was scattered out because of the high gas pressure.

It was found that the optimum pressure was 1.5×10^5 Pa in terms of the morphology because the thin area was largest at the thickness of about 100 μ m.

(2) Surface structure and composition

The typical SEM micrographs of the top surface are shown in Fig. 3 for the gas pressure of 0.1 to 1.5×10^5 Pa. The thickness decreased from 1000 to 100 μ m with increasing pressure.

The surface structure and calculated cooling rate of top surface strongly depended on the thickness. In the case of 1000 μ m in thickness (2.6×10^2 K/s), large dendritic structure was predominant. In the case of 400 μ m (1.5×10^3 K/s), small dendrites were developed. In the case of 100 μ m (1.5×10^4 K/s), there were two kinds of microstructure; small dendrites and equiaxed grains. With decreasing thickness to 70 μ m, the area of dendrites became smaller.

For the bottom surface, the structure composed of fine equiaxed grains which did not depend on the thickness. The cooling rates at the bottom surfaces corresponding to the thicknesses were 6.0×10^4 – 5.4×10^5 K/s (for 1000 to 100 μ m). This indicates that the developing only equiaxed grains at the bottom surfaces could occur by a

Fig. 2 Relationship between the gas pressure and the thickness of samples and the schematic illustrations of the cross-sections, each for the gas pressure 0.1, 0.5, 1.5 and 2.0×10^5 Pa.

little difference in the cooling rate among all the samples.

The surface structure changed with the cooling rate, as summarized in Fig. 4. With increasing cooling rate, the microstructures changed from larger dendrites to equiaxed grains.

The small bright particles were observed in SEM for both the bottom and top surfaces, in the case of the sample thickness being less than 200 μm (see Fig. 3(c) for example). These particles were developed only at high cooling rates.

The compositions of the matrix of the surfaces were stoichiometric CIS independent of the cooling rate. The bright particles were deficient in Se, where the Cu:In ratio was in the range of 73:27–62:38 (at%).

(3) Cross-sectional structure

Figure 5 shows back scattering electron images from the cross sections of the samples with different thicknesses, (a) about 1000 μm and (b) about 100 μm . The center parts are magnified as the right-side micrographs. The cooling rates were estimated to be 7.4×10^2 and 3.1×10^4 K/s for (a) and (b), respectively. The center parts consisted of columnar grains, and other parts consisted of equiaxed grains in both cases at low magnifications though the grain number density was different. The development of the second phase strongly depended on the specimen thickness. The composition of the CIS matrix was stoichiometric in both cases.

When the thickness was less than 400 μm , there was only one type of precipitates lacking in Se whose composition was Cu:In=70:30–63:37 (at%) with about 5 at%Se. These precipitates existed regardless of the difference in sample thicknesses.

When the sample thickness was larger than about 600 μm , two types of precipitates appeared, which were black and white contrasts in the SEM micrograph. The black contrast indicates the metallic Cu–In precipitates which was developed also in the sample less than 400 μm thickness. The composition of the white contrast part

Fig. 3 SEM micrographs of the top surfaces of the sprayed samples. (a) 0.1×10^5 Pa (~ 1000 μm , 2.6×10^2 K/s), (b) 0.5×10^5 Pa (~ 400 μm , 1.5×10^3 K/s), (c) 1.5×10^5 Pa (~ 100 μm , 1.5×10^4 K/s). The numbers inside the parentheses are the approximate thickness and the calculated cooling rate, respectively. The arrows indicate metallic Cu–In particles which were observed on the top surfaces of samples thinner than about 200 μm and on the bottom surfaces.

Fig. 4 The changing surface morphology as the function of cooling rate.

Fig. 5 SEM micrographs (back scattering electron image) from the cross-sections of samples with the thicknesses of (a) ~ 1000 μm (0.1×10^5 Pa) and (b) ~ 100 μm (1.5×10^5 Pa), each under low and high magnifications.

was Cu:In:Se=4:53:43 (at%) and the main constituent was supposed to be InSe. InSe precipitates were not observed at faster cooling rates in the SEM micrograph.

The thickness of 400–600 μm is a transient condition, where metallic Cu–In precipitates were observed in all the samples but the InSe phase was contained in some cases.

(4) XRD data

Figure 6 shows the XRD patterns from (a) the sprayed sample at 1.5×10^5 Pa and (b) the sample before spraying (as synthesized in the electric furnace). The peaks of the chalcopyrite CIS can be seen in both patterns. The peaks of the metallic Cu–In precipitates are supposed to be the ones marked by the triangles in Fig. 6(a), because CIS and these precipitates were dominant in the sample by the SEM observation and other peaks belong to the chalcopyrite CIS. Moreover, those two peaks were not observed in Fig. 6(b). These peaks were observed in the XRD patterns regardless of sample thickness but their intensities were so weak that we could not identify them in XRD. However, these precipitates were estimated to be mixture of Cu_9In_4 , Cu_2In , Cu_7In_4 and $\text{Cu}_{11}\text{In}_9$ by comparing their compositions in the Cu–In system. The InSe phase was not detected by XRD even in the sample of 1000 μm thickness though it was observed remarkably in the SEM images.

(5) Grain number density

The grain number densities were measured after etching and are plotted against the thickness in Fig. 7. The measured areas were the center and bottom of the specimen. The calculated cooling rates are also indicated along the abscissa axis. The density decreases monotonously with increasing thickness at both center and bottom parts. Their behavior was similar when the thickness was small and there was almost no difference in the cooling rate. The densities were different when the thickness was large and there was some difference in the cooling rate. However the relationship between the cooling rate and the grain number density did not depend on the part in the sample. With increasing cooling rate, the number density increased because the large cooling rate would enhance the nucleation probability. The two curves shown in Fig. 7 do not agree with each other strictly at the same cooling rate. This reason is supposed to be that the cooling rates at the bottom parts were smaller than the estimated ones which might be caused by that there were spaces between the specimen and the copper block.

