The growth and thermodynamical feasibility of tungsten diselenide single crystals using chemical vapour transport technique

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Abstract. Thermodynamical feasibility study and the growth of layer structured transition metal dichalcogenide single crystals of WSe_2, using iodine as transporting agent, has been reported in this paper. The characterization of the grown samples have been done by X-ray analysis.

Keywords. Transition metal dichalcogenide; tungsten diselenide; chemical vapour transport; thermodynamical feasibility.

1. Introduction

The transition metal disulphides and diselenides have attracted considerable attention during the past few years (Legma *et al* 1991; Patel 1992; Agarwal *et al* 1993; Gallagher *et al* 1994). These MX_2 (M = transition metal; X = chalcogen) compounds are formed by a layer of transition metal atoms between two layers of sulphur or selenium atoms. There is a strong covalent bonding within the layers, but a weak Van der Waals bonding between them. These materials are used in such diverse applications as catalysis, batteries and lubricants. Recently, these materials have found potential use in the fabrication of photoelectrochemical (PEC) solar cells for solar energy conversion (Gobrecht *et al* 1978; Fan *et al* 1980; Tributsch 1980). It has also been realized that selenides are more efficient as solar cell materials than sulphides (Canfield *et al* 1981). In the light of this realization, the growth of tungsten diselenide single crystals using chemical vapour transport technique and the fabrication of PEC solar cells have attracted more attention recently (Agarwal *et al* 1989a). The PEC cell characteristics have however not reached up to the predicted level due to the lack of good quality crystals. Theoretical thermodynamical investigations may help to grow these crystals with better characteristics.

In the method of chemical vapour transport, an exploratory work is needed to avoid the ineffective and time consuming empirical trial and error fashion for the transport of a particular material. In many cases the models (Seaki 1967; Richardson 1978; Wolf *et al* 1978; Benard *et al* 1981; Nolang 1983) allow one to predict the composition of solids to be deposited in the crystallization zone or to determine the pre-conditions for the deposition of solid(s) of desired composition. It is also obvious that the theoretical models (Emmenegger 1968; Wehmeier 1970) are not adequate to explain the successful growth of binary as well as ternary chalcogenides taking the constituent elements in the stoichiometric ratio as the source material. Nitsche (1975) and Paorici *et al* (1982) established that the constituent elements could be employed as the starting materials.

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Vengatesan *et al* (1986) proposed a thermodynamical analysis of chemical vapour transport of ternary chalcogenides taking the elements as the source materials. Prediction of minimum source temperature (T_s), minimum growth temperature (T_d) and the influence of temperature and the transporting agent concentration on growth are successfully done on the basis of this model. In the present work, an attempt has been made to consider the growth and thermodynamical analysis of the layered structured binary compound tungsten diselenide using iodine as the transporting agent.

2. Model and calculations results

The constituent elements tungsten and selenium are taken in stoichiometric proportions along with the transporting agent, -iodine- at the source end. They react to form the gaseous binary iodide and selenium at high temperature. This gaseous binary iodide diffuses into the colder growth zone due to drop in temperature. At the growth zone, the binary iodide plus selenium react back to form the binary chalcogenide with the release of iodine. The iodine diffuses back to the source end to form the metal iodide once again. This process is represented by the equation

$$W(s) + 2Se(s) + I_2(g) \overset{T_s}{\rightleftharpoons} WI_2(g) + Se_2(g) \overset{T_d}{\rightleftharpoons} WSe_2(s) + I_2(g). \tag{1}$$
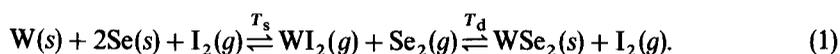
The transport of the binary compound is feasible only if the Gibb's free energy change ΔG of the reaction is negative.

The hypothetical transport reaction is

$$W(s) + Se(s) + I_2(g) \rightleftharpoons WI_2(g) + 1/2 Se_2(g). \tag{2}$$
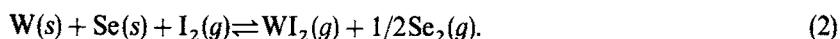
The general ΔG function is

$$\Delta G = \Delta G^\circ + RT \ln K_p.$$

where ΔG° is the standard free energy change, R, the universal gas constant, T, the absolute temperature, and K_p, the equilibrium constant.

