Electrical properties of molybdenite single crystals

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Abstract. Molybdenite crystals used in the present work were grown by direct vapour transport or sublimation method. The electrical resistivities and I-V characteristics were measured at different temperatures in the symmetry plane. The room temperature resistance of a specimen annealed for different periods has also been measured. These results are described and discussed.

Keywords. Electrical properties; molybdenite single crystals; crystal-growth.

1. Introduction

Chalcogenides of transition metals have been the subject of recent interest because of their highly anisotropic properties that produce unusual electronic (Thompson 1975) and chemical (Gamble *et al* 1971) behaviour. Naturally occurring crystals or single crystals grown by using either the bromine or iodine vapour transport have been employed for investigation. It is quite possible that the probable incorporation of iodine or bromine in crystals grown by vapour transport and of various impurities in natural crystals has some adverse effects for certain applications. The object of this work is to report the growth of MoS_2 crystals by a method which does not involve the transport reagent (iodine or bromine) and their electrical properties (Al-Hilli and Evans 1972).

2. Experimental

For crystal growth, stoichiometric amounts of 99·95% pure molybdenum and 99·9999% pure sulphur were sealed under pressure less than 10^{-5} torr in a thoroughly cleaned quartz ampoule, 220 mm in length and 22 mm in outer diameter. The ampoule was kept in a two-zone horizontal tube furnace at 700°C for 36 hr for pre-reaction of the elements. After thoroughly mixing the contents of the ampoule, it was again heated at 1040°C to 1080°C with a temperature gradient of 2°C per centimetre distributed over the entire length of the ampoule for 12 days. The resulting crystals were all in the form of mica-like platelets. The largest size crystal had the dimensions of $8·0 \times 5·5 \times 0·1$ mm³ (figure 1). The lattice parameters of the crystals obtained by using electron diffraction and x-ray diffraction technique agree with the values earlier reported.

Since the MoS_2 crystals grown have exceptionally flat faces, surface topographic

studies were also carried out and there were regions where the hexagonal and triangular features were present on the same face (figure 2). Since the morphology of the growth features follows the symmetry of the crystal structure, a triangular feature clearly belongs to a rhombohedral polytype and a hexagonal feature to a hexagonal polytype, thereby showing the coexistence of 2H+3R polytypes in the same crystal. The crystals used in the present investigation possess this characteristics and are therefore taken as mixtures of 2H and 3R polytypes.

For electrical conductivity measurements, samples were cleaved to thickness of the order of 200 μm such that their faces were flat. Four thick silver electrodes were deposited on the periphery of the crystal flakes, and copper wires were joined to each electrode with silver paste. Good ohmic contacts were made between the lead and the specimen. The ohmicity of the contacts was verified from the I.V. characteristics and this showed a straight line passing through the origin in the first and third quadrant. The dc electric field was generated by Aplab electronically regulated power supply and the current and voltages were independently measured. Electrical conductivity in the plane of the sample was measured by the four probe technique (Van der Pauw 1958). Conductivity measurements at a high temperature were carried out by keeping the specimen in a vacuum chamber which is capable of heating upto 450°C. All measurements were made at a pressure of 10^{-5} torr. The temperature measurements were made by a calibrated Pt/Pt-Rh thermocouple.

3. Results and discussions

Electrical resistivity of three different samples at room temperature before they undergo any heat treatment, given in table 1, shows that these values agree with those reported by previous workers (Fivaz and Mooser 1967; Evans and Young 1965). It may be noted from the I-V curves in figure 3 that MoS_2 crystals behave like a symmetric varistor, that is, the curves retain their shape for both direct and reverse currents. However, it is seen from the curves that the crystals are more current sensitive at higher temperatures, which means that for the same change in voltage a large change in current is obtained. This implies that the number of current carriers increases with the increase in temperature.

The plot of dc conductivity versus temperature of the specimen (figure 4) shows that there is an initial increase of conductivity to a maximum at a particular temperature of 433°K followed by a gradual decrease and again a subsequent increase. The nature of the curve, however, remains the same while recycling the conductivity experiments repeatedly.

Previous studies have shown that there is a disagreement concerning the magnitude of the band gap in MoS_2 (Mathesis 1973). Wilson and Yoffe (1969) attribute a weak indirect edge at 0·2 eV to be the semiconducting energy gap. Huisman *et al* (1971) propose an intrinsic gap of about 1·4 eV. A careful look at the data on MoS_2 conductivity reported by Wilson and Yoffe (1969) reveals that the band gap values obtained by various workers at different temperature ranges vary. Lagrenaudie (1954) and Mansfield and Salaam (1953) studied the *p*-type semiconducting crystals of 2H polytype and have shown that E_a values increase from 0·03 eV to 1 eV as one goes from lower temperature range to higher temperature. On the other hand, Evans and
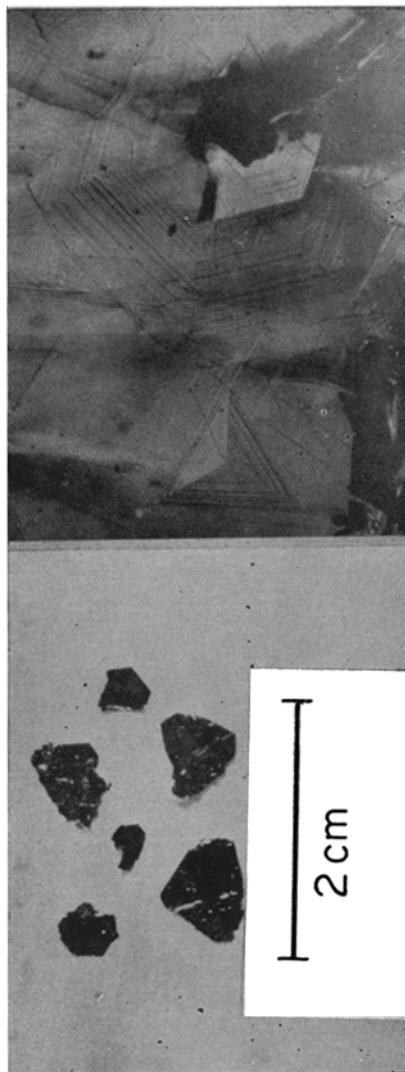
(1)

