CHAPTER III

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EFFECT OF SUBSTRATE TEMPERATURE ON THE PROPERTIES OF SPRAYED MOLYBDENUM SULPHIDE THIN FILMS

3.1 Introduction

The structural, electrical and optical properties of the transition metal dichalcogenides like MoS_2, $MoSe_2$ and WSe_2, in the form of single crystals have been studied[1,2] during the last decade. However, not much information is available on the study of thin films of these compounds. Very little attention is paid towards the study of thin films of molybdenum sulphide prepared by spray pyrolysis technique. In the spray pyrolysis technique the preparative parameters like substrate temperature, spray rate, height of the nozzle from the substrate are found to affect the properties of the films. In the present work the effect of substrate temperature on the electrical and optical properties of molybdenum sulphide thin films is studied.

Molybdenum sulphide films were prepared by pyrolytic decomposition of a mixture of aqueous solutions of ammonium heptamolybdate and thiourea. The films were deposited on non conducting glass substrates of the size 3.9 cm x 0.9 cm. The experimental set-up used for deposition of films is described in Chapter II (2.2.1). The substrate temperature was varied and controlled from 250°C to 400°C in the intervals of 25°C with the help of temperature controller (Aplab 9601). The films prepared at various substrate temperatures are denoted by S_{250}, S_{275}, S_{300}, S_{325}, S_{350} and S_{400}, where the subscript denotes the substrate temperature.

3.2.1 Experimental Set-up for Conductivity Measurements :

The schematic diagram of the experimental set-up used to measure the dark conductivity of the films is shown in fig.3.1. Two heating elements (Toni 30 W) fixed parallel with the help of two brass plates of the same size give uniform temperature. Press contacts to the films were made with copper strips. Silver paint used provides good contact. In order to avoid the contact between brass plates and film a mica sheet is introduced in between them. Radiation losses are reduced by using the cover of asbestoss sheet. The chromel-Alumel thermocouple measures the temperature of the sample at the center. The transistorised electronically regulated power supply was used to pass the current through the sample. The potential drop and current through the sample was measured with the help of digital multimeter (pla-Dm-14-B) and Aplab FET nanoammeter (TEM - 13) respectively.

3.2.2 Thermoelectric Power Measurements

The experimental arrangement used for measurement of the thermoelectric power (α') is shown in fig.3.2. Two mini-heaters (H_1 & H_2) having different heating capacities were used for heating the sample. A brass block serve as a sample holder. The typical shape of the block provides uniform temperature gradient along the length of the sample holder. The films (2.3 cm x 0.5 cm) deposited on glass substrates were used for thermoelectric power measurements. Press contacts were made to the sample with copper strips and silver paint was used for perfect contact. Two chromel-Alumel thermocouple, one for measuring temperature gradient and another for measuring mean temperature of the sample, were used. Mean temperature was measured with pla digital voltmeter (DPM - 10). The thermoelectric voltage was measured by VASAVI digital microvoltmeter (VMV-15).

3.2.3 Optical Absorption :

The optical absorption of the molybdenum sulphide films deposited on glass substrate were studied with the help of monochromator spekol [Carl Zeiss Jena].

3.3 Results and Discussion :

The films prepared are uniform and adhere tightly to the substrate. However, the nature of the films changes with substrate temperature. The films prepared at higher substrate temperature are thinner which may be due to reevaporation of the deposited material. At lower substrate temperature films are bluish green and the colour of the films changes to gray at higher substrate temperature. It is observed that the films prepared at 300°C substrate temperature are more uniform in nature.

The thickness of the films formed at different substrate temperatures was measured and found to decrease with increase in substrate temperature. The variation of film thickness with substrate temperature is shown in fig.3.3. The decrease in thickness at higher substrate temperature may be due to the higher evaporation rates at that temperature.

3.3.1 Dark Conductivity :

The dark conductivity σ was measured for all the samples in the temperature range 300 k to 550 k. The conductivity of a semiconductor is given by

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \qquad \ldots \quad 3.1$$

where the symbols have their usual meanings. The plots of log σ versus $\frac{1}{T}$ for typical samples denoted by S_{250}, S_{300} and S_{350} are shown in fig.(3.4) to (3.6). The plots show that there are two different regions corresponding to high and low temperatures. The activation energies in the high and low temperature regions are determined by employing the relation (3.1)[7]. The activation energies in both the regions are calculated and given in table III below :

TABLE III

Activation energy (eV) in high and low temperature regions

Temperature region	Films prepared at different substrate temperatures					
	S_{250}	S_{275}	S_{300}	S_{325}	S_{350}	S_{400}
high	0.84	0.8	0.9	0.7	0.52	-
low	0.059	0.023	0.042	0.033	0.03	-

The activation energy in the high temperature region decreases with increase in substrate temperature. However, there is no systematic variation in activation energies at low temperature regions. In case of the film prepared at 400°C substrate temperature there are no two distinct regions corresponding to low and high temperatures, hence the activation energy in high and low temperature regions is not listed in table III. It is also observed that the conductivity increases with increase in substrate temperature (fig.3.7). The lower conductivities at low substrate temperatures may be due to incomplete reactions of the initial ingradients and poor crystallinity of the films.