The formation of the binary compound from binary iodide and selenium can be represented by the equation

$$WI_2(g) + Se_2(g) \rightleftharpoons WSe_2(s) + I_2(g). \tag{1a}$$

Free energy function for (1a)

$$\Delta G_{1a} = \Delta G^\circ_{1a} + RT \ln K_{p1a},$$

where the equilibrium constant,

$$K_{p1a} = \frac{P_{1a}(I_2)}{P_{1a}(WI_2)^2},$$

where $P_{1a}(I_2)$ and $P_{1a}(WI_2)$ are the partial pressures of the iodine and the binary iodide. From the stoichiometry of (1),

$$P_{1a}(WI_2) = P_{1a}(Se_2), \tag{3}$$

where $P_{1a}(Se_2)$ is the partial pressure of selenium.

At equilibrium, $\Delta G_{1a} = 0$.

i.e. $\quad\quad -\Delta G^{\circ}_{1a} = RT[\ln P_{1a}(I_2) - 2\ln P_{1a}(WI_2)]$. $\quad\quad\quad\quad$ (4a)

Similarly for (2)

$$\Delta G_2 = \Delta G^{\circ}_2 + RT \ln K_{p_2}, \quad\quad\quad\quad (4b)$$

and

$$\Delta G_2 = \Delta G^{\circ}_2 + RT[3/2\ln P_2(WI_2) - \ln P_2(I_2)], \quad\quad\quad (5)$$

since (3) is also valid for (4b).

By combining (5) and (4a)

$$\Delta G_2 = \Delta G^{\circ}_2 + 0.75\Delta G^{\circ}_{1a} - 0.25\ln RTP_2(I_2). \quad\quad\quad (6)$$

Since heat capacity functions are not available, ΔG° function is evaluated from ΔH° and ΔS°. The standard thermodynamic datas for (6) are listed in table 1.

$$\Delta G_2 = -50205 + 40T - 0.495T\ln P(I_2). \quad\quad\quad (7)$$

It is found that ΔG_2 is negative at any temperature below 1177°K for iodine concentration of $5\,mg/cm^3$. So the source temperature (T_s) should be kept below 1177°K for effective transport.

The dependence of ΔG_2 on the amount of iodine at any constant temperature is represented in figure 1. The transport of binary compound is more feasible at lesser concentration of iodine as revealed by the negative ΔG_2 at much lower temperature of 1148°K. Since the partial pressure is in the logarithmic term, the influence of partial pressure of iodine is comparatively less than that of temperature. The variation of ΔG_2 on temperature for fixed iodine concentration is also represented in figure 2. From figure 2, it is evident that sign of ΔG_2 changes at a particular temperature for fixed iodine concentration.

Due to the fixed temperature gradient between the hot zone and cold zone, the binary iodide and selenium diffuse to the colder zone. At the colder zone two types of reactions are possible.

$$WI_2(g) + Se_2(g)W(s) + 2Se(s) + I_2(g), \quad\quad\quad (8)$$

$$WI_2(g) + Se_2(g) \rightleftharpoons WSe_2(s) + I_2(g). \quad\quad\quad (9)$$
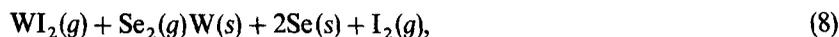
Equations (8) and (9) are for elemental formation and material formation, respectively.

Table 1. Thermodynamic datas.

	Hf°(cal/mol)	S°(cal/mol)	Refs.
$W(s)$	0.0000	7.80	(Weast 1987)
$Se(s)$	0.0000	10.144	(Weast 1987)
$I_2(g)$	+ 14923	62.28	(Wagman *et al* 1968)
$Se_2(g)$	+ 34900	60.20	(Wagman *et al* 1968)
$WI_2(g)$	− 16000	− 32.00	(Rolsten 1961)
$WSe_2(s)$	− 45000	21.50	(Mills 1974)

