

THE PREPARATION AND PROPERTIES OF  
NEAR-STOICHIOMETRIC, NON-STRATIFIED, THIN FILMS  
OF INDIUM ANTIMONIDE

by

DAVID HENRY HUEBNER

B. S., Kansas State University, 1958

---

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

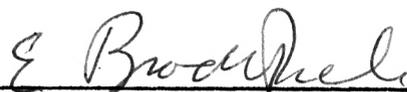
MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1963

Approved by:

  
Major Professor

LD  
2668  
T4  
1963  
H84  
c.2  
Document

TABLE OF CONTENTS

INTRODUCTION . . . . . 1

THEORY . . . . . 2

    Vapor Pressure and Raoult's Law . . . . . 2

    Hall Coefficient, Conductivity and Mobility . . . . . 6

EXPERIMENTAL PROCEDURE . . . . . 7

    The Vacuum Evaporator . . . . . 7

    The Substrates . . . . . 8

    Substrate Cleaning . . . . . 8

    Vapor Source . . . . . 11

    Thickness Measurement . . . . . 11

    Electrical Measurements . . . . . 12

    Some Details of the Experiment . . . . . 14

RESULTS AND DISCUSSION . . . . . 16

CONCLUSION . . . . . 36

ACKNOWLEDGMENT . . . . . 37

REFERENCES . . . . . 38

## INTRODUCTION

Thin films have been widely used to explore many properties of crystalline materials. The methods of producing thin films include electrodeposition, chemical attack, and growth from the vapor phase (13). Growth from the vapor phase, which includes vacuum deposition, cathodic sputtering and gaseous reduction, is the most widely used method.

Elemental semiconducting thin films have been studied extensively and they can be produced without much difficulty. Compound semiconducting thin films sometimes present difficulties with stoichiometry because of the difference in vapor pressures of the constituent elements. Indium antimonide (InSb) is such a semiconducting compound.

InSb is of great interest because it can be obtained in high purity, it is easy to prepare in bulk, and because of its high mobility, low effective mass and small energy gap. It has spherical energy surfaces, and therefore yields to rather simple theoretical treatment. InSb is the most extensively studied semiconducting compound. Whelan (7) states "The conductivity and Hall effect of InSb above its melting point are characteristic of liquid metals. This is consistent with thermodynamic arguments that the compound exists only as a solid and that its melt has the properties of an ideal solution."

Some specific methods of surmounting the problem of different vapor pressures in producing InSb films include sputtering, sprinkling small amounts of InSb on a hot filament (11),

pressing molten InSb between optical flats (2), and evaporating from two boats at different temperatures onto a heated substrate (5, 6).

Senecal (15) evaporated a small charge in its entirety and then annealed the film to recombine the elements into InSb. This method gives evidence of layering.

The work described in this paper is an attempt to produce near-stoichiometric, non-stratified thin films of InSb by vacuum evaporation from a single vapor source, and to evaporate the films, once produced. Such a method of evaporation, if successful, should provide a quick, easily controlled method of producing thin InSb films.

## THEORY

### Vapor Pressure and Raoult's Law

Raoult's Law gives the relationship of vapor pressures, at a constant temperature, for an ideal solution; it can be stated mathematically for a binary solution as

$$P_A = P_A^{\circ} N_A \quad (1a)$$

$$P_B = P_B^{\circ} N_B \quad (1b)$$

where  $P_A^{\circ}$  and  $P_B^{\circ}$  are the vapor pressures at the given temperature of pure elements A and B, and  $N_A$  and  $N_B$  are their respective mole fractions in the liquid. Fig. 1 is a vapor pressure diagram of a binary solution that obeys Raoult's Law.

The evaporation rate is proportional to vapor pressure as

EXPLANATION OF PLATE I

Fig. 1. Vapor pressure diagram at a constant temperature for a binary solution that obeys Raoult's Law.

