CHAPTER 3

GROWTH AND CHARACTERIZATION OF THE $W_{1.02}Se_2$ AND $W_{1.04}Se_2$ SINGLE CRYSTALS

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3.1 Introduction

The vapour transport technique described in the earlier chapter has been found to be a suitable tool by several workers[1-5] for growing single crystals of transition metal dichalcogenides. Author has used this technique to grow single crystals of $W_{1+x}Se_2$ where X = 0.02 and 0.04. After X-ray characterisation of the as grown crystals, thermoelectric measurements have been made to judge this semiconducting nature. The crystals have been also studied optically by reflectivity measurements at oblique angles of incidence. The optical constants at a few wavelengths have been determined . All these results have been reported and discussed in this chapter.

3.2 Experimental

To grow single crystals of $W_{1.02}Se_2$ and $W_{1.04}Se_2$, stoichiometric amounts of 99.999 % pure tungsten powder and 99.95 % pure selenium powder were sealed under a pressure of 10^{-5} torr in 2.5 cm bore X 24 cm long fused quartz ampoules. The total charge used in each experiment was about 10 to 15 gms.

Prior to the introduction of the elements, the quartz ampoules were thoroughly cleaned, etched and vacuum backed. The free flowing shining polycrystalline material required for the growth of single crystals of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ was prepared in the manner described in Chapter 2.

3.2.1 Crystal Growth

For growth of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ the polycrystalline powder prepared above was distributed along the entire length of an ampoule, (2.5 cm bore x 24 cm long), which was then kept in the furnace. The furnace temperature was increased slowly to the required final temperature for growth. The growth conditions for both the composition is listed in Table 3.1.

In both the cases, the crystals obtained were black, opaque and plate-like with C-axis normal to the plane of the plates. All of them grew vertically over the distributed charge inside the ampoule. The dimensions of the largest size crystals of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ [Fig. 3.1(a) and Fig. 3.1(b)]

Table 3.1

Growth Conditions employed to prepare single crystals of $W_{1.02}Se_2$ and $W_{1.04}Se_2$

Crystal	Reaction temperature ^oC	Growth temperature ^oC	Growth time hours
$W_{1.02}Se_2$	800	750	72
$W_{1.04}Se_2$	975	950	212

was found to be of the order of 8 mm x 5 mm x 0.25 mm and 5 mm x 5 mm x 0.20 mm respectively.

3.2.2 Structure

$W_{1.02}Se_2$ and $W_{1.04}Se_2$ crystallises in a layered structure. The space group of these crystals is $P6_3/mmC$ and the crystal system for these structures is a trigonal prism. The metal atom at the centre of the prism is co-ordinated with six selenium atoms at the corners. A layer is composed of alternatively occupied prisms placed side by side and no strong bond exists across the gap between the layers while only long range Van der Waals forces hold atomic sandwitches together.

3.2.3 Lattice Parameter Determination

The X-ray diffractometer traces were used to determine the unit cell dimensions and are depicted in Figure 3.2. The values of 'a' and 'c' parameters obtained from the analysis of X-ray diffractometer traces are given in Table 3.2.

Table 3.2

Lattice parameters of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ single crystals

Crystal	c Å	a Å
$W_{1.02}Se_2$	12.9769 ± 0.01	3.2922 ± 0.001
$W_{1.04}Se_2$	12.9768 ± 0.00	3.2819 ± 0.002

3.2.4 Composition

The composition of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ crystals was studied by EDAX. The compositions as determined from EDAX are given in Table 3.3.

3.2.5 Thermoelectric Measurements

Seeback coefficients were measured for the two compositions at elevated temperatures by employing standard techniques[6]. A thermal gradient was imposed across the sample by placing it between two nichrome wound heaters. Chromel-Alumel (40 SWG) thermocouples were located immediately behind the copper foil strips which contacted the sample. The copper foil contacts were used as voltage probes. The entire apparatus was mounted in an evacuated glass chamber at a pressure less than 10^{-5} torr. The Seeback coefficient was measured from 46°C to 300°C and its variation with temperature for the two compositions is shown in Figure 3.3.

