Indian J. Phys. **81** (1) 131-135 (2007)

Growth and characterization of tungsten substituted molybdenum disulfide

A K Shah and P N Gajjar*

Sheth R A Bhavan's Science College, Khanpur, Ahmedabad-380 001 Gujarat, India
* Department of Physics, University School of Sciences, Gujarat University, Ahmedabad-380 009, Gujarat, India

E-mail pngajjar@rediffmail.com

Abstract : Single crystals of $Mo_{0.5}W_{0.5}S_2$ have been grown by chemical vapour transport technique with iodine as transporting agent The identity of the grown crystals has been verified using EDAX technique Electrical resistivity measurements have been carried out using Van der Pauw technique The resistivity at room temperature along the basal plane has been found to be 10 62 ohm cm The temperature variation of electrical resistivity for low temperature (70–300 K) and high temperature (313– 443 K) is reported The Hall effect measurements on the grown crystals have also been carried out thereby evaluating the Hall mobility and carrier concentration in the grown crystal The obtained value of negative Hall coefficient conform *n* type nature of the crystal having carrier concentration 2 2 × 10^{14} cm^{-3}

Keywords : Crystal growth, electrical resistivity, Hall measurement

PACS Nos. : 71 20 Be, 81 10Aj, 81 10 Dn

1. Introduction

Transition metal dichalcogenide of Group IVB, VB and VIB elements have received a fair amount of attention due to their striking feature and considerable diversity in most of their physical properties [1,2]. Tungsten substituted molybdenum disulfide possess semi conducting properties which has been used as energy conversion devices as photo-voltaic/photo catalytic solar energy converter, Schottaky and liquid junction solar cell, catalysts in many industrial applications and secondary batteries [3–10]. Due to property of the compound that atomic planes can slide over one another in its structure, it found important application as solid-state lubricants [11]. The layered structure of tungsten substituted molybdenum disulfide facilitates the process of intercalation or insertion of foreign atoms and molecules into host materials allowing thereby convenient methods for altering structure and electronic behavior [12,13]. MoS_2 and WS_2 of Mo and W is identical and very close as a result due to lanthanide contraction which suggests that the amorphous single phase of $Mo_{1-x}W_xS_2$ mixed crystal could be obtained over entire range of composition [14–20]. All these facts have motivated us to undertake the study on growth and characterization of tungsten

*Corresponding Author

substituted molybdenum disulfide. In this paper we report the study of electrical resistivity, Hall mobility, Hall coefficient and carrier concentration of single crystals of $Mo_{0.5}W_{0.5}S_2$.

2. Crystal growth

Single crystals of $Mo_{0.5}W_{0.5}S_2$ have been grown by chemical vapor transport method using iodine as the transporting agent [20,21]. A 10 gm mixture of Mo, W (purity 99.95%) and S (purity 99.99%) (Koch light laboratory, England make) was filled in thoroughly clean quarts ampoules. The quartz ampoules used in the present crystal growth have dimension of 22 mm in internal diameter and 180–200 mm in length. A small amount of transporting agent iodine was introduced inside, sufficient to give concentration of 5 mg/cm^3 of ampoule volume. Then ampoule was sealed at the pressure 10^{-5} torr. The sealed ampoule was introduced into two-zone muffle furnace at a constant reaction temperature 850°C for five days to obtain the charge. The charge so prepared was rigorously shaken to ensure proper mixing of constituents and kept in the furnace again for six days with reaction zone at 1200°C and growth zone at 1130°C temperatures. After this, slow cooling up to room temperature was followed. The opaque black shining crystals of the size (4 to 0.55 mm), (4 to 0.6 mm), (0.066 to 0.002 mm) are obtained. The crystals obtained in the form of flat platelets with straight edges and corners having mirror–like surface. Since the crystals grown in the form of thin platelets directly over the charge, they are strain-free. The composition of grown crystals was studied with the help of energy depressive analysis of X-rays (EDAX). LEO 440i with stereo scan 440 computer controlled digital scanning electron microscope having 3×10^6 magnification power with 3.5 nanometer resolution was utilized to confirm stochiometry of grown crystal. This EDAX analysis has confirmed the stochiometry as $Mo_{0.5}W_{0.5}S_2$ From the X-ray diffraction powder method, the evaluated lattice parameters for the grown single crystal of $Mo_{0.5}W_{0.5}S_2$ are a = 3.1677± 0.010 Å, c = 12.305 ± 0.0250 Å.

3. Electrical resistivity

The room temperature electrical resistance of grown crystals was measured using Vander Pauw method. Electrical connections for resistivity measurement were made by four copper wires on peripheries of very thin crystals and attached to the crystal surface by means of conductive silver paste to ensure the ohmic contacts. The sample was flat so that the sample contacts lies in the same plane. The applied electrical field was low enough to avoid any kind of breakdown in the sample. Then the resistivity of crystals was calculated by

$$\rho = \left(\frac{\pi d R}{\ln 2}\right), \tag{1}$$

where d is the thickness of the crystal and R be the measured resistance of the crystal parallel to the C-axis. Thus obtained room temperature resistivity of the crystal perpendicular to C-axis along the basal plane was 10.62 ohm.cm.

