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Electrical Properties of $HfSe_2$ Single Crystals Grown by Chemical Vapour Transport Technique

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In the present work, an attempt has been made to concentrate upon the family of layered materials having a CdI_2 type structure. Single crystals of hafnium di selenide ($HfSe_2$) have been grown by chemical vapour transport (CVT) technique, with iodine as the transporting agent using a two-zone horizontal furnace. Electrical resistivity of the grown crystals were measured using two probe and four probe methods. The measurements showed that resistivity decreases with increase in temperature showing semiconducting behaviour. Activation energy of charge carriers were determined. Hall mobility, Hall coefficient and carrier concentrations were determined. All crystals were found to be of *n*-type conductivity. The electrical conductivity, Hall effect and their temperature dependence concludes the characteristic features of the semiconducting properties of these compounds.

Key Words: $HfSe_2$ single crystals, Resistivity, Hall parameters.

INTRODUCTION

The semiconducting transition metal dichalcogenides, which crystallize with a layered structure have demonstrated sunlight to electrical energy conversion efficiencies and remarkable stability to photocorrosion when employed in a photoelectrochemical cell[1]. The transition metal disulphides and diselenides have attracted considerable attention during the past few years[2]. There is a strong covalent bonding within the layers, but a weak van der Waals bonding between them. It has been realized that selenides are more efficient as solar cell materials than sulphides[3]. Photo electro chemical cell characteristics have however not reached up to the predited level due to the lack of good quality crystals.

Electrical properties of Group IV A transition metal dichalcogenides have been reviewed by Wilson and Yoffee[4]. $HfSe_2$ are semi conductors with energy gap in the range 1.3 ev.[5]. The band gap of these compounds are ideal for photovoltaic applications[6]. Anomaly in the resistivity due to phase transition was identified[7]. It was reported that $HfSe_2$ crystallizes with lattice

parameters a = 3.748 Å and c = 6.159 Å[8]. From the previous survey of literature it was evident that there is not a uniform point of view concerning the nature of semi conducting behaviour of these compounds.

Therefore the main aim of the present work is to investigate the electrical resistivity, Hall effect and temperature dependence in order to conclude the characteristic features of the semi conducting properties of this compound.

EXPERIMENTAL

Single crystals of $HfSe_2$ were grown by chemical vapour transport (CVT) method using iodine as the transporting agent. Total charge used in each experiment was about 10 g. The charges were taken in stoichiometric proportions and were placed in shaped quartz ampoules (length 200 mm and diameter 28 mm) along with transporting agent iodine (3 mg/cm^3). The ampoules were evacuated to a pressure of 10^{-5} torr using oil diffusion pump and sealed off at the constriction of 3 mm diameter.

The ampoules were then placed in a muffle furnace for 72 h for poly crystal-lization. Thoroughly shaken ampoules were transferred to a specially designed two zone horizontal furnace with appropriate stationary temperature profile. Temperature of the furnace is increased in steps of 70 ºC/h. After 432 h of uninterrupted heating crystals were formed. The growth parameters were shown in Table-1.

TABLE-1
GROWTH PARAMETERS OF $HfSe_2$ SINGLE CRYSTALS GROWN USING CHEMICAL VAPOUR TRANSPORT TECHNIQUE

Crystal	Hot zone (ºC)	Cold zone (ºC)	Temperature gradient (ºC)	Growth time (h)	Size (mm^3)
$HfSe_2$	820	770	50	432	13 × 10 × 0.09

Crystals were grounded to powder and patterns were taken by means of a slowly moving radiation detector and recorded on a moving strip of paper with CuK_α radiation The resulting patterns were computer refined to give lattice parameters. Selected crystals were examined by electron probe micro-analysis. Energy dispersive analysis (EDAX) confirms the stoichiometry of the grown crystals.

Electrical resistivity was measured on reasonably well shaped single crystals using van der pauw method and two probe methods at room temperature.

Low temperature resistivity measurements were performed for a constant current in the temperature range 93 to 293 K using a pyrex cryostat designed for the purpose. High temperature resistivity measurements was also performed in the temperature range 303-413 K using a four probe

setup. Anisotropy of different samples are determined in the temperature range 303-433 K.

The sign, mobility and concentration of charge carriers were determined by Hall effect measurements in the magnetic field range 0 to 10 KG.

RESULTS AND DISCUSSION

Typical data are presented in Fig. 1 which show the resistivity as a function of square of temperature (93-293 K). From the plots it is seen that resistivity increases with increase in temperature and propotional to T^2.

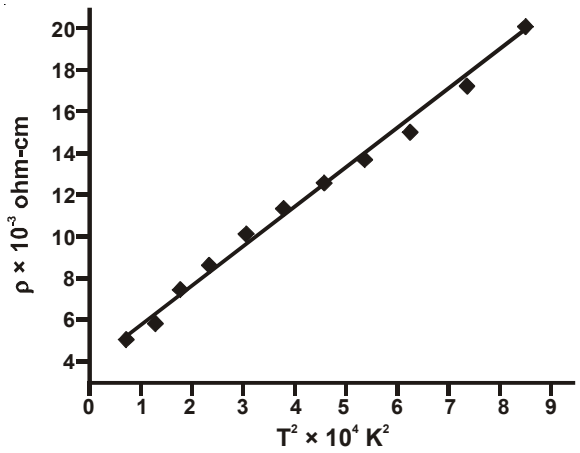

Fig. 1. Variation of resistivity with square of temperature

Fig. 2 depicts the variation of resistivity with temperature in the range 323-423 K. The present plot has two distinct straight line regions. The activation energy of charge carriers were calculated using the formula:

$$Ea = 2.303 \times K \times 10^3 \times \text{slope}$$

were $K = 8.62 \times 10^{-5}$ eV k^{-1} and are seen to be 0.0416 eV in the temperature range 303-373 K and 0.126 eV in the temperature range 373-423 K.

