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Growth and Electrical Characterization of $GeSeFe_{0.02}$ single Crystals

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Abstract

In present investigation, we have grown $GeSeFe_{0.02}$ single crystals by direct vapor transport technique (DVT). Detailed growth parameters for these crystals are reported here like temperature profile, ampoules dimension and furnace dimension etc. The as grown crystals were found to have fairly large dimensions and we used these crystals for electrical measurements at different temperature and different frequency. Using Lakeshore 7504 series system, Hall measurement were performed and we determine the properties such as carrier resistivity, Hall coefficient (R_H), carrier concentration (n) and mobility (μ) of these single crystals and its variation in the temperature range 300 K to 400 K by using magnetic field 1 kG, 2 kG and 3 kG. This electrical characterization is important to use these crystals for device fabrication up to temperature of 400 K and applied magnetic field of 3 kG.

Keywords: $GeSeFe_{0.02}$ single crystals, crystal growth, hall coefficient and mobility.

Introduction

The IV– VI compounds have been the subject of considerable attention, owing to their technological importance in the IR field. In addition, their unusual characteristics make them a preferred subject for solid state basic research. The fabrication of devices with alloys of these compounds with photo detection and injection laser capabilities has been an important recent technological development[1]. Many of the metal chalcogenides, compounds of metals and nonmetals with S, Se or Te are important in the new technologies[2]. These chalcogenides considered as "high – tech" materials have many applications, including the tribology (high temperature lubricants), semiconductors, thin films, glasses, photoresists, photomicrography (electronics) and catalysis (dehydrosulphurisation), intercalation of alkali and other metals (battery technology), solar energy conversion, extractive metallurgy (de-sulphurisation as practiced in steel industry), Corrosion in sulphur containing atmospheres (e.g. H_2S).

Among these metal chalcogenides, the binary IV – VI layered compounds formed with Ge as cations, Se and Fe as anions form a very interesting class of semiconductors. The well-known lead salts (PbS, PbSe and PbTe) crystallise in a cubic (NaCl) structure, are very easy to produce both in bulk and epitaxial form. In this third group of IV-VI compounds GeS and GeSe can be produced in both crystalline and amorphous forms[3]. In crystalline form they have an orthorhombic structure and an exceptionally easy (001) cleavage perpendicular to c-axis[4,5]. This cleavage is so easy, in fact, that GeSe are expected to exhibit extreme anisotropy in their lattice vibration. Optical and electronic properties and perhaps show some features characteristic of the two dimensional or layer type semiconductors[6-11]. It would appear; therefore, that GeS and GeSe provide an excellent opportunity for investigating the relations among structure, bonding and the electronic properties of solids with comparisons possible between i. crystalline and amorphous forms ii. two and three dimensional structures, iii. members of the isomorphic series GeS, GeSe, SnS and SnSe and iv. Structurally different compounds GeS, GeTe and GaS.

Structure of these layered materials can be described as solid containing molecules which are in two dimensions extends to infinity and which are loosely stacked on top of each other to form three-dimensional crystals. Several layered materials possess favorable semiconducting properties and have attracted attention as a new class of solar cell materials. Significant optical to electrical/chemical energy conversion efficiencies have been obtained in solid state photovoltaic and photoelectrochemical cells[11]. The potential of this class of materials has not been fully explored yet but appears to be limited mainly by the availability of suitable materials. Attempts have therefore been made to produce good quality crystals and thin films of the layered semiconductors for photoelectronic device applications.

As the first rays of the Sun creep over the horizon, billions of nature's tiny power plants kick into action. In these small molecules, photons of light from the Sun begin to power the chemical reactions which are essential to life[12].

Our vision is to conversion of solar energy into electrical energy in photogalvanic cell through redox reaction because solar energy is currently high on absolute costs compared to other sources of power such as non –renewable sources. The photogalvanic cell was used as a converter device which converts solar energy (photon) in to electrical energy[13].

Owing to its various physical, mechanical and electronic properties of semiconductor material can be used for semiconductor device application. It can also be used on polycarbonate (PC) in outdoor applications, the coating protects PC from solar radiation and decreases the oxidation rate and photo- yellowing of PC. Particularly, ZnO nanowires can be used in dye sensitized solar cells and in field emission devices. It also has potential applications in laser diodes and light emitting diodes (LEDS)[14].

