CHAPTER 7

EXISTING INFORMATION ON TUNGSTEN DISULPHIDE

7.1 INTRODUCTION

The layered transition metal dichalcogenides (TMDCs) are the most widely investigated of the layered materials with regard to their electrical properties. The TMDCs are very interesting solids since they display the whole spectrum of electronic properties covering insulators, semiconductors, normal metals and super conductors, [1-4]. Such a variation in the electronic behaviour of the transition metal dichalcogenides is due to the mainly d-electronic character of the valence and conduction bands that are derived from the non-bonding d-states of the

transition metal.

Among the transition metal dichalcogenides MoS_2 and WS_2 are mass produced since MoS_2 is used for high temperature lubrication and also for catalysis in the oil industry while WS_2 is also used as a lubrication agent at high temperature and also in UHV stations. MoS_2 and WS_2 also serve as suitable materials for thin film photovoltaic studies, either as p/n homojunctions or as "window" materials for WSe_2 and $MoSe_2$.

InSe, WSe_2 and $MoSe_2$ are at present, the leading candidates for their use in solid state solar cells with efficiencies of 10.9 %, 8.0 % and 6.1 % respectively [5] but MoS_2 and WS_2 are also of similar interest in particular for thin film studies.

Looking to the tremendous potential of tungsten disulphide author has taken up the growth of large size single crystals of WS_2 by direct vapour transport (DVT) and chemical vapour transport (CVT) techniques and use the crystals thus grown in high pressure and PEC studies to be described in the forth coming chapters. The present chapter describes in brief the existing information on the preparation, structure, properties and important uses of WS_2.

7.2 METHOD OF PREPARATION

Tungsten disulphide belongs structurally and chemically to a well defined family of compounds having a general formula TX_2, where T represents tungsten metal and X is a chalcogen S, Se or Te. The methods of preparation of tungsten disulphide are discussed below.

Tungsten disulphide is one of the most metal rich sulphide of tungsten which exists in only two types of polymorphs, namely, two layer hexagonal form (2H) and three layer rhombohedral form (3R).

Tungsten disulphide was first synthesised by Glemser et al. [6] from the thermal decomposition of WS_3 at 800°C for 24 hrs, whereas Wildervanck and Jellinek [7] obtained WS_2 by heating WS_3 at 1100°C. Voorhoeve and Wolters [8] observed that decomposition of WS_3 is an irreversible process which leads to the product $W_{1-x}\ S_2$, where x decreases with increasing decomposition temperature. The procedure of Zeilkman et al. [9] involved decomposition of ammonium thiotungstate in the temperature range of 300 to 600°C with final heating at 800°C.

Van Arkel [10] synthesised WS_2 from the direct union of elements at 800 to 900°C in a pure N_2 atmosphere.

It can be obtained by calcination of WO_3 with CS_2 at 1000°C [11] or by the reaction of WO_3 with metal sulphide MS (M = Zn, Cd, Mg), when heated in the temperature range of 500 to 1200°C in an argon atmosphere [12]. Sulphurization of the powdered tungsten metal at $\lesssim$ 400°C [13] or WO_3 at 1400°C has also been used [14]. When H_2S reacted with WO_3 [15] or WCl_6 heated at 375 to 550°C [16], tungsten disulphide was formed.

According to differential thermal analysis (DTA) studies WS_2 is formed at a temperature always higher than 400°C, although to obtain a well crystallised product without any stacking disorders a temperature of 900°C to 1000°C is preferred [17].

A hydrothermal method for WS_2 has also been reported, where WS_2 crystallised from strongly reducing sulphide solution containing $\geq 2 \times 10^{-3}$ MW. The synthesis of WS_2 was also attempted using 0.02 to 1 M Na_2WO_4, 0.5 to 0.02 M H_2S and 1 to 4 M HCl solutions at 88 to 500 atm. and 300°C in a titanium autoclave [18].

The rhombohedral polymorph of WS_2 was synthesised by Wildervanck and Jellinek [7] by the carbonate melt method, where WO_3 reacted with sulphur in a flux of an alkali carbonate at about 900°C. Silverman [19] successfully employed high pressure - high temperature for the synthesis

of rhombohedral WS_2. When an elemental mixture of tungsten and sulphur was compressed at 45 K bar and heated to 1800°C for 2-3 min., a silver grey coloured product of WS_2 was formed which was completely rhombohedral.