The Hall mobility was found to be 1.0742 $cm^2\ V^{-1}\ s^{-1}$. The values of Hall coefficient (R_H) and carrier concentration (n) at room temperatures were -1.838×10^{-1} cm^3/coul. and 3.40×10^{19} cm^{-3}, respectively.

The variation of Hall mobility with temperature is shown in Fig. 3. The graph shows a positive temperature dependence of mobility due to scattering mechanism in the crystals. The behaviour of carrier concentration as a function of $10^3/T$ is shown in Fig. 4. The graph confirms the linear relation between log n and 1/T.

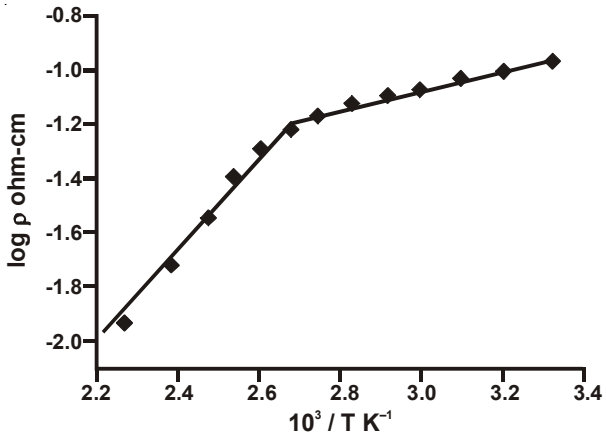

Fig. 2. Variation of resistivity with temperature

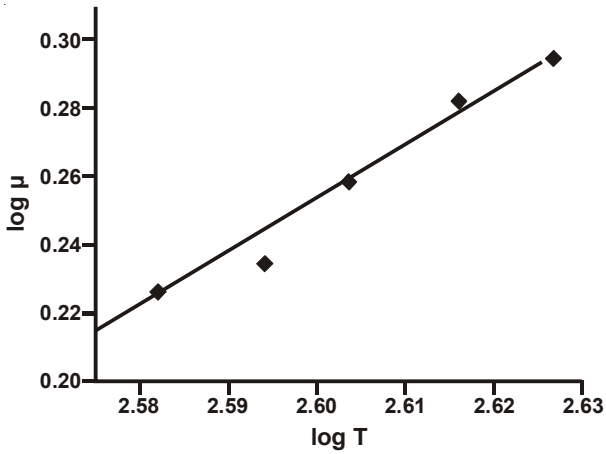

Fig. 3. Variation of Hall mobility against temperature

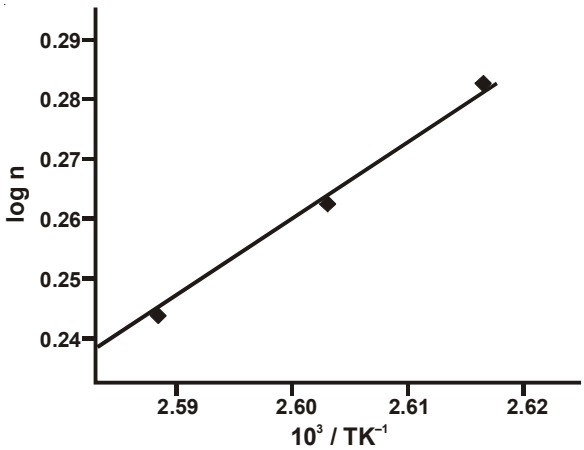

Fig. 4. Temperature dependence of carrier concentration

The low value of resistivity along the basal plane and high value of resistivity perpendicular to it confirms the anisotropic behaviour of the crystals.

The anisotropic bahaviour is similar to other transition metal dichalcogenides. The anisotropic behaviour suggests that electronic conduction in the crystals is mainly anisotropic. The T^2 dependence of electrical resistivity may be due to carrier scattering.

The positive temperature dependence of mobility implies that scattering mechanisms may be due to the ionized impurity scattering in the observed temperature range. Scattering obeys the relation $\mu \propto T^x$ were x = the mode of scattering.

From the behaviour of carrier concentration with temperature, it is observed that as temperature increases, the carrier concentration also increases. The slope of the curve is relatively low due to the presence of deep donor like levels in the material.

Conclusion

Single crystals of hafnium di selinide grown using iodine as the transporting agent exhibits metallic behaviour in the range of 93-293 K and semi conducting behaviour in the range of 303-433 K. The crystals were of *n*-type semi conductors. The positive value of temperature dependence on carrier mobility indicates that ionized impurity scattering is dominant.

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