Several approaches including a novel extension of molecular beam epitaxy for the preparation of layered materials are being actively pursued to produce high quality single crystals and thin films. It appears from the literature that majority of germanium monosulphide and germanium monoselenide compounds in the form of single crystals, polycrystalline and thin film form have been reported as p- type semiconductors. The main conclusions which can be drawn from these measurements are that GeSe is always found to be p- type. The room temperature resistivity is usually of the order of 10^3 to10^5 Ω.cm, with considerable sample to sample variation. Conduction is extrinsic at all temperatures below ≈ 400°C and a great variety of impurity and trapping levels are found in the band gap. It is exceptionally difficult to obtain good quality ohmic contacts needed for reliable electrical measurements.

CuO and Cu_2O materials are known to be p- type semiconductors in general and hence potentially useful for constructing junction devices such as p- n junction diodes. Apart from their semiconductor applications, these materials have been employed as heterogeneous catalysts for several environmental processes, solid state gas sensor heterocontacts and microwave dielectric materials. Their use in power sources has received special attention. Thus, in addition to photovoltaic devices, copper oxides have been used as electrode materials for lithium batteries[15].

Measurement of Hall coefficient and resistivity of GeSe between 320 and 1.5 K and they estimated the ionization energy of the acceptor from the temperature dependence of the Hall coefficient[16]. The ionisation energy changed from 3.9 to 5.3 meV according to the heat treatment given to the samples. The impurity conduction was found to occur at low temperatures. There appeared two activation energies corresponding to impurity conduction, the first one was at about 1.5 meV and the other one was at ~ 0.5meV. The resistivity and hall coefficient measured parallel to the GeSe layer at temperature between 77 K and 14K. They showed that there will be a metal to nonmetal transition at p= 4 X 10^{17} cm^{-3}.

GeSe crystals grown by vapour transport technique. They have done electrical resistivity and hall coefficient and the TEP in the temperature range 78 to 300 K and they have calculated effective mass of holes along a, b, c crystallographic axies as 0.20 m, 0.37 m and 6.2 m respectively where m is the electron mass[16]. Other experiment carried out a comprehensive investigation of the electrophysical properties (i.e. Hall effect, electrical conductivity and thermoelectric power) of GeSe crystals in a wide range of temperatures in solid and liquid states[17]. In a later study performed electrical property measurements in GeSe single crystals grown by a chemical vapour transport method using iodine as the transporting agent[18].

Material and Methods

Growth: In order to avoid the contamination by the transporting agent and hence to obtain pure crystals, a better method is the direct vapour transport technique. Many researchers have used the direct vapour transport technique in order to avoid the contamination due to the transport agent. Their work showed that it is possible to grow fairly large crystals of transition metal chalcogenides and their solid solutions. A useful procedure for the calculations of the rate of the transport of solid, based on knowledge of initial condition as well as thermodynamic and diffusion coefficient data has been derived in past.

High quality fused silica tubes of various diameters, having a melting point of about 1773 K were used for growth experiments. Tubes having inner diameter 22 mm, outer diameter 25 mm and length 250 mm were found to be more suitable. One end of the ampoule was sealed and the other end was drawn into a neck and joined to another 8 mm inner and 10 mm outer diameter quartz tube to connect it to the vacuum system for evacuation after introducing the source materials. Such an ampoule is generally used for the crystal growth.

In the present investigations $GeSeFe_{0.02}$ crystals have been grown by direct vapor transport (DVT) technique. Two zone horizontal furnace having required dimensions has been used which is shown in figure 1**.** The furnace was constructed by a special sillimanite threaded tube closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm, imported form from Koppers Fabriken Feuerfester, Germany. High quality quartz ampoules were used for growth experiment having dimensions of 24 cm length, 2.4 cm outer diameter and 2.2 cm inner diameter.