Figure 1. Single crystals of MoS$_2$

(2)

Figure 2. Coexistence of a triangular spiral with a hexagonal spiral on the as grown face of MoS$_2$ crystal Mag 240

Table 1. Comparison of resistivity at room temperature with previous investigators.

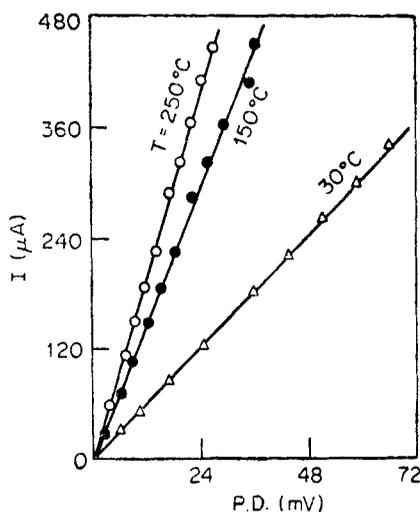| Reference	Specimen preparation	Resistivity (ohm cm)
Fivaz and Mooser (1967)	Bromine	10·50
	Transport	11·84
Present work	Direct vapour	11·33
	Transport	10·19
		12·79
		12 22

Figure 3. Current voltage characteristics plots for different temperaures

Young (1965) while studying n type 2H polytype crystals showed a decrease in E_a values with an increase in the temperature range. Hermann (1973) has given a plot for the conductivity versus temperature for a pure 2H type MoS_2 crystal and has obtained a value of 0·04 eV for E_a. In the light of these results, the conductivity data on the mixtures of 2H and 3R polytypes obtained in the present studies seem interesting.

It is seen from figure 4 that there is an anomalous dependence of conductivity on temperature. This behaviour is true for the majority of the samples investigated. From the plot it may be inferred that from room temperature to about 433°K MoS_2 behaves as a semiconducting material having a band gap of 0·1161 eV, while above 493°K it acts as a semiconductor with a band gap of 0·3271 eV. The accuracy of the band gap measurements for all specimens was $\pm 0·001$ eV. Thus there is an increase in the band gap values with an increase in the temperature and this agrees with the results of Lagrenaudie (1954) and Mansfield and Salaam (1953). The change in the band gap values and the anomaly may be attributed to the creation and ordering of the stacking faults in the specimen. The presence of a large number of stacking faults in our crystals was verified from their electron microscope study. Since the

temperature at which the anomaly occurs varies from sample to sample, it is probably dependent on the nature and the amount of imperfections present. It is known that lattice defects including stacking faults give rise to deep and shallow energy levels in the forbidden band of any material (Prasad and Srivastava 1971). The formation of these energy levels corresponding to a localised state is the result of the splitting of the external energy level and its transition to the forbidden band. The type of perturbation associated with the stacking faults above the temperature of 453°K is expected to eliminate the localised levels near the valence band. Their elimination would change the forbidden band and in effect the band gap increases.

In the present study, it was observed that the room temperature resistance of the specimen changes after heat treatment. A number of specimens were annealed by heating in vacuum at different temperatures 373°K, 423°K, 473°K, 523°K, 573°K, 623°K, 673°K for about an hour and their resistance was measured after cooling the specimens to room temperature. The data on the dependence of change in the resistance occurring at room temperature for different annealed temperatures are plotted in figure 5.
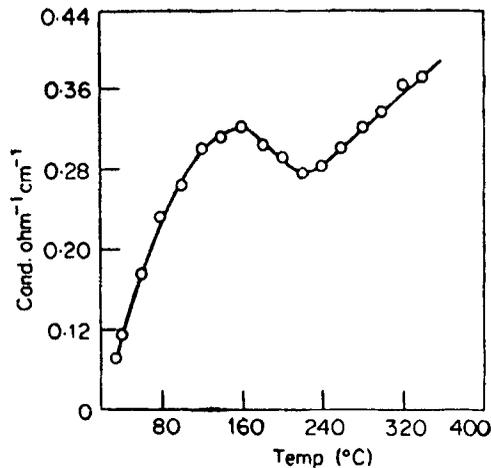

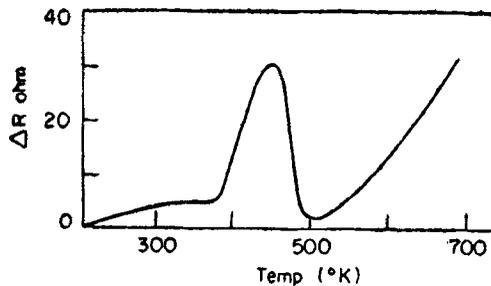**Figure 4.** Conductivity versus temperature plot.

Figure 5. Change in resistance ($\triangle R$) versus annealing temperatures.

4. Conclusions

(i) I.V. curves at different temperatures show that the crystals grown by direct vapour transport method are symmetric varistors.

(ii) The room temperature resistivities of specimens annealed at different temperatures are found to be different.

(iii) The conductivity versus temperature curve shows an anomalous behaviour and an increase in the band gap values with an increase in temperature.

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