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GROWTH, PHYSICAL, STRUCTURAL AND CHEMICAL CHARACTERIZATION OF LAYERED SEMICONDUCTOR MOLYBDENUM DISELENIDE

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$MoSe_2$ is known to have layered structure with various polytypes having different stacking structures developing on conditions prevailing during the synthesis of crystals. Looking to its potential for application in electronic devices, it will be important to investigate growth conditions vis a vis electrical properties which depends on structure. In this paper we explain the growth of Molybdenum diselenide single crystals by direct vapor transport technique. The chemical nature and physical structure of grown crystals have been studied with the help of EDAX and XRD techniques. It has been found that for obtaining high carrier mobility in such crystals, DVT technique has greater chances of success in comparison to CVT technique.

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1. Introduction

Molybdenum dichalcogenides belong to the large family of layered transition metal dichalcogenides. It consists of weakly coupled sandwiched layers i.e. Se – Mo – Se in which a Mo atom layer is enclosed within two Se layers [1]. The metal atom is always coordinated by six chalcogenide atoms. Two geometries are possible: trigonal prismatic and trigonal antiprismatic (commonly referred to as octahedral, although distorted). The interlayer binding forces are of van der Waals nature resulting in large interlayer distances. This structure makes $MoSe_2$ extremely anisotropic in character and leads to unusual structural properties [2]. In addition, $MoSe_2$ possess flexible nature along with good carrier mobility to make them potential candidate for fabricating flexible high mobility electronic devices such as Schottky barrier devices, FETs, solar cell etc. Further, this material has also been used as catalyst and are known to be extremely good lubricants [3-5].

Due to the weak interlayer interactions, several stacking polytypes are found. $MoSe_2$ generally crystallizes in the 2H and 3R poly forms. 2H has two layers per unit cell stacked in hexagonal symmetry and 3R has three layers in rhombohedral symmetry. The present paper aims to report the growth of molybdenum dichalcogenides by direct vapor transport technique along with its structural characteristics. This is expected to contribute to greater objective of correlating growth conditions with structural properties as it has been reported to possess properties which are highly dependent on growth conditions [6]. An attempt has also been made to compare present growth conditions with those reported in last three to four decades. Such an exercise is expected to help in exploring the suitable growth conditions for obtaining good crystals with required properties in case of this potential material.

2. Experimental

Crystals of $MoSe_2$ were grown by direct vapour transport (DVT) method inside a dual zone horizontal furnace [7, 8]. In present case such a furnace controlled by a micro controller

(Honeywell, Model: DCP 50) with thermal profile programming facility and Solid State Relay (SSR) based power unit for the two zones of the furnace with suitable back up to take care of power supply breakups has been used .

High quality fused quartz tubes having a melting point of about 1500°C were used for growth experiments. The length of the ampoule was chosen to be around 24 cm as per the requirement of the furnace dimensions and the temperature profile within it. The inner and outer diameters of the ampoules were 23 mm and 25 mm respectively. One end of the ampoule was sealed and the other end was drawn into a neck, which was then joined to another quartz tube with smaller dimensions (8 mm of inner diameter, 1 mm thickness and 30 cm in length). This kind of arrangement is required for connecting it to the vacuum system for evacuation after filling it with the source material.

The ampoules were cleaned prior to filling them with stoichiometric elemental mixture of molybdenum and selenium. They were washed with boiling water along with a suitable detergent and then rinsed with concentrated H_2SO_4. This was followed by washing with double-distilled water. The above cycle of acidic rinsing and washing was repeated with HNO_3. For good results above kind of cyclic cleaning were repeated 2-3 times. Then, the ampoules were filled with concentrated HF and heated till boiling for some time so that the inner surfaces of the ampoules become rough due to etching. This was absolutely necessary to create ample growth sites for preferential nucleation to assist the growth of crystals. A thorough and final washing was done again with double-distilled water to remove any residue of these chemicals. The clean ampoule was then transferred into a constant temperature oven (SlCO make) at 100°C and left overnight to make it dry and moisture free.

