The Crystal Growth of In-Se by Vapor Transport Method

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The thermophotovoltaic (TPV) system has been attracted as the waste heat recovery system. A TPV system consists of the heat source, the selective emitter and the TPV cells. For high conversion efficiency, it needs the wavelength matching between emitter radiation and the bandgap of TPV material. The Yb2O3 emitter is a high temperature resistant material with a selective emission spectrum. The peak wavelength of this spectrum is 980 nm. The bandgap of \(\alpha\)- and \(\beta\)-In2Se3 is 1.2-1.3 eV, so that \(\alpha\)- and \(\beta\)-In2Se3 are promising as the TPV material for this emitter radiation. We investigated about the crystal growth of In-Se by vapor transport method in two conditions of temperature gradients which were 0.83 and 0.33 Kmm\(^{-1}\). In addition, an effect on substrate which has Si-O layer on the surface was also investigated.

The hollow hexagonal cylinders with diagonal dimension of approximately 10 \(\mu\)m were obtained at both growth conditions. The layers with thickness of approximately 200 nm were stacked in a longitudinal direction of the hollow hexagonal cylinder. From the results of powder XRD analysis, it was revealed that these hollow hexagonal cylinders were mixed phase of In2Se3. In addition, the similar morphological crystals as hollow hexagonal cylinder were obtained onto Si-O layer.

Key words: Crystal growth, In-Se, Vapor transport method, Thermophotovoltaic

1. INTRODUCTION

A combustion apparatus as an industrial system or a residential heating system produce a heat which mostly becomes waste heat. The temperature range of the waste heat is between 1300 and 1800 K, it can become a heat source with sufficient quality convertible into electricity. A thermophotovoltaic (TPV) system is one of the attractive candidates as the waste heat recovery system. The TPV system basically consists of three different parts as the heat source, the selective emitter and the TPV cells. The heat source heats up the selective emitter. The selective emitter radiates photons in a narrow wavelength range. The emitted photons will directly be converted to electricity by the TPV cells which have a bandgap well matched to the emitted peak wavelength. The Yb2O3 emitter is a high temperature resistant material with a selective emission spectrum. The emission shows its maximum value at photon energy of 1.27 eV [1]. The bandgap of \(\alpha\)- and \(\beta\)-In2Se3 is 1.2-1.3 eV, \(\alpha\)- and \(\beta\)-In2Se3 are promising as the TPV material for this emitter radiation [2, 3].

The TPV material include In2Se3, which is a direct transition semiconductor. The basic structure of the layered In2Se3 is zinc blende structure. The crystal structure of In2Se3 is commonly layered structure or defect wurtzite with highly ordered vacancies, where every atom is located at the wurtzite or zinc blende sites and one third of the cation sites are occupied by the structural vacancies [4]. Fig. 1 shows the structure models of In2Se3. The layered structure consists of rather loose stacks of covalently bonded layers, including five atomic layers of Se-In-Se-In-Se, by van der Waals force.

The bandgap of In2Se3 can be controlled by the element substitution. Since this can achieve wavelength matching between emitter radiation and bandgap of TPV cells, this will be the advantage as component of TPV system.

Fig. 1 Structure models of In2Se3: (1) hexagonal layered structure (\(\alpha\)-phase) with planar cationic vacancy ordering; (2) distorted wurtzite-like structure (\(\gamma\)-phase) with screw-type cationic vacancy ordering.

In order to keep the costs low, it would be interest to obtain the photoconductive material in thin films by using simple techniques. The crystal growth of In2Se3 has been realized in other laboratories [5-6], the obtained films, however, were strained as the method is based on the solid state reaction. The crystal grown by
the vapor transport method is considered to be without strain, which is caused by inner wall of reactive chamber, because of vapor state reaction. In order to acquire the scientific knowledge into crystal growth condition, we investigated the crystal growth of In\textsubscript{2}Se\textsubscript{3} by vapor transport method.

2. EXPERIMENTAL PROCEDURE

2.1 Preparing of starting material

The melt grown material of In\textsubscript{2}Se\textsubscript{3} as the starting material for vapor transport method was prepared by vertical Bridgman method. Indium (99.999 %) and selenium (99.999 %) were weighed to stoichiometric composition and encapsulated into a quartz ampoule under vacuum at 10\textsuperscript{-3} Pa. The reaction temperature was 1160 K. The reaction time was 24 h. The crystal growth rate was 1.6 mm h\textsuperscript{-1}.

The phase identification of sample was achieved by powder XRD analysis.

2.2 Crystal growth of In-Se by vapor transport method

The quartz ampoule encapsulated only bulk In\textsubscript{2}Se\textsubscript{3} as starting material was heated by temperature gradient furnace. The bulk In\textsubscript{2}Se\textsubscript{3} was placed at hot side in quartz ampoule under vacuum at 10\textsuperscript{-3} Pa. The temperature of In\textsubscript{2}Se\textsubscript{3} placed side was kept at 1050 K, and the opposite side was kept at 850 K. For this study, two crystal growth conditions of temperature gradient were carried out by the control of ampoule length. At the first condition, the gradual temperature gradient 0.33 Kmm\textsuperscript{-1} was achieved with a 600 mm ampoule. At the second condition, the steep temperature gradient was achieved 0.83 Kmm\textsuperscript{-1} with a 240 mm ampoule. The heating time was 168 h, respectively.

The surface of each sample was observed by SEM. The phase identification of each sample was achieved by powder XRD analysis.