PLATE I

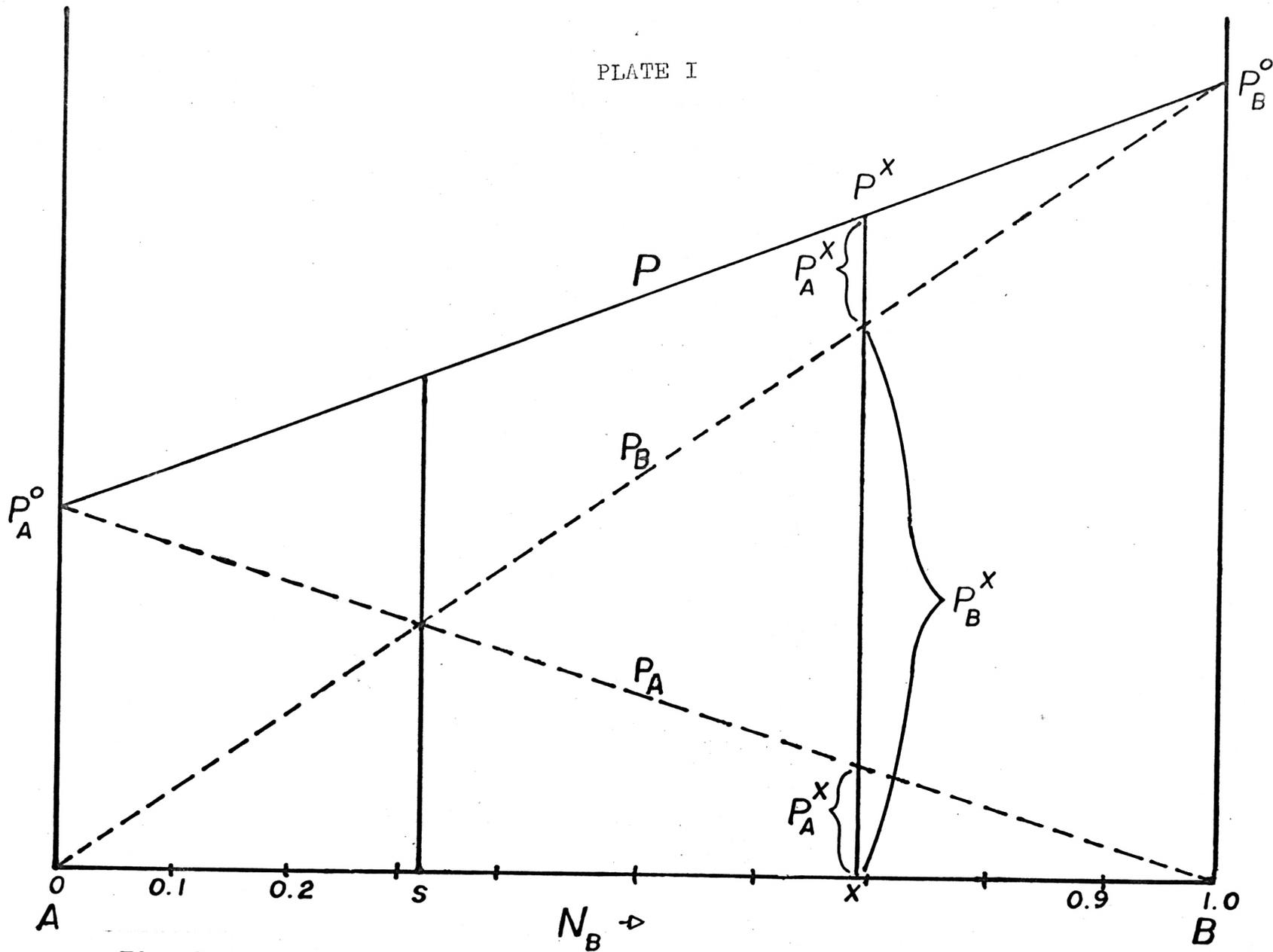


Fig. 1

given by Dushman (4)

$$\log W_A = 5.7660 + 0.5 \log M_A + \log P_A - \log T \quad (2)$$

where  $W_A$  is the rate of evaporation of A in grams per square cm per second, and  $P_A$  is the vapor pressure in microns. Thus for a binary solution at a high temperature, whose composition is such that each element has an equal vapor pressure, an equal number of moles of each element will be evaporated. This composition is represented in Fig. 1 by the point S.

Element B in Fig. 2 has a higher vapor pressure than element A, and a melt with a composition X will produce a vapor containing more B than A. Thus, evaporation will change the composition of the melt toward S. Even when the composition of the melt reaches S, it will continue to change toward a smaller  $N_B$ , even though more A than B is now being evaporated, until  $N_B = N_A (P_A^0/P_B^0)$ . At this point, the composition of the melt and the vapor will be the same and will remain constant. It may be seen from Fig. 1 that if  $N_B$  is close to 1.0, the composition of the melt will change rapidly, while as  $N_B$  moves toward smaller values, the rate of change becomes slower.

Suppose after a small part of the melt has been evaporated, the evaporation is stopped and an amount of compound AB is added to the melt equal in weight to the amount of material evaporated from the melt. If  $N_B$  before the evaporation was greater than S, more B will be evaporated than was added by the compound, and if  $N_B$  before the evaporation was less than S, less B will be evaporated than is added. In either case, the composition of the

melt will approach S.

If this process is repeated a sufficient number of times with equal amounts of A and B being added each time, composition S will be reached, such that the vapor will contain equal amounts of A and B. This method was used to produce all films discussed in this paper.

#### Hall Coefficient, Conductivity and Mobility\*

If charge flows in the x direction in an extended medium, and a magnetic field is applied in the z direction, then the electric field in the y direction can be written as

$$E = R_h j B \quad (3)$$

where  $R_h$  is the Hall coefficient and is defined by this equation,  $j$  is the current density and  $B$  is the magnetic induction.

The force experienced by a moving negative charge in a magnetic field is  $(\underline{B} \times \underline{v})e$ , where  $v$  is the velocity and  $e$  is the magnitude of the charge. If the charge is constrained to a medium, an electric field will be built up to oppose the force so that the charge will flow as before the magnetic field was applied. This condition can be written as

$$(\underline{B} \times \underline{v})e = \underline{E}e \quad (4)$$

If  $n$  is the number of charges

$$j = nev \quad (5)$$

---

\* This treatment is essentially that of Putley, Ref. 14.

and upon substitution of (4) and (5), (3) becomes

$$E = -(1/ne)Bj$$

or

$$R_h = -1/ne$$

The conductivity,  $\sigma$ , is

$$\sigma = j/E_x = neV_x/E_x = ne\mu$$

where  $\mu$  is the mobility. Thus

$$\sigma |R_h| = \mu \quad (6)$$

When  $\mu$  is computed from Eqn. 6 it is generally known as the Hall mobility. It is used in this paper as a figure of merit because it is sensitive to the dislocation density and to the concentration on ionized impurities. Hereafter, mobility will refer to the Hall mobility.

#### EXPERIMENTAL PROCEDURE

Glass substrates were cleaned and placed in a vacuum chamber. Thin films were deposited on the substrates by evaporation from a resistance-heated boat. The thickness of the films thus produced was determined, and electrical measurements were made as a function of temperature.

#### The Vacuum Evaporator

The evaporation chamber was a ten inch glass bell jar, 15 inches high, mounted on a metal base plate with a polystyrene gasket. The chamber was evacuated by an oil diffusion pump

using silicone oil, backed by a mechanical pump. An ionization gauge was used to measure the pressure. A vacuum of  $10^{-6}$  Torr was reached occasionally, and during evaporation the pressure was near  $10^{-5}$ .

### The Substrates

Two films were made simultaneously in each evaporation, one on a one inch square cut from a glass microscope slide (hereafter referred to as the substrate), the other on a 28 mm square, nearly optically flat, glass spectroscopy window (hereafter referred to as the optical flat). The film on the substrate was used for electrical measurements, and the film on the optical flat was used for thickness measurement. The masks used are shown in Fig. 2. A copper-constantan thermocouple of size 30 wire was cemented on the substrate with Eccobond 58C, a high-conductivity metal-filled resin.

