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NATIVE DEFECTS IN MoSe₂ CRYSTALS GROWN BY DIRECT VAPOR TRANSPORT

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ABSTRACT

The presence of native defects in crystals of MoSe₂ grown by direct vapour transport has been investigated. The XRD and EDAX shows the presence of MoO₂, MoO₃, Se and SeO₂ along with MoSe₂. The formula assigned to grown crystals is MoSe₂.₀₃ accounting for excess of selenium as seen from EDAX. This excess in selenium may be attributed to the use of molybdenum in formation of MoO₂ and MoO₃ with residual oxygen in the ampoule which outweighs slightly the use of selenium in formation of SeO2 in addition to unreacted selenium. The n-type conductivity of grown crystals can be attributed to the compensating nature of defects incorporated during growth. The extrinsic electrical behavior of MoSe₂ is therefore ascribed to the presence of both donors and acceptor impurities originating from the defect structure of MoSe₂ crystals.

Key words: crystal growth; direct vapor transport technique, EDAX, native defects, XRD.

INTRODUCTION

The transition metal based semiconductor MoSe₂ belongs to the family of dichalcogenides with a layer-type structure. MoSe₂ has been studied widely for its properties and applications using growth of this material by various techniques [1-12]. Among the layered compounds, MoSe₂ has been recognized as ideal model compound for the studies involving surfaces, photoreactions, adsorption phenomena and catalysis, scanning tunneling microscopy, spectroscopy and epitaxial growth of thin films [3, 5, 8]. The extremely anisotropic character of the layered compounds, built in at the atomic level, dominates all the properties of such materials, both mechanical and electrical. It opens up new opportunities for the application of layered materials [2, 4, 7, 10]. It is a well-known fact that in the layered crystals like MoSe₂, the bonding within the layers is strong and primarily covalent, while that between the layers are Van der Waals bonding and thus weak enough to permit intercalation of foreign atoms or molecules into the gap between the layers [4, 6, 12].

Native or intrinsic defects are imperfections in the crystal lattice that involves only the constituent elements. They include vacancies (missing atoms at regular lattice positions), interstitials (extra atoms occupying interstices in the lattice) and antisites. Native defects can strongly influence the electrical and optical properties of a semiconductor, affecting doping, minority carrier lifetime and luminescence efficiency, and are directly involved in the diffusion mechanisms connected to growth, processing and device degradation [13-15]. Native defects are, in general, related to the compensation of the predominant acceptor or donor dopants, i.e. donor defects are easier to form in p-type material, whereas acceptor defects are easier to form in n-type material, always counteracting the prevailing conductivity. Identification of the processes controlling the incorporation of native defects during semiconductor material preparation and /or processing is of primary importance since so many electronic and structural properties critically depend on the presence of such defects. However incorporation of such defects in DVT grown crystals has been seldom dealt in detail. Present paper discuss this aspect and its influence reflected in semiconducting behavior of DVT grown MoSe₂ crystals.

MATERIAL AND METHODS

Crystals of MoSe₂ were grown by direct vapor transport (DVT) method inside a dual zone horizontal furnace [1, 9-12]. Highly pure molybdenum (AR 99.9%) and Selenium (AR 99.6%) elements were used as starting elements. Growth and source zone temperatures were 1030K, 1060K respectively and the duration of transport was about 72 hours. 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. 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, α2 elimination, peak search, indexing, and generation of simulated powder X-ray diffraction patterns.

RESULTS AND DISCUSSION

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 figures 1. 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 crystal shows characteristic property of growth from gaseous phase [16-18].

It is observed to contain 37 sharp lines of varying intensities in the diffractogram (figure 2). 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 = 3.280Å and c = 13.020Å. 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 be present. When analyzed in this way it is seen that three d-spacings of 3R-MoSe$_2$ as seen from JCPDS data are present in the X-ray diffractograms of grown crystal. However, the intensity of one of the prominent line among the three for 3R-MoSe$_2$ as given in JCPDS data sheet is down by 66%. Therefore presently grown crystals may contain only a little proportion of 3R polytype form.
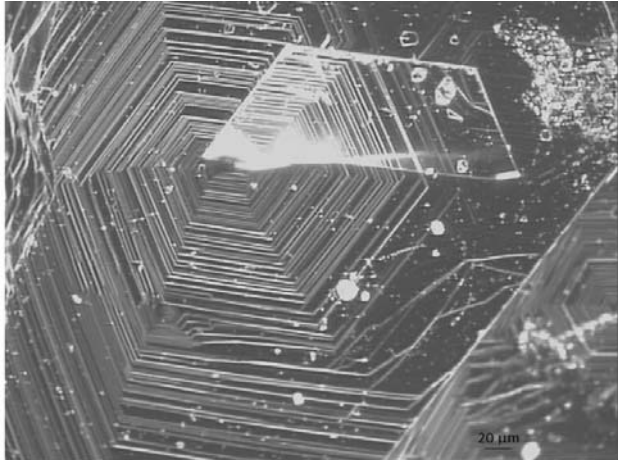