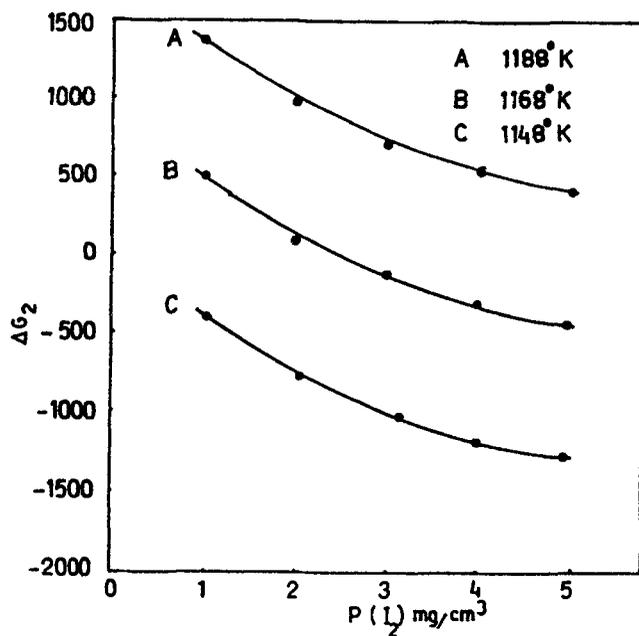**Figure 1.** Dependence of ΔG on iodine concentration at various temperatures.
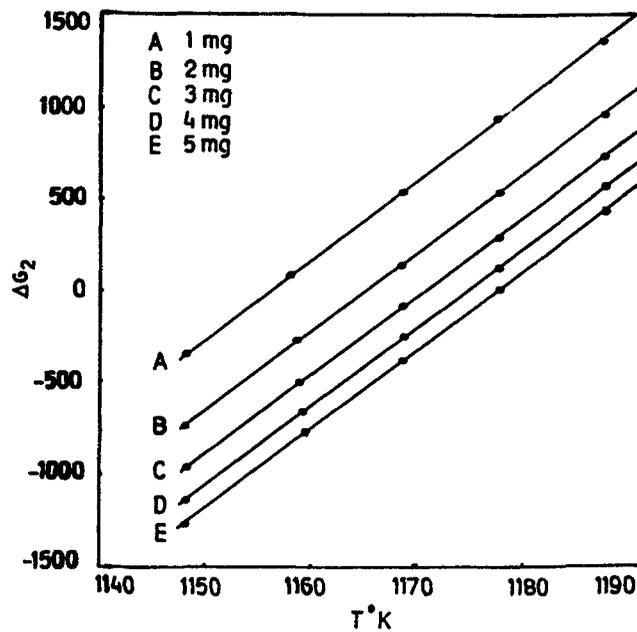

Figure 2. Variation of ΔG with temperature for different iodine concentrations.

For the effective transport, assume $K_p = 1$ for both equations. Then the free energy functions ΔG_8 and ΔG_9 are

$$\Delta G_8 = \Delta Hf^\circ{}_8 - T\Delta S^\circ{}_8,$$

$$\Delta G_9 = \Delta Hf^\circ{}_9 - T\Delta S^\circ{}_9.$$

By using thermodynamic data of table 1,

$$\Delta G_8 = -3977 - 6.116\,T, \tag{10}$$

$$\Delta G_9 = -48977 - 55.58\,T. \tag{11}$$

These equations show that the formation of the element as well as material is possible at any temperature.

Take the ratio of the two equations as

$$\left[\frac{\Delta G_9}{\Delta G_8}\right]_T = 10.28,$$

it is found that for a constant temperature, the ratio is 10.28. It shows that the feasibility for (11) is 10.28 times higher than that for (10).

Theoretical thermodynamical calculations have shown that reaction is possible in order to have a stable WSe$_2$ phase as the growth zone. In order to verify this detailed experiments were conducted.

3. Experimental

Single crystals of tungsten diselenide have been grown by many workers (Al-Hilli and Evans 1972; Agarwal and Rao 1989; Agarwal *et al* 1989b; Legma *et al* 1993) using different kinds of transporting agents. Since the iodine possesses the least bond energy among the halogens (Emeleus and Sharpe 1973), attention has been given to grow WSe$_2$ using iodine as transporting agent. The growth parameters selected in the present investigation are different from those used by other workers (Al-Hilli and Evans 1972).

99.99% Pure tungsten and selenium powders obtained from Merk were taken in stoichiometric proportions and were placed in transparent quartz ampoules (length $= 200$ mm and diameter $= 24$ mm) which were etched and vacuum baked. The total charge used in each experiment was 10 g. The transporting agent iodine (5 mg/cm^3) was also placed in the quartz ampoule along with the powders. The ampoule was evacuated and sealed at a pressure of 10^{-5} torr. Thoroughly shakened ampoule was placed in the two zone horizontal furnace having appropriate temperature profile.