For compound preparation the cleaned ampoule was filled with stoichiometric proportion of Ge (99.999%), Se (99.99%) and Fe (99.99 %) pure of about 10 g for growth then ampoule was sealed under pressure of 10^{-5} Torr. All the chemicals/ powder used for this characterization were from Alfa Aesar, U. S. A. and of the A.R. Grade. The sealed ampoule was kept in two-zone horizontal furnace. The temperatures of both the zones were slowly but gradually raised upto desired temperature and maintained that temperature for specific time, after that furnace was cooled off at the room temperature. The ampoule was broken and shaken well with help of agate mortar to prepare fine powder of this compound.

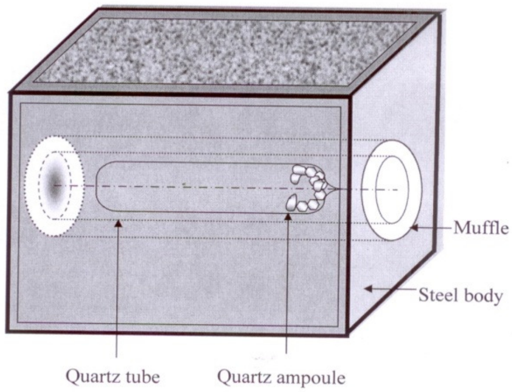

Figure- 1
The dual zone horizontal furnace with co-axially loaded ampoule

The growth parameters for $GeSeFe_{0.02}$ (DVT) single crystals are shown in table 1. The temperature was increased at the rate of 50 K/hr, till it attained the required temperature in both the zones. For the growth of $GeSeFe_{0.02}$, the ampoule was left in the furnace for 168 hour after that the temperature was decreased at the rate of 30 K/hr up to the room temperature. Then the furnace was switched off and the ampoule was carefully taken out from the furnace. The ampoule was finally broken and resulting crystals were collected.

Table- 1
Growth condition for $GeSeFe_{0.02}$ single crystals

Crystal	Temp. range in furnace (T_1-T_2) (^{0}C)	Time for which ampoule was kept in temp. range (T_1-T_2) in hours	Size of the crystals (cm × cm)	Thickness of the crystals (µm)
$GeSeFe_{0.02}$	45	168	0.8 × 0.75	35

Hall Effect Measurements: The Lakeshore 7504 Series Hall effect/ electronic transport measurement system which were design to measure the electronic properties of electrically conductive materials. The systems consist of advanced, integrated hardware and software. The Hall system software controls system instrumentation during an experiment and determines sample resistance, resistivity, Hall coefficient, Hall mobility and carrier concentration. It also controls magnetic field during the Hall effect measurements. Variation in temperature is made possible with the help of ASABA DTC temperature controller.

The system consists of electromagnet which can produce a magnetic field of maximum 10 kG, with 4 inch air gap between the two pole pieces. The necessary current is being supplied by the magnetic power supply (LS 689) with current and voltage limits of 0 to ± 32 V respectively. The Model 450 is an extremely accurate full featured Gaussmeter that covers a wide range of magnetic fields and applications. The instrument provides easy to use front panel programming and a vacuum fluorescent alphanumeric display. This alphanumeric format allows for message-based front panel operation. Most operations can be performed and monitored through the front panel keypad and message display. The Model 450 measures fields in either Gauss (G) or Tesla (T). Set magnetic field can be varied manually or with auto ranging. The gauss meter measures both DC and AC magnetic field values. In DC operation, the display shows the DC field at the probe with the sign followed by the appropriate filed units. In AC operation, the display shows a Peak or RMS value for the field at the probe.

Sample holder is built on PCB which contains in built four pressure contact probes made up of stainless steel, heater and Cr-Al thermocouple. The thermocouple and heater are directly connected with the power supply in series. The temperature can be controlled and displayed with the help of temperature controller model ASABA DTC-07DP. At particular temperature all the Hall parameters has been measured under the variation of a magnetic field (up to ±3KG).