### Substrate Cleaning

The substrates were washed in concentrated sodium hydroxide for several hours, boiled in detergent twice, rinsed in vigorously boiling distilled water several times and dried under an infrared lamp. Care was taken not to touch the substrates or anything that came in contact with the substrates. When being dried, a uniform film of water formed on the substrates and interference fringes could be observed as this film dried. After being dried, the substrates were immediately placed in the vacuum chamber, a heater placed on top of them, and the chamber

### EXPLANATION OF PLATE II

Fig. 2. The mask used for the substrate. Dimensions are given in mm.

Fig. 3. The mask used for the optical flat. Dimensions are given in mm.

Fig. 4. The arrangement of the boat used as the vapor source.

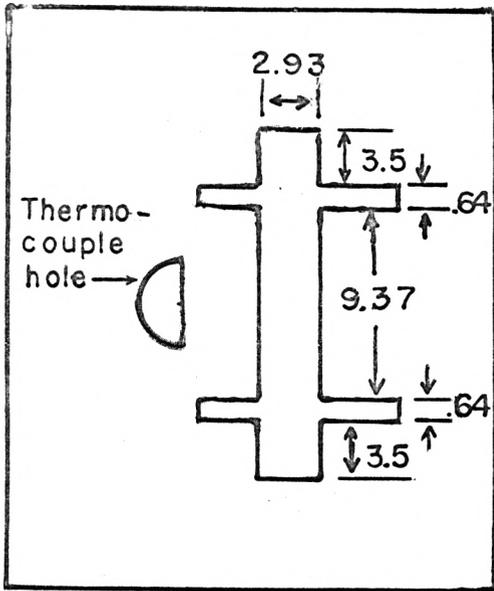


Fig. 2

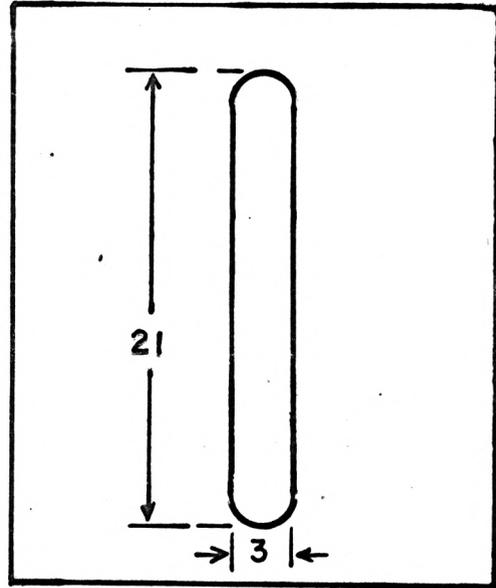


Fig. 3

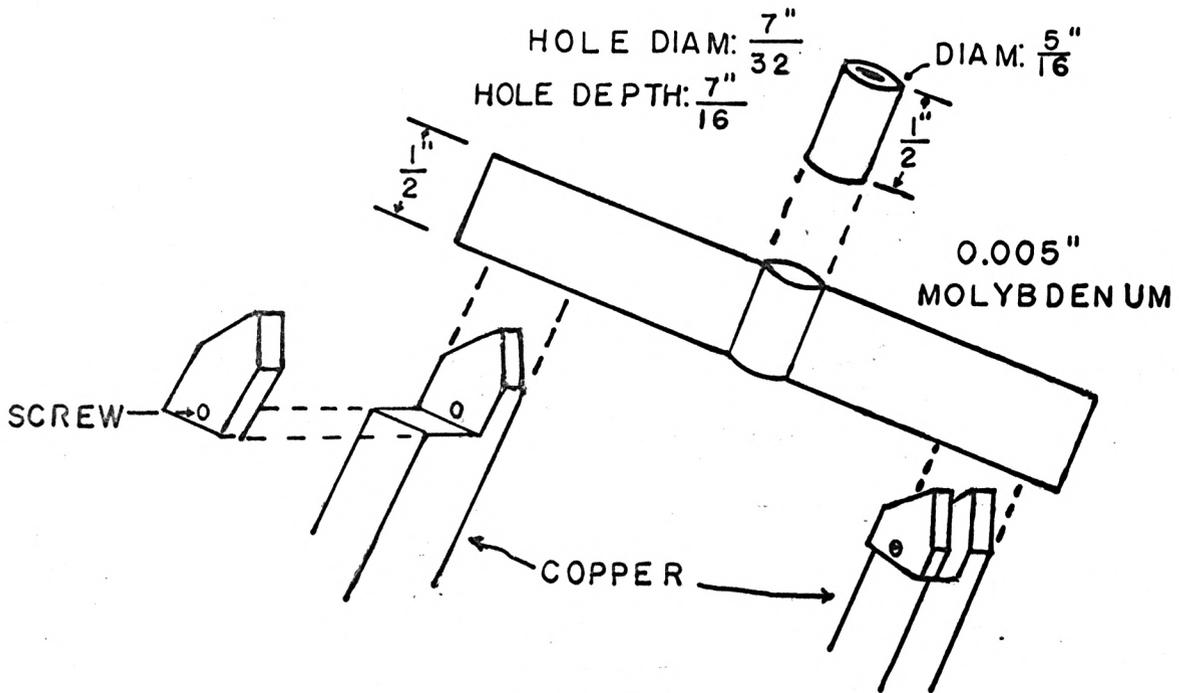


Fig. 4

evacuated. The substrates were then heated to  $400^{\circ}$  C for three to five hours before being allowed to cool to the temperature desired for the particular evaporation. The optical flats were cleaned in the same manner, omitting the washing in sodium hydroxide.

### Vapor Source

The boat used as a vapor source was made from reactor grade graphite. It was heated by a double strip of molybdenum, into which the boat was inserted. This arrangement is illustrated in Fig. 3.

### Thickness Measurement

Thickness was measured by the method of fringes of equal thickness. Aluminum was evaporated on the film side of the optical flat. The optical flat was then placed under a sodium vapor lamp and a half-reflecting optical flat placed over the coated film and adjusted until reasonably wide-spaced fringes were obtained. The distances between fringes were measured with a telescope equipped with a micrometer eyepiece.