3.2.6 Optical Constants Determination

The determination of optical constants

Table 3.3

Weight percentage of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ single crystals obtained by EDAX

Crystal	Weight % of element present	
	W	Se
$W_{1.02}Se_2$	54.26	45.74
$W_{1.04}Se_2$	54.80	45.20

by the method of reflectivity measurements is normally employed for the substances which have got high absorptivity. The various reflectivities which can be determined experimentally are P R_p, the reflectivity corresponding to plane polarized radiation with its plane of polarization parallel to the plane of incidence, R_s, the one corresponding to plane polarized radiation with its plane perpendicular to the plane of incidence, R_p/R_s, the ratio of these reflectivities or $1/2(R_p+R_s)$, the reflectivity of unpolarized radiation. From these reflectivities any two measurements at non-normal incidence are sufficient to obtain the optical constants, Humpreys-Owen [7] have discussed the various methods that can be employed to determine the optical constants. Of all these methods, the "R_p/R_s" method has got some special advantage as it eliminates the measurement of absolute values of reflectivity. Avery[8] first proposed this method and discussed its advantages over the other methods. This method in principle, measures $p^2 = R_p/R_s$ at two angles of incidence θ_1 and θ_2. Here $p^2(\theta_1) = F(n, k, \theta_1)$ and $p^2(\theta_2) = F(n, k, \theta_2)$, where P_1 is the appropriate Fresnel function. The simultaneous solution of these equations then yield (n,k) pairs. As

the analytic solution of these functions are difficult they have solved graphically (Avery).

Greenaway and Harbeke[9] have analysed Freshel's equation for anisotropic materials and derived the reflectivity equation. The method of R_p/R_s was employed to study the optical properties of graphite. In the present study this method has been employed for the determination of optical constant of $W_{1.02}Se_2$ single crystals at few wavelengths.

A spectrophotometer has been improvised from an ordinary spectrometer by attaching a monochromator consisting of a Hg-vapour lamp, appropriate filters and a lens system,on the movable arm and a photodetector on the fixed arm. The prism table was replaced by a goniometer meant for holding the crystals. A polaroid on a rotatable mount was attached on the exit slit of the monochromator with rotation axis along the beam direction (Fig. 3.4).

The expressions for R_p and R_s have been given by Goswami and Rao[10]. Curves relating (R_p/R_s) and k for the values of K upto 6 were computer

generated for various values of n(n = 1, 1.5....., 5.0). Using the experimentally determined values (R_p/R_s) for a given θ and λ a the possible values of (n,k) pairs were evaluated from these curves. For a given λ such (n,k) pairs were determined at various θ values. The true values of n and k were then determined from the common intersection of the plot of n versus k (Fig.3.5).

The absorption coefficient, α were calculated from the experimentally determined k values using the relation.

$$\alpha = \frac{4\pi k}{\lambda}$$

The functional relationship between the absorption coefficient to the photon energy for various types of transmission are given by Lee et al[11]. For direct allowed transmissions, $\alpha \gtrsim (h\nu - E_g)$ where E_g is the optical energy band gap. A plot of α^2 versus $h\nu$ should be a straight line intercepting $h\nu$ axis at $(E_g)_{opt}$ value.[10,12,13]

The Table 3.4 shows the values of n, k and α for $W_{1.02}Se_2$ single crystals at different wavelengths. Figure 3.6 shows a typical plots of α^2 Vs $h\nu$. The $(E_g)_{opt.}$ value has been determined from the units in the plot of X- intercept.

3.2.7 Microstructures

The surface microstructures observed on the growing faces of a typical $W_{1.02}Se_2$ crystal is shown in Fig. 3.7. A hexagonal spiral emerging from screw dislocation is clearlysee seen in the picture.

3.3 Conclusions

1. Single crystals of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ have been grown by direct vapour transport technique in which crystals are ought to be free from contamination of any transporting agent.

2. The positive Seeback coefficient implies that the crystals under investigation are p-type semiconductors.

Table 3.4

Optical constant of $W_{1.02}Se_2$ single crystals

λ in Å	n	k	$\alpha \times 10^8$ m^{-1}
6328	4.48	1.52	0.30
5461	1.85	2.88	0.66
4050	1.77	3.82	1.17

3. The optical constants for $W_{1.02}Se_2$ by R_p/R_s method of reflectivity has been obtained and also the $(E_g)_{opt.}$ has been determined.

