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TRANSPORT PROPERTY MEASUREMENTS IN WSe_{2-X} CRYSTALS

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ABSTRACT

Electrical resistivity and Hall effect measurements have been carried out on crystals of WSe_{2-x} grown by Direct Vapour Transport technique. The effect of changing the selenium content on the electrical properties of the grown crystals has been thoroughly investigated and its implications have been discussed.

Keywords: WSe_{2-x}, Hall effect, Activation Energy.

INTRODUCTION

The dichalcogenides of tungsten (WSe_2) possess C7 type crystal structure. In this structure each W atom is in 6- fold co-ordination with the chalcogen (Se) atoms lying in a hexagonally packed plane.

The atoms in sandwich layers are bonded partly by ionic and partly by covalent bonding and the interlayer interaction is due to the van der Waal's bonding. Because of this strong anisotropy in the bonding, the layered transition metal dichalcogenides show marked anisotropy in their physical properties.

The effective use of solar energy in photovoltaic or photoelectrochemical applications depends in part on the development of materials that can show high conversion efficiency and longterm stability under operation. In addition, the desirable material should have a band gap that closely matches the solar spectrum and be made of readily available and inexpensive materials. Single crystals of transition metal dichalcogenides have band gaps (1.1 – 1.6 eV) that closely match the solar spectrum and exhibit high conversion efficiencies. In addition, they can achieve long term stability due to the fact that the transitions are localized in the non-bonding d-orbitals of the metal. Among TMDC's WSe_2 occupies a favorable position with suitable band gap of 1.57 eV and is one of the most promising material in PEC solar cell applications [1]. Since changing the content of Se in WSe_2 single crystals alter its electrical properties, which in turn has an effect on its photoelectrochemical behavior, it was thought worthwhile to carry out electrical resistivity and Hall effect measurements on single crystals of WSe_{2-x} grown by direct vapour transport method.

In order to see the effect of defects such as stacking faults etc., it is desirable to measure the resistance in the direction normal to the basal plane, hence resistance measurements normal to the basal plane were carried out on WSe_{2-x} single crystals in the temperature range 298K to 853K.

EXPERIMENTAL

The single crystals of WSe_{2-x} used in the present investigations were grown by direct vapour transport technique [2]. The room temperature electrical resistivity, Hall mobility, Hall coefficient and carrier concentration were determined using the standard method of Van der Pauw.

The electrical resistivity measurements in the temperature range 77-300K were carried out using the conventional four probe technique with the help of a low temperature resistivity set up (Figure1) manufactured by Scientific Solutions Bombay. The system is designed to fit directly into any of the standard liquid nitrogen containers. The system is supplied with a standard ½ inch valve for evacuating and a ¼ inch valve for introducing the exchange gas, monitoring vacuum etc.

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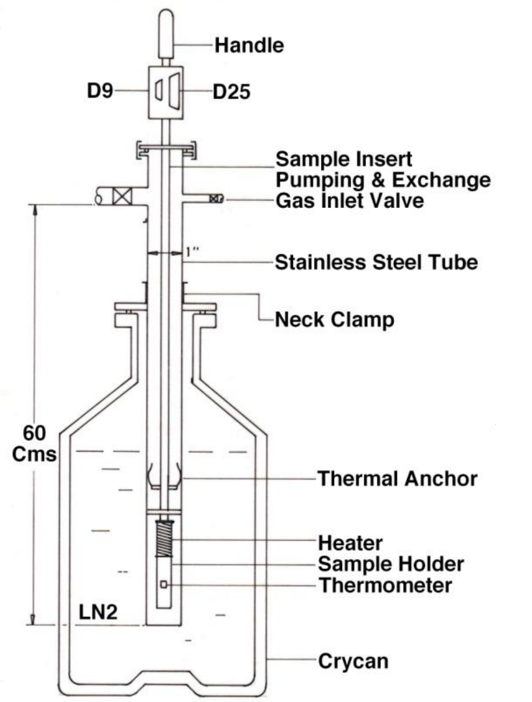

Fig.1. Experimental Set – up for Low – Temperature Resistivity Measurements.

Four copper wires were attached with the conducting silver paste on each specimen. Samples whose ohmic contacts were checked before measurements were fixed on a sample holder. The sample holder consists of a gold-plated copper assembly mounted with a standard platinum thermometer and a heater in close thermal contact with the sample holder. The temperature was varied with the use of a heater.

The experimental set up for the measurement of resistance normal to the basal plane was fabricated in University Science and Instrumentation Centre (USIC).

The experimental set up is shown in figure 2. The crystal was mounted on the sample holder , which was then inserted into the sample chamber , and then closed from the top. The temperature of the sample could be raised by introducing the sample chamber assembly into a furnace. The temperature of the sample was measured with the help of a Cr-Al thermocouple kept in the vicinity of the sample. Starting from room temperature, the temperature of the sample was increased slowly in steps of 10^{o} C till the final temperature was reached, and at each step the corresponding value of the resistance of the sample was noted. To avoid excessive heating of the sample chamber, it was cooled by circulating water around it with the help of tubing wound around it.

