Growth and characterization of single crystals of the quaternary TlGaSeS compound

S. R. Alharbi†

Physics Department, Faculty of Sciences, King Abdulaziz University, Kingdom of Saudi Arabia

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The electrical conductivity and Hall effect for TlGaSeS crystals have been investigated over a wide temperature range. The crystals we used are grown by a modified Bridgman technique and possess p-type conductivity. The energy gap has been found to be 1.63 eV, whereas the ionization energy is 0.25 eV. The variations of the Hall mobility as well as the carrier concentration with temperature have been investigated. The scattering mechanisms of the carrier are checked over the whole investigated temperature range. Furthermore, the diffusion coefficient, relaxation time, and diffusion length of holes are estimated.

Keywords: crystal growth, DC electrical conductivity, Hall effect, TlGaSeS compound

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1. Introduction

Most of the technological electronic and opto-electronic applications utilize materials in crystalline forms.[1,2] Particularly, complex semiconductor compounds $TlA^{III}_{2x}B^{VI}_{2(1-x)}$ have been attracting much attention recently.

In preparing such crystalline materials, continuous series of solid solution $TlGaS_{2x}Se_{2(1-x)}$ are built from elements of 3rd (Tl, Ga, In) and 6th (S, Se) subgroups of the periodic table, these compounds being indicated as $A^{III}B^{III}C^{VI}_{2x}D^{VI}_{2(1-x)}$. In this study, x is equal to 0.5. Thallium gallium selenite sulphur[3] crystallizes in a monoclinic structure with the space group C^4_5. The quaternary layered TlGaSeS belongs to the group of layered semiconductors. The crystals are formed from $TlGaS_2$ and $TlGaSe_2$ crystals by replacing half of the sulphur (selenium) atoms with selenium (sulphur) atoms. The crystal lattice has two-dimensional layers arranged parallel to the (001) plane.[4,5] The bonding between Tl and Se (S) atoms in TlGaSeS is an interlayer type, whereas the bonding between Ga and Se (S) is an intralayer type. These crystals have received a great deal of attention due to their optical and electrical properties in view of possible optoelectronic device applications.[6] The optical and photoelectric properties have been studied,[7–9] and photo-luminescence (PL) spectra of layered TlGaSeS crystals have been reported.[6,10] Information on trap state in undoped layered TlGaSeS crystals using the well-established technique of thermally stimulated current TSC measurements were studied in Refs. [11]–[14]. Information about the energy gap width, impurity level, concentration, mobilities, scattering mechanism, type of conductivity, and the position of impurity level are essential in the characterization of materials that are used in the fabrication of electronic devices. Thus, it is very useful to gain detailed information of electrical conductivity and the Hall effect in order to obtain high-quality devices. To our knowledge, there is no information about the electrical conductivity and Hall coefficient, and its temperature dependence. Hence, in this work, we report the measurements of the DC electrical conductivity and the Hall effect in the temperature range from 278 K to 563 K. The results were used to estimate the main physical parameters of the TlGaSeS semiconductor compound.

2. Experimental arrangement

2.1. Crystal growth

In the present work, the chemicals used in preparing the TlGaSeS sample were 26.5662 g of Tl (purity 99.9999%), 8.9940 g of Ga (purity 99.9999%), 10.2677 g of Se (purity 99.9999%), and 4.1721 g of S (purity 99.9999%). The percentages of the charge elements are 53.1323% for Tl, 17.9880% for Ga, 20.5355% for Se, and 8.3442% for S. The chemicals were obtained from Aldrich. The materials were introduced into a silica tube with the tip down, which was then evacuated to 10^{-6} Torr, and sealed under this vacuum. The ampoule with its charge was supported in the holder inside the three-zone tube furnace. Single crystals of TlGaSeS were grown by a modified Bridgman method. More details about this technique and apparatus used for crystal growth are available in previous work.[15] The ampoule with its charge was exposed to high enough temperature (850 °C) in the first zone, and kept at this temperature for two days to homogenize the melt. During heating, the melt was shaken several times to accelerate the diffusion of the constituents through each other. The crucible was then lowered from the cold side to the hot side at 480 °C at a rate of 1.6 mmh^{-1}. Solidification process was completed, as long as the temperature is below the crys-

†Corresponding author. E-mail: sr_alharbi@yahoo.com

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tallization temperature. The solidified sample was then cooled slowly to room temperature. The duration time required for this process was about 18 days, which was enough to obtain high-quality crystal. The resulting ingot appears red in color, and the freshly cleaved surface was mirror-like.

Identification of the product crystal was performed by using an X-ray diffractometer with monochromatic Cu K_α radiation ($\lambda = 1.54049$ Å).

