

Synthesis, growth and characterization of AgInSe₂ single crystals



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ARTICLE INFO

Article history:

Received 19 April 2015

Received in revised form

14 July 2015

Accepted 15 July 2015

Keywords:

X-ray diffraction

Single crystal growth

Growth from melt

Bridgman technique

Nonlinear optic material

Infrared devices

ABSTRACT

Single crystal of the ternary semi-conductor AgInSe₂ has been grown by Bridgman technique. The AgInSe₂ crystal crystallizes in the tetragonal chalcopyrite structure. Using melt temperature oscillation method polycrystalline charge was synthesized. The synthesized charge was subjected to powder X-ray diffraction analysis. Thermal property of AgInSe₂ was analyzed using differential scanning calorimetry (DSC) technique. The melting and solidification temperature is 777 °C and 761 °C respectively. The synthesized polycrystalline charge was employed to grow AgInSe₂ single crystals. The grown crystal was confirmed by single crystal X-ray diffraction. The crystal exhibits 60% transmission in the Infrared region. The stoichiometric composition of AgInSe₂ was confirmed by Energy dispersive X-ray analysis (EDAX). The electrical properties of the crystal were studied by Hall Effect measurements and photoconductivity.

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1. Introduction

The I–III–VI₂ ternary compounds crystallize in the tetragonal chalcopyrite structure and can form a large number of semi-conducting materials. Such ternary compounds have been widely studied because of their potential applications. Complex silver-containing chalcogenides have found wide application in various semi-conductor fields [1]. Certain representatives are used as superionic semi-conductors [2], photocells, and narrow-band optical filters [3]. Many of them possess a non-centrosymmetric structure [4] and are thus prospective for non-linear optics. The compounds with general formula AgA^{III}X₂ (A^{III}—Ga and In; X—S, Se and Te) that crystallize in the chalcopyrite structure belong to such phases.

Silver indium diselenide (AgInSe₂) is one of the I–III–VI₂ ternary compounds. AgInSe₂ is also promising candidate for solar cells. AgInSe₂ has band gap energy of 1.20 eV. The optical properties of AgInSe₂ have been studied by various techniques [5–7]. The material is more electrically conductive due to the absorption of the electromagnetic radiation. Most of these studies were carried out on polycrystalline AgInSe₂ samples [8–10]. The growth techniques and properties of AgInSe₂ have been studied by many authors [5]. It is very difficult to obtain large sized, crack-free AgInSe₂ single crystal for practical applications. We had many problems in synthesis and single crystal growth and this paper reports successful results of crystal growth of AgInSe₂.

The major difficulties are (i) anomalous thermal expansion

behavior along *c* axis during cooling, which causes cracking and possible formations of dislocations [11,12], (ii) Selenium is more volatile compared to silver and indium. This may cause Selenium vacancies in the AgInSe₂ structure and (iii) retrograde phase transformation during growth, which allows the formation of secondary phase. Due to these problems, it is very difficult to grow high-quality crack-free and void-free AgInSe₂ single crystal.

In this paper, we report the details of synthesis and growth of AgInSe₂ single crystal and its physical properties. The melt temperature oscillation method was used to synthesize the AgInSe₂ polycrystalline charge. The synthesized polycrystalline charge was used to grow AgInSe₂ single crystal using Bridgman technique. The grown single crystal was subjected to single crystal XRD, powder XRD, TG-DSC, UV–vis–NIR transmission and absorption, Energy dispersive X-ray analysis (EDAX), Hall effect and photoconductivity measurements.

2. Experimental method

2.1. Synthesis

AgInSe₂ polycrystalline material is not available commercially in the market. 6 N purity elements were used as starting materials. Without high quality AgInSe₂ polycrystalline charge we cannot achieve good quality, void free single crystals. In accordance with the stoichiometry, the mole ratio 1:1:2 of silver, Indium and selenium, with an excess of 2% selenium was chosen as the starting composition. The starting materials were taken in a quartz

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ampoule. The length of the quartz ampoule was 260 mm and the inner diameter was 23 mm. The quartz ampoule was evacuated upto 1×10^{-6} m bar at room temperature and then sealed. The evacuated sealed ampoule was placed in a suitable horizontal furnace. The 3 rpm DC gear motor was connected to the quartz ampoule and the ampoule was continuously rotated. The quartz ampoule was slightly tilted for not allowing the materials into another end. This process is used to achieve the stoichiometric composition. During the synthesis process the temperature was controlled by Eurotherm thermo controller.

The temperature was raised to 680 °C (to be reached in 24 h) and maintained for 24 h. The temperature was increased to 940 °C (to be reached in 24 h) and maintained for 48 h. The melt was cooled to 670 °C and the temperature was rapidly changed twelve times approximately, alternating between 860 °C and 670 °C. This step is called as melt temperature oscillation method. Excess of selenium exists in the gaseous state in the melt at 860 °C. When the temperature was rapidly reduced to 670 °C, the melt condensed to the solid state and the temperature in the inner part of melt was higher than that of the surface; therefore, the selenium vapor in the center of the melt was rapidly transported out of the melt. The temperature was then rapidly raised again from 670 °C to 860 °C, and it was reduced from 860 °C to 670 °C alternately, so that the excess of selenium vapor in the melt would rapidly transport out of the melt. During the temperature oscillation, the state of the melt alternated between melt and polycrystal. After several cycles the furnace was cooled down in 24 h. After this process the polycrystalline charge was harvested.