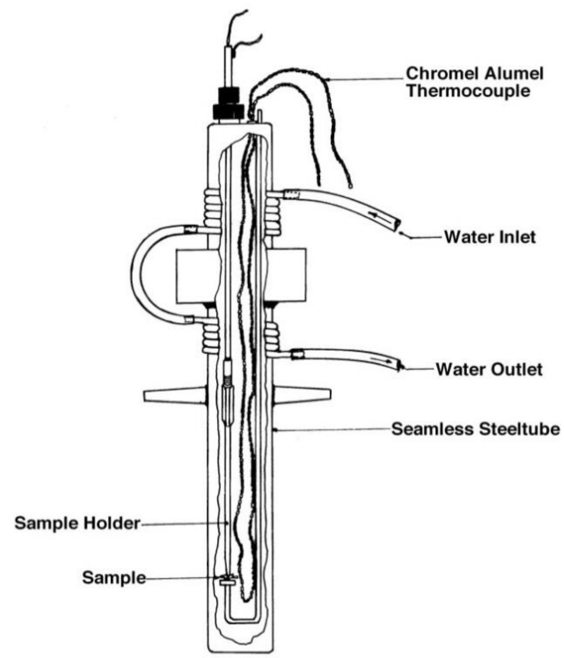

Fig.2. Cross – section of the Two Probe set – up for Resistivity Measurements parallel to c – axis.

RESULTS AND DISCUSSION

The Hall effect measurements on the grown crystals are reported in Table 1. The Hall coefficient R_H and the carrier concentration 'n' have been calculated, assuming the single carrier conduction model and using the relation,

$$\mu_H = \frac{R_H}{\rho} \quad \text{and} \quad n = \frac{-1}{eR_H}$$

where 'e' is the electronic charge. The Hall coefficient has a positive value.

A study of Table 1 reveals the following facts: The room temperature resistivity decreases with the decrease in selenium content. All the crystals are essentially p-type. The Hall coefficient decreases with the decrease in selenium content.

Crystal	ρ (Ωcm)	R_H (cm^3/C)	μ_H (cm^2/V.sec)	n (cm^{-3}) x10^{17}	Ea (eV)
WSe_2	0.81	146	178	0.43	0.06
$WSe_{1.98}$	0.59	143	242	0.44	0.06
$WSe_{1.97}$	0.40	133	345	0.47	0.05
$WSe_{1.93}$	0.35	125	357	0.50	0.04
$WSe_{1.90}$	0.32	100	312	0.62	0.04

The Hall mobility increases as the selenium content is decreased. The carrier concentration of all the crystals is more or less of the same order, but still there is a definite increase in the value of carrier concentration with the increase in the value of x.

Table 1 : Data of WSe_{2-x} Crystals

The plots of log ρ vs 1/T are shown in Fig.3 for all the off-stoichiometric crystals used in this study. All the plots exhibit a classical semiconducting nature. The values of the activation energies calculated from the above plots show a decreasing trend with the decrease in selenium content.

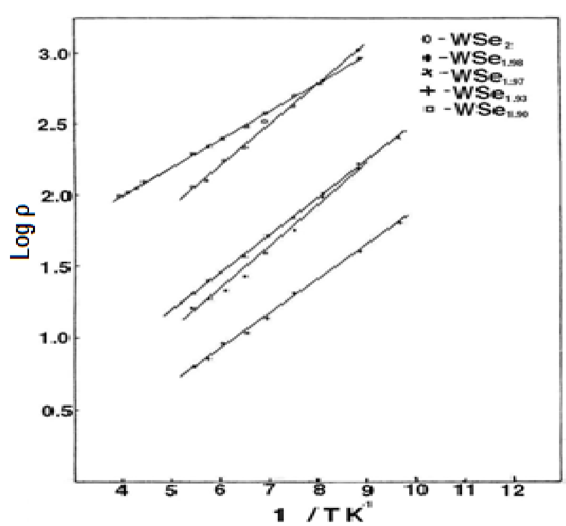

Fig.3 Low Temperature (77K – 303K) electrical resistivity plots (log ρ vs 1/T) for all p-type off – stoichiometric WSe_{2-x} single crystals

The p-type nature of the WSe_{2-x} crystals can be explained by considering a proper electronic sharing between $5d^4 6s^2$ electrons from tungsten and $4s^2 4p^4$ electrons from selenium. From the chemistry of these two elements we know that there exist two valence states (+4 and +6) for tungsten and three valence states (+2, +4 and +6) for selenium.