3.3.2 Thermoelectric Power :

Thermoelectric power measurements were made as a function of temperature in the temperature range 300 k to 550 k. The polarity of the thermoelectric voltage developed in the films determines the type of the semiconductor. It is found that the hot end of the film is positive which reveals that films are of n-type. This is in agreement with the results reported earlier[3-6]. Fig.3.8 shows the variation of the thermoelectric power as a function of the mean temperature. Thermoelectric power increases with increase in temperature. This is attributed to an increase in electron concentration with rise in temperature. Thermoelectric power is higher for the films prepared at higher substrate temperature and is hold responsible for better crystallinity of the films.

3.3.3 Optical Absorption :

The optical absorption of the films was studied by varying the wavelength between 770 nm to 400 nm and is reported in fig. 3.9. The films having very small thickness (.1 μm) was used for the optical absorption study. It is observed that absorption coefficient (α) increases with increase in substrate temperature, except at substrate temperature 400°C. The better crystallinity accounts for higher values of α [8]. The absorption data are analysed by plotting the $(\alpha h\nu)^2$ versus $h\nu$ (fig. 3.10). The plots are linear indicating that the transitions are direct and allowed[4,6]. The values of the band gap are determined by the extrapolation of the graph on energy axis. The values of the band gap energy are found to be 1.9 eV. The results are in fair agreement with the results reported by others near the direct band gap[9-11].

Figure Captions

3.1 Schematic diagram of conductivity measurement unit.

3.2 Schematic diagram of Thermoelectric Power measurement unit.

3.3 Variation of film thickness with substrate temperature.

3.4 Plot of log σ versus 1/T for sample S_{250}

3.5 Plot of log σ versus 1/T for sample S_{300}

3.6 Plot of log σ versus 1/T for sample S_{350}

3.7 Variation of log σ versus 1/T for samples S_{250}, S_{300} and S_{400} .

3.8 Plots of thermoelectric power as a function of mean temperature for typical samples.

3.9 Variation of absorption coefficient as a function of wavelength.

3.10 Plot of $(\alpha h\nu)^2$ versus $h\nu$ for typical samples.

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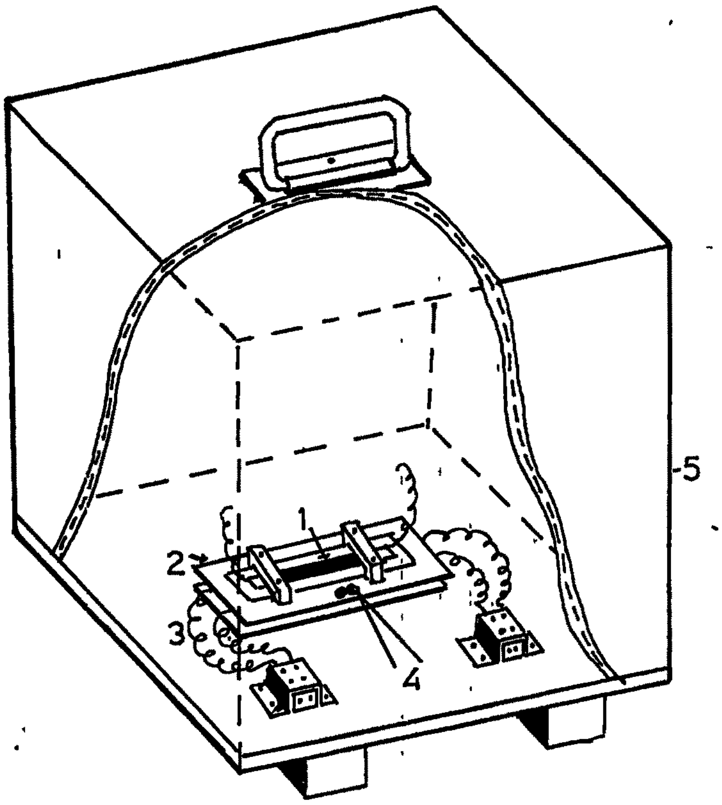


Fig. 3.1

1 - Sample

2 - brass strips

3 - Heater

4 - Thermocouple

5 - Shield

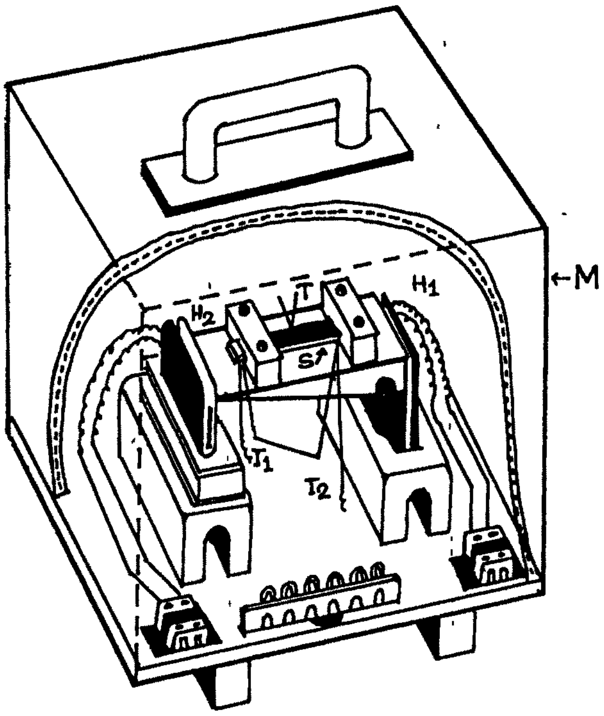


Fig. 3·2 Schematic diagram of Thermoelectric power unit. S—sample, M — metal shield, T — mean temperature thermocouple, T_1, T_2 — Differential thermocouple junctions and H_1, H_2 — heaters

