Silver gallium telluride (AgGaTe2) single crystal: Synthesis, accelerated crucible rotation-Bridgman growth and characterization

K. Aravinth, G. Anandha Babu, P. Ramasamy

Centre for Crystal Growth, SSN College of Engineering, Kalavakkam 603110, India

Available online 20 March 2014

Keywords: Bridgman growth Characterization X-ray diffraction

Abstract

A silver gallium telluride single crystal of diameter 12 mm and length 80 mm was successfully grown by the vertical Bridgman method using accelerated crucible rotation technique. To confirm the unit cell parameters of the grown silver gallium telluride (AgGaTe2) crystal, single crystal X-ray diffraction studies were carried out. AgGaTe2 has been studied using differential scanning calorimetry and is found to have supercooling of 13°C. AgGaTe2 shows Fourier transform infrared transmission in the spectral range of 6000–500 cm⁻¹. The composition of Ag, Ga and Te in the grown crystal was measured with energy dispersive X-ray analysis spectroscopy. The optical band gap for AgGaTe2 is 1.8 eV. In the positron lifetime measurements, the average lifetime 267 ps corresponds to vacancy clusters in AgGaTe2 crystal. Hall measurements confirm p-type nature of AgGaTe2.

1. Introduction

Ternary compounds of types A⁺⁺B⁺⁺⁺⁻⁻⁻ and A⁺⁺B⁺⁺⁺⁻⁻ are known to have attracted considerable attention because of their interesting semiconducting, electrical, structural, and optical properties. Compared to their binary analogues (III–V and II–VI compounds) ternary compounds have higher energy gaps and lower melting points because of which they are considered to be important in crystal growth studies and device applications [1]. AgGaS₂ and AgGaSe₂ are ternary semiconducting compounds that crystallize in chalcopyrite structure whose non-linear optical properties have been used for many years to convert the frequency of solid-state and CO₂ lasers into the mid-infrared spectral region. AgGaSe₂ has a large non-linear coefficient (dₓᵧ = 39 pm/V) and excellent transmission in the mid-IR (1–18 μm) range. Continuation of this trend, by substituting Te for Se, should result in an additional 3-fold increase in dₓᵧ and a transparency range that is further red-shifted but still desirable for mid-IR laser application [2]. The chalcopyrite structure is similar to the zinc blende non-centrosymmetric, leading to non-zero second order nonlinear susceptibility, χ(2). Silver gallium telluride (AgGaTe₂) is of chalcopyrite structure and it belongs to the I42d space group and is black in colour at room temperature and its melting point is 724°C [3]. The material has a direct band gap of 1.32 eV. The value is well adapted to the solar spectrum and together with a high absorption coefficient, these materials are very attractive for thin film solar cells [4–7]. Most chalcopyrites also possess essential property, birefringence, which is the result of a uniaxial tetragonal distortion (c/a) from their underlying diamond like face-centered cubic structure. The distortion ranges from 0% to 10% and it is usually described by c/a, the ratio of its lattice parameters. The unit cell is tetragonal due to some uniaxial distortion of the lattice cell (c/a ≠ 2), causing additional interesting anisotropy of the physical properties. In particular, sufficient birefringence is needed to achieve the phase matching condition for nonlinear optical devices. The c/a ratio of AgGaTe₂ crystal...
is found to be 1.90 from X-ray diffraction studies. As the value is significantly different from 2.0, AgGaTe$_2$ is expected to have substantial birefringence [8–10].

In the compound semiconducting crystals, like binary and ternary, one of the most important complicated parameters to be controlled is the stoichiometry. Non-stoichiometry enhances the generation of intrinsic point defects that contributes to compensation level, type of conductivity, carrier concentration, absorption behaviour etc. It promotes the generation, multiplication and three dimensional movement of dislocations. Finally, the incorporation of the excess component at the interphase in the form of inclusions and the precipitation of dislocations. This process was repeated several times between the cooling process of the as grown crystal can impair the nucleation of second phase in the form of precipitates during growth challenges mentioned above, we followed a relatively lower temperature synthesis method. The method was used to synthesise high purity AgGaTe$_2$ at 745 °C, which is slightly above its melting point (724 °C). It reduces the material losses. The composition is maintained to its starting stoichiometric ratio. The synthesised material and grown crystals were characterized by single crystal X-ray diffraction (SXRD), powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), UV–vis–NIR, energy dispersive X-ray analysis spectroscopy (EDS), Hall measurement and positron annihilation studies.