If  $D$  is the distance between successive fringes and  $A$  is the distance a fringe is displaced due to the film, then the thickness of the film,  $t$ , is

$$t = (A/D) \lambda/2 \quad (7)$$

where  $\lambda$  is the wavelength of the light source, and for the sodium vapor lamp has a value of  $5892 \text{ \AA}$ . At least ten

measurements were made for each film, and an average was taken to be the value of the thickness. The mean square deviation for a set of ten measurements was approximately 30 Å.

### Electrical Measurements

Electrical contacts to the film on the substrate were painted on with G. C. Electronics Company's air drying silver conductive paint. To maintain thermal contact, the substrate was attached to a metal surface with Dow Corning silicone high vacuum grease. Pressure contacts were placed on the painted contacts and the substrate placed inside a working dewar, which was held between the poles of an electromagnet. The dewar was evacuated to approximately  $10^{-4}$  Torr. The temperature of the dewar, and hence of the film on the substrate, was controlled either by an electric resistance heater or by liquid nitrogen or a mixture of ethyl alcohol and liquid nitrogen. The temperature of the film was measured by the thermocouple on the substrate.

The circuit used in measuring resistivity and Hall coefficient is shown in Fig. 4. Resistivity measurements were made using the low voltage as the power supply, and Hall measurements used the high voltage. Two independent measurements of both resistivity and Hall coefficient were made at each point.

At zero magnetic field, the value of  $V_h$  was not zero, due to misalignment of the probes shown in Fig. 4. Careful alignment of the probes minimized, but did not eliminate, this potential. To offset this difficulty, and also to eliminate the Nernst and the Righi-Leduc effects (12), six potential

measurements were used to find each Hall voltage, i.e., with current in both directions, and with the magnetic field off, on, and reversed.

Computation of  $V_h$  was made by use of the formula

$$V_h = \frac{|V_o^+ - V_+^+| + |V_o^+ - V_-^+| + |V_o^- - V_+^-| + |V_o^- - V_-^-|}{4} \quad (8)$$

where the superscript refers to the direction of the current, and the subscripts o, +, and - denote the magnetic field as being off, on, and reversed, respectively. These sign conventions were arbitrarily chosen.

The equation used to compute the conductivity is

$$\sigma = \frac{L V_s}{W t R_s V_f} \quad (9)$$

where L, W and t are the length, width and thickness of the film in cm.,  $V_s$  and  $V_f$  are the potentials in volts across the standard resistance and the film, respectively, and  $R_s$  is the value of the standard resistance in ohms.

The equation used to compute the Hall coefficient is

$$R_h = \frac{10^8 t V_h R_s}{B V_{s1}} \quad (10)$$

where B is the magnetic induction in gauss,  $V_h$  is the Hall voltage from Eqn. 8 in volts, and t,  $R_s$  and  $V_{s1}$  are defined above. Note that the value of  $V_s$  in Eqn. 9 is in general, different from the value of  $V_{s1}$  in Eqn. 10.

The value of L/W was found to be 3.2 (see Fig. 2), and a

magnetic field of 2.86 kilogauss was used throughout the experiment. Inserting these values in (9) and (10), and inserting (9) and (10) in (6):

$$\mu = \sigma |R_h| = 1.12 \cdot 10^5 (V_s/V_f) (V_h/V_{s'}) \quad (11)$$

it is seen  $\mu$  can be computed independently of the film thickness

#### Some Details of the Experiment

Two series of films were made. The first series began by an evaporation from a 500 mg. charge of n-type InSb, containing about  $10^{15}$  electrons/cm<sup>3</sup>. New InSb was added to the charge to replace the weight lost in evaporation. Two successive evaporations were made from this charge, then new InSb was added to restore the 500 mg. weight. For the first three films 5 to 10% of the charge was evaporated each time. A series of 20 films were then made, each one from the residue of the charge from the previous evaporation plus enough new InSb to make the charge weigh 500 mg. For the last 20 films of the series, less than 5% of the total charge was evaporated each time. A summary of the last 14 films of this series is given in Table 1.

The first 21 films were deposited on substrates maintained at 200° C, allowed to anneal at this temperature for 24 hours and then allowed to cool to room temperature before removal from vacuum. The last two films of the series, H-46 and H-48, were deposited on substrates maintained at room temperature and were not annealed in the evaporator.

TABLE 1

Summary of the first series of films

Film	Evapo- ration number	Evapo- ration time (min.)	Weight lost in evapo- ration (mg)	Thick- ness (A)	Room Temperature		Type
					Conduc- tivity	Mobil- ity	
H-23	10	3	31.5	1090	284	2.9	n at 178° p at 26°, below
H-25	11	3	38.3	1800	95	3.0	n
H-27	12	4	33.1	1760	2.65	37.4	n
H-29	13	5	38.7	1770	No measurements		
H-30	14	3	15.8	680	1.17	36.3	n at 214° p at 22°, below
H-32	15	4	11.2	720	3.0	14.4	n
H-34	16	5	10.7	970	2.08	20.6	n
H-36	17	6	18.5	1180	4.93	22.7	p at -70° n at 23°, above
H-38	18	4	17.9	1000	1.63	21.7	n
H-40	19	5	18.1	970	2.21	25.2	n
H-42	20	5	13.2	720	1.60	1.6	n
H-44	21	6	25.7	910	5.52	41.5	n
H-46	22	5	25.3	1150	25.8	0.05	p
H-48	23	4	16.4	750	56.7	Not measurable	n

A second series of 11 films, using 99.999% indium and InSb in a proportion computed from vapor pressure data given by Honig (10) as the charge for the initial evaporation, was made. At  $1000^{\circ}$  C the vapor pressure of In and antimony (Sb) are  $2.10^{-2}$  and 13 Torr respectively. Using Raoult's Law, the required composition is 0.1 molar Sb and 99.9 molar In. The procedure for the rest of the second series may be seen from Table 2.

All evaporations were made at  $1000^{\circ} \pm 10^{\circ}$  C, as measured with an optical pyrometer. The boat was first heated to approximately  $800^{\circ}$  C for ten to 15 minutes to allow the charge to mix. No evaporation was observed at this temperature.

The films, deposited on heated substrates and annealed, were placed in the dewar, where the resistivity and Hall coefficient were measured as a function of temperature.

The films deposited on room temperature substrates (unannealed) were annealed in the dewar in a step-wise fashion, and the conductivity and Hall voltage recorded as a function of time. After annealing, measurements were made as with the other films.