The measurements of low temperature electrical resistivity along the basal plane were carried out on a four probe set up designed by cryostate LNDP Scientific Solutions, Mumbai in the temperature range 77–300 K. The results of low temperature electrical resisitivity of $Mo_{0.5}W_{0.5}S_2$ are shown in the Figure 1.

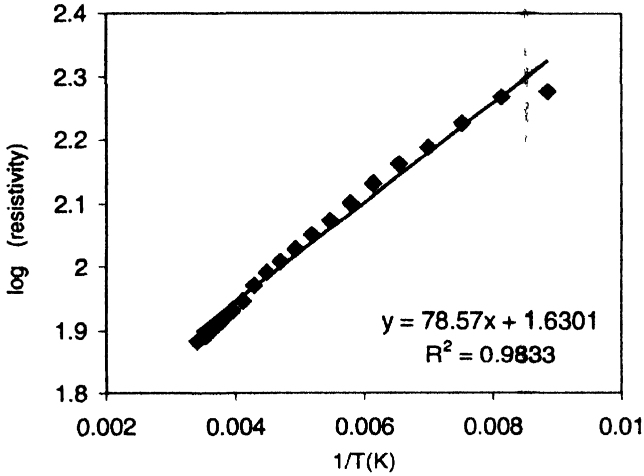

Figure1. Low temperature resistivity of $Mo_{0.5}W_{0.5}S_2$.

From these measurements, the activation energy for the grown crystal was calculated using

$$\rho = \rho_0 \exp \frac{Ea}{k_B T}$$

and $$\log \rho = \log \rho_0 + \left| \frac{Ea}{2.303 k_B} \right| T \qquad (2)$$

where ρ is the resistivity, ρ_0 be the constant, Ea the activation energy for electrical conduction, k_B the Boltzmann constant and T is absolute temperature. Hence from the slope of the graph of log ρ *versus* $1/T$, the obtained value of activation energy is 0.015 eV.

The high temperature electrical resistivity parallel to basal plane ($\rho_{||}$) was measured in the temperature range 303–443 K. A four probe set up manufactured by Scientific Equipments, Roorkee was used for the purpose. The measurements of electrical resistivity normal to basal plane ($\rho_\perp$) were carried out on an experimental set up designed and prepared by University Science and Instrumentation Center (USIC), Sardar Patel University, Vallabh Vidyanagar. Starting from room temperature (303 K), the temperature of sample was increased slowly in steps of 10 K until temperature reached to 443 K. At each step the corresponding value of resistivity was calculated. The results for high temperature electrical resistivity ($\rho_{||}$) and ($\rho_\perp$) of $Mo_{0.5}W_{0.5}S_2$ are shown in Figures 2 and 3, respectively.

The activation energies were also obtained from the graphs and we found that in the temperature range 313–383 K it is 0.1818 eV and for temperature range

383–443 K it is 0.4232 eV. Anisotropy measurements have been carried out in the temperature range 303–443 K and the results are displayed in Figure 4. The anisotropy ratio $((\rho_\perp)/(\rho_{||}))$ increases linearly with increase in temperature.