2.2. Crystal growth

The polycrystalline material was powdered and taken in the specially designed quartz ampoule. The length of the ampoule was 300 mm and the diameter was 8 mm. The quartz ampoule was evacuated upto 1×10^{-6} m bar at room temperature and then sealed. The specially designed Bridgman furnace is used to grow the single crystals. The furnace contains one zone of kanthal winding. The temperature profile was taken for the entire length of the growth furnace. Using TG-DSC analysis we found that the melting temperature of the AgInSe₂ polycrystalline material was 777 °C and the freezing point of the material was 761 °C. The ampoule was placed at suitable place in the furnace. The temperature profile of the furnace is shown in Fig. 1.

The ampoule was rotated clockwise and moved down using the suitable mechanical arrangement. The ampoule was rotated at 5 rpm and then the ampoule lowered at 10 mm per day. To achieve good quality, void free single crystals the ampoule was rotated.

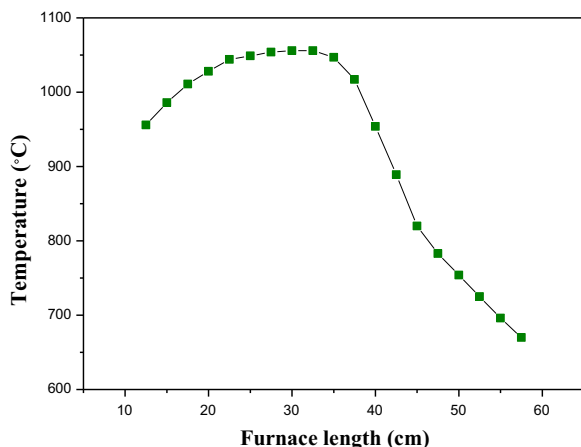


Fig. 1. Axial temperature profile of the growth furnace.

With the help of mechanical arrangement and microcontroller assembly the ampoule was rotated and lowered successfully. After many trials we have optimized the experiment and got successful results. We achieved good quality, void-free, crack-free single crystal with 8 mm diameter and 70 mm length as shown in Fig. 2. The cut and polished AgInSe₂ single crystal ingots are shown in Fig. 3.

2.3. Material characterization techniques

The crystal structure was determined by single-crystal X-ray diffraction studies using ENRAF NONIUS CAD4 single-crystal X-ray diffractometer. The powder X-ray diffraction pattern was recorded using Rich Seifert X-ray diffractometer employing CuK α (1.54058 Å) radiation, scanning angle ranging from 10° to 70° at a scan rate 1°/min to study the crystallinity of the grown crystal. Differential scanning calorimetry/Thermogravimetric analysis was performed in a SDT (simultaneous DSC-TGA) STA 449F3 Model. The optical studies were measured by Perkin-Elmer Lambda-35 spectrophotometer for the wavelength range from 200 to 1100 nm with slits restricting the spectrum segment to a near-monochromatic radiation beam with spectral band pass of 2 nm and scan speed 240 nm/min, which covers near ultraviolet, visible and higher energy part of near IR region. Low energy part of near IR, mid-IR and far-IR region was covered by the ALPHA-BRUKER spectrophotometer for the wave number range from 500–6000 cm⁻¹ with an accuracy of 0.01 cm⁻¹. The electrical properties of the AgInSe₂ crystal were examined by an ECOPIA-HMS3000 type Hall measurement apparatus in the Vander Pauw configuration at room temperature with a permanent magnet of 0.57 T. Photoconductivity studies were measured using Hind Hi-vacuum cryostat CMT 25 coupled with Keithly Picoammeter (model 6487).

3. Results and discussions

3.1. X-ray diffraction analysis

The grown AgInSe₂ single crystal was subjected to single crystal X-ray diffraction analysis, the crystal belongs to tetragonal system and I42d space group with the following dimension $a=6.09$ Å and $c=11.64$ Å in close agreement with previously reported value [13]. The powder X-ray diffraction of AgInSe₂ pattern is shown in Fig. 4. The peak positions matched with the powder diffraction files (PDF 38-0952) of AgInSe₂.

3.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used to study the heat flow rate during the melting and freezing phase transitions. The AgInSe₂ polycrystalline charge was subjected to DSC analysis as shown in Fig. 5. The melting point and solidification temperature of AgInSe₂ polycrystalline were identified as 777 °C and 761 °C from the endothermic and exothermic peaks on the measured DSC curve. The temperature gradient was adjusted to 15 °C/cm at the growth interfaces, and the growth rate was about 10 mm/day.

3.3. Optical properties

The transmission spectrum plays an important role in identifying the potential nonlinear optical materials. The transmission of the AgInSe₂ single crystal was measured by FTIR spectrometer with wavenumber range from 500 cm⁻¹ to 6500 cm⁻¹. The cut and polished AgInSe₂ crystal with 1 mm thickness was used for FTIR transmittance. It shows 60% transmittance in the entire Mid

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