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Synthesis, growth and physical properties of silver gallium sulfide single crystals

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ABSTRACT

The temperature oscillation method was used to synthesize dense single-phase polycrystalline $AgGaS_2$ from high purity elements. $AgGaS_2$ single crystal of 8 mm diameter and 45 mm length, free of voids and crack was obtained by the descending ampoule with steady ampoule rotation method using the synthesized polycrystalline charge. The grown crystal was subjected to powder X-ray diffraction and single crystal X-ray diffraction. The $AgGaS_2$ has been studied using differential scanning calorimetry (DSC) technique. The single crystal has high transmission of 75% in the Mid IR region. The band gap energy was calculated using absorption spectrum. The stoichiometric composition of $AgGaS_2$ was measured using energy dispersive spectrometry (EDAX). The structural and compositional uniformities of $AgGaS_2$ were studied using micro-Raman scattering spectroscopy at room temperature. The photoluminescence behavior of $AgGaS_2$ has been analyzed. It shows the maximum emission at 538 nm. The resistivity of the grown single crystal has been measured.

1. Introduction

Ternary chalcopyrite compounds with the general formula $A^{I}B^{III}C_2^{VI}$ (A=Li, Na, Cu, Ag; B=Al, Ga, In; C=S, Se, Te) are currently being investigated for a wide variety of device applications. $AgGaS_2$ is a I-III-VI_2 ternary semiconductor compound with a chalcopyrite type structure, has been extensively studied because of its potential use for nonlinear optical devices, detectors and solar cells [1–3]. $AgGaS_2$ is an important infrared nonlinear optical material with the band gap 2.68 eV [4]. The $AgGaS_2$ single crystal has a relatively large nonlinear optical coefficient ($d_{36}=18\times10^{-12}$ m/V) [1]. The crystal has wide transparency region from 0.5 to 13 μm [5] and can be phase matched for second harmonic generation (SHG), sum of frequency generation, difference frequency generation and optical parametric oscillator [6–9]. $AgGaS_2$ is very promising for use in an optical parametric oscillator by reasons of high nonlinear coefficients, sufficiently high optical birefringence for phase matching [10,11]. $AgGaS_2$ single crystal has resistivity of 108–1011 Ω cm [12]. $AgGaS_2$ is one of the most important infrared nonlinear optical materials for device application, it can be widely used in laser communication, lidar gas analyzers, optoelectronics station for suppression, laser radar and IR tracking and IR guidance [13].

It is very difficult to grow large, crack-free high quality ingots for device application. The reasons are (i) anomalous thermal expansion behavior along *c* axis during cooling, which causes cracking. (ii) large differences in vapor pressure of the elements, specifically the more volatile sulfur. (iii) Presence of the large degree of super cooling effect during the growth which allows multi nuclei formation and (iv) retrograde phase transformation during growth, which allows the formation of a secondary phase [14]. It is very crucial to determine appropriate procedures and to optimize growth parameters for crystal growth process. We are using melt temperature oscillation method for synthesis of the $AgGaS_2$ polycrystalline charge and descending ampoule with rotation for growth of $AgGaS_2$ single crystal. We have grown single crystal successfully and it has good transmittance in the Mid-IR region compared to the previous report. The crystal has an average transmittance of 75% in the Mid-IR region. We have carried out the composition analysis of various parts of the grown single crystal.

In this paper, we describe the details of synthesis, growth and characterizations of $AgGaS_2$. The melt temperature oscillation method was used to synthesize the $AgGaS_2$ polycrystalline charge. The synthesized polycrystalline charge was used to grow $AgGaS_2$ 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 spectrometry (EDAX), micro-Raman, photoluminescence and electrical measurements.

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2. Experimental method

2.1. Synthesis

The growth of $AgGaS_2$ is done in two steps. First synthesis of the polycrystalline material from the starting elements. Secondly the synthesized material is employed to grow a single crystal. $AgGaS_2$ polycrystalline material is not available commercially in the market. 6N purity elements were used as starting materials. Without high quality $AgGaS_2$ polycrystalline charge we cannot achieve good quality, void free single crystals. In order to get the final crystal with the stoichiometric composition of the mole ratio 1:1:2 of silver, gallium and sulfur, an excess of 5% sulfur was chosen as the starting composition. The reason for the excess of sulfur is to prevent the sulfur losses from all possible process during synthesis and growth.