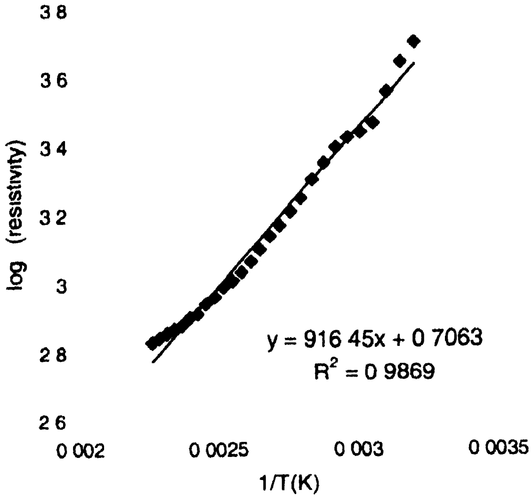

Figure 2. High temperature resistivity $(\rho_{||})$ of $Mo_{0.5}W_{0.5}S_2$

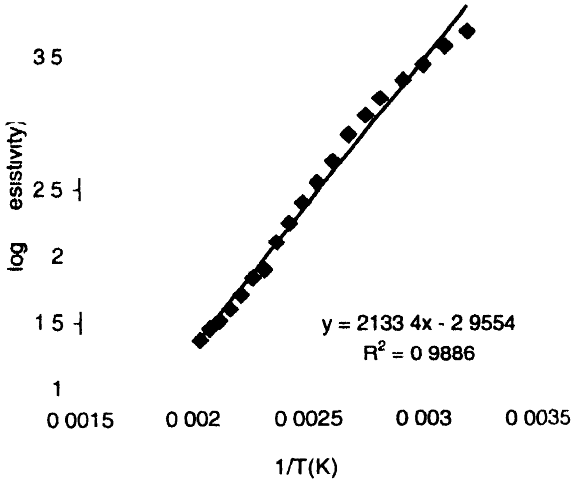

Figure 3. High temperature resistivity $(\rho_\perp)$ of $Mo_{0.5}W_{0.5}S_2$

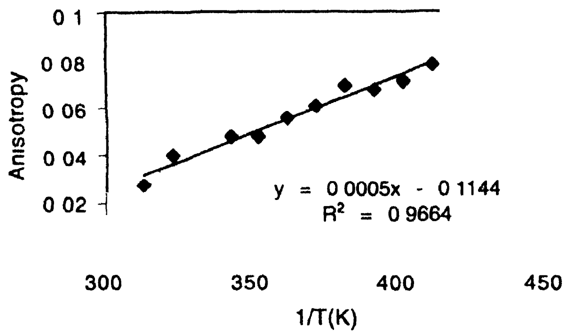

Figure 4. The anisotropy ratio $((\rho_\perp)/(\rho_{||}))$ in $Mo_{0.5}W_{0.5}S_2$

4. Hall mobility, Hall coefficient and carrier concentration

The Hall mobility of the crystal was determined by measuring the change in resistance *R* upon applying magnetic field perpendicular to basal plane of the sample [20]. The Hall mobility, Hall coefficient and net carrier concentration as obtained is –2582 cm^2 $volt^{-1}sec^{-1}$, –27549 cm^3 $coul^{-1}$ and 2.2×10^{14} cm^{-3}, respectively. The obtained value of negative Hall coefficient conform *n* type nature of the crystal.

5. Conclusions

The single crystals of $Mo_{0.5}W_{0.5}S_2$ have been grown successfully by chemical vapour transport technique. The Hall mobility and net carrier concentration as obtained from Hall effect measurement is –2582 cm^2 $volt^{-1}$ sec^{-1} and 2.2×10^{14} cm^{-3}. The value of activation energy was obtained in the range of 0.1818–0.4232 eV in the temperature range 313–443 K. The negative value of Hall coefficient indicates that the $Mo_{0.5}W_{0.5}S_2$ crystals grown in the present work are *n*-type.

References

[1] F Jellink *Ark Kemi* **20** 447(1963)

[2] J Pouzet and J C Bernde Metter *Chem. Phys.* **36** 304(1994)

[3] A A Balchain and F Levy (eds) *Crystallography and Crystal Chemistry of Materials with Layered Structure* (1976)

[4] F Hulliger *Structural Chemistry of Layered Phases* (Dordrecht : D Reidel) (1976)

[5] H Tributch *J. Electrochem. Soc.* **125** 1087(1978)

[6] R Span, M Lux-Steinr, M Oberfell and E Bucher *Appl. Phys. Lett.* **47** 871(1985)

[7] B A Parkinson, T E Furtak, D Canfield and K Kam *Faraday Discuss. Chem. Soc.* **70** 253 (1980)

[8] R R Tenne and A Wold *Appl. Phys. Lett.* **110** 707 (1985)

[9] Wiesser and S Landa *Sulphide Catalysts, their Preparation and Application* (Oxford : Pergamon) (1973)

[10] M S Whittingham and F Levy *Intercalated layered material* (Dordrecht : Reidel) p307 (1979)

[11] G V Suba Rao and C S Sunanduna in J M Honing *C.N.R.res Preparation and Charaterization of Materials* (London : Academic) p269 (1981)

[12] G V Suba Rao and M W Schafer in F Levy (ed) *Intercalated Layered Materials* (Dordrecht : Reidel) p 99 (1979)

[13] A J Barreta, A Vazquez and E Camarillo *J. Crystal Growth* **96** 685 (1989)

[14] S K Srivastave, B N Avasthi and S Basu *J. Indus. Res.* **42** 656 (1982)

[15] S K Srivastave and B N Avasthi *J. Mater Sci.* **20** 3801 (1985)

[16] J A Wollam and R B Somano *Phys. Rev.* **13** 3483 (1976)

[17] R J H Bvoorholve and J C M Stuiver *J. Catal.* **23** 243 (1971)

[18] P R Bonneaus *Inorg. Chem.* **32** 6084 (1993)

[19] S K Srivastave, T K Mandal and B K Samantaray *Synth. Metals* **90** 135 (1997)

[20] A K Shah *Growth and Characterization of Single Crystals of $Mo_{0.5}W_{0.5}$ S_2, (PhD. Thesis)* June (1999)

[21] F Levy, P Schmid and H Berger *Phil. Mag.* **34** 1129 (1976)