In WSe_{2-x} crystals, two selenium atoms are effectively associated with one tungsten atom. Therefore it is possible for the eight electrons from the incomplete p sub shells of selenium to go for a covalent bonding with the six $5d^4 6s^2$ electrons. This would ultimately give rise to vacancies for two more electrons to perform the complete covalent bonding. This vacancy would obviously be at the heavy metallic sites provided by tungsten atom. These vacancies will provide a positive hole like character to the material thus making them behave like p-type semiconductors.

An EDAX analysis of the specimens of WSe_{2-x} carried out [3] clearly points out that crystals of WSe_{2-x} grown by direct vapour transport method grow with hybridized valence states due to the presence of higher valence states of selenium.

Since the higher valence states in selenium are formed by the electronic transition from p-level to d-level in the N-shell, the generation of holes will take place a little bit deeper in the valence band and will affect the semiconducting properties of the materials.

Now a change in stoichiometry in WSe_{2-x} gives rise to a "local strain field" which pumps the selenium into higher valence states. Accordingly, the development of higher valence states will be related to the composition of WSe_{2-x}. The greater the value of x in WSe_{2-x} more will be the off-stoichiometry and greater will be the number of positive charge carriers leading to a reduction in resistivity as experimentally observed. This increase in the number of charge carriers is confirmed from the Hall effect measurements.

The systematic decrease in the value of activation energy of the samples with the decreasing selenium content in the low temperature resistivity measurements can only be explained in terms of off-stoichiometry introduced in the samples with the change in the selenium content. Since all these crystals are grown by direct vapour transport method there is no transporting agent to account for this change in activation energy.

As a representative example of WSe_{2-x} the resistance of WSe_2 and $WSe_{1.97}$ parallel to c-axis was measured as a function of temperature. Figures 4 and 5 show the plot of resistance versus temperature.

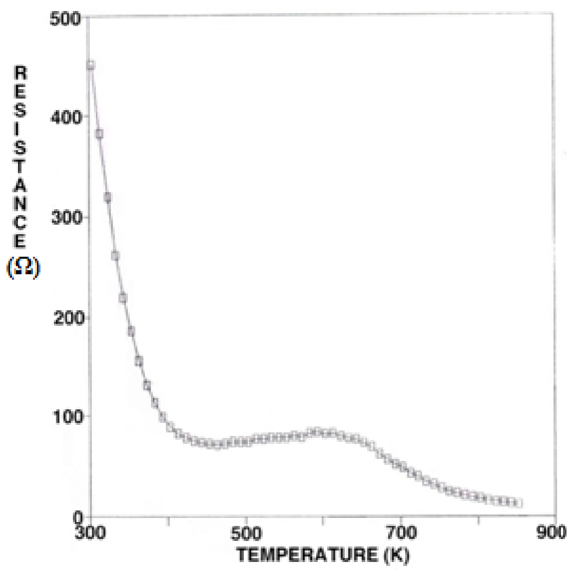

Fig.4. Plot of resistance versus temperature for WSe_2.

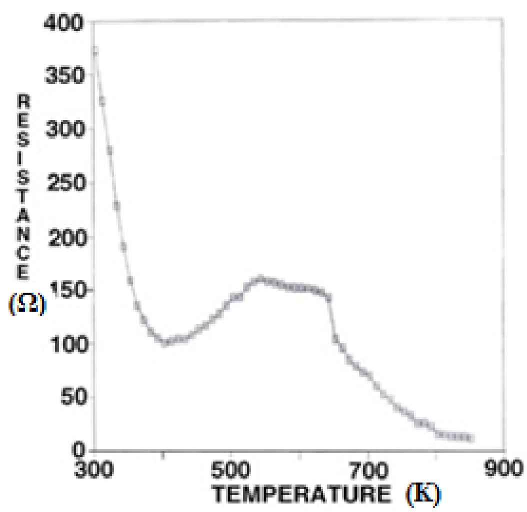

Fig.5. Plot of resistance versus temperature for $WSe_{1.97}$.

A comparison of the values of resistance at room temperature with the similar values along the basal plane clearly brings out the anisotropic character of our specimen. The anisotropic ratio for WSe_2 and $WSe_{1.97}$ is found to be 9.95 and 9.38 respectively.

A close inspection of the curves brings out the following facts:

In the case of WSe_2 the resistance goes on decreasing with an increase in temperature as is seen in the case of any normal semiconductor.

However in case of $WSe_{1.97}$ the resistance at first decreases up to the temperature of 403 K, thereafter there is an increase in resistance from 403K to 543 K. Once again the resistance remains constant from 583 K to 643 K and thereafter decreases in the same manner as seen for WSe_2.

The apparent change in behavior of the two samples has to do with the stoichiometry of the two samples. More experiments are needed for understanding the exact mechanism involved in the process of conduction along the c-axis.

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