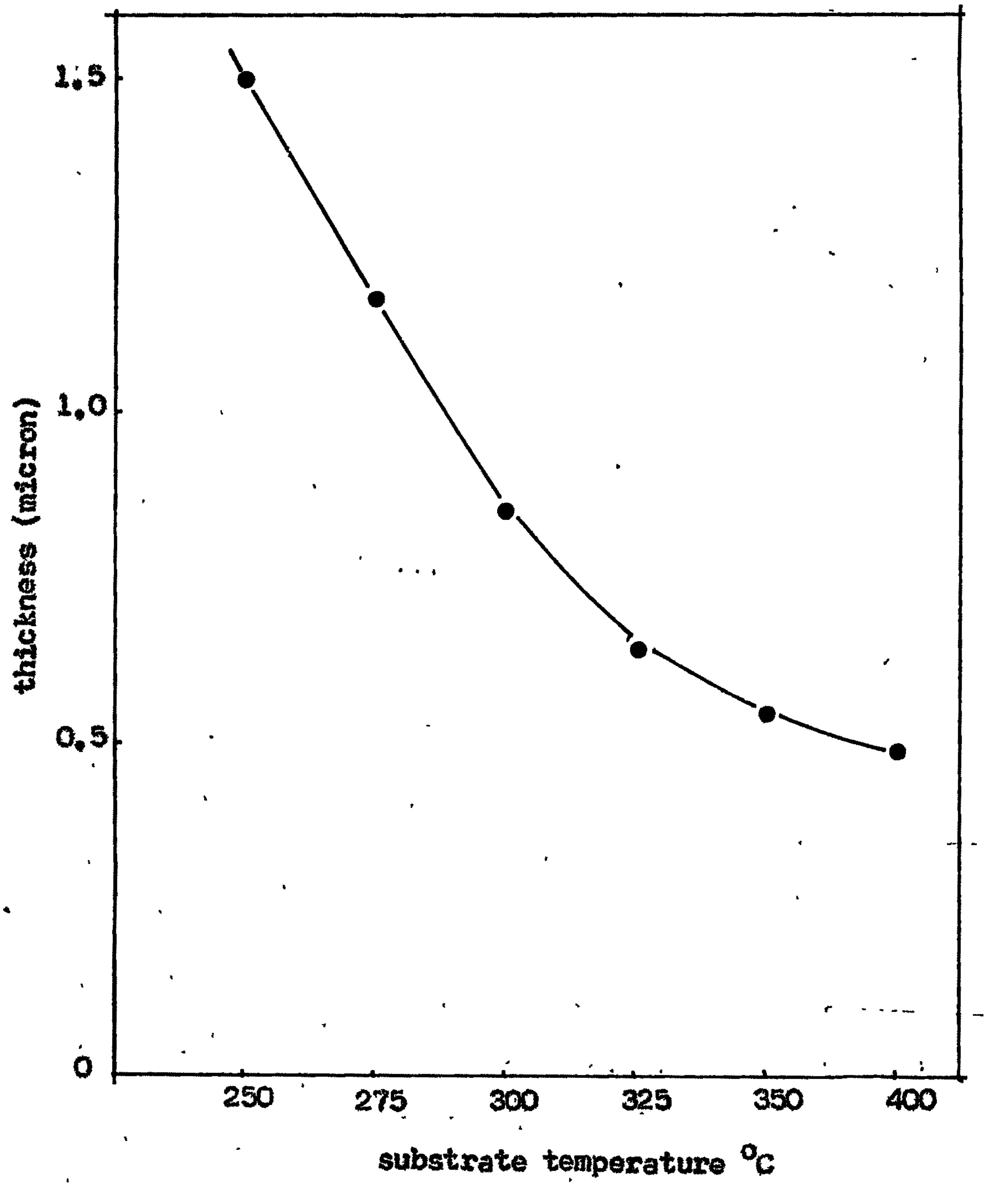

thickness (micron)
1.5
1.0
0.5
0
250
275
300
325
350
400
substrate temperature °C