However, the most interesting aspect concerning synthesis of WS_2 is the growth of WS_2 in the form of single crystals, which are needed for the study of various physical properties. The first attempt in this direction was made by Nitsche [20]. He was able to synthesize WS_2 single crystals using Br_2 as a transport agent. Widervanck [21] obtained it by using Cl_2 and Br_2, I_2 and NH_4Cl and observed that in the later case transport was incomplete. The preparative techniques used by Shafer et al. [22, 23] have shown the possibility of sulphur assisted transport of WS_2. Agarwal et al. [24] reported that single crystals of WS_2 can be grown from polycrystalline WS_2 powder by a sublimation method without the addition of a transporting agent. Baglio et al [25] synthesised WS_2 single crystals from the chlorine and bromine transport technique. Table 7.1 summarises important results on growth of tungsten disulphide single crystal.

7.3 STRUCTURE

Tungsten disulphide crystallises into a layer

Table 7.1 Conditions to grow single crystals of tungsten disulphide

Workers	Temperature (°C)		Transport agent	Duration	Remarks
	Source	Growth			
Nitsche	900	800	Br_2	48 h	Product is 2H-WS_2
Wildervanck	960-1030	875-945	Cl_2	10 days-2.5 week	Yields 2H as well as 3R-WS_2
	865-1090	787-1009	Br_2	1-2 week	
	830-930	800-870	I_2	2-4 week	Yields 2H + 3R WS_2
	900	800	NH_4Cl		Transportation was incomplete; yields 2H-WS_2
Agarwal et al.	1055	1035	Without transport	5 day	15 mm x 10 mm x 25 mm large platelets
Baglio et al.	1200	1140	Cl_2	100 or 160 h	2H-WS_2 } source yields
	1175	1125	Br_2	120 h	W + S_2 } good quality crystal
Brixner	800-850	750	Br_2	10 g of the	Bright shining n-type
	1055	890	I_2	sample could be transported during 10-15 h	2H-WS_2 crystals having shape of hexagonal plates

type structure similar to C_7 (MoS_2) [Fig. 7.1] [27]. Within each layer there is a trigonal prismatic co-ordination between tungsten and sulphur atoms. The structure of WS_2 is characterised by the presence of W^{2+} and S^{2-} sheets, but each W^{2+} sheet is sandwiched between two S^{2-} sheets. The sandwiches are held together by weak van der Waals forces. The variation in the stacking sequence of layers leads to the formation of hexagonal (2H) or rhombohedral (3R) polymorphs.

The lattice parameters for tungsten disulphide are recorded in Table 7.2.

7.4 APPROACH TOWARDS A BAND MODEL

The general features of the band structure of WS_2 are similar to MoS_2. It consists of a valence band made up of sulphur s and p orbitals, above which is a broad antibonding or conduction band made up of tungsten s and p orbitals and in between a non-bonding band made mostly of tungsten d-character. If the tungsten atom is in trigonal prismatic co-ordination, a narrow d_z2 band is lowest in energy. The energy difference between the valence band and low lying d_z2 band as well as electron occupancy will determine the optical and electrical properties of WS_2. However, in case of WS_2 the d_z2 band is full and it exhibits