4. The presence of growth spirals on the growing faces of $W_{1.02}Se_2$ single crystal suggests that growth involves a screw dislocation mechanism.

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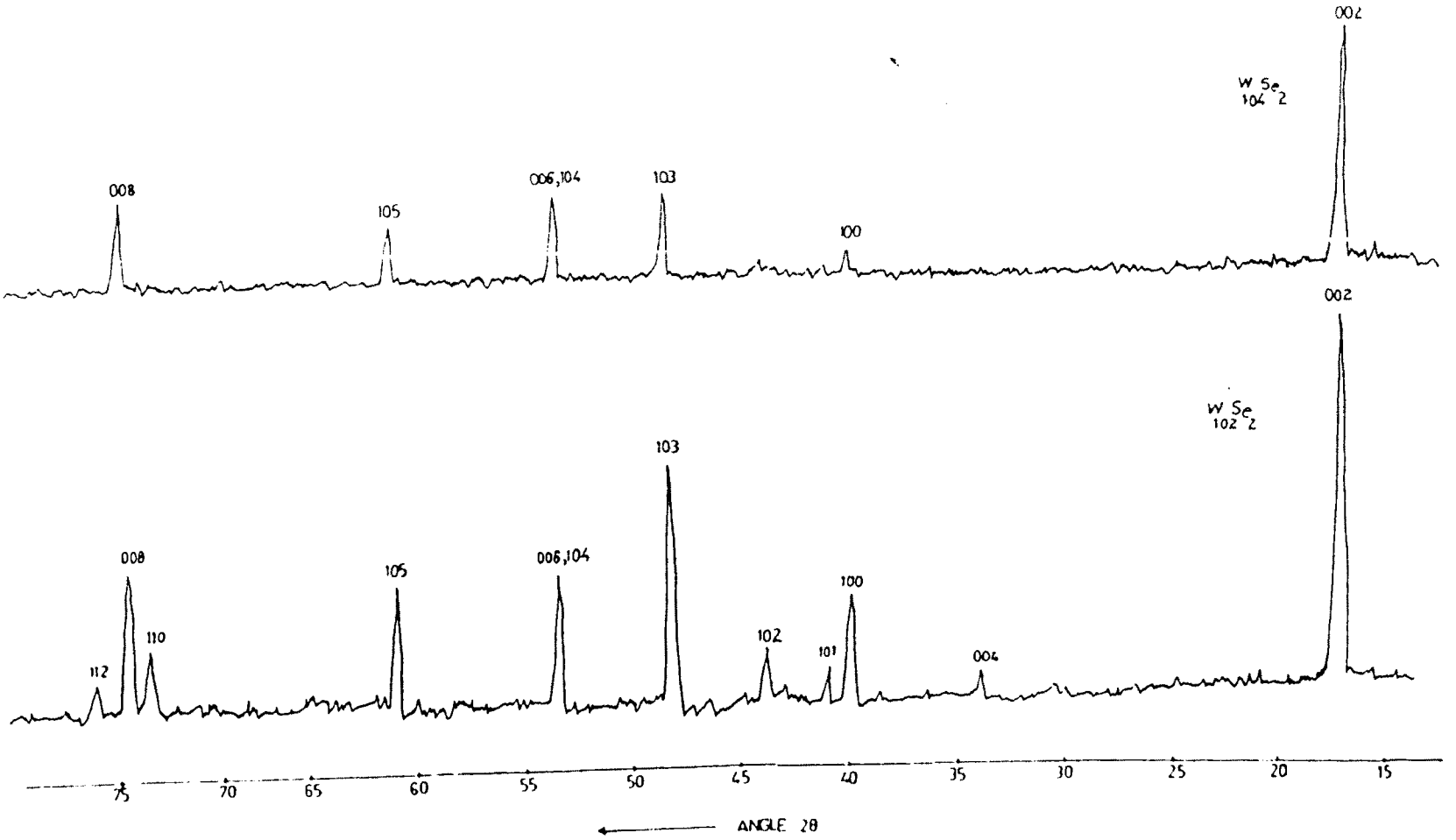

Fig. 3.2 X-ray diffractometer traces of $W_{1.02}Se_2$ and $W_{1.04}Se_2$ single crystals.

