TWOFOLD CONDUCTION MECHANISMS IN MOLYBDENUM DISELENIDE SINGLE CRYSTALS IN THE WIDE TEMPERATURE RANGE OF 300K TO 12K

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Molybdenum dichalcogenides, a member of VIA-VIB transition metal dichalcogenides has been looked as a potential semiconducting material for electronic devices. Thispaper reports temperature variation of (12K - 300K) electrical conductivity and carrier concentration in semiconducting crystals grown by direct vapor transport technique. It is found that the conductivity behavior is extrinsic in character with three different values of activation energy in the investigated temperature range. This behavior seems to be originating from presence of defects incorporated during growth and can be explained in the frame of a model consisting of one donor level along with one shallow acceptor level.

1. Introduction

Molybdenum dichalcogenide belongs 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. The interlayer distances in these materials are large and the interlayer binding forces are of van der Waals nature. This structure makes $MoSe_2$ to exhibit anisotropic properties in general and has been looked as potential material for various applications including that for electronic devices [1-5].

Electrical properties play an important role in determining the behavior of solid state devices and thereby their potential for such applications. In this paper we report our investigations regarding the electrical behavior of molybdenum diselenide single crystals grown by direct vapor transport technique, which has been reported to be highly dependent on growth conditions [6].

2. Experimental

Crystals of $MoSe_2$ were grown by direct vapor transport (DVT) method inside a dual zone horizontal furnace [7, 8]. 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. For present study the crystals with flat shining surfaces were chosen with the help of optical microscope (Carl Zeiss Jena, Germany). These were then washed in acetone to remove contamination and dried in an oven for a couple of minutes at 60^0C. The physical and chemical structure was chcked with XRD and EDAX analysis. Ohmic contacts on crystals were made along the basal plane by fusing of indium and attaching low strain Ag alloy wires to them at 275^0C. The Hall effect measurements were made using Lake Shore Hall measurement system 7504 over a range of temperature (300-12K)

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with the help of Lakeshore temperature controller (Model 340) and a Closed Cycle Refrigerator (CCR 75014) under a magnetic field of $\pm 5kG$.

3. Results and discussion

The temperature variation of the conductivity of crystals is shown in figure.1. It is seen that it has an activated nature with negative temperature coefficient confirming that the crystals are semiconducting in nature. Since $MoSe_2$ crystals have been seen to have transition to intrinsic nature around 600-700K [9], the observed conductivity is in extrinsic region. This is also confirmed by values of activation energies (Table 1) as evaluated from figure. 1 for the three identified temperature regions. The conductivity of a semiconducting material can have contributions from temperature dependence of carrier concentration and their mobility. The temperature dependence of carrier concentration found by us is shown in figure.1.
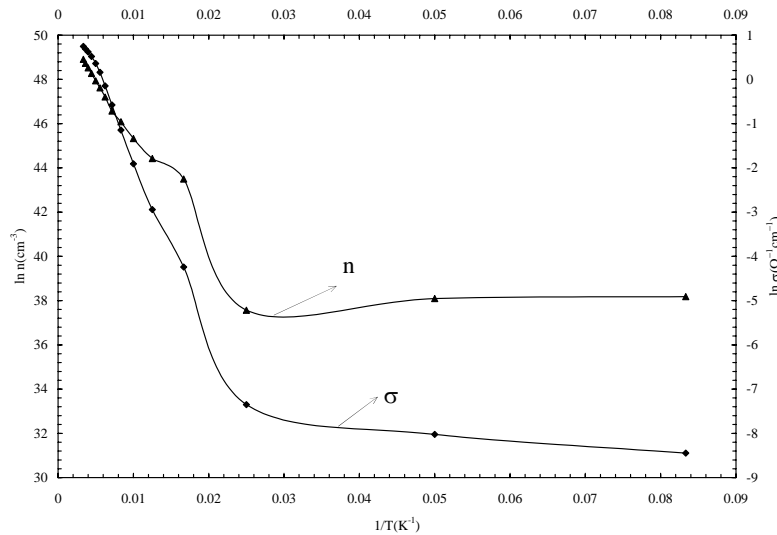

Fig. 1. Temperature dependence of conductivity and carrier density.