Highly pure molybdenum (AR 99.9%) and selenium (AR 99.6%) were used as starting elements and powders of these elements in stoichiometric proportion, were loaded in the quartz ampoule. A total charge of about 12 g for a volume of 87cm^3 of the ampoule was used in the experiment. The ampoule containing the source material was then connected to a vacuum system, and evacuated to a pressure of 10^{-4} -10^{-5} Torr. This helps to minimize the reaction of the elements with residual gases within the evacuated ampoule at elevated temperatures and further helps to create a lower inside pressure so that the vapour pressure developed at high temperature within the ampoule does not lead to explosion. Proper care was taken while evacuating the ampoule so that the loaded material from ampoule does not enter into the vacuum system. Once the required vacuum was reached, the loaded ampoule was sealed off at the neck. The sealed ampoule with the elemental powders was shaken thoroughly to ensure proper mixing of the contents. The ampoule was then inserted into the two zone horizontal furnace and the temperature was raised slowly for reaction between elements keeping it same for the two zones. The slow heating was necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements. The typical temperature profile and the nature of variation of the zone temperatures used during the growth run of $MoSe_2$ crystal is shown in Figure 1. Growth and source zone temperatures were kept as 1030 K and 1060 K and the duration of transport was about 96 hours with charge of around 12gm. It may be noted that before arriving at the optimum conditions described above for the growth of $MoSe_2$ crystals of good size, several runs of growing this material by DVT under different conditions of temperature , temperature gradients and material stoichiometry have been attempted.

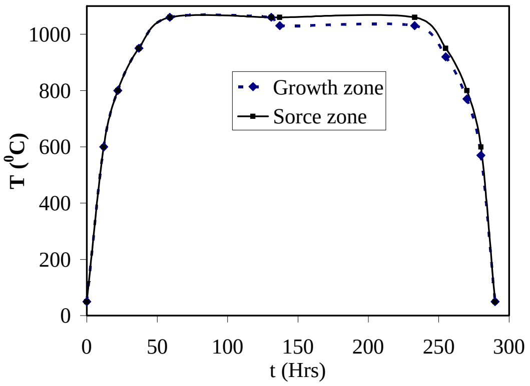

Fig. 1. Typical temperature profile for $MoSe_2$.

The microstructural investigations of as-grown surfaces of the crystals were done with the help of Axiotech 100 reflected light microscope (Carl Zeiss Jena, Germany make). The physical structure was studied by X-ray diffractometer (XRD) unit (Make: Phillips, Model: X'Pert MPD). The lattice parameters, hkl reflections and d spacing of the grown crystals were determined by comparison with JCPDS data as well as by using suitable software. This program facilitates for data smoothening, background subtraction, α_2 elimination, peak search, indexing, and generation of simulated powder X-ray diffraction patterns. The chemical proportions of elements in grown crystals were obtained from the Energy Dispersive Analysis of X-rays (EDAX) using (Phillips, Model: XL 30 ESEM).

3. Results and discussion

After the completion of DVT cycle and cooling of the ampoule, the growth zone of the ampoule was found to contain grey, shiny irregular shaped platelets of $MoSe_2$ crystals. The average crystal dimensions were 3-5mm^2 in cross sectional area and few micrometers in thickness.

The grown crystals as observed under light microscope with X-20 magnification revealed the presence of hexagonal spirals on the growing faces as shown in Figure 2. This microstructure showing presence of large number of crystallographically oriented spirals suggests screw dislocation mechanism of growth. In general, presence of screw dislocations in grown crystals shows characteristic property of growth from gaseous phase. The pattern of growth spirals both with unique or with multiple Burger vectors strongly depends on the rate of movement of dislocations and atomic steps in different crystallographic directions relative to the faces [9]. The growth speed depends on the crystallographic orientation. Further, the feature of polygonized spirals reflects the symmetry of that face of the crystal and the formation develops perpendicular to the direction of crystal growth.

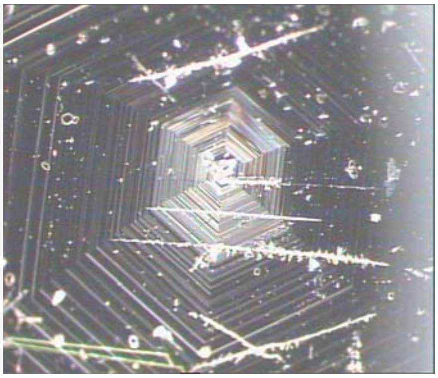

Fig. 2. Microstructure (20x) showing hexagonal spiral growth pattern of as grown $MoSe_2$ crystal.

Thus the peculiarities of the growth of faces are directly reflected with the distinctive features of the growth conditions. As seen from micrograph (figure 2) the spirals are formed in groups of four suggesting that four active dislocations are responsible for growth of faces in present crystal and suitable conditions for this are present in the vapor transport followed in present case.