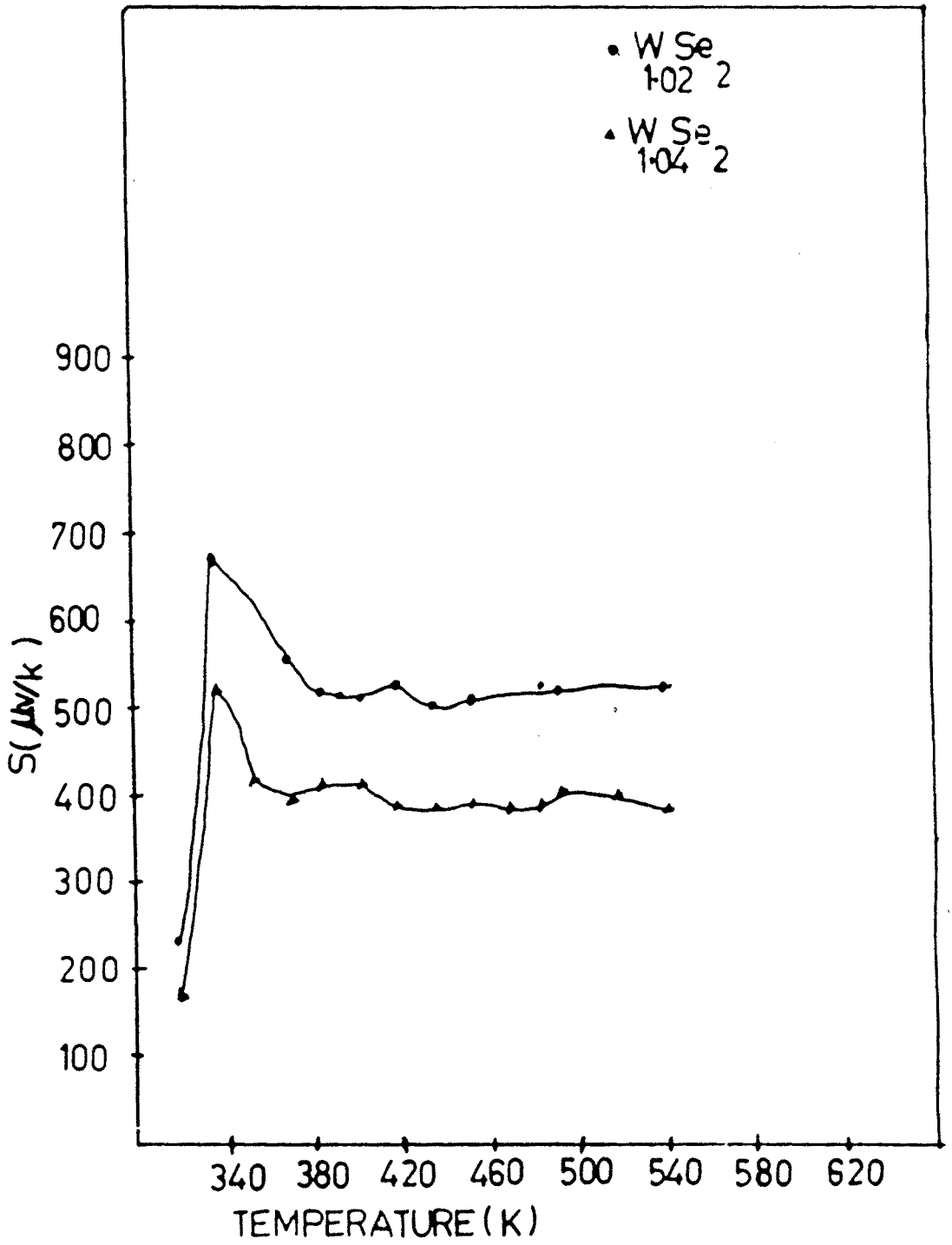

Fig. 3.3 Variation of Seeback coefficient with temperature for $W_{1.02}Se_2$ and $W_{1.04}Se_2$ single crystals.

