The growth and characteristic features of the quaternary chalcogenide Tl_2GaInS_4

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Abstract: The preparation and electrical characterization of quaternary chalcogenide Tl_2GaInS_4 crystals are reported in this work. Measurements of the electrical conductivity and Hall coefficient were performed over the temperature range of 200 K to 452 K. This study was conducted with the current flowing parallel to the c-axis and the magnetic field direction perpendicular to the c-axis. The crystals were obtained by a modified Bridgman technique for crystal growth and exhibited p-type conductivity with a hole concentration of $1.318\times10^{9}cm^{-3}$ at room temperature. The conductivity and Hall mobility at 300 K were found to be 2.913×10^{-6} $\pi^{-1}cm^{-1}$ and 1.38×10^{4} cm^2/V sec, respectively. The energy gap width was calculated at 2.085 eV.

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Key words: crystal growth, **Tl_2GaInS_4**, electrical conductivity, Hall coefficient.

1.Introduction:

For many years, the properties of layered crystals have constituted a major research area in solid state physics [1, 2] due to their structural properties and potential optoelectronic applications. Over the past three decades, significant interest has arisen in chalcogenide semiconductors because of their interesting physical properties as well as their wide-ranging technological applications [3]. Tl_2GaInS_4 is formed from the $TlGaS_2$–$TlInS_2$ system of layered crystals, which belong to the monoclinic system. The temperature-dependent photoluminescence spectra of Tl_2GaInS_4 crystals at temperatures of 10-150 K have been investigated [4]. The optical [2], photo-electronic and electrical properties of Tl_2GaInS_4 layered crystals have also been published [5]. A determination of the trapping centre parameters of Tl_2GaInS_4 layered crystals has been conducted based on thermally stimulated current measurements [6]. In addition to these properties, the optical constants and the interband transitions of anisotropic layered structured Tl_2GaInS_4 crystals have been studied via spectroscopic ellipsometry [7]. As can be deduced from a review of the literature, little work has been performed on the optical and photoelectric properties, band structure, transmission, reflection spectra or thermally stimulated currents. Thus, this work presents detailed information on the main physical parameters, obtained by measuring the Hall effect and electrical conductivity and their temperature dependence. This study provides precise and straightforward information on the carrier density, mobility, energy gap, impurity level position and conductivity type in order to obtain high-quality devices. To the best of our knowledge, there is currently no information on the Hall effect or electrical conductivity of Tl_2GaInS_4 or their temperature dependence in the literature.

2. Experimental Procedures

2.1 Crystal growth

Tl_2GaInS_4 single crystals were grown using a modified Bridgman method with polycrystalline $TlGaS_2$ and $TlInS_2$ compounds, with stoichiometric starting materials sealed in evacuated $(\sim10^{-6}$ mbar) and carbon-coated quartz ampoules with a tip at the bottom. $TlGaS_2$ and $TlInS_2$ polycrystals were synthesised from high-purity elements (>99.999% purity). The ampoule was moved through a thermal gradient of $30^{\circ}Ccm^{-1}$ at a rate of $1.7\ mmh^{-1}$. We used a three-zone tube furnace, and each zone was approximately 20 cm in length. Details of the experimental equipment used for the crystal growth and the preparation procedures are described elsewhere [8]. The resulting ingots had no cracks or voids on the surface, which was yellow-green in colour, and cleaved easily along the layer plane. The freshly cleaved surfaces were mirror-like, such that no further polishing or cleaning treatments were required.

X-ray analysis confirmed that Tl_2GaInS_4 single crystals were obtained. The XRD patterns show that these crystals have a monoclinic structure with lattice parameters of a = 1.0639, b = 1.0441, c = 1.5334 nm and $\beta = 100.12^{\circ}$. These results are in good agreement with previous X-ray structure investigations for Tl_2GaInS_4 [4]. In fig. 1, the peaks of the X-ray powder diffraction as a function of 2θ (twice the Bragg angle) are shown, indicating the single phase nature of the produced crystal. The samples were prepared by cleaving an ingot parallel to the crystal layer, which is perpendicular [2] to the c-axis.

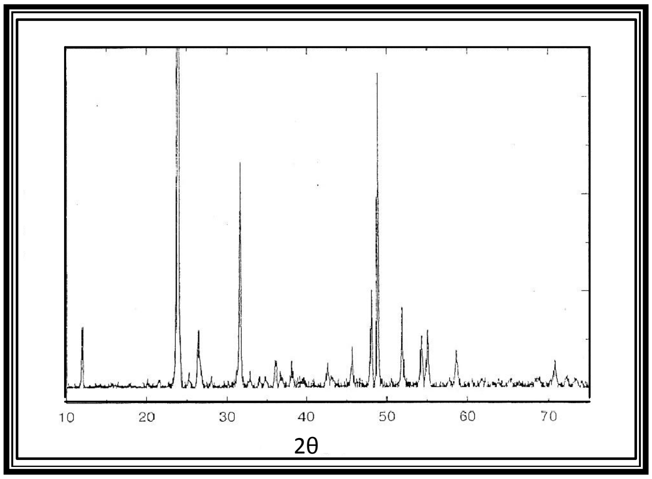

Fig. 1: X-ray diffraction pattern for the Tl_2GaInS_4 compound.

