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C-Axis Resistivity Measurements in WS_{2-x} Single Crystals

GK Solanki[1], YA Patel[2] and MK Agarwal[1]

[1]Department of Physics, Sardar Patel University, Gujarat, India
[2]NV Patel Pure and Applied Science College, Sardar Patel University, Gujarat, India
solankigunvant@yahoo.co.in

ABSTRACT

Single crystals of p-type WS_2 and $WS_{1.9}$ have been grown by a Physical Vapour Transport (PVT) technique. DC electrical resistivity measurements have been made along the c-axis in both these crystals. Electron microscopic examinations revealed the presence of large concentration of defects in these crystals. The observations described in this paper clearly indicate how far two dimensional these layered crystals can be considered.

Key words: Single crystal, layered material, resistivity, activation energy, electron microscopy

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INTRODUCTION

Among the transition metal dichalcogenides, the stability and non-toxicity of tungsten disulphide makes this layered semiconductor interesting material in photovoltaic energy conservation [1]. WS_2 is a layered material consisting of S-W-S slabs. The binding energy between S-W-S slabs is 0.14 eV [2]. WS_2 pays a favourable role as solid lubricant under severe conditions where fluids are unable to support the heavy load [3]. They are also used in scanning probe microscopy [4], heterogeneous catalysis [5] and electrochemical hydrogen storage [6]. WS_2 is emerging electrocatalyst for hydrogen evolution reaction (HERs) [7]. Two dimensional sheets of WS_2 and MoS_2 have gained wide attention in recent years as graphene analogues. Monolayer WS_2 with direct band gap in the visible and NIR frequency range, works as novel building block for realizing unique hetero-structures with tailored optoelectronic, electrolytic and photocatalytic functionalities [8]. Recently Jo et al [9] have used mono – and bilayer WS_2 in the fabrication of light emitting transistors. Since monolayers are obtained from synthetic WS_2 crystals grown by a vapour transport technique using exfoliation techniques, it will be worthwhile to make a study of c-axis resistivity in the grown crystals. Such a study will help in deciding the true 2D character of WS_2 crystals. Authors therefore report c-axis resistivity measurements in WS_2 and its off-stoichiometric compound $WS_{1.9}$ in the present paper.

EXPERIEMNTAL

Single crystals of WS_2 and its off-stoichiometric compound $WS_{1.9}$ were grown by physical vapour transport technique [10]. Single crystal nature of the grown crystals was confirmed from electron diffraction. EDAX analysis of the crystals revealed that the weight percentage of elements obtained from this analysis matched with the weight percentage of the elements taken from their synthesis and it was possible to grow WS_{2-x} (x=0, 0.1) in single crystal form. The positive values of Seebeck coefficient and the Hall coefficient indicated that both WS_2 and $WS_{1.9}$ were p-type and majority charge carriers in them were holes.

Two probe contacting system [11] with zinc based pressure contacts was employed for measuring the dc electrical resistivity parallel to the c-axis. A Phillips EM 400 electron microscope operating at 100 KV was used for the observation of structural defects.

RESULTS AND DISCUSSION

The value of resistivity for WS_2 and $WS_{1.9}$ obtained from c-axis measurements at 313K, 473K, 673K and 873K are given in Table 1. A graphical variation of the log $\rho_{||}$ versus 1000/T for both cases is registered in Fig. 1**.** A careful study of the data reveals the following points:

- For both the samples WS_2 and $WS_{1.9}$ there is a decrease in resistivity with increase in temperature.

- At all temperatures, the values of resistivity in off-stoichiometric $WS_{1.9}$ crystals are less than the stoichiometric WS_2.
- The graph showing the variation of log $\rho_{\|}$ versus 1000/T can be divided into three distinct linear regions in the different temperature ranges. The variation of ρ predicts a non-metallic conduction characterized by thermally activated conduction defined by; $\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)$

The values of activation energies for the three regions are shown in Table 1.

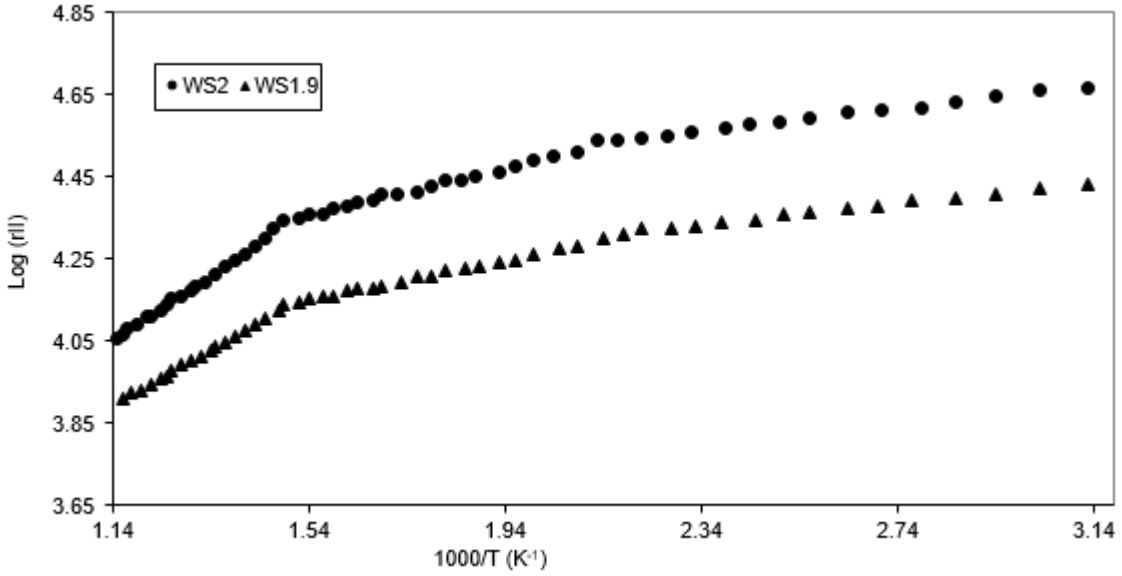

Fig.1 1000/T vs c-axis resistivity for WS_2 and $WS_{1.9}$ single crystals in the temperature range 313-873K