## RESULTS AND DISCUSSION

Fig. 6 shows the mobility vs evaporation number for points of constant or near constant temperature. Each curve should not be considered to be continuous, but rather a series of distinct points where connecting lines have been drawn to identify points of equal temperature. In the first series of films, the mobility is extremely low until evaporation H-23 where it begins to

TABLE 2

Summary of the second series of films

Film	: :Evapo- :ration :number :	: :New :InSb :added :(mg) :	: :Total :weight :of :charge :(mg) :	: :Evapo- :ration :time :(min.) :	: :Weight lost :in evapo- :ration (mg) :	: :Thick- :ness :(A) :	: :Type :	: :Remarks :
H-52(a)	1	1.7	347.7	2 1/2	5.2	--	--	Film almost invisible
H-52(b)	2	3.5	346.0	4	12.0	--	--	Film white, transparent
H-52(c)	3	12.1	346.0	5	17.9	--	--	Film white, transparent
H-52(d)	4	17.9	346.0	5	13.0	--	--	Film white, transparent
H-53	5	21.7	354.7	5	14.9	970	n	Film brown, nearly opaque
H-54	6	14.9	354.7	4	10.5	620	p	Film brown, semi-transparent
H-55(a)	7	10.5	354.7	5	12.9	--	--	Film white, transparent
H-55(b)	8	12.9	354.7	5	14.5	--	--	Film white, transparent
H-56	9	19.5	359.7	5	18.1	590	n	Film brown, semi-transparent, appeared nonuniform in color, density
H-57	10	23.1	364.7	5	14.0	350	--	Film white, semi-transparent
H-58	11	22.1	372.8	5	14.3	940	n	Film brown, nearly opaque

EXPLANATION OF PLATE III

Fig. 5. Diagram of the circuit used to measure the electrical properties of the films.

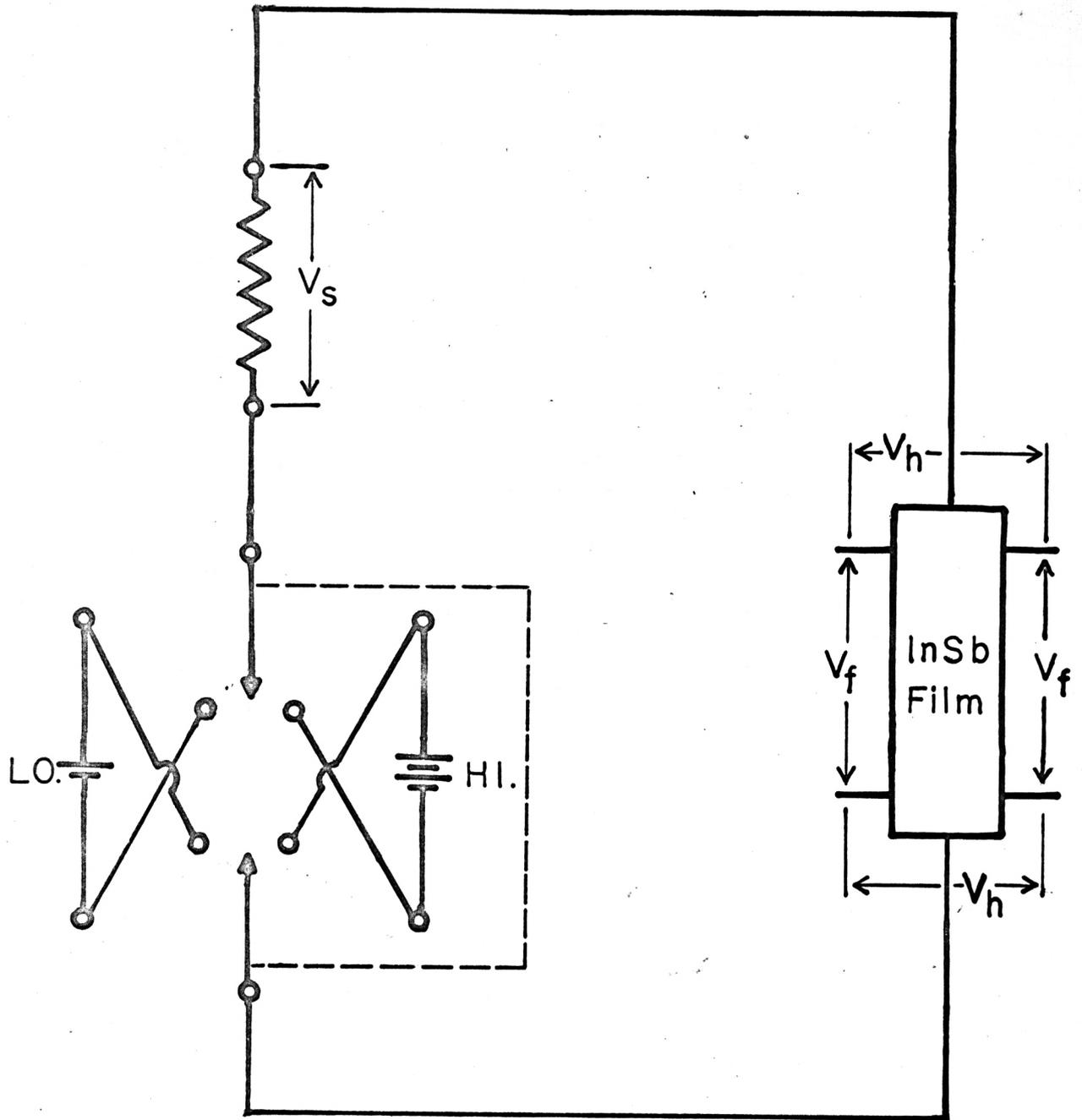


Fig. 5

EXPLANATION OF PLATE IV

Fig. 6. Mobility for points of constant temperature versus evaporation number.

