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Study of Electrical Property of Single Crystals of Tungsten Diselenide

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ABSTRACT

The requirement for inexpensive and highly efficient solar cell requires continuous exploration of new semi-conductors which satisfy the photo-voltaic criteria established by solar cell base materials like Tungsten Diselenide. Single crystals of $W_{0.80}Se_2$ belonging to transition metal dichalcogenides MX_2 group are synthesized in the laboratory. Since the crystals are insoluble in water and decompose before melting point temperature, crystals are grown by Direct Vapor Transport (DVT) technique. The electrical transport properties of $W_{0.80}Se_2$ single crystal are studied and resistivity through Van der Pauw method in the high temperature range (313K –388K) is obtained. Employing the Hall effect measurements, Hall coefficient, mobility as well as carrier concentration have been studied. The Van der Pauw technique is also used to evaluate the type, mobility and carrier concentration of $W_{0.80}Se_2$ single crystals.

Keywords: Dichalcogenides, Decompose, Non-Stoichiometry

I. INTRODUCTION

The requirement for inexpensive and highly efficient solar cell requires continuous exploration of new semi-conductors which satisfy the photo - voltaic criteria established by solar cell base materials like Tungsten Diselenide. From the recent photo electrochemical studies on the transition metal dichalcogenides $W_{0.80}Se_2$ single crystals have emerged as the most efficient photo electrode materials used in the photo electrochemical solar cells. Among the layered compound group VI transition metal dichalcogenides, WSe_2 is the most promising semiconducting material for the photo electrochemical (PEC) conversion of solar energy to electricity, because of its high absorption coefficient in the visible and near infrared [1] and its excellent output stability as photo electrodes in polyiodide electrolytes [2,3]. A large number of investigators [3] have therefore focused their attention on the PEC studies of WSe_2. However, very little work appears to be done on off-stoichiometric crystals of Tungsten diselenide. The author has therefore decided to concentrate his attention on off-stoichiometric $W_{0.80}Se_2$ single crystals. Since these materials exhibit semiconducting behavior, it is worth studying them from the point of view of transport properties. It is obvious that these properties are of primary importance in the evaluation of these semiconducting materials for device fabrication.

The crystals possess facile basal cleavage, lubricity and marked anisotropy in their physical and chemical properties. Since the material of $W_{0.80}Se_2$ possesses a semiconducting nature, the author decided to study its transport properties like the resistivity (µ), Hall coefficient (R_H), as well as carrier concentration (n).

II. METHODOLOGY

Since single crystals of $W_{0.80}Se_2$ are not available in nature, they have to be synthesized in the laboratory. There are several methods of growing single crystals. The techniques have been fully described in [1-7]. The crystals of transition metal dichalcogenides MX_2 (M is W and X is Se) group are insoluble in water and they decompose before their melting points are reached. So, the growth of such crystals from the melt and aqueous solution is not possible. Therefore, one goes for growing these crystals by the method of growth from the vapour phase. Depending upon the phenomena involved, the vapour phase method is classified in the following two categories: (i) Chemical vapour transport and (ii) Direct vapour transport.

Single crystals of $W_{0.80}Se_2$ have been grown using a direct vapour transport technique. A stoichiometric mixture of 99.999% pure tungsten powder and 99.95% pure selenium powder were sealed under a pressure of 10^{-5}Torr in 2.5 cm bore x 24 cm long high quality fused quartz ampoules. The sealed ampoule containing the mixture was then introduced into a two zone furnace at a constant-reaction temperature to obtain the charge of $W_{0.80}Se_2$. The charge so prepared was rigorously shaken to ensure proper mixing of the constituents and kept in the furnace under appropriate conditions to obtain single crystals of $W_{0.80}Se_2$. The growth conditions used for the synthesis are given in Table 1 and 2. The resulting crystals from the growth were black opaque and plate like with c-axis normal of the plates.