Fig. 3.3

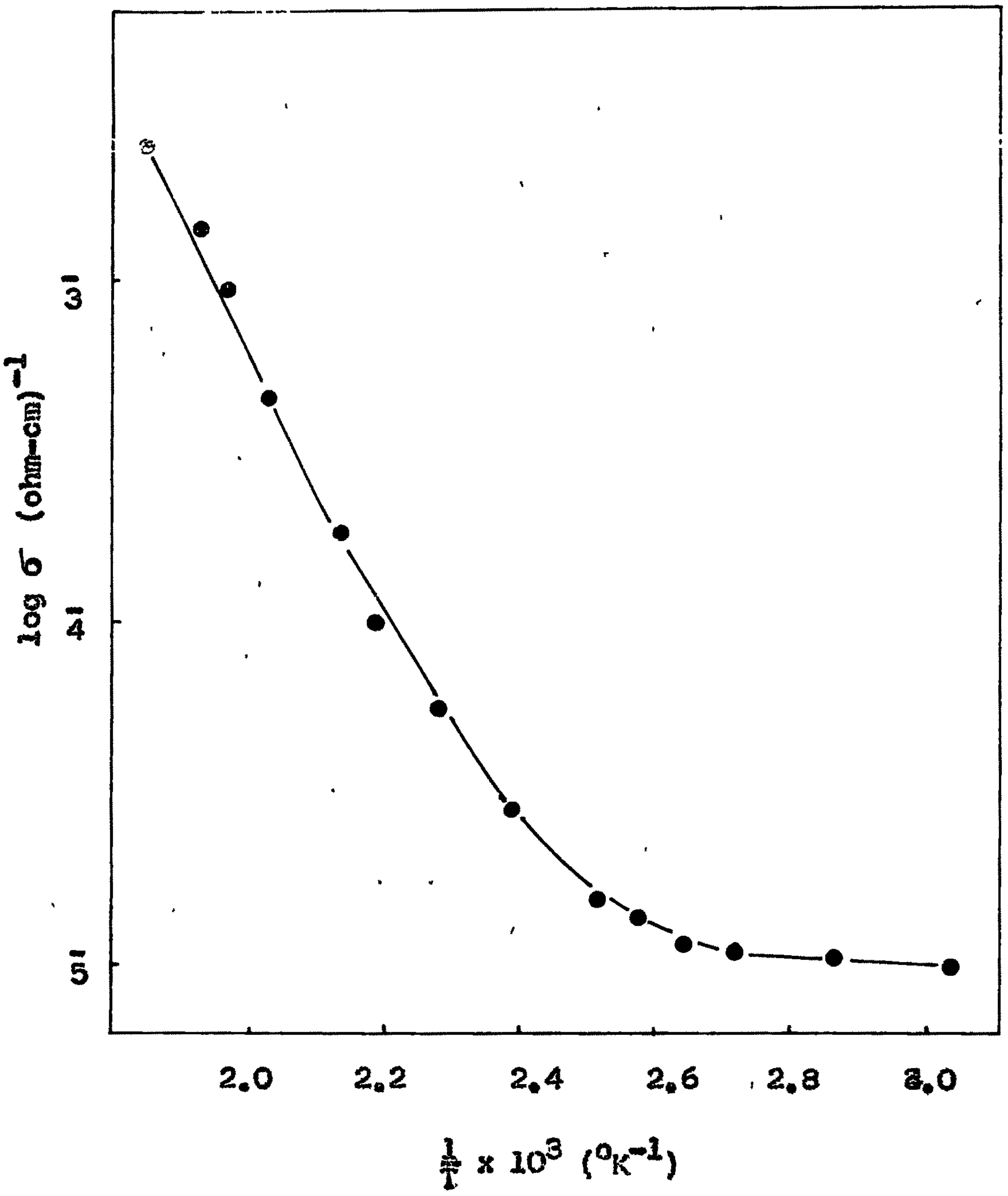


Fig.3.4