Fig. 1 The branching of the growth spirals on the surface of MoSe$_2$ crystal formed by several dislocations of one and the same sign.
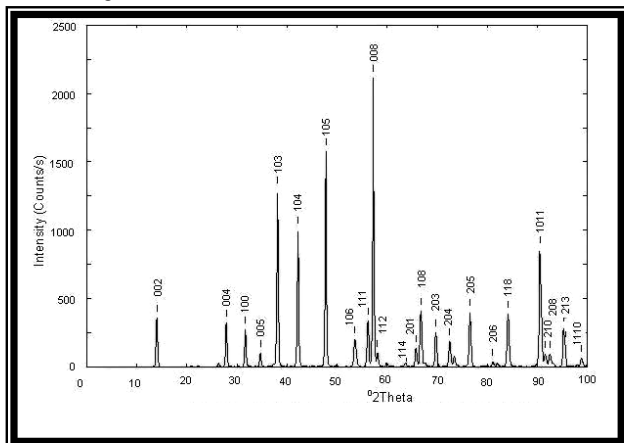

Fig. 2 X-Ray diffractogram of molybdenum diselenide crystal grown by DVT technique.

Even after such analysis, 10 lines of present crystal's 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 present growth process was 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 fairly low intensity. Thus only a small amount of these may be found in present crystal resulting probably from incomplete reaction or insufficient vapour pressure during reaction and residual oxygen. It may be further

noted that the three lines which are still left, are of very low intensity and these may be considered as a part of the background. At the high temperature associated with crystal growth, the solid phase of a compound semiconductor in equilibrium with the liquid or gas can exist over a narrow but finite range of atomic composition that is with small deviation from exact stoichiometry. As the temperature drops, the extent of this so-called existence region shrinks and eventually goes to zero. As the temperature is lowered atomic diffusion rates fall and hence small deviations from stoichiometry gets frozen into the crystals. Any deviation from exact stoiciometry implies the existence of defects to accommodate imbalance. EDAX analysis was also carried out to estimate the amount of stoichiometry and confirm this kind of evolution of defects. The energy dispersive spectrum of MoSe$_2$ is shown in figure 3. The analysis shows that there is a slight excess of selenium and with the excess of selenium the formula assigned to present crystal 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 with residual oxygen in sealed ampoule.
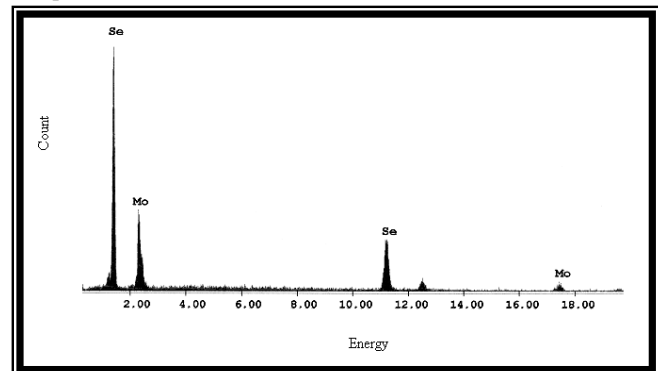

Fig. 3 Typical EDAX of the as grown MoSe$_2$ crystal.

The electrical transport behaviour studied for the grown crystals show n-type conductivity. Details regarding the electrical transport properties of grown crystals were explained elsewhere [19, 20]. The extrinsic electrical behavior of MoSe$_2$ is attributed to the presence of both donor and acceptor impurities originating in defect structure of MoSe$_2$ crystals incorporated during its growth. The n-type electrical conductivity of grown crystal is due to the compensating nature of such defects. In the case of DVT grown crystals it is very likely that selenium excess results in giving larger number of donor defects in comparison to shallower acceptor defects.

CONCLUSION

In summary we have studied and discussed the evolution of native defects incorporated in the crystals of MoSe$_2$ grown by direct vapour transport technique. The study revealed that various kinds of defects are incorporated in the crystals of MoSe$_2$ during growth process. The n-type electrical conductivity of grown crystals is due to the compensating nature of native defects. In the case of DVT grown crystals it is very likely that selenium excess results in giving larger number of donor defects in comparison to shallower acceptor defects.

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