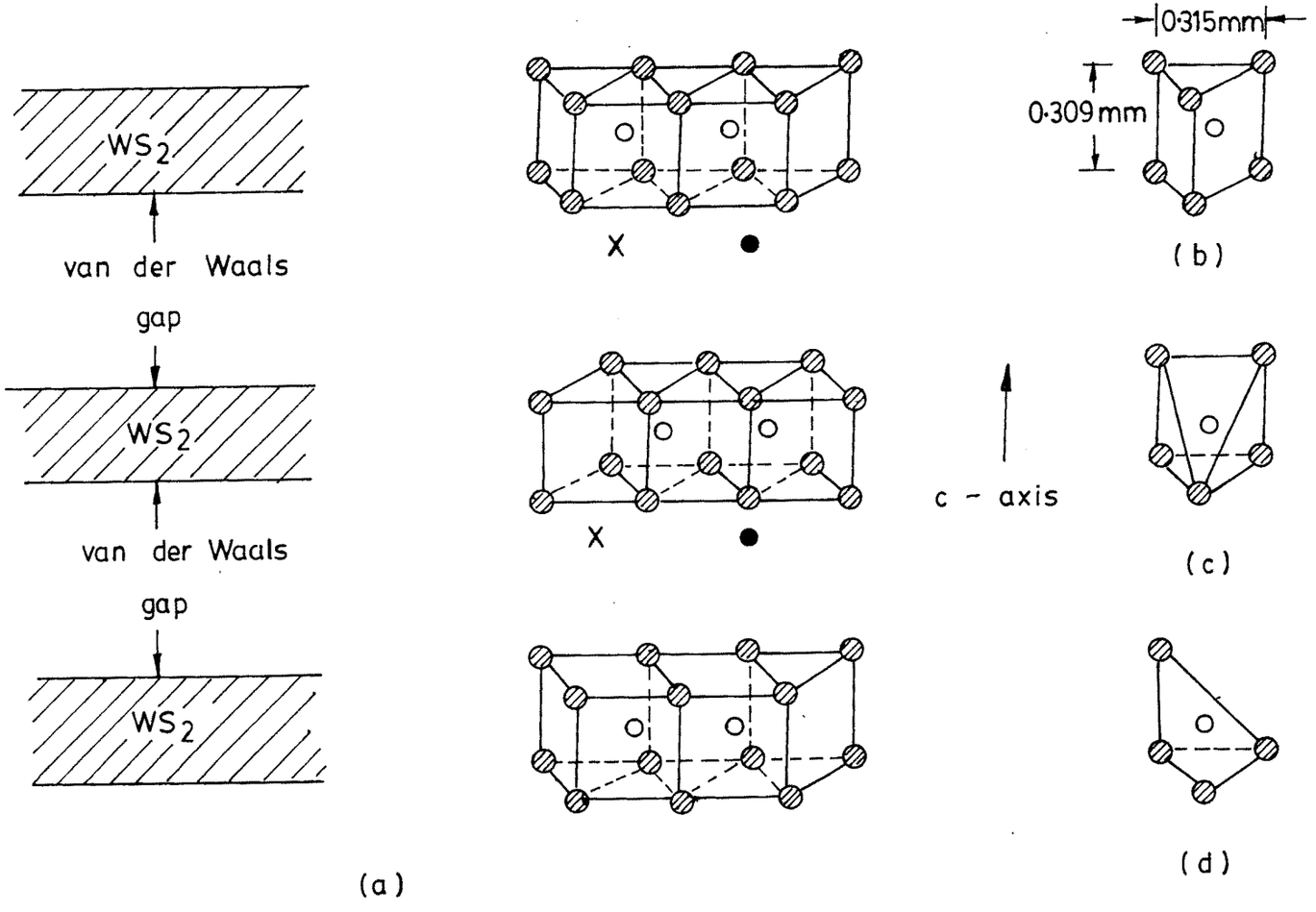
WS2
van der Waals
gap
WS2
van der Waals
gap
WS2
(a)
X
●
X
●
0·315mm
0·309mm
(b)
c - axis
(c)
(d)
O - S
O - W
X = Octahedral hole,
● - Tetrahedral hole.

fig. 7·1

Table 7.2 Lattice parameters for tungsten disulphide

Compound	a (nm)	c(nm)	c/a	References
WS_2 (2H)	0.3155	2 x 0.6195	1.957	7
(3R)	0.3162	3 x 0.6117	1.935	7
(2H)	0.3161	2 x 0.6179	1.955	28

diamagnetism and semiconducting behaviour. Wilson and Yoffe [29] assigned this d_z2 band in the gap between the valence band and the Fermi level, E_f [Fig. 7.2a]. Huisman et al [30] placed it at the top of the valence band as shown in Fig.[7.2b]. McMenamin and Spicer [31] and William and Shephered [32] from their photoemission studies concluded that this band is somewhere between these two positions, the top of the band falling above the top of the valence band, with the bottom at or slightly below the top of the valence band as shown in Fig. [7.2c].For transitions involving visible radiations, Tributsch [33] has regarded the valence band of WS_2 as made up by d_z2 states of tungsten and conduction band as made up by d_{xy} and $d_{x^2-y^2}$ states of tungsten. The complete band diagram as suggested by him is shown in Chapter 10.