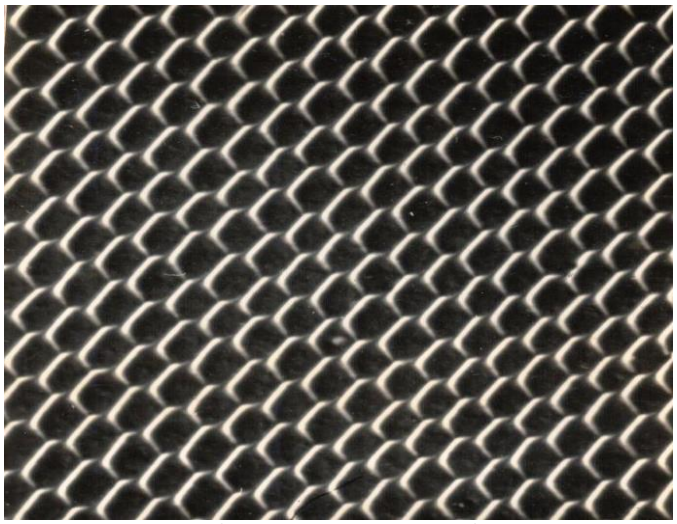

Fig.2 Weak beam dark field Electron micrograph of WS_2 crystal showing extended and contracted nodes

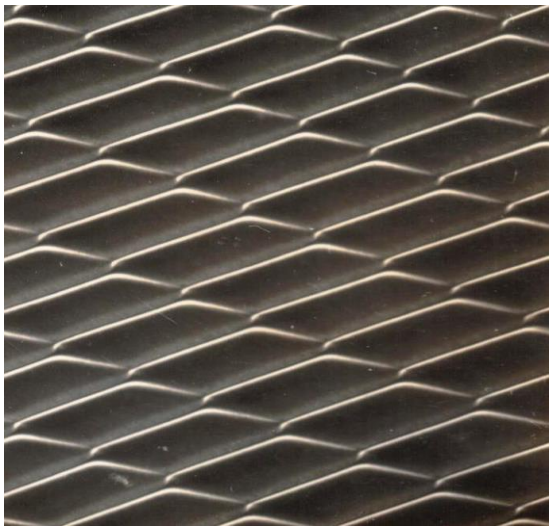

Fig. 3 Weak beam dark field Electron micrograph of WS_2 crystal showing a network pattern

Inspite of the fact that WS_{2-x} are layered compounds having a two dimensional character, this conduction along c-axis, at first sight is difficult to understand. The only way we can understand this conduction is by supposing the presence of stacking faults in them. The weak beam electron microscopy of WS_{2-x} has indeed shown the presence of stacking faults in them. Fig. 2 shows a weak beam dark field picture of extended and contracted nodes, while Fig. 3 shows a weak beam picture of a network pattern.

The disorder produced by stacking faults is sufficient to localize the electron states along the layer normal. While considering stacking between adjacent crystals, the total crystal is always seen to remain invariant under the primitive translation parallel to the layers. The electron states, therefore transform like Bloch functions under these translations and dc transport parallel to the layers is not much affected by the presence of stacking disorder.

Perpendicular to the layers however there is a possibility of transport due to localization of the electron states because of the presence of stacking faults. This will therefore give conduction parallel to the c-axis. Further the amount of conduction will be more where the likelihood of stacking faults is more. It has been observed [12] that the number of stacking faults in off-stoichiometric WS_{2-x} is larger as compared to the samples which are stoichiometric. This is precisely what is confirmed by the observations presented in Fig. 1 and Table 1.

Table -1 Resistivity ($\rho_{\parallel}$) and Activation Energies for WS_2 and $WS_{1.9}$ Single Crystals

Sample	$\rho_{\parallel}$ (Ω cm)				Activation energies (meV)		
	Temperature (K)				Temperature range (K)		
	313	473	673	873	313-473	473-673	673-873
WS_2	48322	34145	21752	11317	27.3	56.6	160.3
$WS_{1.9}$	27347	19953	13740	8072	24.8	47.5	154.4

It may be mentioned here that the samples used for electron microscopy were not having monolayer thickness but are many monolayers thick. If samples of monolayer thickness are observed under high resolution they may not show the presence of any defects and c-axis conduction in such crystals will be absent. That this is indeed true is clear in the work of Wang et al [8]. They showed using atomic force microscopy that monolayer of MoS_2 of the high purity and clean with no evidence of defects. Author evidence supporting this is given by Pradhan et al [13] who showed that atom resolved electron microscopy of TMDC $MoTe_2$ shows no evidence of defects indicating a high level of uniformity and cleanliness.

CONCLUSION

The values of c-axis resistivity at room temperature in WS_2 are fairly high so that one can consider them as 2-dimensional. It will be easy to obtain monolayer from such 2D-materials by proper exfoliation techniques. Such exfoliated monolayers will be devoid of defects and can therefore be fruitfully used as analogues to graphene.

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