Results and Discussion

Ohmic contacts are required for accurate Hall effect measurements. It is recommended that we test the current-voltage characteristics between contacts to verify ohmic behavior before making Hall effect measurements on unknown sample. With experience, we knew that some samples almost always have ohmic contacts and do not require contact testing. Van der Pauw suggested different geometries of the samples such as circular, square, rectangle and cross. The cross structure is generally used for films and other bulk crystals. According to the invention made for different geometries, the preferred geometry is square rather than circle to reduce the effect of contact lead placement errors in the transport parameters such as resistivity and Hall coefficient [19]. The square shape is the most convenient sample shape to fabricate and this will also reduce the effect of errors in the van der Pauw method arising from either the size or the displacement of contacts leads from the edge of the sample. The lead placement in the square sample must be near the corners in order to minimize errors.

For van der Pauw samples, connection 1 and 3 are opposite to each other (as are contacts 2 and 4). Measuring $R_{12,\ 12}$ sends the excitation current from the switch card down cable 1 and back on cable 2. The voltage is measured between the same cables, so the resistance measured includes the cable resistance, contact resistance at both contacts and the sample resistance between two contacts. The voltage measured across the same contacts used to supply current (e.g. $R_{13,\ 13}$ or $R_{24,\ 24}$) will tell us the voltage levels at the current source and other instruments connected to the switch card. Using the voltages measured in all the test had been kept within the limits of our measurement configuration.

The ohmic nature of the electrical contacts made on all the sample using I- V characteristic. It has been verified before extracting the Hall parameters. In order to get the linear nature of the prepared electrical contacts, the contacts have been annealed. Measuring both $R_{13,\ 13}$ and $R_{24,\ 24}$ tests all four contacts on a van der Pauw sample and is the minimum number of tests required to determine if all four contacts are ohmic. If one or more of the contacts is non- ohmic, additional, additional test may be required to identify the bad contact(s). We have tested $R_{12,\ 12}$, $R_{23,\ 23}$, $R_{34,\ 34}$ and $R_{14,\ 14}$ to verify ohmic behavior of all the contacts. In order to get the linear nature of the prepared electrical contacts, the contacts have been annealed under different conduction. Figure 2, 3, 4 and 5 show linear plot of I-V characteristic between $R_{12,12}$, $R_{23,23}$, $R_{34,34}$, $R_{41,41}$ contacts of $GeSeFe_{0.02}$(DVT) crystal respectively it is required to verified before extracting the Hall parameters.

After the confirmation of the ohmic nature, experiments were conducted for Hall parameters. The change in the Hall parameters/ electrical parameters with temperature and with magnetic field has been shown in figure 6, 7, 8, 9 and 10. From the positive value of Hall coefficient, grown crystals are p- type in nature even their temperature are raised to 400 K. from figure 7, it has been observed that the value of carrier concentration increases with the temperature due to the excess number of charge carriers made available as the temperature increases. The variation of mobility with the temperature as well as magnetic field is shown in figure 10.

