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Synthesis and Characterization of Tungsten Diselenide Single Crystals

D. K. Patel

Physics Department, C. U .Shah Science College, Ahmadabad, Gujarat, India

ABSTRACT

The semiconducting compound tungsten diselenide (WSe_2) possess interesting electrical properties and has been the subject of numerous investigation.it is used as photovoltaic/photo catalytic solar energy converter. The development of photo based material was simulated largely by the need for working out a photo electrochemical (PEC) solar energy conversion method as a new ecologically clean and inexhaustible source of energy. In the most promising variant method of converting solar energy in to electrical energy using solar cells (PEC) with semiconductor electrode. Single crystals of tungsten diselenide (WSe_2) emerged as a most efficient photo electrode material used in the PEC solar cells have been grown by using Direct vapors transport technique (DVT). The electrical properties of $W_{0.90}Se_2$ single crystal are studied and resistivity through vander-Pauw method in the High temperature range (313K – 388K) is obtained. The vander-Pauw technique is also used to evaluate the type, mobility and carrier concentration of $W_{0.90}Se_2$ the single crystals of photovoltaic cells.

Keywords: Dichalcogenides, Decompose, Non-Stoichiometry, Semiconductor, Resistivity

I. INTRODUCTION

The incident solar radiation are useful for alternative green power source of energy.The$W_{0.90}Se_2$ crystallize in a layered structure. The space group of these crystals is $P6_3/mmc$ and the basic co-ordination unit for these structures is a trigonal prism. The metal atom (W) at the centre of the prism is co-ordinate with six selenium atoms at the corners. A layer is composed of alternatively occupied prisms places side by side and no strong bond exists across the gap between the layers while only long range Vander walls forces hold atomic sandwiches together. This gives growth and pronounced cleavage perpendicular to c-axis. As a consequence the crystals possess facile basal cleavage, lubricity and marked anisotropy in their physical and chemical properties. Since the material of $W_{0.90}Se_2$ possesses a semiconducting nature, the purpose of present study of tungsten Diselenide transport properties like the resistivity (ρ), Hall coefficient (R_H), Mobility (μ) as well as carrier concentration (n). (Perker, R.L., 1970)

II. METHODS AND MATERIAL

Since single crystals of $W_{0.90}Se_2$ are not available in nature, they have to be synthesized in the laboratory. There are several methods of growing single crystals. (Buckley, H.F.1951) In the recent years (Lawson, W.D. & Nielson,S.1958) There has been much interest in transition metal dichalcogenides of the form MY_2 (M=Transition metal W and Y=chalcogen Se_2) for potential use in the conversion of solar energy in to electrical or chemical energy. Very high conversion of efficiencies has been reported with tungsten diselenide for the conversion of solar energy in to electrical energy (Salvador, P.Chaparro A.M.and Mir, and A.1996). It is seen (campet.et.al.,1989). that variation of stochiometry in WSe_2 affect its photovoltaic performance. E.g. lowering the selenium excess during the crystal growth increases overall quantum efficiency of WSe_2 diodes.Additionally,the open circuit voltage V_{oc} could be increased by reducing the selenium excess down to 1%. Therefore there is a need for a systematic study of non-stoichiometric compound of WSe_2. Recently

(Molenda, J.and Bak.T. 1993) have reported a study of electronic and electro-chemical properties of non-stoichiometric The importance of tungsten diselenide WSe_2 in the fabrication of liquid junction photo-electrochemical cells has been shown by (Aruchamy A.and Agarwal, M.K. 1992) WSe_2 Since the electrical transport properties of semi-conducting material plays an important role in deciding the photo-conversion efficiency of a solar cell fabricated with semiconductor. 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 $W_{0.90}Se_2$ 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 $W_{0.90}Se_2$. 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 $W_{0.90}Se_2$. 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.

Table 1. Growth Parameters used to Synthesize Single crystals of $W_{0.90}Se_2$

Material Growth Parameters	Reaction Temperature	Growth Temperature	Growth Time	Crystal Size	Appearance
$W_{0.90}Se_2$	1073 K	1248 K	212 hrs	8mm × 6 mm × 0.2 mm	Black Opaque

Table 2. Structural data of $W_{o.90}Se_2$

Material	Lattice Parameters	
	A	c
$W_{0.90}Se_2$	12.978 ± 0.01	3.292 ± 0.001

The resistivity measurements perpendicular to c-axis (i.e. along the basal plane) can be investigated using following techniques: (i)Vander Pauw Method and (ii) Four Probe Resistivity Method. The room temperature resistivity measurements were made using Van der Pauw method. The resistivity of $W_{0.90}Se_2$ single crystals can be measured at different temperatures in the temperature range (313 K - 388 K) 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. Many conventional methods for measuring resistivity are unsatisfactory for semiconductors because metal semiconductor contacts are usually rectifying in nature. 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 offers 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