7.5 PROPERTIES OF TUNGSTEN DISULPHIDE

7.5.1 Physical Properties

Some of the physical properties of tungsten disulphide are listed in Table 7.3.

7.5.2 Chemical Properties

WS_2 is insoluble in water. Mineral acids have no action on WS_2, but it reacts readily with the mixture of

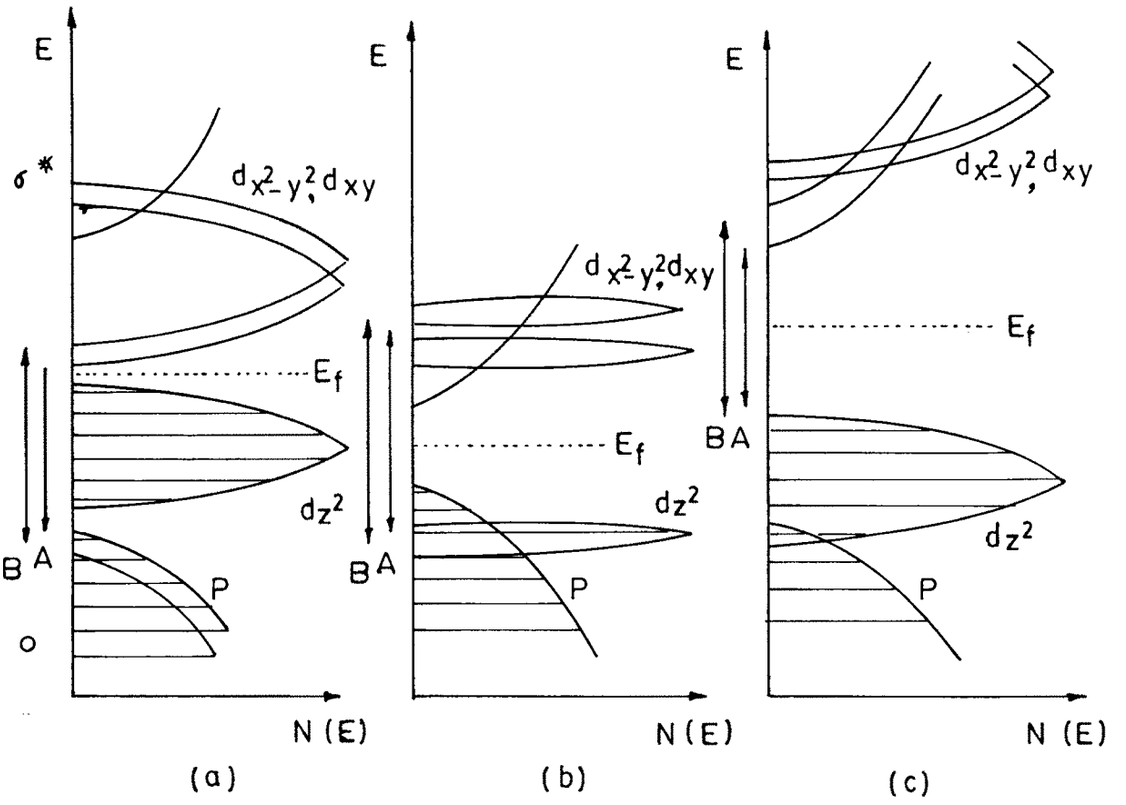
E
σ*
$d_{x^2-y^2}$ d_{xy}
E_f
d_{z^2}
B A
P
o
N (E)
(a)
E
$d_{x^2-y^2}$ d_{xy}
E_f
d_{z^2}
B A
P
N (E)
(b)
E
$d_{x^2-y^2}$ d_{xy}
E_f
B A
d_{z^2}
P
N (E)
(c)