2.2. Measuring technique

For studying the electrical conductivity and the Hall coefficient, the sample was prepared in a rectangular shape with dimension of 8.3 mm × 1.8 mm × 1.0 mm. The plate-like samples were extracted by means of a blade from the product version. The resultant surfaces were mirror-like, and there was no need for any mechanical polishing. In this way, the length of the sample was made three times its width to avoid the Hall voltage drop according to the Isenberg recommendations.[16] Both the electrical conductivity and the Hall effect measurements were carried out in an evacuated Pyrex cryostat designed for this purpose.[17] Ohmic contacts were formed on the specimen surface by means of silver paste, and the ohmic nature of the contact was checked by recording the current–voltage characteristics. The investigated specimen was placed in its holder inside a glass cryostat. DC compensation method was adopted for measuring voltages without drawing appreciable current by using a Tensily UJ33E potentiometer. The Hall voltage was taken as the average of four readings using a reverse switch to reverse the direction of the current as well as that of magnetic field to avoid the spurious voltage included in the value of Hall voltage except Ettingshausen voltage, which is so small that it can be neglected. The electrical conductivity was measured when the current was oriented parallel to the cleavage plane, also the Hall coefficient was measured with the magnetic field oriented at right angle to the cleavage plane. All measurements were carried out under vacuum with the magnetic field intensity being 0.5 T.

3. Results and discussion

Figure 1 shows the powder XRD pattern of our compound. The X-ray chart indicates that the crystalline product has the required phase. The calculated d-spacing and lattice parameters are consistent with the results reported by Guler *et al.*[7] The Miller indices (hkl), the calculated and reported d-spacing, and the relative intensities (I/I_0) of diffraction lines are given in Table 1. The TlGaSeS crystal has a monoclinic structure with lattice parameters $a = 7.588$ Å, $b = 7.645$ Å, $c = 8.714$ Å, and $\beta = 111.85°$.

The electrical conductivity behavior in response to temperature is an important tool for understanding the electronic

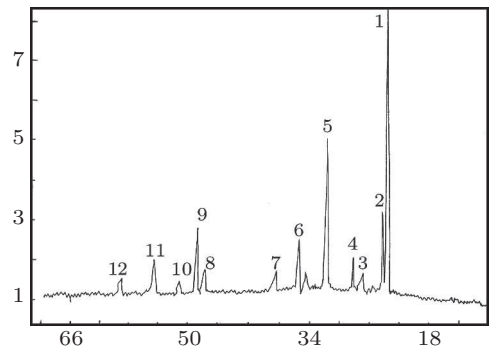


Fig. 1. X-ray diffraction pattern for TlGaSeS compound.

Table 1. X-ray powder diffraction data for TlGaSeS crystals.

No.	$d_{(\text{calc.})}$/Å	$d_{(\text{repo.})}$/Å	$h\,k\,l$	I/I_0
1	3.7903	3.823	0 2 0	100
2	3.700	3.720	2 1 –1	37.7
3	3.324	3.343	2 0 -2	18.7
4	3.184	3.199	0 1 2	23.5
5	2.830	2.845	2 2 –1	59.4
6	2.534	2.543	3 1 0	28.92
7	2.337	2.348	0 0 3	19.28
8	1.901	1.903	1 3 2	20.12
9	1.865	1.869	4 1 –3	32.53
10	1.780	1.785	3 1 2	16.27
11	1.674	1.680	0 4 2	23.49
12	1.560	1.560	3 4 0	17.47

transport properties of semiconductors. The temperature dependence of the electrical conductivity σ was studied for TlGaSeS crystals in a temperature range of 278–563 K. Figure 2 shows this dependence, where the curve shows a typical semiconductor behavior. From this curve, it is noticed that σ increases slowly in the low temperature range (the extrinsic region). However, as the temperature rises, the conductivity grows very rapidly because of the rapid increase in the current density. From the same curve, one can also notice that an intermediate region appears between 358 K and 448 K. The measured data of σ–T dependence are obtained by the following relations:

$$\sigma_{\text{imp}} = \sigma_{0\text{imp}} \exp\left(\frac{-\Delta E_{\text{a}}}{KT}\right) \quad \text{(in the extrinsic region)}, \quad (1)$$

$$\sigma_{\text{i}} = \sigma_{0\text{i}} \exp\left(\frac{-\Delta E_{\text{g}}}{2KT}\right) \quad \text{(in the intrinsic region)}, \quad (2)$$

where $\sigma_{0\text{imp}}$ and $\sigma_{0\text{i}}$ are the pre-exponential factors, ΔE_{a} is the impurity ionization energy, and ΔE_{g} is the energy gap width.