## PLATE IV

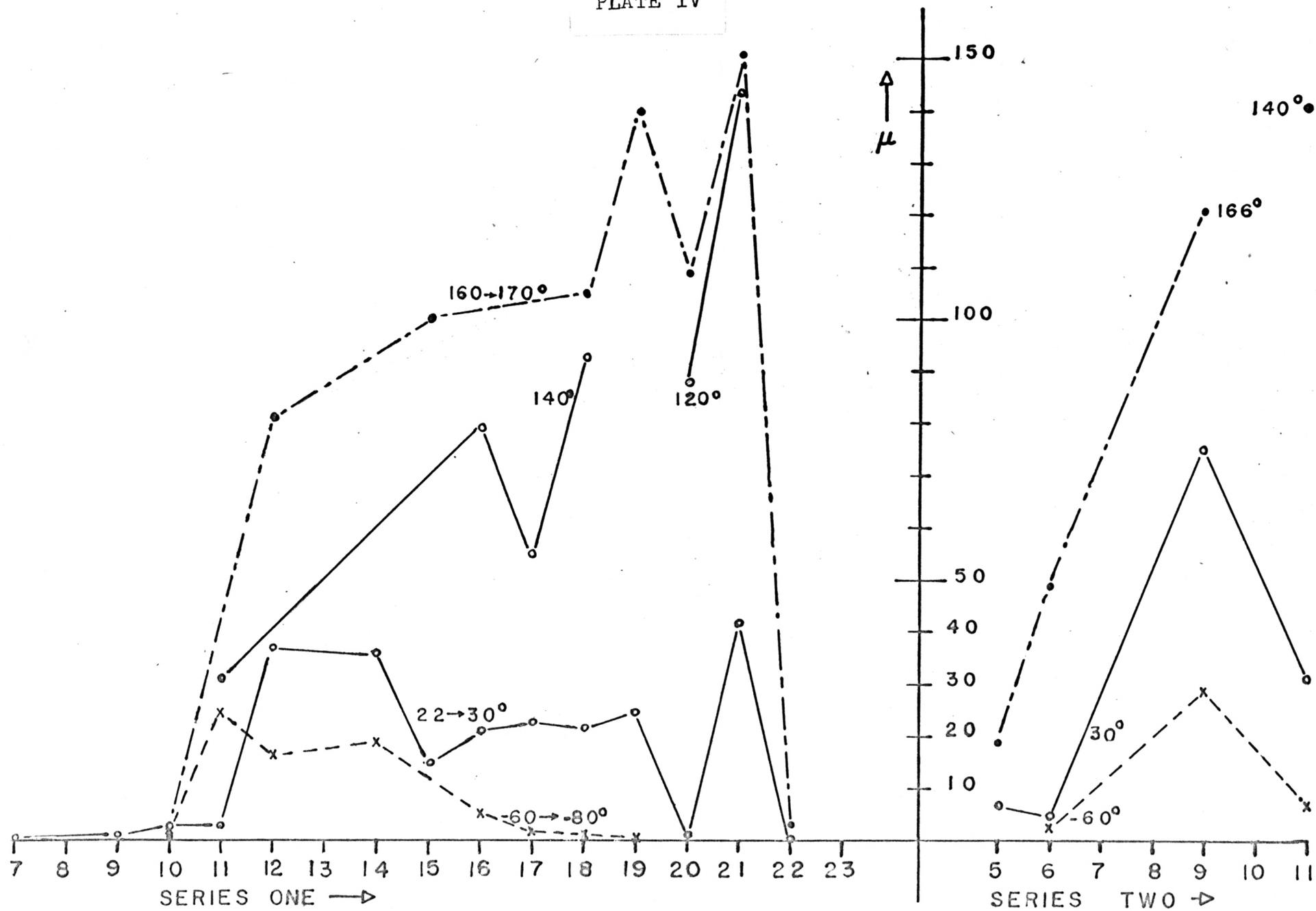


Fig. 6

rise, and continues to rise until evaporation H-46. After evaporation H-44 a thermocouple hole was bored in the carbon boat, and contamination of the charge is suspected as the cause of the low mobility of films H-46 and H-48.

The room temperature conductivity was above 200 (ohm-cm.)<sup>-1</sup> in all films preceding H-25. Values for room temperature conductivity for three consecutive films about this point are:

H-23 . . . . .	284	(ohm-cm) <sup>-1</sup>
H-25 . . . . .	95.0	
H-27 . . . . .	2.65	

Thereafter, the room temperature conductivity was between 1 and 5 (ohm-cm)<sup>-1</sup>, until H-46, when it rose to 25.8 (ohm-cm)<sup>-1</sup>.