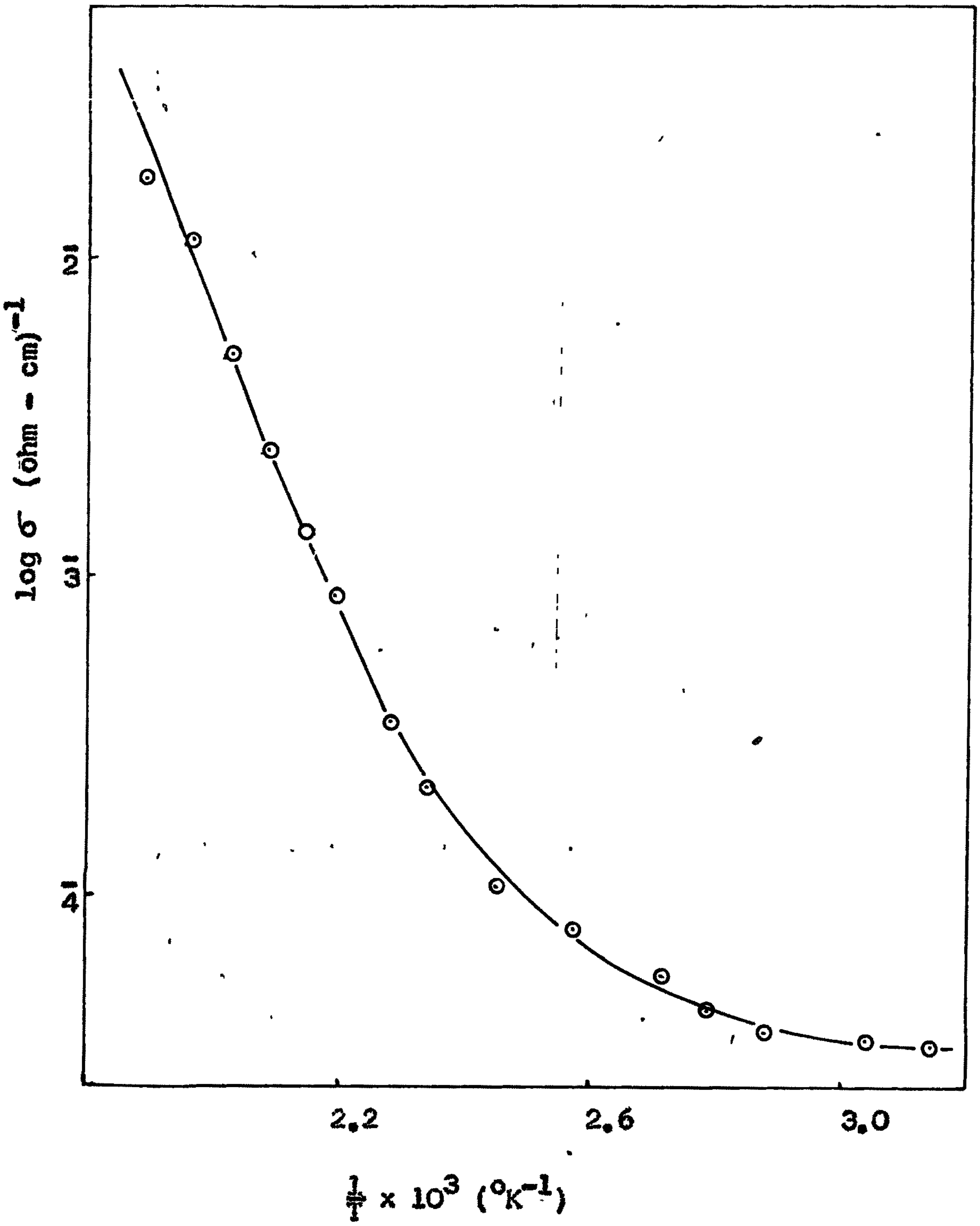


Fig. 3.5

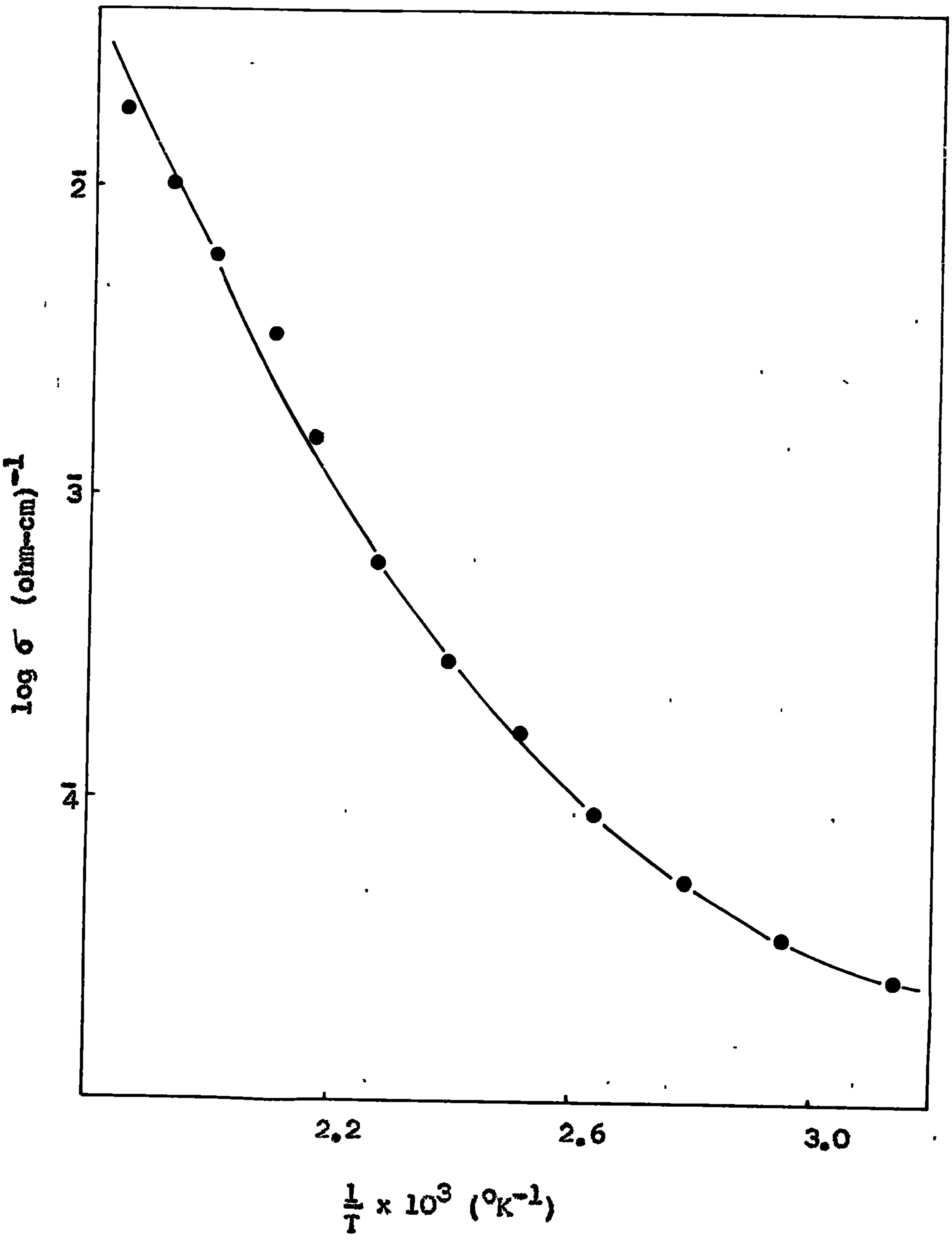