From the results of the electrical conductivity, we can sum up the following remarks. The extrinsic conduction appears in the temperature interval of 278–358 K. The value of ΔE_{a} was found to be 0.25 eV. This value suggests that the extrinsic conductivity is due to impurity carriers, which will be confirmed later from the Hall data. The intrinsic conduction becomes more favorable between 448 K and 563 K. The energy band gap width ΔE_{g} was found to be 1.58 eV. The middle region

which begins from 358 K up to 448 K has a steepness, indicating the slight increase of the mobility. This is acceptable if we consider this temperature range where the conductivity behavior is a result of the carrier concentration and the carrier mobility effects.

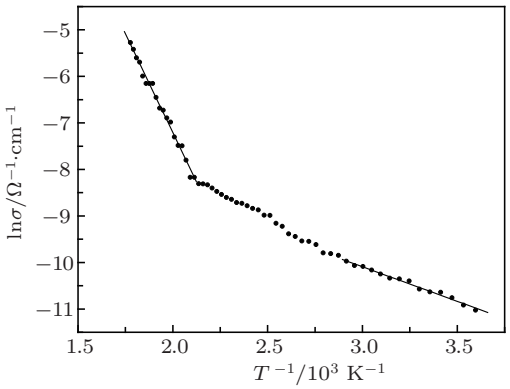


Fig. 2. Temperature dependence of the electrical conductivity for TlGaSeS crystal.

For instance, the value of the electrical conductivity at room temperature equals 2.56 $\times 10^{-5}$ $\Omega^{-1}\cdot$cm^{-1}. Three regions are also observed in Fig. 3, which illustrate the mode of variation of the Hall coefficient with temperature. It is evident from the measurements that the Hall coefficient is positive all over the temperature interval under investigation. The positive sign of $R_{\rm H}$ indicates the p-type nature of the TlGaSeS crystals, which is in complete agreement with the previous data.[4] Also we can observe that the Hall coefficient in the low temperature range is less temperature-dependent compared with the high temperature range. At room temperature, $R_{\rm H}$ equals 6.52×10^{6} cm^3/C.

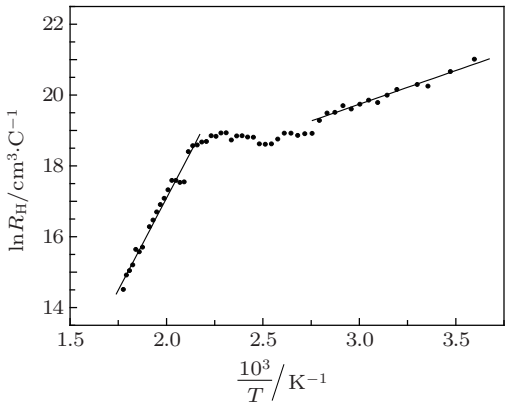


Fig. 3. Variation of the Hall coefficient with temperature for TlGaSeS crystal.

Figure 4 shows the relation between $R_{\rm H}T^{3/2}$ and $10^3/T$. The depth of the acceptor level and the width of the forbidden zone deduced from this figure have the values of 0.25 eV and 1.62 eV, respectively. They are obtained from the following relation:

$$R_{\rm H}T^{3/2} = c\exp\left(\frac{\Delta E_{\rm g,a}}{2KT}\right), \qquad (3)$$

where c is a constant. We extend our work to cover the effect of temperature on the carrier concentration of TlGaSeS crystals. They are calculated by the relation $P = 1/(eR)$, which is shown in Fig. 5. The figure shows the remarkable increase of carrier concentration in the high temperature range, where the crystal exhibits an intrinsic behavior. The expected value for the intrinsic concentration can be given as follows:

$$n_i = 2\left(\frac{2\pi K}{h^2}\right)^{3/2}\left(m_{\rm p}^* m_{\rm n}^*\right)^{3/4} T^{3/2}\exp\left(\frac{-\Delta E_{\rm g}}{2KT}\right), \qquad (4)$$

where $m_{\rm p}^*$ and $m_{\rm n}^*$ are the effective mass of holes and electrons, respectively. Using this formula, we can calculate the energy gap width of TlGaSeS to be 1.7 eV. The value of $\Delta E_{\rm g}$ calculated from the Hall work deviates slightly from the value obtained from the electrical conductivity work. As for this situation, we used to consider the average of $\Delta E_{\rm g}$ as 1.63 eV.

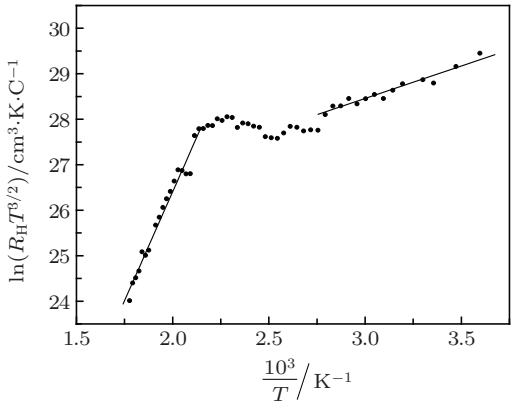


Fig. 4. Illustration of $\ln(R_{\rm H}T^{3/2})$ versus the temperature of TlGaSeS single crystal.