Resistivity along the basal plane by van der Pauw method

The room temperature resistivity of $W_{0.90}$ Se_2 single crystals, perpendicular to c - axis (i.e. along the basal plane) was investigated using vander Pauw method. The results of such measurements for representative samples are given inTable3.Using the values of R_1 and R_2, resistivity (ρ) can be calculated. The basal plane resistivity for $W_{0.90}$ Se_2 crystals was evaluated and are reproduced in Table 6. From Table 3, average R_1 = 5.77Ω and R_2 = 5.71 Ω(maximum)

Table 3 . Measurement of Resistivity through Van der Pauw Method

Sample: $W_{0.90}Se_2$, Thickness t = 0.002 cm, Length ℓ= 0.6cm, Breadth b= 0.3cm

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	2.30	4.60	0.5	2.30	4.60
1.0	5.70	5.70	1.0	5.30	5.30
1.5	8.90	5.90	1.5	8.60	5.73
2.0	11.7	5.85	2.0	12.1	6.05
2.5	15.3	6.12	2.5	15.2	6.08
3.0	18.3	6.10	3.0	18.2	6.06
3.5	21.5	6.14	3.5	21.5	6.14
4.0	---	---	4.0	---	---

High Temperature Resistivity Measurement Perpendicular to c-axis

The high temperature resistivity measurement perpendicular to c-axis i.e. along the basal plane were carried out on single crystals of $W_{o.90}$ Se_2 using the four probe technique as described earlier. Table 4 and 5 show the variation of resistivity with temperature (313 K - 388 K) for representative samples of $W_o.{}_{90}Se_2$.In all cases it is seen that resistivity increases with decreasing temperature, thereby indicating that the samples show a classical semiconducting behavior.

Table 4. Result of High Temperature Resistivity Measurement

Sample : $W_{0.90}Se_2$ thickness t=0.002cm length ℓ=0.6cm breadth b=0.3cm

Temp (^oC)	Temp T K	$\frac{1}{T}$ x 10^{-3} (k^{-1})	Resistance R k Ω	Resistivity $\rho = \frac{Rbt}{l}$ Ω cm	log ρ
40	313	3.19	8.44	8.44	0.92
45	318	3.14	8.02	8.02	0.90
50	323	3.09	7.60	7.60	0.88
55	328	3.04	7.15	7.15	0.85
60	333	3.00	6.72	6.72	0.82
65	338	2.95	6.22	6.22	0.79
70	343	2.91	5.74	5.74	0.75
75	348	2.87	5.26	5.26	0.72
80	353	2.83	4.74	4.74	0.67
85	358	2.79	4.33	4.33	0.63
90	363	2.75	3.98	3.98	0.59
95	368	2.71	3.61	3.61	0.55
100	373	2.68	3.24	3.24	0.51
105	378	2.64	2.95	2.95	0.46
110	383	2.61	2.63	2.63	0.41
115	388	2.57	2.43	2.43	0.38

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 measurement is the only tool to provide basic electrical parameter of material. The sample $W_{0.90}Se_2$, 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. The calculated value of $R_{H,}$ mobility (μ) and carrier concentration (n) for each case are represented in Table 5. The results obtained from Hall Effect Measurement for sample are given in Table 8.

Table 5. Result of Hall Effect Measurement

Sample $W_{0.90}Se_2$ Thickness t = 0.002 cm Constant current I= 1 mA

Magnetizing Current I Amp	Magnetic Field B K.Gauss	Hall Voltage mV	Resistance R = V/I Ω	△ R	△ B	Hall Coefficient R_H Cm³/coul	Mobility U cm²/V.sec	Carrier Concentration n cm³
0.5	2.58	-30.7	6.14	0.04	2.26	3.53	49.02	1.76 x 10^{18}
1.0	4.84	-30.39	6.18	0.04	1.89	4.23	58.75	1.47 x 10^{18}
1.5	6.73	-31.1	6.22	0.04	1.55	5.16	71.66	1.21 x 10^{18}
2.0	8.28	-31.3	6.26	0.04	1.24	6.45	89.58	0.96 x 10^{18}
2.5	9.52	-31.5	6.30	0.04	0.92	8.69	120.69	0.71 x 10^{18}
3.0	10.44	-31.7	6.34	0.02	0.75	5.33	74.02	1.17 x 10^{18}
3.5	11.19	-31.8	6.36	0.02	0.52	7.69	106.82	0.81 x 10^{17}
4.0	11.71	-31.9	6.38	---	---	---	---	----

Table 6. Result of Measurement on off-stoichiometric Crystals of $W_{0.90}Se_2$

Sample Examined	Resistivity ρ Ω. Cm	Hall coefficient R_H Cm^3/coul	Mobility µ cm^2/V.sec	Carrier Concentration cm^{-3}
$W_{0.90}Se_2$	0.0072	5.86	81.50	1.15 x 10^{18} (n)

III. RESULTS AND DISCUSSION

The variation of resistivity along the basal plane with temperature clearly brings out the classical semiconducting nature of $W_{0.90}Se_2$ 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 $W_{0.90}Se_2$ 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 coefficient for $W_{0.90}Se_2$ indicate that these crystals are p-type semiconductor.

IV. CONCLUSION

The electrical transport property measurements are carried out on $W_{0.90}Se_2$ single crystals. The experiments may be carried out on their photo electrochemical characterization. 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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