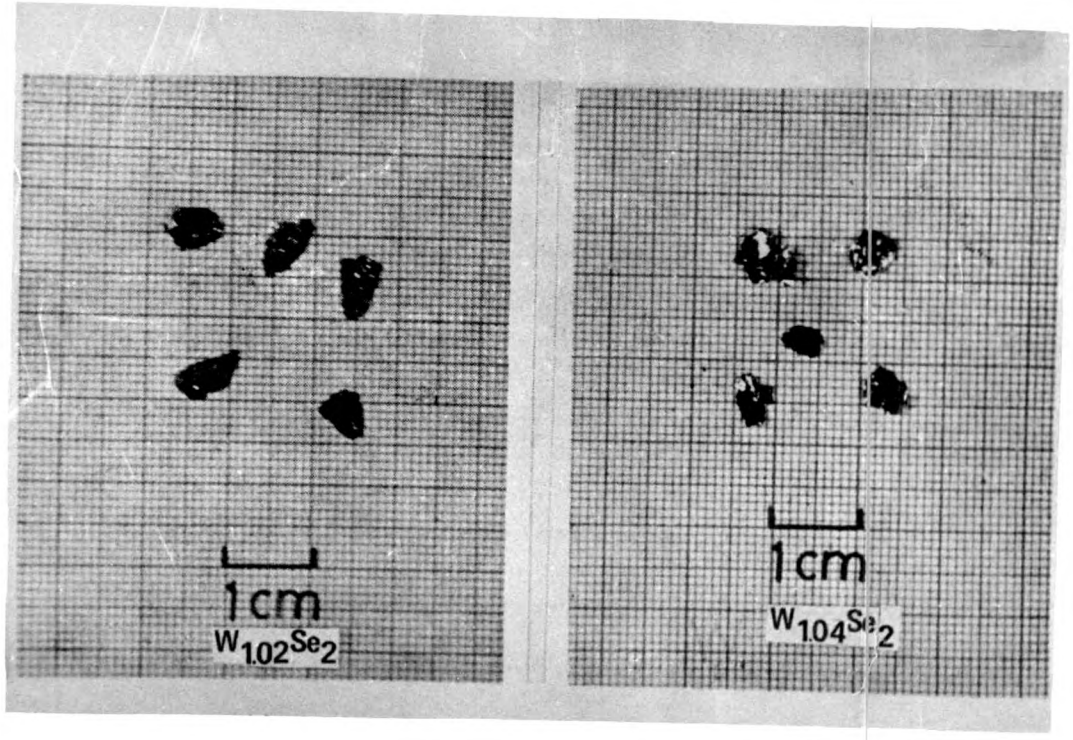

Fig. 3.1(a) and 3.1(b) Typical crystal sizes for the $W_{1.02}Se_2$ and $W_{1.04}Se_2$ single crystals respectively.