fig. 7·2

Table 7.3 Physical properties of tungsten disulphide

Mol. wt. (g)	247.98
Colour	Black
m.p. (°C)	1150° (d)* [34] 1200° (d) [35,36]
Density (g cm^{-3})	7.5 [36]
Crystal structure and polymorph	Trigonal prismatic layer structure 2H and 3R
Space group and stacking Sequence	2 H : $P6_3/mmc$ BaB AbA 3R : $R\bar{3}_m$ BcB CaC AbA
Magnetism	Diamagnetic
Heat of formation (k cal mol^{-1})	-64 ± 4 [36] -36.71 [37]
Entropy ($_1$ cal k^{-1} mol^{-1} at 298 K)	15.5 ± 1.5 [36]
Heat capacity ($_1$ cal k^{-1} mol^{-1})	7.81 [36] (in the temperature range of 298-623 K)

* Decomposition temperature (d)

nitric acid and hydrofluoric acid or hydrochloric acid. It is oxidised by aqua regia to H_2SO_4 and WO_3. It is readily soluble in molten alkali hydroxide and alkali carbonate in the presence of an oxidation agent. Fluorine at ordinary temperature reacts with WS_2 to form the fluoride, whereas chlorine at 400°C yields the hexachloride. It is attacked by bromine at 700°C. WS_2 is found to be stable in dilute non-oxidising acids at room temperature but dissolves on heating.

7.5.3 Magnetic Properties

Tungsten disulphide with the trigonal prismatic co-ordination is diamagnetic [38]. The effects of temperature (2 to 300 K) on a single crystal of WS_2 have indicated that magnetic susceptibility is temperature independent and strongly anisotropic [39].

7.5.4 Optical Properties

Liang [40] studied the reflectivity spectra of 3R-WS_2 grown by bromine transport at 77 K. The transmission spectra of iodine grown crystals have been measured by Beal et al [41]. They characterised the general feature of the spectra by the presence of absorption peaks A, B, C, D, α, β, etc. in the direction of increasing photon energy. Further, they subdivided the spectra into regions at low

energy which were dominated by sharp excitonic transitions (.e.g. A and B) on a relatively low absorption back ground and a region of strong absorption at higher energies where the absorption coefficient rises to a maximum (e.g. C, D and beyond).

Liang [42] also made reflectance measurements on 3R-WS_2 parallel to the crystal c-axis at liquid nitrogen temperature and room temperature, where crystals were grown by bromine transport.

7.5.5 Electrical Properties

WS_2 is found to be diamagnetic semiconductor. Its electrical properties have been studied in detail by various workers. Table 7.4 records the electrical data and band gaps of WS_2.

7.6 USES OF WS_2

WS_2 has been used as a catalyst in hydration, hydrogenation, hydrogenolysis, hydrodesulphurization and isomerization reactions either in pure form or supported on carriers. The most significant property of WS_2 is that it is widely used for removing sulphur compounds from petroleum or coal derived liquids.

Due to its good adhesive characteristics and

Table 7.4 Electrical and Band gap data for tungsten disulphide

Band gap	Carrier type	Resistivity Ωcm	Carrier concentration n (cm^{-3})	Hall mobility ($cm^2V^{-1}sec^{-1}$)
1.78 [44] (Direct) 1.34 (Indirect)	n	33.33(300K) [25]	-	105 (300K) [25]
1.34 [45] (Indirect) 1.3 [46] (Indirect)	p	Semiconducting E_a = 0.14 eV (300-620K) [43]	1.057×10^{16} [43]	1.347×10^{3} [43]

stability against moisture it is extensively employed as a solid lubricant.

Recently WS_2 has also been widely considered as a suitable material for the fabrication of liquid junction solar cells. Author's attempts in this direction will be discussed in Chapter 13 of the present thesis.

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CAPTIONS TO THE FIGURES

Fig. 7.1 The structure of tungsten disulphide

(a) Stacking of layers illustrating the position of holes Site symmetry of tungsten ion,

(b) in the bulk,

(c) in the surface, and

(d) on an edge parallel to the c-axis.

Fig. 7.2 Band structure of trigonal prismatic tungsten disulphide as suggested by

(a) Wilson and Yoffe [29]

(b) Huismann et al. [30]

(c) McMenamin and Spicer [31], and William and Shephered [32].