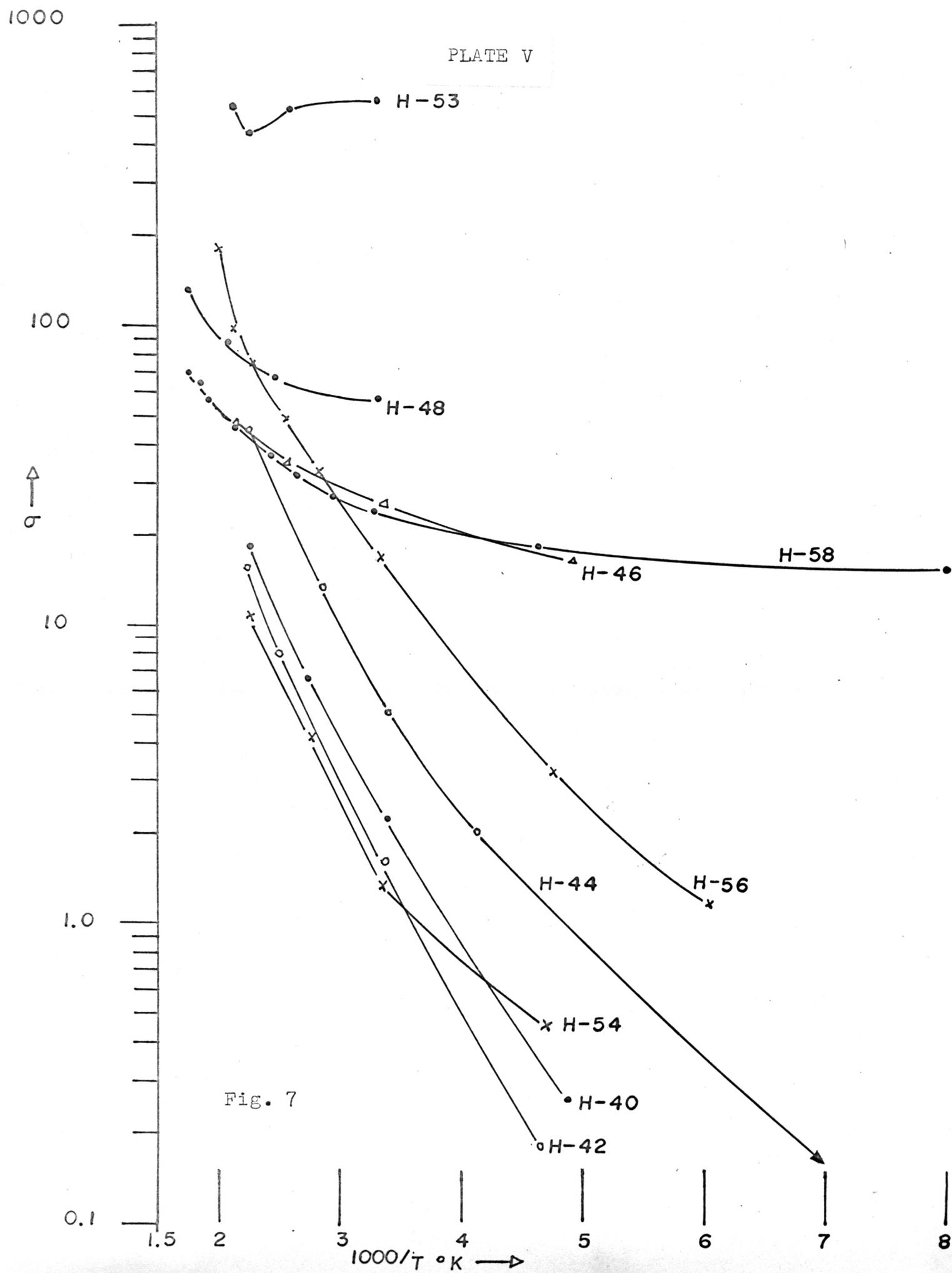
Fig. 7 gives the conductivity vs temperature<sup>-1</sup> for some of the later films. The curves for films deposited on heated substrates resemble the conductivity vs temperature<sup>-1</sup> curves given in the literature (such as Hilsum and Rose-Innes (8)). The curves for films that have been annealed after being deposited on room temperature substrates have much smaller slopes and the conductivity is somewhat higher than for the other films. Although the curve for H-58 is much like those for H-46 and H-48, the mobility of H-58 is the highest of any film measured, and a mobility was measured at -188° C, which could not be done for any other film.

Figs. 8 and 9 are plots of mobility vs temperature for several films. The slopes of all curves drawn are approximately the same in the high temperature region, with the mobility changing as T<sup>3</sup> or T<sup>4</sup>. However H-54 and H-58 change slopes, and vary as approximately T in the low temperature region. The

EXPLANATION OF PLATE V

Fig. 7. Conductivity in  $(\text{ohm-cm})^{-1}$  vs  $1000/^\circ\text{K}$  for some films.