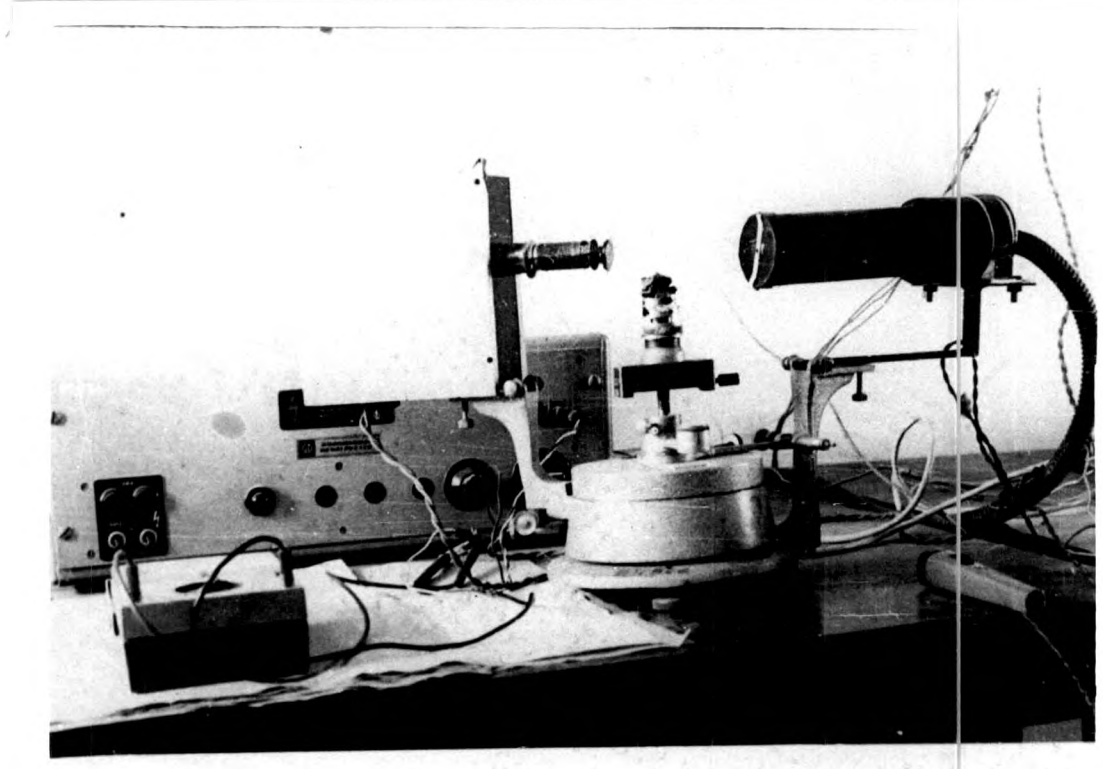

Fig. 3.4 Experimental set up for the determination of optical constants.