The XRD diffractograms of grown crystals is shown in figure 3. There are observed 37 sharp lines of varying intensities in the diffractogram. The analytical indexing of the pattern thus obtained was done to calculate the lattice parameters for the hexagonal layered structure. The values thus obtained are a = b = 3.280 Å and c = 13.020 Å. In order to affirm that these lines belong to molybdenum diselenide, the d spacing and relative intensities of these lines were compared with JCPDS data for 2H-$MoSe_2$ polytype. It is noted that 24 of the d-spacing of JCPDS data match with the present diffractogram.

However relative intensities do show deviations. This deviation along with the presence of other lines, although not very prominent ones indicate that along with 2H-$MoSe_2$ 3R-polytype form of this compound may also to be present. When analyzed in this way it is seen that three d-spacings of 3R-$MoSe_2$ as seen from JCPDS data are found in the X-ray diffractograms of present crystal, though the intensity of one of the prominent line among these three for 3R-$MoSe_2$ as given in JCPDS data sheet is down by 66% in the diffractograms of present crystal. Therefore presently grown crystals may contain only a little proportion of 3R polytype form.

Even after such an analysis, 10 lines of present crystals diffractogram remain to be assigned. For this JCPDS data sheets of possible elements and compounds (such as Mo, MoO_2, MoO_3, Se and SeO_2) in preset growth process were searched. Such analysis shows that none for Mo; 1out of 39 for MoO_2; 1 out of 58 of MoO_3; 1 out of 23 of Se and 4 out of 104 for SeO_2 are present with low intensity. Thus only a little amount of these may be found in present crystal resulting probably from incomplete reaction or insufficient low pressure during reaction. It may be further noted that the lines which are still left are of very low intensity and these may be considered as part of the background.

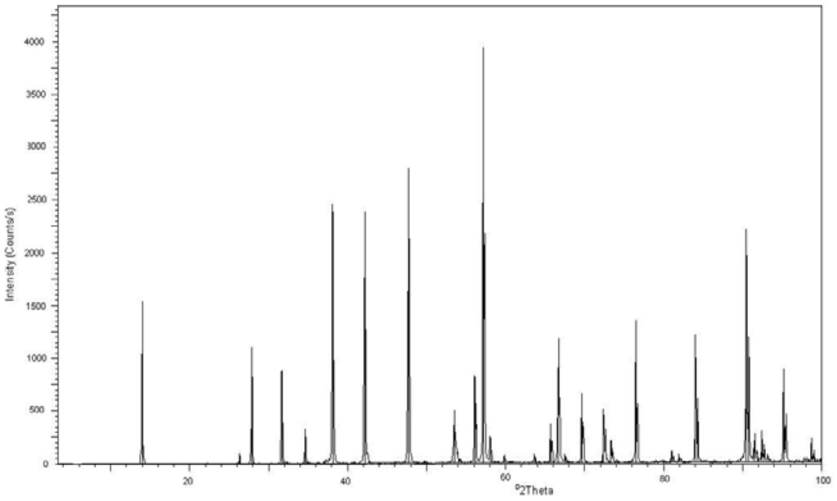

Fig.3. X-ray diffractogram of molybdenum diselenide.

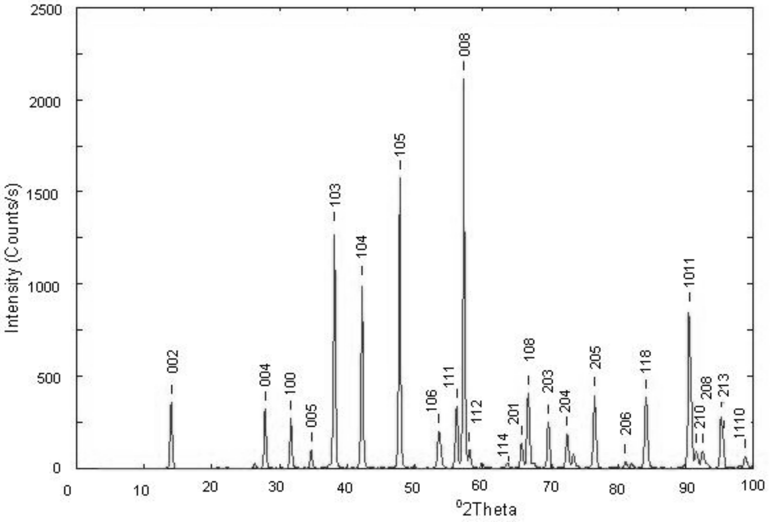

Fig.4. X-Ray diffractogram of molybdenum diselenide showing matching reflections with 2H-$MoSe_2$ generated by software.