2. Experimental procedure

2.1. Synthesis of AgGaTe$_2$

The following elements were used without further purification: Ag (99.9999%), Ga (99.9999%), Te (99.99%) Alfa make. AgGaTe$_2$ was synthesised from stoichiometry amount with the mole ratio 1:1:2 of Ag, Ga and Te. In order to prevent deviation from stoichiometry resulting from all possible volatile losses of tellurium during initial steps, the excess 1% of Te was chosen as the starting composition. The starting materials were loaded into a quartz ampoule with an inner diameter of 19 mm and then sealed at 2 × 10$^{-6}$ mbar. The ampoule was placed in a muffle furnace inclined at an angle of 45° and rotated at 3 rpm for uniform melt mixing. It is heated to 500 °C within 60 h, held for 24 h, subsequently heated to 745 °C at the rate of 6 °C/h and held for 24 h. This process was repeated several times between 500 °C and 745 °C. After completion of several cycles, the ampoule was adjusted carefully to be inclined at 20° to prevent the quartz cracking. Finally the furnace was cooled to room temperature at the rate of 15 °C/h.

2.2. Single crystal growth of AgGaTe$_2$

AgGaTe$_2$ single crystal of size 80 mm length and 12 mm diameter was grown by the vertical Bridgman technique using the synthesised polycrystalline material of the title compound in a high quality conical quartz ampoule in two zone tubular furnace. The conical bottom of the ampoule was used to encourage the spontaneous nucleation and propagation of a single grain. Preceding crystal growth, the silica ampoule charged with polycrystalline material was continuously evacuated and then sealed at 2 × 10$^{-6}$ millibar pressure. The well-sealed charged ampoule was hanged in the vertical Bridgman furnace from the top of the setup in the hot zone of the furnace cavity where it was heated gradually upto 745 °C, 20 °C above the melting point of AgGaTe$_2$ at the rate of 15 °C/h and held at this temperature for 24 h. The temperature profile of the furnace is shown in Fig. 1. Temperature gradient of the growth interface was kept at 3 °C/cm in the furnace. The ampoule was allowed to move downwards along the axis of the furnace cavity with a rate of 5 mm/day. The ampoule was also rotated by ACRT mode at 15 rpm periodically to ensure complete homogeneity of the melt. This improvement in the crystal growth process helps in improving crystal quality. After the entire melt had traversed through the growth face, the temperature of the furnace was cooled to room temperature at a very slow rate of about 5 °C/h. The as grown single crystal is shown in Fig. 2. The cut and polished AgGaTe$_2$ crystal wafer is shown in Fig. 3.

2.3. Instrument for characterization

To confirm the crystal structure and lattice parameters of the grown AgGaTe$_2$ single crystal, a small piece of the crystal was subjected to SXRD using Enraf (Bruker) Nonius CAD40 diffractometer with graphite monochromated MoK$_\alpha$ radiation ($\lambda=0.71073$ Å). X-ray powder diffraction analysis was performed using a Xpert-Pro diffractometer with continuous X-ray wavelength of 1.54 Å (CuK$_\alpha$) with 2θ

![Fig. 1. Temperature profile of two zone vertical Bridgman furnace.](image)