The calculated band gap is found to be smaller than that obtained by Guler *et al.*[7] using optical property measurements of the compound. This contradiction in the measured $\Delta E_{\rm g}$ values is clarified by Panich,[4] who attributed it to the existence of structural constraints upon electron transfer between the chemically distinct Tl^{1+} and Tl^{3+} ions that occupy two different crystallographic positions.

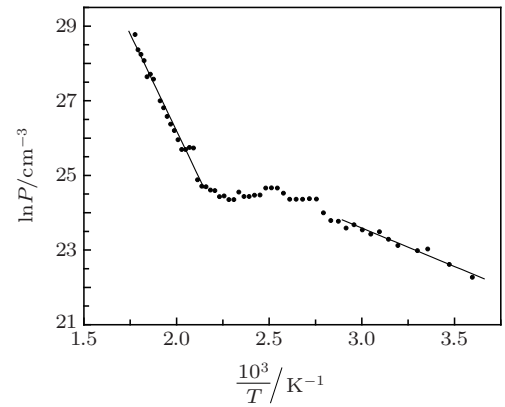


Fig. 5. Dependence of the concentration of holes P on the temperature of TlGaSeS specimens.

Finally, the charge carrier concentration at room temperature is equal to 9.59×10^{9} cm^{-3}. The present work has dealt with the effect of temperature on the Hall mobility which was calculated by the following relation:

$$\mu = \frac{\sigma}{Pe}. \tag{5}$$

Figure 6 illustrates this dependence for TlGaSeS sample. The general behavior of μ in response to T can be divided into two regions. 1) Low temperature part. The Hall mobility increases with increasing temperature. In this region, $\mu(T)$ can be described as $\mu \sim T^{4.8}$. 2) High temperature part. The Hall mobility decreases with increasing temperature. In this region, μ decreases with increasing temperature according to the law $\mu \sim T^{-5.4}$. From this relation, it seems that the value of exponent n in the relation $\mu \sim T^{n}$ is usually large, compared with those obtained for impurity and lattice scattering in other semiconductors. This behavior, in our opinion, may be associated with the presence of a high density of stoichiometric vacancies and the creation of defects. The room-temperature value of the mobility equals 1.67×10^{4} cm^2/(V·s). The diffusion for holes is calculated to be 432.18 cm^2/s. Assuming that the effective mass for holes is equal to the rest mass and using the value for the hole mobility at room temperature, the mean free time is determined and its value is found to be 9.5×10^{-13} s. In addition, diffusion coefficient as well as the diffusion length for TlGaSeS crystals were evaluated to be 432.18 cm^2/s and 2.02×10^{-5} cm, respectively.

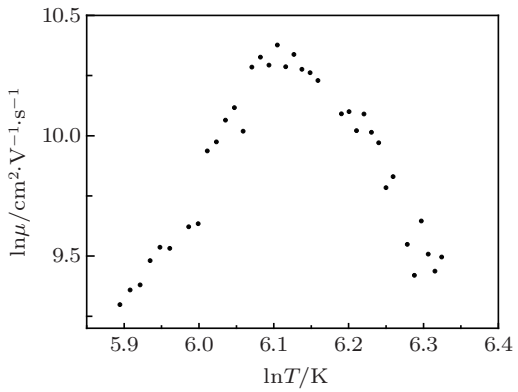


Fig. 6. Plot of $\ln\mu$ against $\ln T$ for TlGaSeS single crystal.

4. Conclusion

TlGaSeS single crystals were grown by modified Bridgman method. The crystals were identified by X-ray diffraction. Measurements of electrical conductivity and Hall effect were performed in the temperature range of 278–563 K. From these measurements, many physical parameters were estimated. The electrical conductivity, Hall coefficient, Hall mobility, and hole concentration at 300 K were found to be 2.56×10^{-5} Ω^{-1}·cm^{-1}, 6.52×10^{6} cm^3/C, 1.67×10^{4} cm^2·V^{-1}·s^{-1}, and 9.59×10^{9} cm^{-3}, respectively. The diffusion coefficient, relaxation time, and diffusion length of holes were estimated to be 432.18 cm^2·s^{-1}, 9.5×10^{-13} s, and 2.02×10^{-5} cm, respectively. The conductivity type of the crystal was found to be p-type. In addition to these pronounced parameters, the energy gap and the position of the acceptor level were evaluated to be 1.63 eV and 0.25 eV, respectively. This work provides a good picture of the actual physical behavior of the prepared TlGaSeS crystals, which leads to better application in many modern fields.

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