Since majority d-spacings of grown crystals match well (table 1) with those given in JCPDS data sheet for 2H-$MoSe_2$ structure [10], the values of lattice parameters for our crystals can be assumed to be a = b = 3.287±0.007Å and c = 12.925±0.095Å. Therefore it can be inferred that the structure of our crystal belongs to 2H-$MoSe_2$ polytype of molybdenum diselenide.
Using the above values of lattice parameters, the x-ray diffraction pattern of 2H-$MoSe_2$ was simulated using the software and its capabilities for data smoothening, back ground elimination etc. The pattern so obtained is given in figure 4 and d-spacings (table 1) of the reflections were also obtained.

Table 1. Comparison of experimentally observed d-spacings of $MoSe_2$ crystals with JCPDS data sheet and software simulated.

d-spacings (A^0)		
d (expt.)	d (calc.)	d (JCPDS)
6.39770	6.45774	6.46
3.21781	3.22887	3.23
2.83808	2.85008	2.845
2.59825	2.58310	2.605
2.36935	2.37650	2.373
2.14927	2.13674	2.153
1.91014	1.91397	1.913
1.71476	1.71771	1.717
1.64160	1.63230	1.643
1.61319	1.61444	1.615
1.59151	1.59454	1.591
1.46100	1.46486	1.465
1.42235	1.41644	1.423
1.40377	1.40472	1.404
1.35085	1.35285	1.351
1.30570	1.30371	1.306
1.24648	1.24776	1.246
1.18721	1.18825	1.187
1.15215	1.15240	1.152
1.08645	1.08562	1.086
1.07661	1.07723	1.077
1.06819	1.06837	1.067
1.04441	1.04501	1.044
1.01621	1.01597	0.9934

24 of such d-spacings of this simulated diffractogram matches with that of figure 4. This can again confirms that crystals grown in the growth conditions used presently belong to 2H-$MoSe_2$ polytype.

Table 2. Chemical composition (wt %) of as grown $MoSe_2$.

wt (%) of the elements	**Mo**	**Se**
Stoichiometric proportion taken for crystal growth	37.792	62.2075
Obtained from the EDAX of grown crystals	36.88	63.12

Table 3. Growth mechanism, growth conditions, crystal type and electrical data of MoSe2 from various authors.

SI. NO.	Crystal Type	Growth mechanism	Growth conditions	$\rho_{\perp}$ (Ω-cm)	n/cm^{3}	μ (cm^{3}/Vs)	Year
1	$MoSe_2$	CVT (Br_2)	960/930 ^{0}C	2.5	$3.5x10^{16}$	31.4	2006 [11]
2	2H-$MoSe_2$	CVT (Br_2)	-	-	$3.5x10^{15}$	-	2006 [12]
3	2H-$MoSe_2$	Vapour transport	-	-	10^{17}	-	1992 [13]
4	$MoSe_2$	CVT(Br_2)	960/800-840 ^{0}C	0.925	-	-	1984 [14]
5	$MoSe_2$	CVT (Br_2)	-	-	$7x10^{16}$	-	1981 [15]
6	$MoSe_2$	Vapour phase transport	-	1	$1.6x10^{17}$	40	1975 [16]
7	$MoSe_2$	CVT (Br_2)	850/740 ^{0}C	1.5	$5x10^{16}$	-	1967 [17]
8	2H-$MoSe_2$ (Present work)	DVT	1060/1030 ^{0}C	47.519	$1.74x10^{15}$	75.58	2007
9	$MoSe_2$	DVT	1050/1000 ^{0}C	11.5	$1.78x10^{16}$	30.30	1992 [18]
10	$MoSe_2$	DVT	1100/1060 ^{0}C	0.1769	$1.1x10^{17}$	213	1990 [8]
11	2H-$MoSe_2$	DVT	1070 ^{0}C	0.47	$1.29x10^{17}$	126	1971 [7]
12	$MoSe_2$	Powder synthesis	Reacted at 550 ^{0}C, sintered at 1000^{0}C	-	$5.6x10^{16}$	15	1964 [19]
13	$MoSe_2$	Powder synthesis	Compact powder synthesis, 1100 ^{0}C.	3.4*	-	-	1962 [20]

* pellet form of compressed powder

Chemical compositions of presently grown crystals were analyzed using EDAX analysis (figure 5). This analysis shows the proportion of the constituent elements and its comparison with starting elements used in stoichiometric proportion in table 2. Such a comparison shows that there is a slight excess of selenium and with the excess of selenium the formula assigned to present crystals is $MoSe_{2.03}$. This excess in selenium may be attributed to use of molybdenum in formation of MoO_2 and MoO_3 which outweighs slightly the use of selenium in formation of SeO_2 in addition to unreacted selenium.