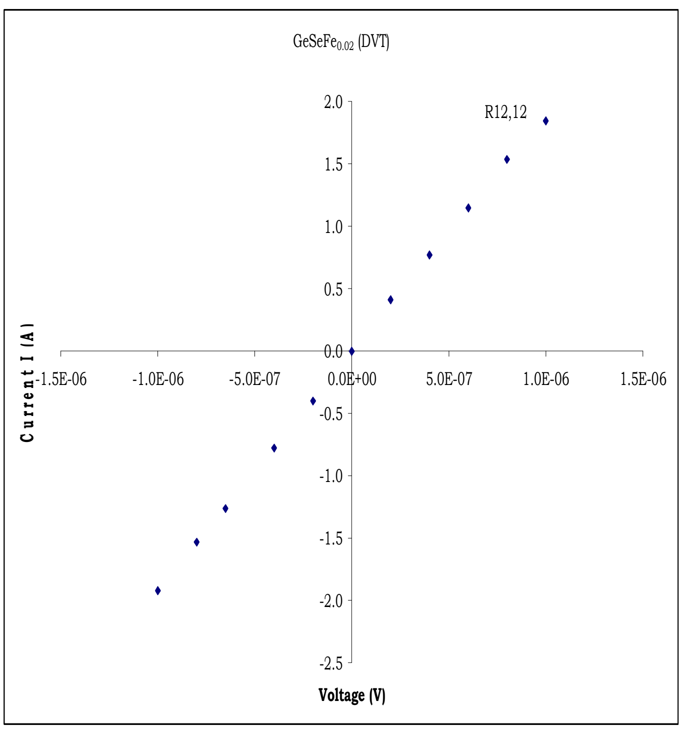

Figure-2
I- V characteristic between $R_{12,12}$ contacts

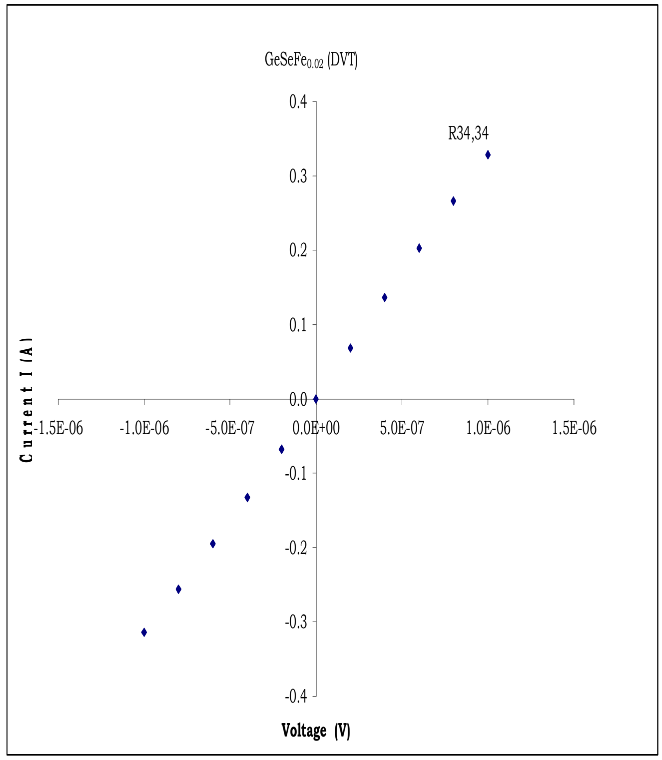

Figure-3
I- V characteristic between $R_{23,23}$ contacts

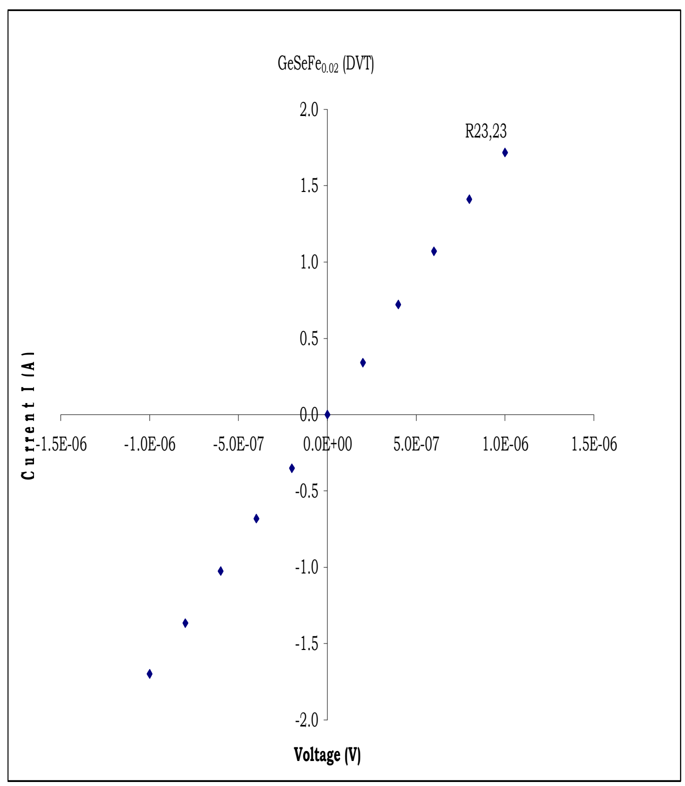

Figure- 4
I- V characteristic between $R_{34,34}$ contacts

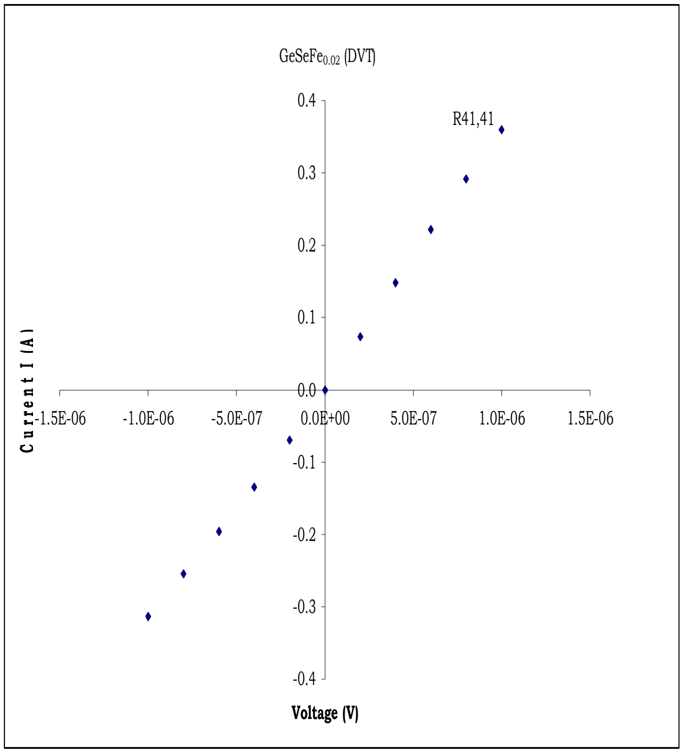

Figure- 5
I- V characteristic between $R_{41,41}$ contacts

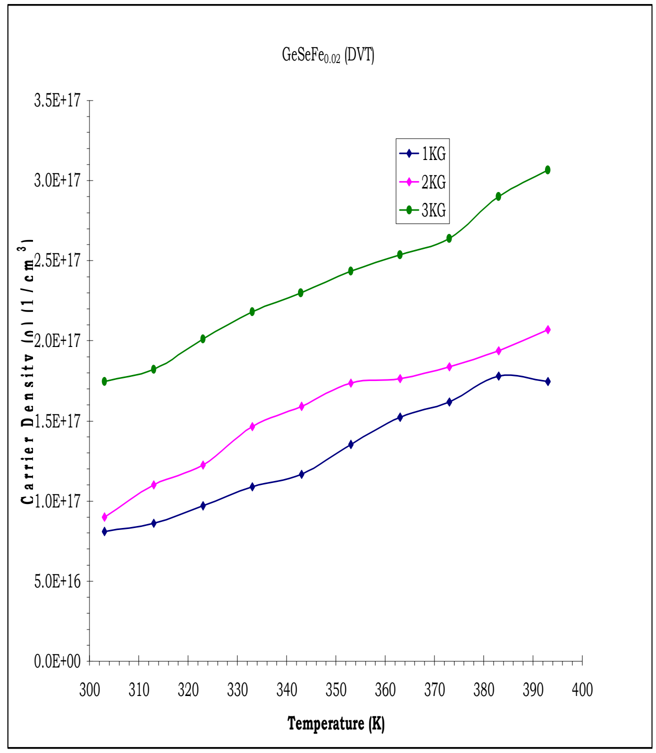

Figure-7
Carrier concentration versus temperature

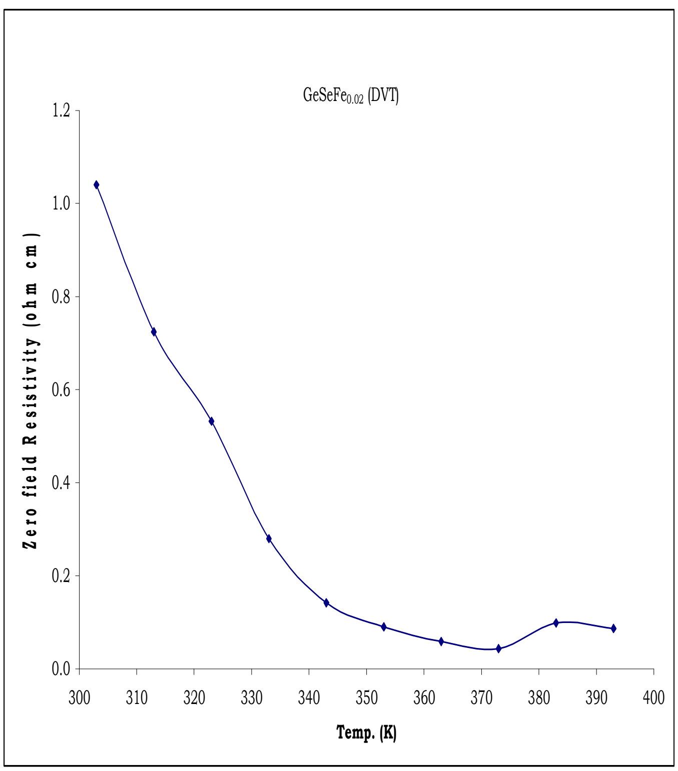

Figure-6
Resistivity with temperature at zero field

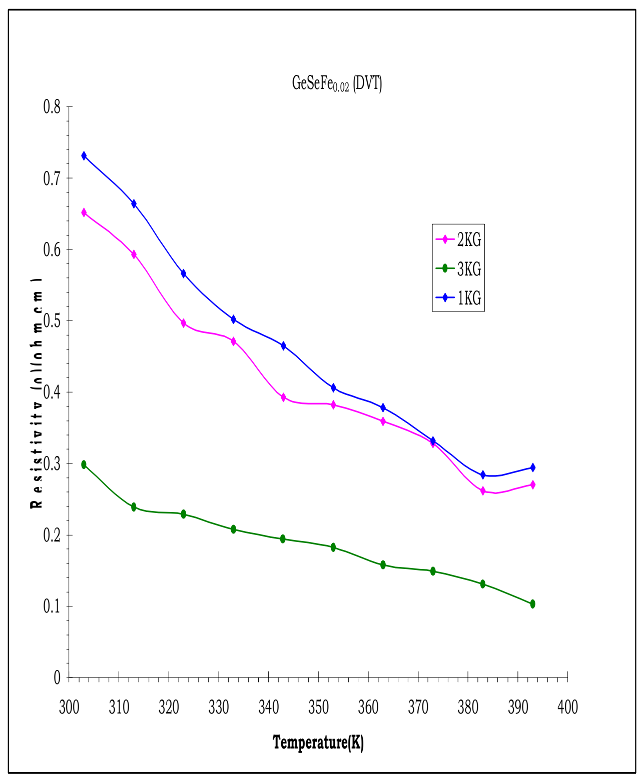

Figure-8
Resistivity versus temperature

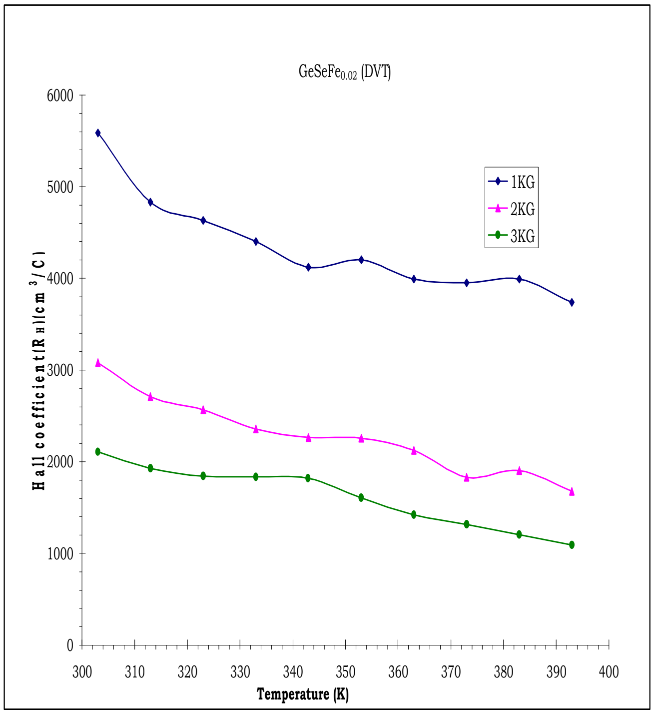

Figure-9
Hall coefficient versus temperature

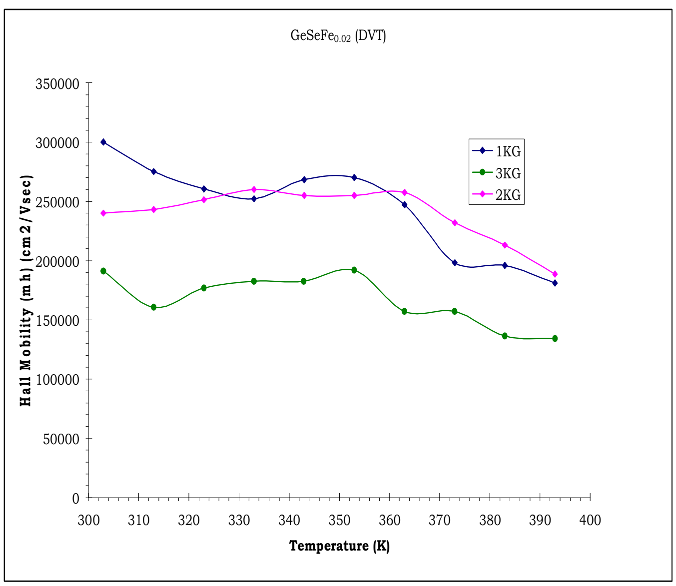

Figure-10
Mobility with temperature