III. Experimental Technique

The resistivity measurements perpendicular to c-axis (i.e. along the basal plane) can be investigated using following techniques: (i)Van der Pauw Method and (ii) Four Probe Resistivity Method. The room temperature resistivity measurements were made using Van der Pauw method. The resistivity of $W_{0.80}Se_2$ single crystals can be measured at different temperatures in the temperature range (313K - 388K) by a four probe method. The high temperature resistivity measurements were evaluated using the Four Probe Method. The four probe set up (Scientific Equipments, Roorkee, India) consists of probe arrangement, oven, constant current source, milliammeter and electronic voltmeter. Large size crystals having proper shape were used for the study of variation of resistivity with temperature using the four probe method. Also there is generally minority carrier injection by one of the current carrying contacts. An excess concentration of minority carriers will affect the potential of other contacts and modulate the resistance of the material. The four probe method overcomes the difficulties mentioned above and also offer several other advantages. It permits measurements of resistivity in samples having wide variety of shapes including the resistivity of small volume within the bigger pieces of semiconductor.

3.1 Resistivity Along the basal plane by van der Pauw method

The room temperature resistivity of $W_{0.80}$ single crystals, perpendicular to c - axis (i.e. along the basal plane) was investigated using van der Pauw method. The results of such measurements for representative samples are given in Table 3. Using the values of R_1 and R_2, resistivity can be calculated. The basal plane resistivities for $W_{0.80}Se_2$ crystals were evaluated and are reproduced in Table 6. From Table 3, average R_1 = 4.928 Ω and R_2 = 4.56 Ω.

3.2. High Temperature Resistivity Measurement Perpendicular to c-axis

The high temperature resistivity measurement perpendicular to c-axis i.e. along the basal plane was carried out on single crystals of W0.80Se2 using the four probe technique as described earlier. Table 4 and 5 show the variation of resistivity with temperature (313K - 388K) for representative samples of W0.80Se2 . In all cases it is seen that resistivity increases with decreasing temperature, thereby indicating that the samples show a classical semiconducting behavior.

3.3 Hall effect measurements

A modification of Van der Pauw technique has been used to evaluate the type, mobility (μ) and carrier concentration (n). The phenomenon in which the production of voltage difference across an electrical conductor transverse to and electric current in a conductor placed in a magnetic field perpendicular to the current is know as hall effect. Hall Effect measurment is the only tool to provide basic electrical parameter of material. The sample $W_{1-x}Se_2$, for this measurement is kept in known magnetic field produced by an electromagnet (Type EMPS-5 Omega Electronics, Jaipur, India). This magnetic field modifies the path of electrons producing the Hall voltage. By knowing the values of difference in resistance (△R), magnetic field (△B) and the thickness of the sample t, the mobility of carriers was evaluated using the following equation

$$\mu_H = \frac{t\Delta R}{\Delta B \rho} \qquad (1)$$

Where ρ is the room temperature resistivity of the samples. The Hall coefficient (R_H) and carrier concentration (n) were calculated using the following formula

$$R_H = \mu_H \times \rho \qquad (2)$$

$$n = \frac{1}{R_H e} \qquad (3)$$

From the sign of Hall coefficient, the nature of the charge carriers in the grown samples could be ascertained. T calculated value of R_H and carrier concentration (n) for each case are represented in Table 5. The result obtained from Hall effect Measurement for sample are given in Table 8 and 9.

IV. RESULTS AND DISCUSSION

The variation of resistivity along the basal plane with temperature clearly brings out the classical semiconducting nature of $W_{0.8}Se_2$ single crystals. Hall effect measurements shown in respective tables. Following are the main results:

(1) The resistivity measurements point out that all the samples of $W_{0.80}Se_2$ indicate a classical semi-conducting behavior.
(2) The off-stoichiometric crystals of tungsten diselenide show a semiconducting behavior in the temperature range 313K to 388K.
(3) The positive values of Hall coefficients for $W_{0.80}Se_2$ indicate that they are p-type semiconductors

V. CONCLUSION

The electrical transport property measurements are carried out on $W_{0.80}Se_2$ single crystals. The suitability of cells so fabricated should be decided in different electrolytes. The Photo electrochemical studies will clearly indicate the effect of non-stoichiometry on the photo electrochemical performance of WSe_2 solar cells.