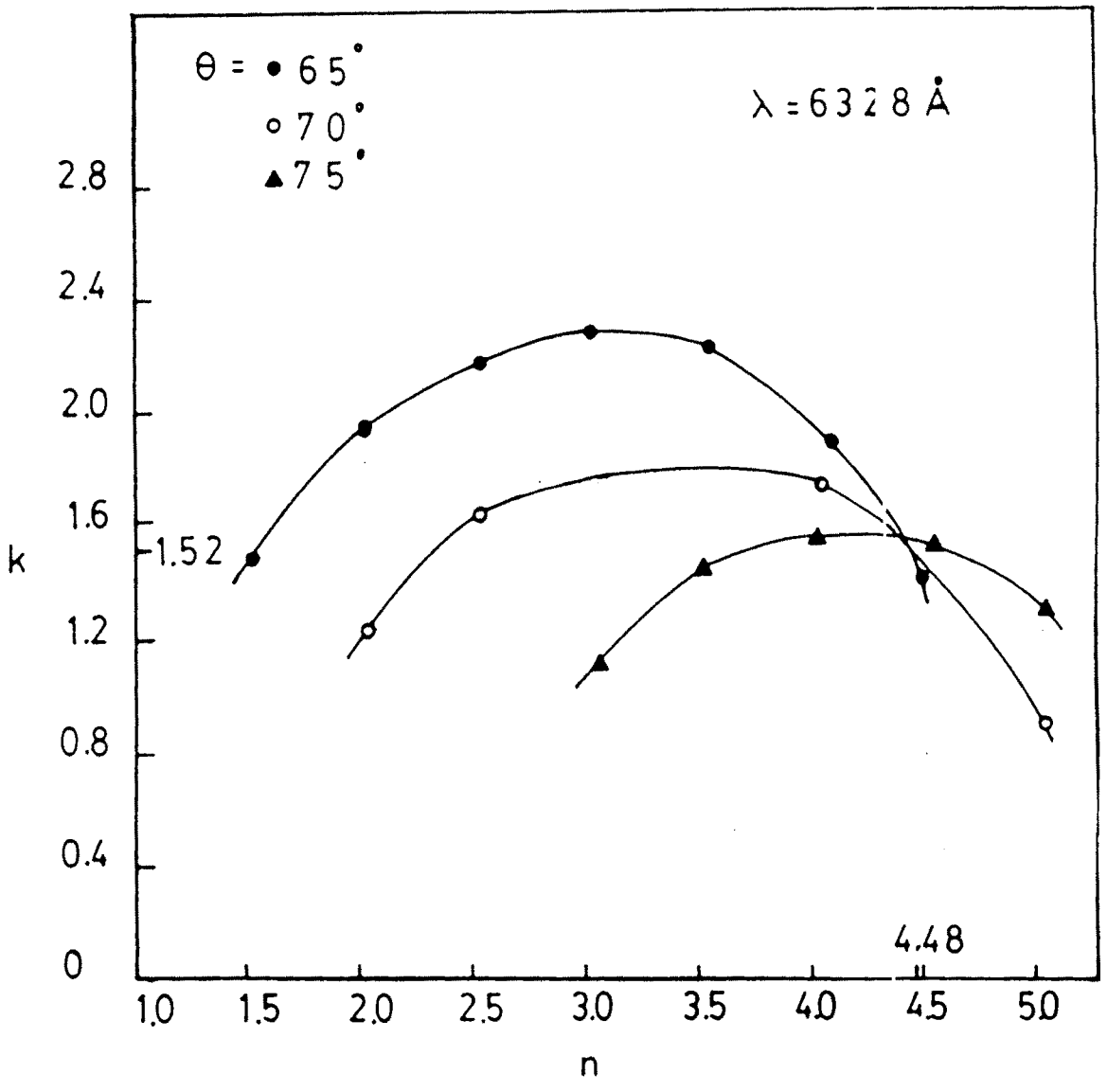

Fig. 3.5 Plot of n versus k for a typical wavelength.