The starting materials were taken in a quartz ampoule. The length of the quartz ampoule was 260 mm with inner diameter 23 mm. The quartz ampoule was evacuated upto 1×10^{-6} mbar at room temperature and then sealed. The evacuated sealed ampoule was placed in a suitable horizontal furnace and the quartz ampoule was continuously rotated with suitable mechanical arrangement. The quartz ampoule was slightly tilted for not allowing the material in to another end. This process is used to achieve stoichiometric composition. During the synthesis process the temperature was controlled by Eurotherm temperature controller.

The temperature was raised to 445 °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. Then the temperature was raised to 1050 °C (to be reached in 12 h) and maintained for 48 h. The melt was cooled to 710 °C and the temperature was rapidly changed several times, alternating between 1050 °C and 710 °C. This step is called as melt temperature oscillation method. Excess of sulfur exists as dissolved in the melt at 1050 °C. When the temperature was rapidly reduced to 710 °C, the melt condensed to the solid state and the temperature in the inner part of melt was higher than that on the surface; therefore, the sulfur vapor in the center of the melt was rapidly transported out of the melt. The temperature was then rapidly raised again from 710 °C to 1050 °C, and it was reduced from 1050 °C to 710 °C alternately, so that an existence of sulfur 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 twelve 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 of the neck was 4 mm. The quartz ampoule was evacuated upto 1×10^{-6} mbar 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 $AgGaS_2$ polycrystalline material was 1002 °C and the freezing point of the material was 917 °C. The difference between melting and solidification is around 86 °C, which may lead to spurious nucleation during the crystal growth. To avoid spurious nucleation growth we tried with various temperature gradients. For a temperature gradient of 25 °C at the growth interface and growth rate of 10 mm/day we got successful results and the temperature profile is shown in Fig. 1. The ampoule was placed at suitable place in the furnace.

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. 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 45 mm length as shown in Fig. 2.

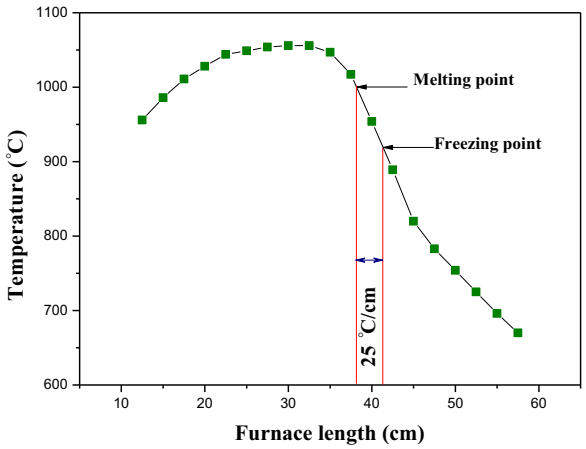

Fig. 1. Axial temperature profile of the growth furnace.

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 CuKα1 (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 to 6000 cm^{-1} with an accuracy of 0.01 cm^{-1}. Photoluminescence emission spectrum was recorded at room temperature, using 'HORIBA JOBIN-YVON FLUOROMAX 4' spectrofluorometer. The Raman measurement was performed at room temperature by Renishaw micro Raman instrument. The electrical properties of the $AgGaS_2$ 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.

3. Results and discussions

3.1. X-ray diffraction analysis

The grown AgGaS2 single crystal was subjected to single crystal X-ray diffraction analysis, the crystal belongs to tetragonal system and space group with the following dimension $a = 5.762$ (3) Å and $c = 10.312$ (3) Å in close agreement with previously reported values [15,16]. The powder X-ray diffraction was done for the AgGaS2 polycrystalline material which is shown in Fig. 3. The peak