2.2 Apparatus and measurements

Specimens for measurements were prepared with typical rectangular dimensions of 5.7×1.7×1 mm^3. Silver paste contacts were used as ohmic contacts. The ohmic nature of the contacts was confirmed by the I-V characteristics, which were found to be linear and independent of current reversal for low applied currents and voltages. The conductivity and Hall coefficient were measured via a compensation method in a specially designed cryostat with a conventional dc-type measurement system. The Hall voltages were measured by reversing the current and the magnetic field directions and by taking the appropriate averages. The measurements were performed under vacuum conditions in a cryostat specially designed for mounting samples between the polar expansions of an electromagnet GMW model 5403, with a DTM-133 digital telemeter. The designed cryostat allows for measurements over a wide range of temperatures. The presence of liquid nitrogen in the inner jacket of the cryostat allows one to obtain temperatures below 300 K, while supplying a current to a small resistance heater provides temperatures above 300 K. For the Hall measurements, the magnetic field was perpendicular to the crystallographic c-direction, with an intensity of 0.45 Tesla. In all measurements, the applied current direction was parallel to the crystallographic c-axis of the sample. Routine precautions were taken into account, as described in the literature.

3. Results And Discussions

The electrical conductivity of Tl_2GaInS_4 single crystal has been investigated over a wide range of temperatures extending from 200-450 K. Fig 2 shows a plot of the electrical conductivity versus the inverse absolute temperature. The curve shows typical semiconductor behaviour and consists of three regions. The first region lies between 200 and 230 K and represents the extrinsic region. In this region, the conductivity was observed to increase slowly in the low-temperature range, due to the liberation of the ionised acceptors and their transition from the impurity level. In the low-temperature region, the relation between the temperature and electric conductivity can be given as follows:

$$\sigma = \sigma_\circ \exp(-\Delta E_a/2KT) \qquad (1)$$

where $\sigma_\circ$ is a pre-exponential factor and ΔE_a is the ionisation energy of the acceptors. From the slope of the curve in this region, the ionisation energy was evaluated to be ΔE_a = 0.08 eV. The second region represents the transition region, where the behaviour of σ is governed by the charge carrier concentration and their mobility. This region extends from 283-413 K and is characterised by exponential increases in electrical conductivity at a relatively high rate. A rapid linear increase in the conductivity is observed in the high-temperature range above 413 K. This finding reveals that both electrons and holes contribute to the conduction in the high–temperature range.

The dependence of this temperature range follows the relation given below:

$$\sigma = \sigma_\circ \exp(-\Delta E_g/2KT) \qquad (2)$$

Using this formula, the energy gap ΔE_g = 2.09 eV, as calculated from the slope of the above formula. This value is close to a previously published value [(2)]. The electrical conductivity at room temperature was measured at approximately $2.913\times10^{-6}\ \pi^{-6}cm^{-1}$. Because the Hall effect is important in determining many physical parameters, this work was extended to cover the effect of temperature on the Hall coefficient R_H, as shown in fig. 3.

Fig. 3 shows the relationship between the Hall coefficient and the temperature for single Tl_2GaInS_4 crystals. This measurement was performed over a wide range of temperatures (200-452 K). The results indicate that the sign of the Hall coefficient of Tl_2GaInS_4 is positive throughout the entire range of investigation. This finding implies that the compound is a p-type semiconductor, which is in reasonable agreement with a previous report [(4)]. The Hall coefficient at room temperature was evaluated as $4.74\times10^9\ cm^3/C$.

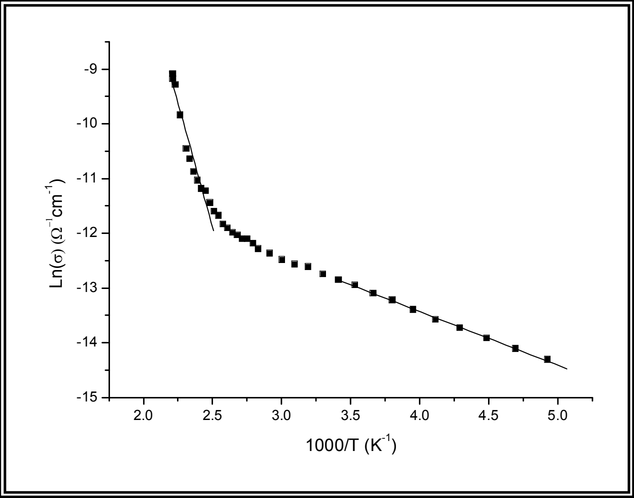

Fig. 2: Temperature dependence of the electrical conductivity for Tl_2GaInS_4 single crystal.