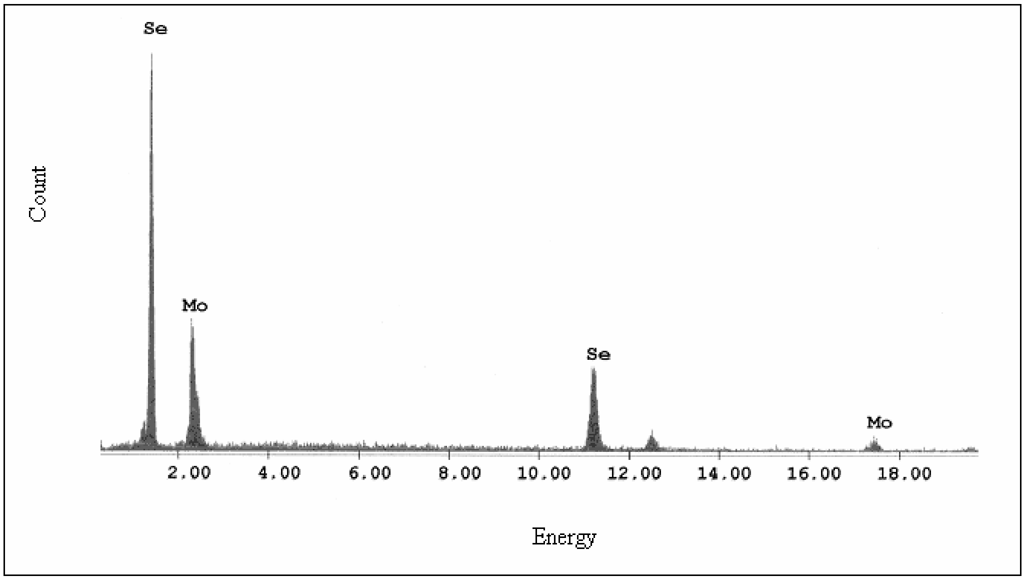

Fig.5. Typical EDAX of the as grown $MoSe_2$ crystal.

In order that above effort helps in exploring suitable growth conditions for obtaining such crystals with tailor made properties, a survey of reported growth conditions of these single crystals in last three to four decades was made from literature. Such a comparison is given in table 3. Where a value of electrical parameters, vital in electronic application of these crystals is also given wherever reported. This table clearly shows the properties of these semiconducting crystals are highly dependant on growth conditions used in synthesis. It also be noted that higher values of carrier mobilities can be obtained in crystals synthesized by DVT mechanism which seems to be related to more trap free crystals resulting from this method in comparison to chemical vapor transport mechanism. However, more elaborate and systematic study needs to be pursued with this technique to obtain crystals with good electrical properties for application in electronic devices.

4. Conclusions

The optimum condition for the growth of molybdenum diselenide single crystal with direct vapour transport technique was found to be growth and source zone temperatures of about 1030K and 1060K and the duration of transport of about 96 hours with charge of around 12gm. Also the direct vapour transport technique has been found suitable to grow crystals of $MoSe_2$, because it yields crystals of moderate size with relative ease having good purity. The optical microscope image of the $MoSe_2$ crystal reveals the layer type structure and the formation of growth spirals on the surface of the grown crystal. Spiral growth is well known for bulk single crystal growth under conditions close to thermodynamic equilibrium, and it is mediated by the existence of screw dislocations in the crystal. The surface structure is completely dominated by growth spirals of single or multiple dislocations. All the grown crystals show the left helical dislocations, which extends up to the boundary of the crystal. Electrical parameters of such crystals are highly dependent on growth conditions and it appears that high carrier mobility in these semiconductors can be obtained by suitably developed DVT growth mechanisms

Using the lattice parameters given above, Miller indices and d-spacing were obtained and these were compared with those obtained from XRD pattern for our crystals. These were again compared with d-spacing in JCPDS for 2H-$MoSe_2$. Again a good match is seen which confirms that our crystal belongs to 2H polytype of molybdenum dichalcogenides. EDAX analysis has shown a slight excess of selenium which leads to a chemical formula 2H- $MoSe_{2.03}$.

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