2. Structure and composition of reference samples

In the standard sample, CIS, InSe (JCPDS #34-1431) and metallic Cu–In phases were detected by the XRD pattern and the SEM observation. Their Cu:In:Se ratios were as follows by XMA; 26:24:50, 1:50:49 and 63:36:1

Fig. 6 XRD patterns of (a) the sprayed sample of 1.5×10^5 Pa case and (b) the sample before spraying (as synthesized in the electric furnace). Open circles indicate the chalcopyrite CIS (JCPDS file #40-1487) and closed triangles are supposed to peaks belonging to metallic Cu-In phase.

Fig. 7 The relationship between the thickness of samples and the grain number density. Open circles indicate the density for the center parts and closed triangles indicate the ones for bottom parts. The thickness scale is common to both parts. The calculated cooling rate is also indicated.

Fig. 8 SEM micrograph of the standard sample.

Fig. 9 TEM micrograph from the sprayed sample at 1.5×10^5 Pa under (a) low and (b) high magnifications.

(at%). **Figure 8** shows the SEM structure. The metallic Cu-In phase also appeared in the XRD pattern of this sample. The precipitation process of the three phases is assumed to be in the order of CIS, metallic Cu-In phase and InSe by two reasons. The first one is that the InSe phase seems to fill in the opening between the CIS and the metallic Cu-In phases by the SEM micrograph. The second one is that their melting points are about 1273, 953 and 933 K, respectively.

In the unsprayed sample, CIS, InSe and metallic Cu-In phases were identified by XRD and SEM observations. Their Cu:In:Se ratios were as follows by XMA; 26.6:24.6:48.8, 1.9:49.7:48.4 and 63:35:2 (at%). The developed phases were the same as the standard sample.

TEM micrographs from the sample at 1.5×10^5 Pa under low and high magnifications are shown in **Fig. 9** at (a) low and (b) high magnifications. Precipitates about 1 μm can be seen along grain boundaries as shown in Fig. 9(a). EDS results indicate that the precipitates are metallic Cu-In phase which were observed also by SEM. Figure 9(b) shows fine precipitates of about 30 nm in

diameter. They are thought to be InSe which could not grow very much at large cooling rate.

V. Discussion

1. Formation process of metallic Cu–In phase

The Cu:In ratios of the metallic Cu–In phases in typical three specimens were as follows: 67.3:32.7 (sprayed under 1.5×10^5 Pa), 64.4:35.6 (unsprayed sample), 63.6:36.4 at% (standard sample). Their standard deviations were 1.4, 1.7 and 0.8 at%, respectively. There was a slight difference in the ratio among the samples. The reason for this difference may be explained as follows. The amounts of In and Se which solve into CIS increased by quenching and lowers the In concentration in the metallic Cu–In phase in the sprayed sample. The solubility limit of In_2Se_3 in the chalcopyrite CIS is large and the 0.5 mol of In_2Se_3 can be solved in 1 mol of CIS at most⁽¹⁵⁾.

The quantity of this kind of precipitates seems to be not sensitive to the cooling rate because the intensity of this phase in the XRD patterns were similar at different cooling rates.

2. Suppression of development of InSe phase

The InSe phase was observed in the standard and unsprayed samples and also in the thicker sprayed samples, but it did not exist in the thinner sprayed samples. By XRD, InSe was confirmed only in the standard and the unsprayed samples. The XRD intensities of both samples ((400) plane) were almost the same compared with the (112) plane of the chalcopyrite CIS.

This behavior can be explained as follows. When the cooling rate is slow enough (below 1.1×10^2 K/s which is the cooling rate of the unsprayed sample), InSe crystals can be developed well. When the cooling rate is faster (sprayed samples of ~ 1000 μm), InSe cannot grow well and can be observed not by XRD but by SEM. At much faster cooling rate (sprayed samples with thickness below 400 μm), it can be identified neither by SEM nor XRD. However, the small precipitates observed by TEM are supposed to be InSe which might not be able to grow well at the fast cooling rate.

VI. Summary

We obtained CIS platelets 30 to 1000 μm in thickness by splat solidification at the gas pressure of $0.1\text{--}3.0 \times 10^5$ Pa. The cooling rate increases with decreasing sample thickness.

The microstructures of the surfaces are dendrites at the

cooling rate of $2.6 \times 10^2\text{--}1.5 \times 10^3$ K/s. With increasing cooling rate from 10^3 to 10^6 K/s, the structure changed from large dendrite to equiaxed grains.

The cross-sectional structure of the sprayed samples consists of CIS matrix, metallic Cu–In and InSe precipitates. The types of the second phases did not depend on the sample thickness, but the size of InSe was related to the cooling rate; several μm for 2.2×10^3 K/s (600 μm) and several tens of nm for 3.5×10^3 K/s (400 μm). The composition of the matrix was stoichiometric, whereas that of the metallic Cu–In precipitates was about Cu:70 and In:30 at%.

When the cooling rate was slow at the same level as the standard samples, three phases of CIS, metallic Cu–In and InSe appeared. They were supposed to be the equivalent phases when the composition was Cu:In:Se = 27.5:27.5:45.0 at%. When the sample was just cooled down in the nozzle, the CIS, metallic Cu–In phase and InSe were also developed. The grain number density was observed to depend on the thickness of the sample, and it increased with increasing of cooling rate. The optimum condition of splat solidification for making good CIS platelets was achieved at the inert gas pressure of 1.5×10^5 Pa.

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