Fig. 3.6

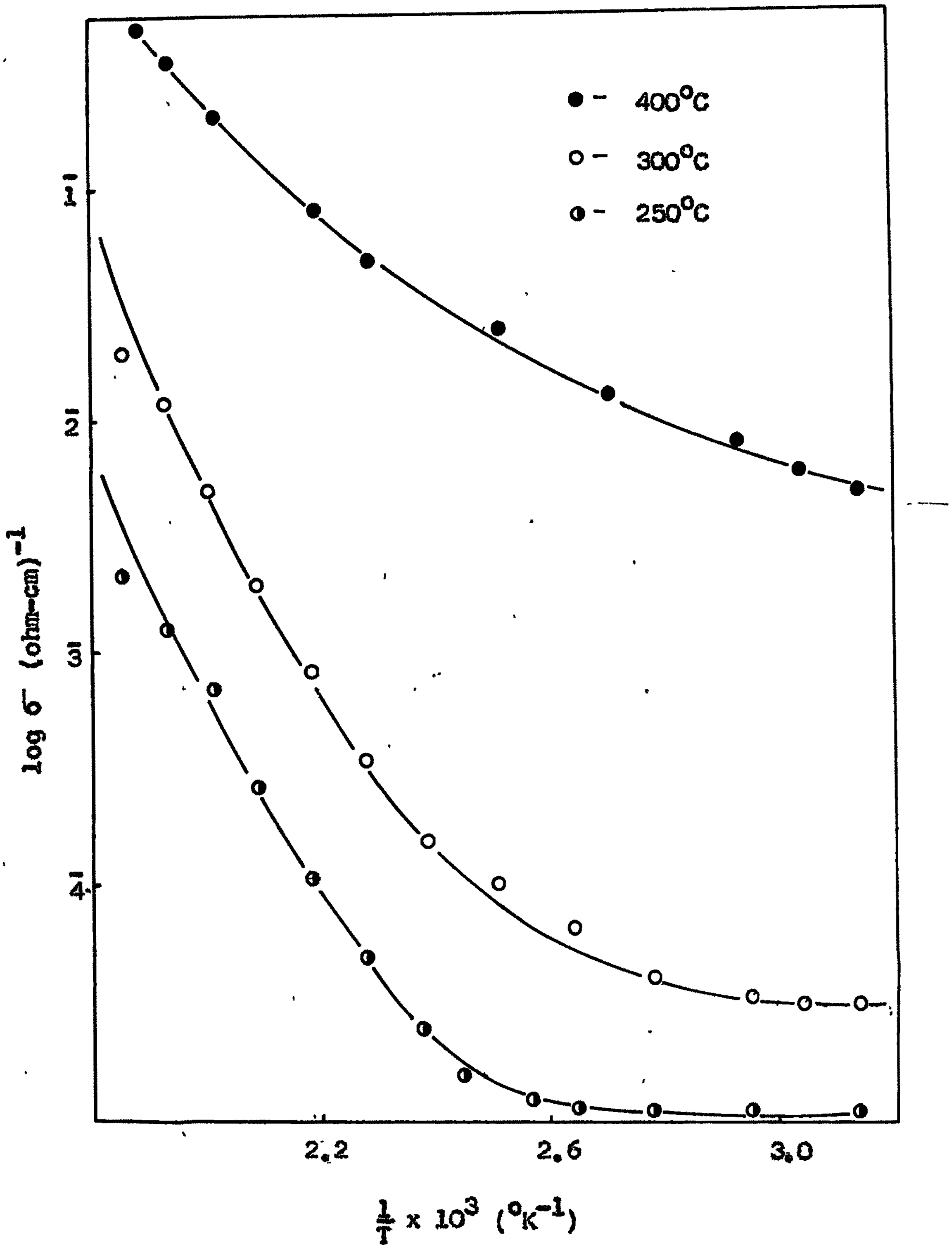


Fig. 3.7