The temperature of the furnace was increased slowly in steps of 343°K/h. The temperature of the vapourization and deposition zones were $T_s = 1173°$K and $T_d = 1103°$K, respectively. After five days of uninterrupted heat treatment, single crystals of WSe$_2$ in platelets form with c-axis normal to the plane of the plates were obtained. The separated crystals were observed under metallurgical microscope in order to ascertain the growth nature. The surface of the platelets were highly reflective and devoid of any bulk defects. In vapour transport mechanism, density of the vapour species need not to be distributed uniformly throughout the capsule due to the local variations in supersaturation. The condition was quite critical at the growth region. The spiral growth usually occurred at lower supersaturation of the species and layer growth initiated at higher supersaturation (Elwell and Scheel 1975; Krishan Lal 1982). In this particular case these two mechanisms occurred at
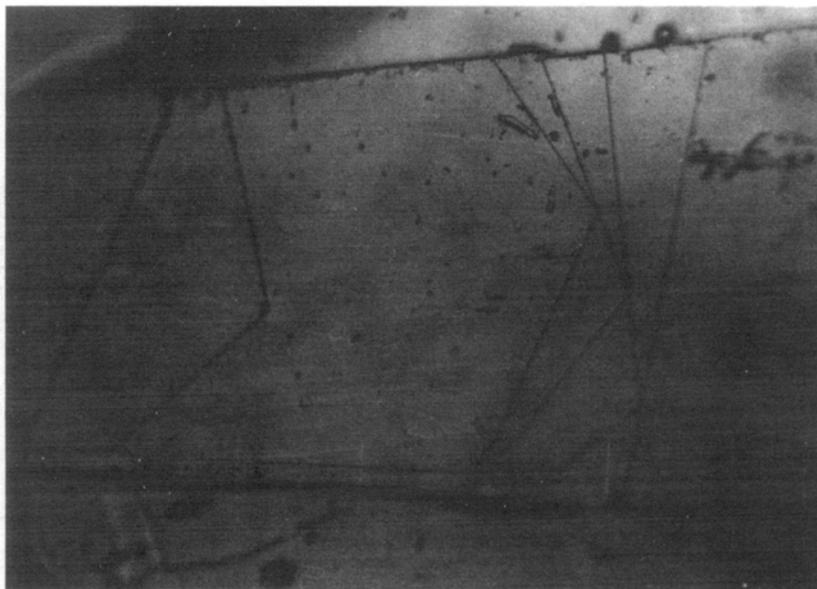
Figure 3. Growth layers.

Figure 4. Growth spiral.

micro regions in the growth locations. Hence both these types of growth were expected. Figure 3 is an example for two dimensional nucleation and figure 4, growth by spiral mechanisms. It was found that 90% of the crystals were grown by former and remaining ones by latter.
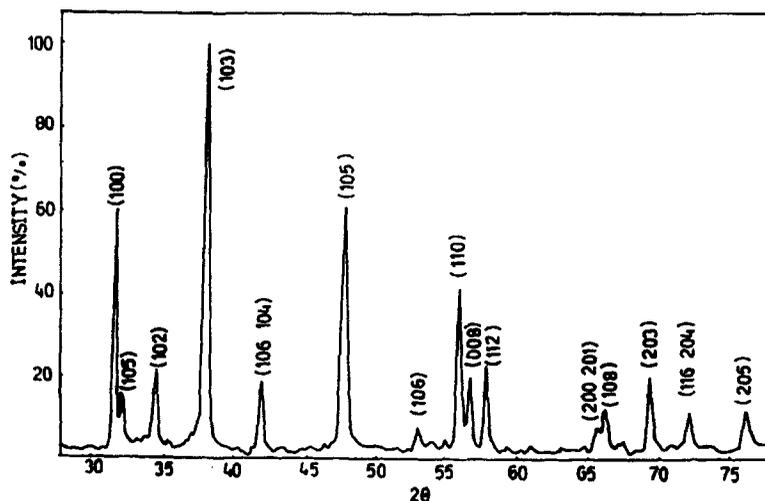
Figure 5. X-ray diffractogram.

4. Characterization

Figure 5 shows the diffractogram of the grown sample using Cu Kα radiation from Shimadzu XD-610 diffractometer. From the XRD peaks, the lattice parameters measured were $a = 3.29$ Å, $c = 12.97$ Å which were consistent with literature values (Glemser 1948).

5. Conclusion

Preliminary thermodynamical calculations show that for efficient transport of binary iodide, the temperature of the hot zone should be around 1177°C. The formation of WSe_2 and its constituent elements have equal probability at wide range of temperatures. The calculations show that the possibility of formation of WSe_2 is 10·28 times higher than that of the formation of the elements in the deposition zone. On this basis the temperature of the growth zone has been assigned to 1103°K for a temperature gradient, $T = 347°$K.

Detailed experiments have been conducted by changing the temperature of growth zone and source zone in order to see the best condition for the formation of good WSe_2 crystals. Platelet single crystals are formed when the temperature zones are fixed near theoretical values. Our results also show that the lower iodine concentration reduces contamination of the crystals. These crystals were characterized using X-ray method. The examination of the crystals showed that the growth is predominantly taking place due to spiral mechanisms, two dimensional nucleation and spreading of layers.

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