![Fig. 2. As grown AgGaTe$_2$ crystal.](image)
values from 10° to 90°. DSC measurements were performed in a simultaneous DSC-TGA STA 449 F3 made by NETZSCH company. About 15.0 mg of polycrystalline sample of AgGaTe2 was placed in Al2O3 crucible and heated (and cooled) at a rate of 10 °C/min between 30 °C and 800 °C under flowing N2 gas. The FTIR transmittance of the AgGaTe2 single crystal was measured using Alpha Bruker FTIR Spectrometer with wave number range from 500 to 6500 cm⁻¹. The above spectral studies were obtained using a crystal of 2 mm thickness. The 1 mm thick cut and polished AgGaTe2 single crystal was used for UV absorption studies. The absorption of the AgGaTe2 crystal was measured by Shimadzu UV–vis spectrophotometer for the wavelength range of 200–900 nm with slit width 2 nm and scan speed 240 nm/min. The composition of the AgGaTe2 sample was determined using scanning electron microscope (Hitachi S34200) linked to an energy dispersive spectrometer (EDS) INCA Energy 250 from Oxford Instruments using an accelerating voltage of 20 kV. The EDS consists of a Link Pentafet X-ray detector with an energy resolution quoted as 133 eV at 5.9 keV, and an INCA Microanalysis Suite Version software package. A 22Na source is used to inject positrons into the AgGaTe2 sample. Lifetime measurement involves a coincidence setup of two BaF2 detectors to measure the time difference between the 1.27 MeV de-excitation gamma ray coming from the 22Na source, and the 511 keV γ ray originating from positron annihilation in the sample. The energy resolution of the high purity Ge detector used is 1.09 ± 0.01 keV at 511 keV, resulting in a high sensitivity to changes in material properties from surface to depth. The motion of the electron-positron pair prior to annihilation causes a Doppler broadening of the 511 keV annihilation line and can be characterized by the line shape parameters S and W. The usefulness of these parameters may be illustrated by an S–W plot, which allows one to conclude whether the changes are due to change in concentration or type of a defect [12,13]. The Hall measurement was carried out using Van der Pauw type (Ecopia-HMS 3000) at room temperature with a permanent magnet of 0.57 T.

3. Results and discussion

SXRD analysis revealed that the grown AgGaTe2 single crystal belongs to tetragonal system with unit cell dimensions \( a=6.314 \) (1) Å; \( b=6.314 \) (1) Å; \( c=12.00 \) (3) Å and \( V=482 \) (8) Å³. The values are in good agreement with reported values [14]. PXRD patterns of AgGaTe2 single crystal at room temperature are shown in Fig. 4. The XRD pattern is consistent with AgGaTe2 and no peak attributable to possible impurities is observed. Bragg’s reflections for AgGaTe2 crystal are observed in XRD pattern at 2\( \theta \) values of 24.7°, 40.20°, 41.55°, 47.80°, and 49.88° representing (112), (220), (204), (312), (116) and (400) planes of AgGaTe2 respectively. DSC was used to study the heat flow rate during melting and freezing phase transitions. In melt growth methods supercooling state of solution may cause a severe problem, the

![Fig. 3. Cut and polished AgGaTe2 crystal wafer.](image)

![Fig. 4. PXRD pattern of AgGaTe2 single crystal.](image)

![Fig. 5. DSC curve for the heating and cooling process of AgGaTe2 crystal.](image)

![Fig. 6. FTIR transmittance spectrum of AgGaTe2 crystal.](image)
Fig. 7. EDS spectra of sample's bottom, middle and top of AgGaTe₂ single crystal.
The presence of the large degree of super-cooling allows multinuclei formation. The thermograms of AgGaTe2 crystal are shown in Fig. 5. This shows the endothermic peak at 724 °C which is the melting point of the compound. This is followed by an exothermic reaction (during cooling) with peak at 711 °C. The FTIR transmission spectrum is as shown in Fig. 6. The transmission is above 30% for AgGaTe2 single crystal in the wave number region 500–6000 cm⁻¹. The uniformity of the composition was investigated by EDS. The semi-quantitative measurements were performed for the axial composition of the sample of AgGaTe2. In the EDS spectra of AgGaTe2 obtained from sample’s bottom, middle and top (Fig. 7), Ag, Ga and Te elements are detectable. The atomic percentages of the Ag, Ga and Te elements for the sample’s bottom, middle and top are given in Table 1. It is seen that the crystal was Ag deficient, gallium, tellurium rich through out of the ingot and no other phases were observed in EDS measurements. From this we conclude that the average stoichiometric composition of grown single crystal was AgGaTe2. Roy et al., have reported that last to freeze region of the horizontal Bridgman method grown AgGaTe2 crystal has higher Ga concentration when compared to Ag and Te [15], but in the present investigation last to freeze region of the vertical Bridgman method grown crystal has higher Te concentration compared to Ag and Ga. The Te content increases gradually along the axial distribution of the crystal due to Te segregation. The fundamental absorption edge lies at around 640 nm at room temperature. Fig. 8(a) shows the absorption spectra of AgGaTe2 single crystal. The value of the band gap was obtained using the following relationship [16]:

\[(ahv)^2 = k(hv - E_g)\]  