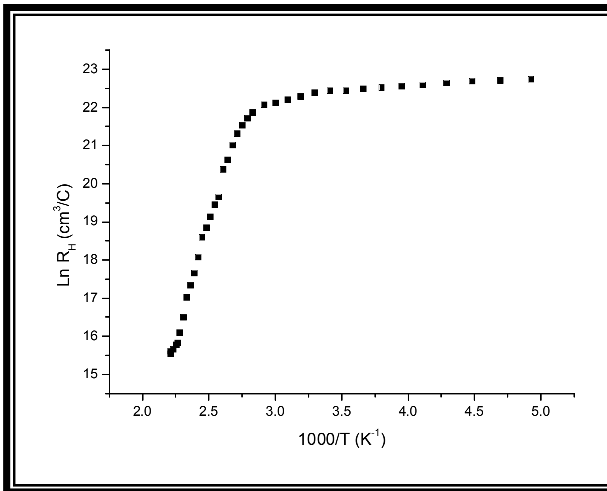

Fig. 3: Temperature dependence of R_H for Tl_2GaInS_4 single crystal.

The energy gap and ionisation energy can be determined from the Hall data by plotting the relationship between $lnR_H T^{3/2}$ and $10^3/T$, as shown in fig. 4 on the basis of the following relationship:

$$R_H T^{3/2} \alpha \exp(-\Delta E_g/2KT) \quad (3)$$

In the temperature region in which the conductivity is predominantly intrinsic, the forbidden gap width was estimated to be ΔEg = 2.08 eV. The depth of the acceptor centre was determined from the region in which the conductivity primarily arises from impurity atoms and was found to be 0.075 eV. The measurement curve leads to the following conclusions: the three regions of the curve indicate that extrinsic conduction occurs from 200 to 283 K while intrinsic conduction arises at 413 to 452K, and the transition region lies between 283 and 413 K, as shown in fig. 2.

Due to the importance of mobility data in the field of solids, especially for semiconductors, the present work investigated the effect of temperature on the free carrier mobility. This approach allows one to gain insight into the scattering mechanism of the charge carrier. The Hall measurements and electrical conductivity data were combined to study the temperature dependence of the Hall mobility of the charge carriers. Fig. 5 depicts the variation of μ as a function of temperature.

From the graph, one can conclude that the general plot of μ versus T can be divided into two regions. In the low-temperature region, which corresponds to extrinsic conduction and mobility, μ seems to increase with increasing temperature, reaching a maximum value at 2.8312×10^4 $cm^2/Vsec$ for 343 K and following a power law, $\mu \approx T^{3.06}$. In the high-temperature region, the mobility decreases with increasing temperature, according to the law $\mu \approx T^{-18.32}$. The high value of the exponent for $\mu \approx T^n$ suggests that the scattering mechanism of the carriers should differ from that of semiconducting single crystal materials. The observed behaviour differs that of a typical semiconductor material and thus cannot be understood by the general theory of semiconductors. However, such behaviour has been previously observed in GaTe(9), Tl_2GaInS_4 (3,10), Ga_2Se(11) and In_2Te_3(12). The Hall mobility behaviour of Tl_2GaInS_4, with its higher resistivity (5), may be due to a change in the transport mechanism between localised states either within the energy gap or in the regions close to the bottom of the conduction band and close to the top of the valence band. However, more work must be performed to determine the mobility behaviour with temperature before any definite conclusions can be drawn from this type of measurement. The Hall mobility at room temperature is 1.38×10^4 $cm^2V^{-1}S^{-1}$; the charge carrier mobility in our material is much higher than that of other semiconducting materials from the $A^{III}B^{VI}$ group, but such behaviour often occurs in defect semiconductors (3, 13).