It shows similar temperature regions but having activation energies (Table 1) different from that observed for the conductivity. The type of carriers as seen from the sign of Hall coefficient is n-type for 300 K-20 K and p-type below 20 K. It is also seen that carrier concentration below 20 K is almost constant around 3.5×10^{10}/cm^3.

Table 1. Activation energy for different temperature regions.

Temperature range (K)	Carrier concentration (cm^{-3})	Activation energy (eV)	
		ln σ vs 1/T	ln n vs 1/T
300-100	10^{15}-10^{13}	0.035	0.048
60-40	10^{12}-10^{10}	0.032	0.085
40-12	10^{10}	1.6×10^{-5}	1.38×10^{-6}

MoSe$_2$ is known to have layered structure with various polytypes having different stacking structures developing on conditions prevailing during preparation [10]. It has been found from XRD analysis that present crystals belongs to 2−H MoSe$_2$ polytype similar to one reported in JCPDS –International Centre for Diffraction Data [11].

However EDAX of our crystals shows a slight selenium excess and the crystals can be assigned a formula MoSe$_{2.03}$. The extrinsic electrical behavior of MoSe$_2$ is generally attributed to the presence of both donors and acceptor impurities originating in defect structure of such crystals incorporated during its growth. Thus electrical behavior of our crystals, which is predominantly n-type in most of the temperature range of investigation, can be attributed to the compensating nature of such defects. In present case it is very likely that selenium excess produces a larger number of donor defects in comparison to shallower acceptor defects. This is also supported by the fact that selenium deficiency has been observed to give p-type [6] behavior with Fermi level moving towards valence band with decreasing selenium content.
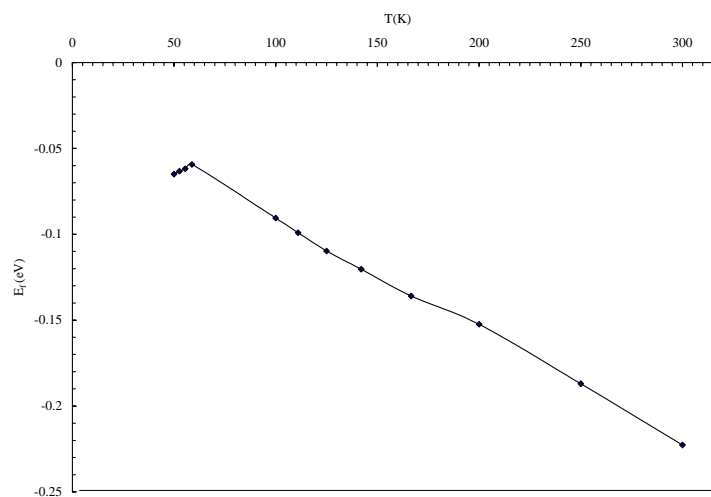

Fig. 2. Temperature dependence of Fermi energy.

Thus observed conductivity behavior of our crystals can be explained in a model with one donor and one shallower acceptor level in association with acceptor density N$_A$, smaller than donor defect density N$_D$. Donor ionization energy is found to be 0.08 eV and at high temperature region the activation energy is almost half of this value. In compensated semiconductors, this is due to a change in the charge neutrality conditions for the two regions [12]. That is, in higher temperature region carrier concentration n >N$_A$ while in lower temperature region n < N$_A$. This transition is also indicated from variation of Fermi level with temperature (figure.2). The Fermi energy [9] has been calculated from,

$$E_f = kT \ln\left(\frac{n}{N_c}\right) \quad (1)$$

Where N$_c$, the effective density of states for the conduction band and is given by,

$$N_c = 2\left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2} \quad (2)$$

It may be noted that in the calculation of Fermi level the effective mass of the carriers m* has been taken 0.5 m$_e$ as reported in [13].

4. Conclusion

MoSe$_2$ crystals grown by DVT technique under given conditions exhibit semiconducting nature which can be explained in terms of one donor and one shallower acceptor defect levels originating from growth conditions. The grown crystal shows mixed conduction behavior in the temperature region 300 K to 12 K. The EDAX results show slight excess of selenium corresponding to the chemical formula MoSe$_{2.03}$.

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