2.3 Crystal growth of In-Se onto Si-O layer by vapor transport method

In order to investigate the crystal growth state to a flat silicon oxide, the Si oxide layer on Si substrate was used. The quartz ampoule encapsulated a melt grown In\textsubscript{2}Se\textsubscript{3} and two Si-O substrates were heated by temperature gradient furnace under vacuum at 10\textsuperscript{-3} Pa. The temperatures of two substrates were approximately 950 K and 880 K. The crystal growth was achieved under the temperature gradient of 0.83 Kmm\textsuperscript{-1}. The heating time was 168 h.

The surface of the sample was observed by SEM. The phase identification of the sample was achieved by thin-film XRD analysis.

3. RESULTS AND DISCUSSION

3.1 Preparing of starting materials

Fig. 2 shows a powder XRD pattern of the ingot obtained by vertical Bridgman method. This sample was contained the α- and δ-In\textsubscript{2}Se\textsubscript{3}. From the result, it is found that this ingot was suitable to be used as the starting material for vapor transport method.

3.2 Crystal growth of In-Se by vapor transport method

From the result of crystal growth by the gradual temperature gradient (0.33 Kmm\textsuperscript{-1}) with 600 mm ampoule, the crystal deposited at three areas in ampoule which were approximately 960, 920 and 880 K. On the other hand, another condition which was achieved the steep temperature gradient (0.83 Kmm\textsuperscript{-1}) with 240 mm ampoule, the deposits obtained at the region between 920-880 K. Fig. 3 shows SEM morphologies of the obtained deposits. There were little differences by deposit conditions in the thickness, length and linearity of deposits.
Fig. 4 shows the detail SEM morphologies at the edge of deposit. The hollow hexagonal cylinders with diagonal dimension of approximately 10 μm in the quartz ampoule were obtained regardless of the temperature gradient. The layers with thickness of 200 nm were stacked in a longitudinal direction of the hollow hexagonal cylinder.

Fig. 4 SEM images of the hollow hexagonal cylinders: (a) gradual temperature gradient (0.33 Kmm⁻¹), (b) steep temperature gradient (0.83 Kmm⁻¹).

Figs. 5 and 6 show the powder XRD pattern of hollow hexagonal cylinders. From the results of powder XRD, hollow hexagonal cylinders contained mixed phase of α-, β-, γ- and δ-In₂Se₃.

There was little difference in the morphology of crystals which grew under each temperature gradient. Thus, the hollow hexagonal cylinders were constructed by mixed phase of In₂Se₃. It may be that the layers observed in a longitudinal direction of the hollow hexagonal cylinder consisted of different phases of In₂Se₃ stacked periodically because of strain release.

Fig. 5 powder XRD pattern of the hollow hexagonal cylinders obtained by gradual temperature gradient (0.33 Kmm⁻¹): (1) obtained at 960 K, (2) at 920 K, (3) at 880 K.

Fig. 6 powder XRD pattern of the hollow hexagonal cylinders obtained by steep temperature gradient (0.83 Kmm⁻¹).

3.3 Crystal growth of In-Se onto Si-O layer by vapor transport method

The high aspect ratio crystals were obtained onto Si-O layer by vapor transport method. Fig. 7 shows the SEM morphology of hollow hexagonal cylinder which obtained onto the Si-O layer. It is clear that there were little differences by presence of substrate in the thickness, length and morphology of deposits.
Fig. 7 SEM image of hollow hexagonal cylinder which obtained onto Si-O layer.

Fig. 8 shows the thin-film XRD pattern of the crystal that was obtained onto Si-O layer. The hollow hexagonal cylinders, which obtained onto Si-O layer, were contained the α-, γ- and δ-In$_2$Se$_3$.

Fig. 8 thin-film XRD pattern of the obtained crystal onto Si-O layer (α= 0.3 degree).

The whisker was observed onto the edge of Si-O layer, i.e., Si substrate. Fig. 9 shows the SEM morphologies of the whisker with a crystal at the bottom onto Si substrate. The diameter of the whisker was about 1 μm and length extends up to 20 μm (Fig. 9(a)). It is confirmed that the whisker grew onto layered crystal (Fig. 9(b)). The small crystals which arranged in a circular pattern were observed in proximity to the layered crystal at the root of the whisker (Fig. 9(c)). The diameter of the circle was approximately 400 nm. It seems that the layered crystal at bottom of the whisker grew from these circular arranged crystals. It is not clear the relationship between these whiskers and the hollow hexagonal cylinders of In$_2$Se$_3$.

![Fig. 9 SEM images of the crystals on substrate: (a) the whisker observed on Si (the Si substrate has a 100 nm oxide layer at the surface.), (b) the crystal at the bottom of the whisker, (c) the circular arranged crystals.](image)

4. CONCLUDING REMARKS

The In$_2$Se$_3$ was grown by vapor transport method. The crystal growth conditions of In$_2$Se$_3$ are as follows: The temperature of starting material side was 1050 K, alternative side in ampoule was 850 K and the temperature gradient was 0.83 or 0.33 Kmm$^{-1}$.

From the results of powder XRD and SEM observation, the hollow hexagonal cylinders which contained mixed phase of In$_2$Se$_3$ were obtained regardless of temperature gradient. In addition, the hollow hexagonal cylinders were obtained onto the Si-O layer. The relation between the crystal growth of hollow hexagonal cylinders and the whisker observed in Si substrate is investigated now.

REFERENCES


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