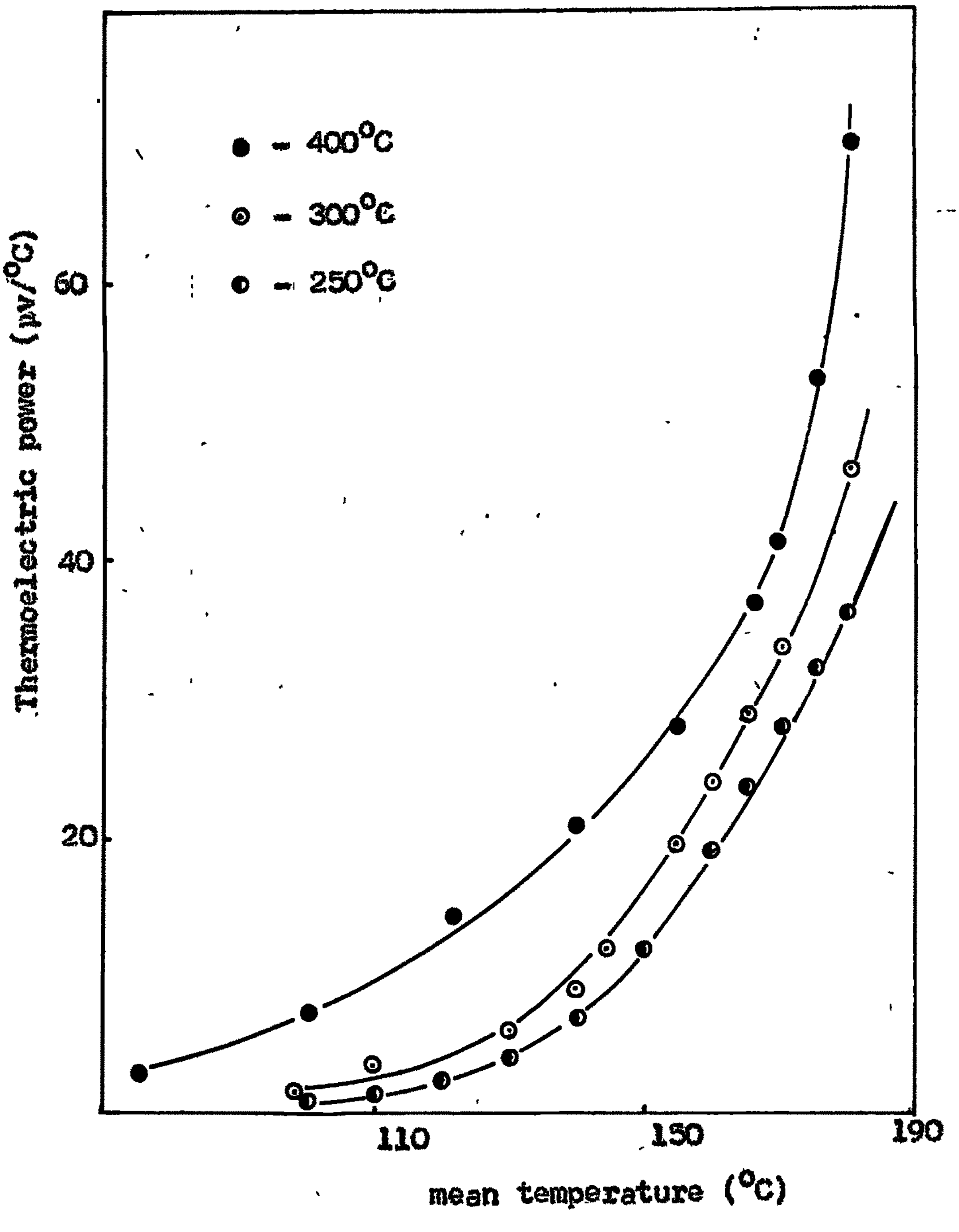
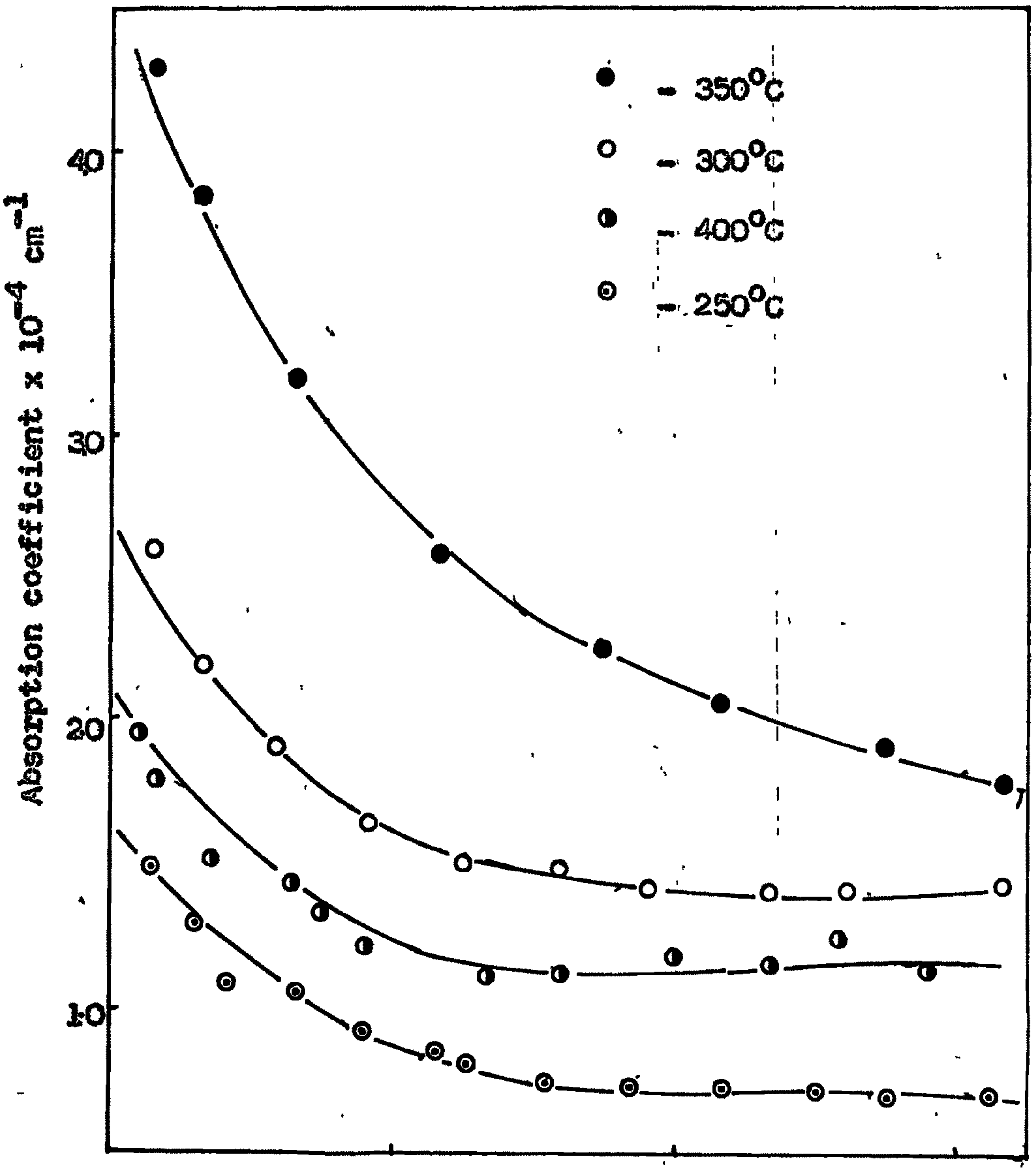