The electronic properties of GeSe were studied for the first time established the existence of shallow impurity levels near the valance band[20]. In past current voltage characteristics of the amorphous and polycrystalline GeSe films had been investigated at different temperature ranges (in low temperature range from 295 to 93 K)[21]. Germanium chalcogenides, GeSe, $GeSe_2$, Ge_xSe_{1-x} and the three component systems of the type Ge-Se-Ga are the objects of increasing interest in view of application in electronic switching, solar cells and memory devices. Here instead of GeSeGa, we grow GeSePb crystals. Another difference is that they prepared thin films for electrical characterization but we have used single crystal as well as we report here high temperature study of the electrical parameters.

Table-2
Elecrical properties of GeSe crystals

Crystal	Resistivity (Ohm-cm)	Hall Coefficient (cm^3/ Vs)	Mobility (cm^2/ Vs)	Carrier concentration (cm^{-3})
GeSe (DVT)	78.19	10067.61	128.75	6.20×10^{14}

It is generally known that the grown by the vapour transport method under similar but not identical conditions, have different residual resistance and resistance anisotropy which is taken as an index of crystal perfection. In our earlier publication work, it was observed that for GeSe single crystals although grown by vapour transport method: using different transporting agents or without any agent show significant change in resistivity. We suggested that these properties can be taken as an index of crystal perfection. We also concluded in past that crystals grown by DVT technique are more perfect as compared to those grown by CVT technique and hence we have grown crystals by DVT method. If we compare value of electrical parameters of GeSe crystals and those of $GeSeFe_{0.02}$ crystals (present work) from the reported graph, then we conclude that there is significant change is found in electrical properties[22].

Conclusion

We have grown successfully single crystal semiconductor $GeSeFe_{0.02}$ by Direct Vapour Transport technique and these as grown crystals are having sufficient dimensions such that we used directly for electrical characterization. We measured electrical parameters like carrier resistivity, Hall coefficient, Carrier concentration and mobility as a function of temperature as well as magnetic field. The value of zero field resistivity and the resistivity is increased with increasing the temperature indicating the typical behavior of semiconductor. The positive value of Hall coefficient in all sample indicate that they have p-type semiconducting nature with majority charge carriers as hoes. The change in Hall parameters with increase in temperature up to 400 K has been explained here. The carrier concentration increases with increase in temperature which causes the decrement in carrier mobility with temperature. This electrical characterization is important to use these crystals for device fabrication up to temperature of 400 K and applied magnetic field of 3 kG.

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