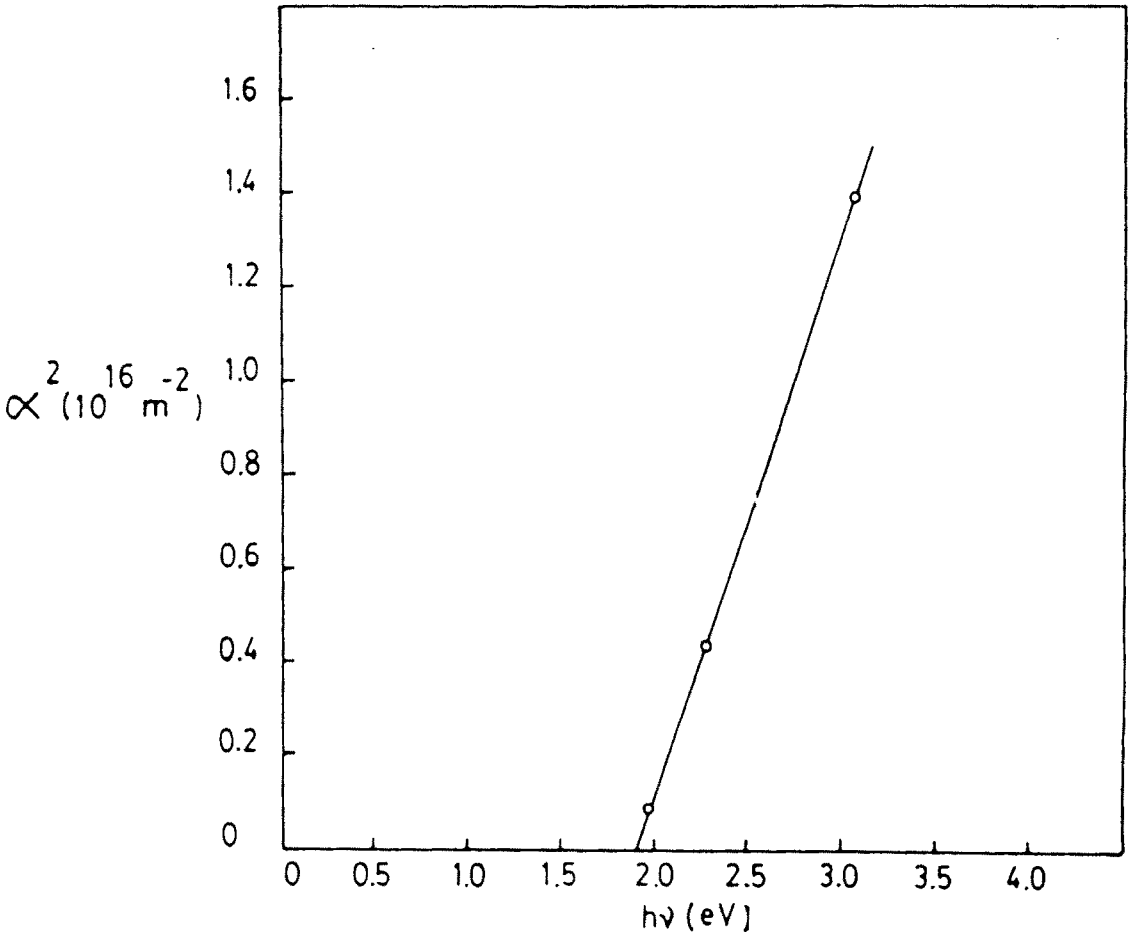

Fig. 3.6 Plot of α^2 versus hν

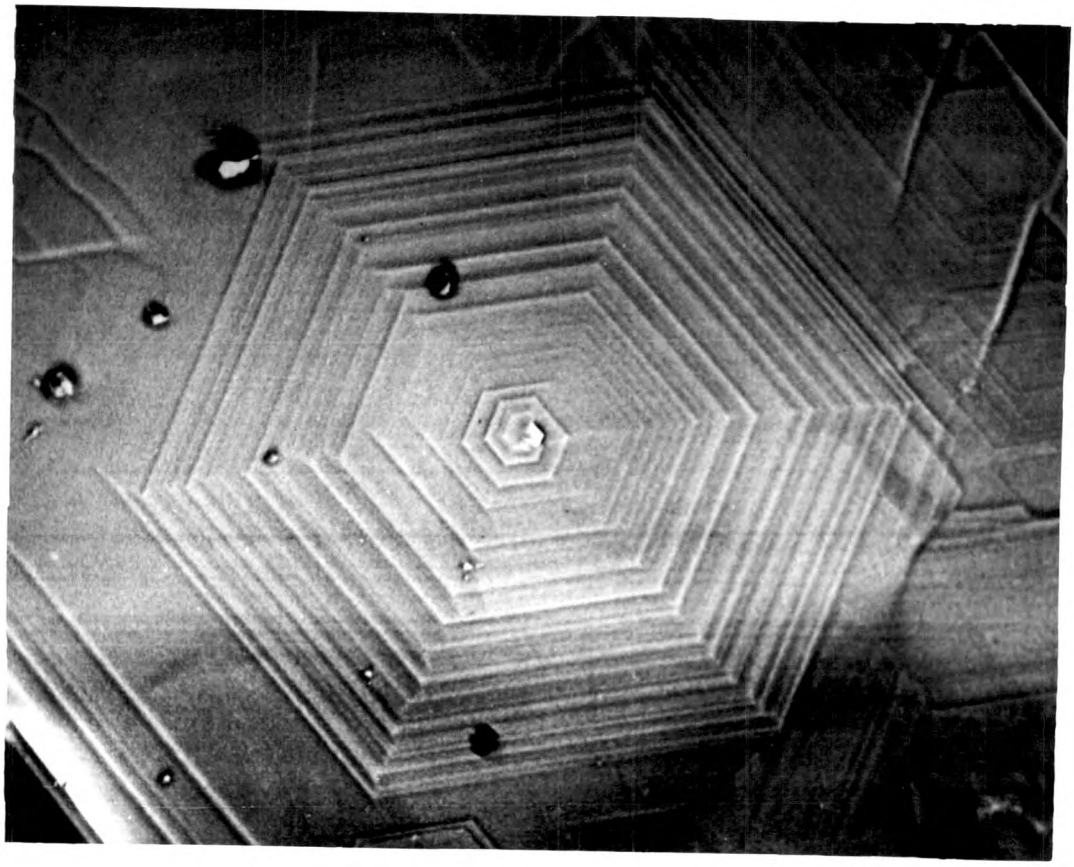

Fig. 3.7 Surface microstructure observed on the as grown crystals of $W_{1.02}Se_2$