● – 400°C
⊙ – 300°C
◐ – 250°C
Thermoelectric power (μv/°C)
60
40
20
110
150
190
mean temperature (°C)

Fig. 3.8



● - 350°C
○ - 300°C
◐ - 400°C
⊙ - 250°C
40
30
20
10
500
600
700
Absorption coefficient x 10^{-4} cm^{-1}
wavelength (nm)

Fig. 3.9

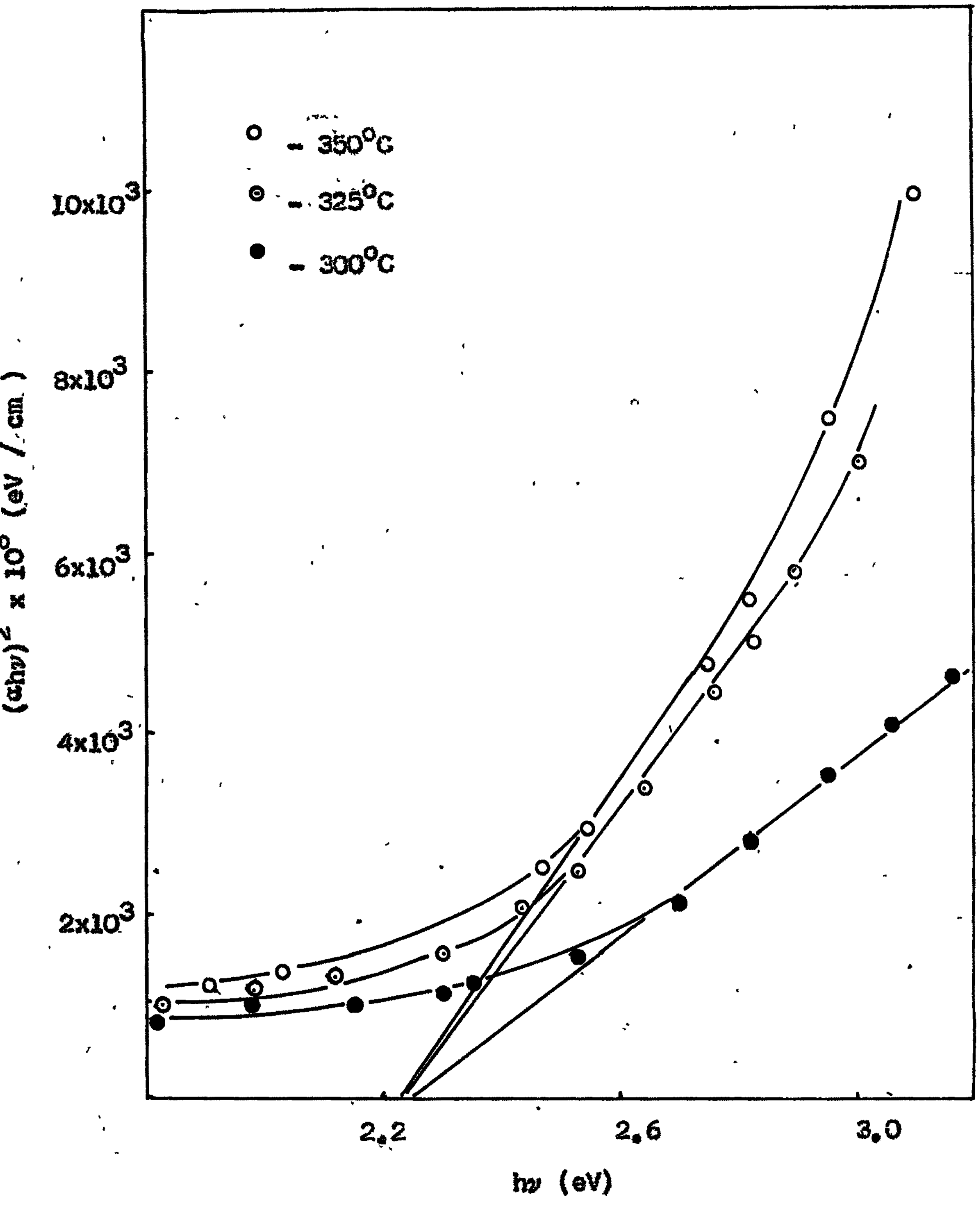

○ - 350°C
⊙ - 325°C
● - 300°C
10x10^3
8x10^3
6x10^3
4x10^3
2x10^3
$(\alpha h\nu)^2 \times 10^8$ (eV /cm.)^2
2.2
2.6
3.0
hν (eV)

Fig. 3.10