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TABLE:1 Growth Parameters used to Synthesise Single crystals of $W_{0.80}Se_2$

Material / Growth Parameters	Reaction Temperature	Growth Temperature	Growth Time	Crystal Size (maximum)	Appearance
$W_{0.80}Se_2$	1073 K	1248 K	212 hrs	9mmX6 mmX 0.2 mm	Black Opaque

TABLE 2. STRUCTURAL DATA OF $W_{0.80}Se_2$

Material	Lattice Parameters	
	a	c
$W_{0.80}Se_2$	12.973 $\pm$ 0.01	3.290 $\pm$ 0.001

Table 3. Measurement of Resistivity through Vander Pauw Method

Sample : $\mathbf{W_{0.80}}Se_2$, Thickness t=0.006cm, Length ℓ=0.7cm, Breadth b=0.5cm

Current I_{AB} mA	Voltage V_{DC} mV	Resistance R_1 Ω	Current I_{BC} mA	Voltage V_{AB} mV	Resistance R_2 Ω
0.5	-2.37	4.74	0.5	-2.3	4.60
1.0	-4.76	4.76	1.0	-4.5	4.50
1.5	-7.39	4.92	1.5	-6.7	4.46
2.0	-9.85	4.92	2.0	-9.1	4.55
2.5	-12.39	4.95	2.5	-11.6	4.64
3.0	-15.10	5.03	3.0	-14.0	4.66
3.5	-17.65	5.04	3.5	-16.1	4.60
4.0	-20.3	5.07	4.0	-18.4	4.51

Table 4. Result of High Temperature Resistivity Measurement

Sample:$W_{0.80}Se_2$ Thickness t=0.006cm length ℓ=0.7cm breadth b=0.5cm

Temp (°C)	Temp T K	$\frac{1}{T} \times 10^{-3}$ (k^{-1})	Resistance R k Ω	Resistivity $\rho = \frac{Rbt}{\ell}$ Ω cm	log ρ
40	313	3.19	33.3	142.71	2.15
45	318	3.14	32.0	137.14	2.13
50	323	3.09	30.6	131.14	2.11
55	328	3.04	28.6	122.57	2.08
60	333	3.00	27.2	116.57	2.06
65	338	2.95	26.7	114.57	2.05
70	343	2.91	23.4	100.28	2.00
75	348	2.87	21.8	93.42	1.97
80	353	2.83	19.4	83.14	1.91
85	358	2.79	15.9	68.14	1.83
90	363	2.75	14.2	60.85	1.78
95	368	2.71	12.4	53.14	1.72
100	373	2.68	10.4	44.57	1.64
105	378	2.64	9.1	39.00	1.59
110	383	2.61	8.2	35.14	1.54
115	388	2.57	7.22	30.94	1.49

Table 5. Result Of Hall effect Measurement

Sample: $W_{0.80}Se_2$ Thickness t = 0.006 cm Constant current I = 1.5 mA

Magnetising Current I Amp	Magnetic Field B K.Gauss	Hall Voltage mV	Residtance R = V/I Ω	△ R	△ B	Hall Coefficient R_H Cm³/coul	Mobility μ cm²/V.sec	Carier Concentration n cm³
0.5	2.58	12.69	8.46	0.06	2.26	15.92	123.41	3.92×10^{17}
1.0	4.84	12.60	8.40	0.05	1.89	16.12	124.96	3.87×10^{17}
1.5	6.73	12.53	8.35	0.07	1.55	27.09	210	2.30×10^{17}
2.0	8.28	12.43	8.28	0.08	1.24	38.70	300	1.61×10^{17}
2.5	9.52	12.30	8.20	0.04	0.92	26.08	202.17	2.3×10^{17}
3.0	10.44	12.36	8.24	0.10	0.75	80	620.15	0.78×10^{17}
3.5	11.19	12.22	8.14	0.04	0.52	46.15	357	1.35×10^{17}
4.0	11.71	12.45	8.10	--	--	---	---	----

Table 6. Result of Measurement on off-stoichiometric Crystals of $W_{0.80}Se_2$

Sample Examined	Resistivity Ω .Cm	Hall coeffcient R_H Cm^3/coul	Mobility μ cm^2/V.sec	Carrier Concentration cm^{-3}
$W_{0.80}Se_2$	0.129	24.78	192.10	2.8×10^{17} (p)