(1)

The band gap energy of AgGaTe2 is shown in Fig. 8(b). The band gap energy was found to be 1.8 eV. The cut and polished piece of AgGaTe2 crystal of 1 mm thickness was used for electrical measurements. The positive sign of the Hall coefficient confirms the p-type conductivity. The measured parameters are Hall coefficient (3.85 × 10⁻² cm²/C), resistivity (6.55 Ω cm), mobility (5.87 × 10² cm²/V s), bulk concentration (1.62 × 10¹⁵/cm³) and conductivity (1.53 × 10⁻¹Ω cm) of the grown AgGaTe2 crystal.

Positron lifetime and Doppler broadening measurements were carried out on AgGaTe2 crystal. In AgGaTe2 single crystal the group VI atom vacancies should act as donors, whereas the group I and III atom vacancies should be acceptors. In a real crystal, defects can trap positrons. Two or more lifetimes were found in the positron lifetime spectra. \(\tau_1\) indicates the positron lifetime of monovacancy-type defects and \(\tau_2\) indicates the positron lifetime of multivacancy-type defects or the larger vacancy-type defects. From the observed experimental spectrum two positron lifetime components i.e., first component \(\tau_1 \sim 226.7\) ps (bulk annihilation) with 81.2% intensity and second component \(\tau_2 \sim 445.4\) ps with 18.2% intensity were observed. Bulk annihilation lifetime for common semiconductors is of the order of 200 ps [13]. This is also evidenced by the observation that the second lifetime component with considerable intensity corresponds to presence of vacancy clustering and void formation in the sample. The mean lifetime is calculated as \(\tau_m \approx 266.740\) ps using the relation [17]

\[\tau_m = (\tau_1 I_1 + \tau_2 I_2)/(I_1 + I_2)\]  

(2)

Doppler broadening S-parameter value is found to be 0.6446 and W-parameter is 0.0136.

4. Conclusion

Single crystals of AgGaTe2 have been grown by the vertical Bridgman growth method. The unit cell parameters of the AgGaTe2 were confirmed by SXRD studies. The melting and freezing temperature of AgGaTe2 crystal were 724 °C and 711 °C respectively. EDS measurement of the different regions of the grown crystal showed the composition uniformity of the ingot. FTIR studies showed that transmittance is 30% throughout the mid-IR region from 1.5 to 20 μm. The absorption edge lies at 640 nm. The band gap energy was calculated to be 1.8 eV for AgGaTe2 single crystal. The measured electrical properties of cut and polished AgGaTe2 crystal at room temperature are Hall coefficient (3.85 × 10⁻² cm²/C), resistivity (6.55 Ω cm) and conductivity (1.53 × 10⁻¹Ω cm). Positron annihilation spectroscopy measurements on as grown crystal indicate the strong presence of vacancy clustering and void formation.

Acknowledgement

The authors are thankful to Prof. K. Ramamurthi, School of Physics, Bharathidasan University, Trichy, for Hall measurement studies and Dr. G. Amarendra, MSG, IGCAR, Kalpakkam, for Positron Annihilation Studies.

Table 1

<table>
<thead>
<tr>
<th>Scanned area</th>
<th>Ag L (at%)</th>
<th>Ga K (at%)</th>
<th>Te L (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>23.35</td>
<td>25.97</td>
<td>50.68</td>
</tr>
<tr>
<td>Middle</td>
<td>23.57</td>
<td>25.14</td>
<td>51.29</td>
</tr>
<tr>
<td>Top</td>
<td>23.09</td>
<td>25.06</td>
<td>51.85</td>
</tr>
<tr>
<td>Average</td>
<td>23.33</td>
<td>25.39</td>
<td>51.27</td>
</tr>
</tbody>
</table>
References