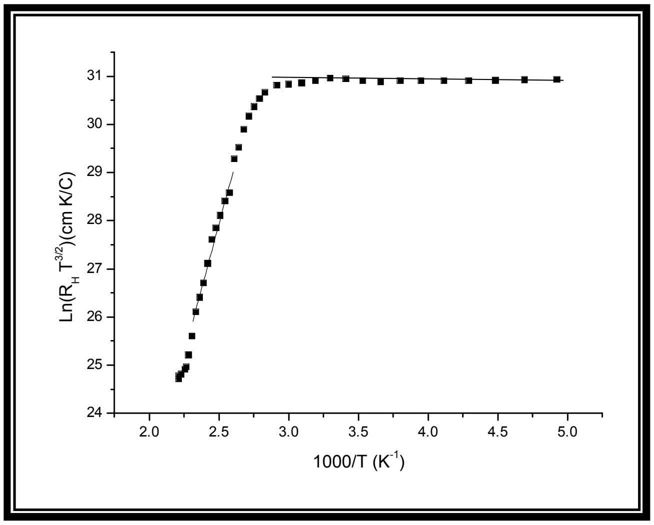

Fig. 4: Temperature dependence of $R_H T^{3/2}$ for Tl_2GaInS_4 single crystal

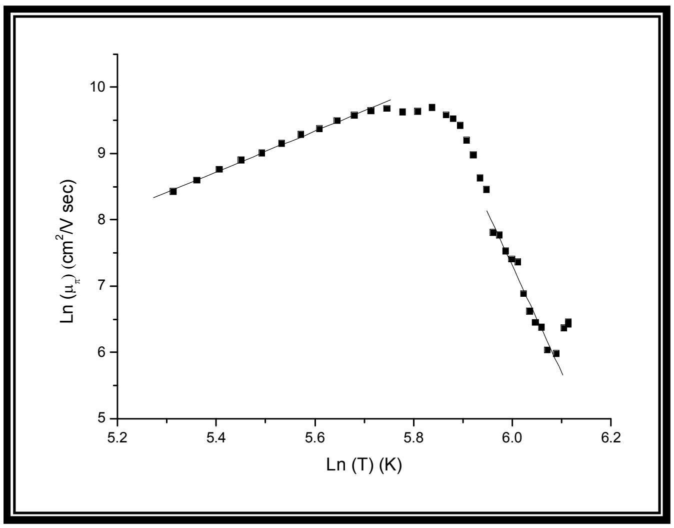

Fig. 5: Hall mobility as a function of temperature for Tl_2GaInS_4 single crystal.

The typical behaviour of the carrier concentration as a function of temperature is illustrated in fig. 6.

It is well known that the following relation can be applied within the intrinsic region of conduction to describe the temperature dependence of the charge carrier concentration.

$$P_i = c\exp(-\Delta E_g/2KT) \qquad (4)$$

This relation allows us to calculate the energy gap. The value of ΔE_g agrees with that obtained from fig. 2 and 3 and a previously published value (2). Furthermore, at room temperature, the carrier concentration is calculated to be 1.318×10^{9} cm^{-3}. A further calculation of the diffusion coefficient for holes gives a value of 397.8 cm^2/sec. 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 was determined to be 8.832×10^{-7} sec. Furthermore, the diffusion length of the holes in the Tl_2GaInS_4 specimen was evaluated at 1.87×10^{-2} cm.

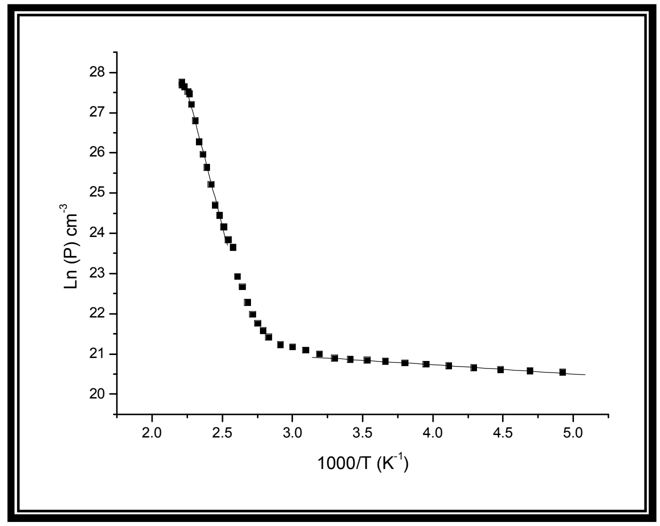

Fig. 6: Variation of ln p with ln T for a Tl_2GaInS_4 single crystal.

4. Conclusion

High-quality of Tl_2GaInS_4 single crystal were grown by a modified Bridgman technique, and the electrical conductivity and Hall effect were measured over a wide temperature range (200-452 K). High-purity starting materials were used for the preparation of Tl_2GaInS_4 in the form of large yellow-green cylindrical ingots, as were identified by XRD analysis. All measurements were taken under vacuum conditions in a specially designed cryostat. The Hall coefficient measurements indicate a p-type conductivity. The energy gap and the depth of the acceptor level were found. The experimental data allowed us to determine the carrier concentration, mobility, diffusive coefficient, diffusive length and relaxation time of the primary carriers.

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