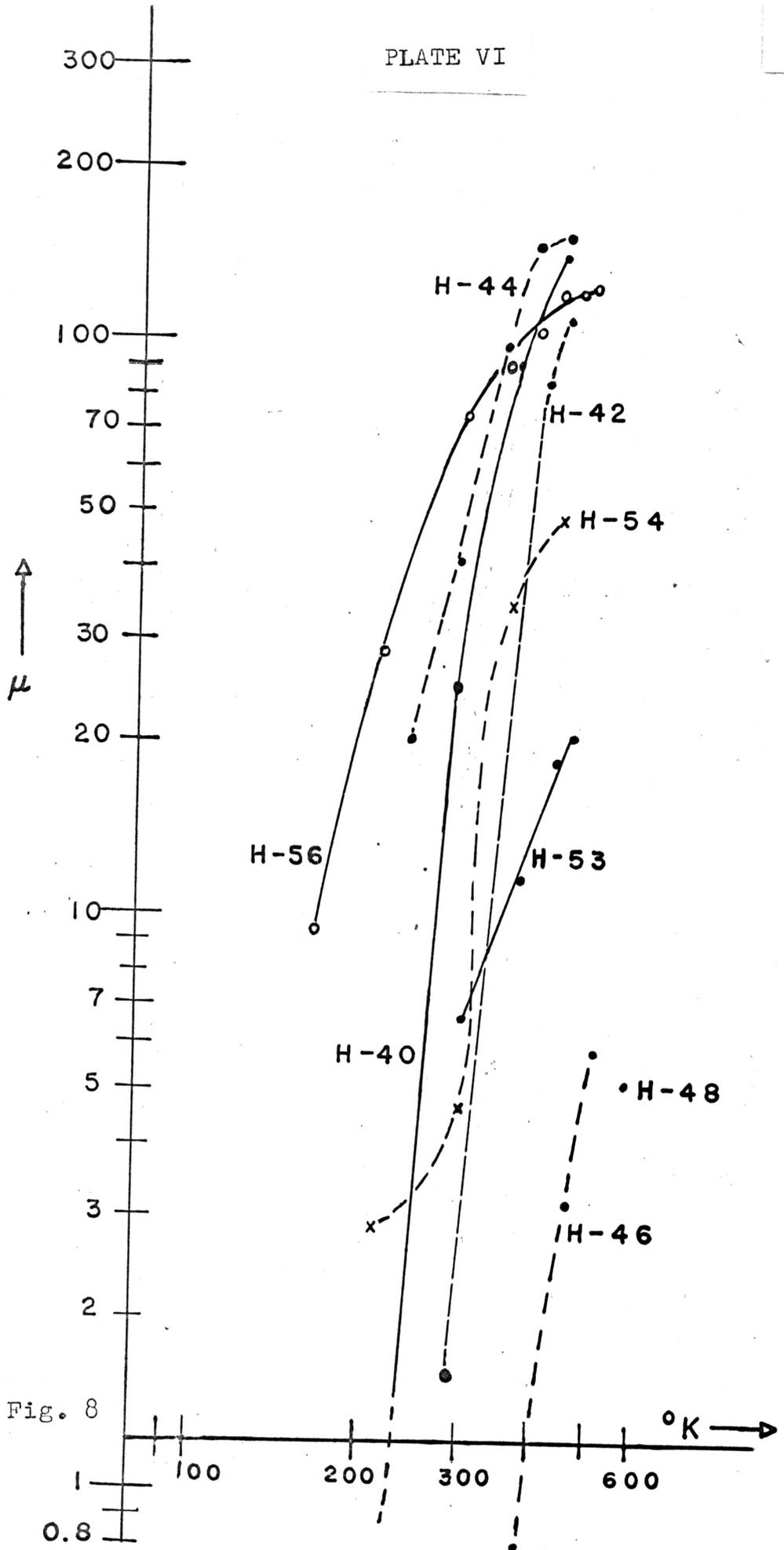
PLATE V



EXPLANATION OF PLATE VI

Fig. 8. Mobility vs absolute temperature for some films.

PLATE VI



EXPLANATION OF PLATE VII

Fig. 9. Mobility vs absolute temperature for some films.

The points for film H-36 are not connected.

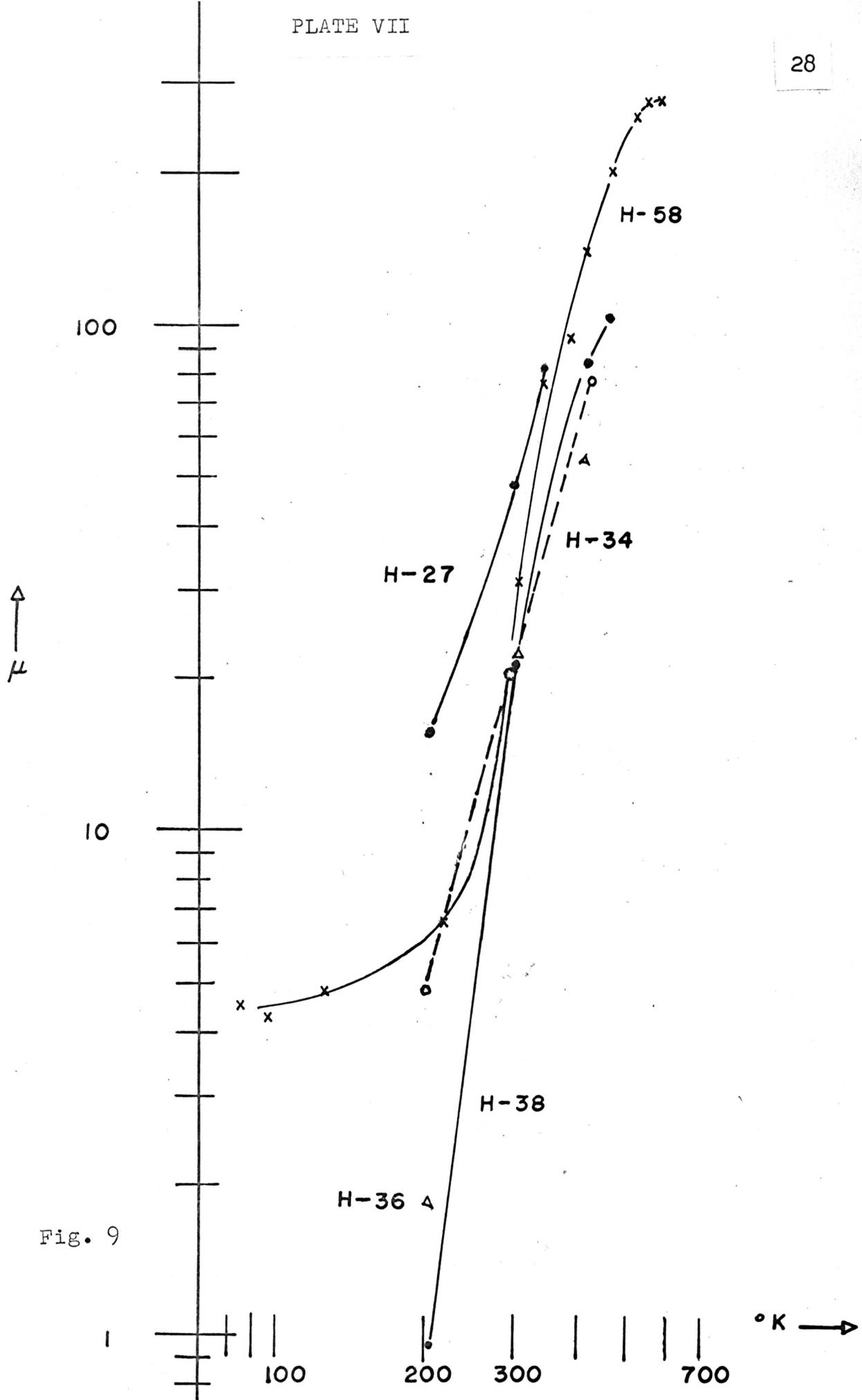


Fig. 9

small mobility of H-46 and H-48 is illustrated; the values for H-46 are seen to be much smaller than for the typical curves, while H-48 is represented by a single point at  $293^{\circ}$  C, below which no Hall voltage could be detected.

Annealing curves are given in Figs. 10 and 11. Earlier work in this laboratory (3) produced annealing curves that reached a maximum conductivity and then decreased, even when the temperature was increased. Films H-46 and H-48 did not reach a maximum. The conductivity would approach a constant value at a constant temperature, but would rise again when the temperature was increased, even at temperatures of  $300^{\circ}$  C. The room temperature conductivity of H-58 before annealing was extremely high (2080/ohm-cm) and it decreased almost continuously with annealing, although each time the temperature was increased, the conductivity would increase before starting to decrease again.

A possible explanation of the difference in the properties of films deposited on heated and room temperature substrates is the re-evaporation of part of the film during deposition or during annealing. The vapor pressure of Sb at  $204^{\circ}$  and  $25^{\circ}$  C is  $10^{-11}$  and less than  $10^{-13}$  Torr respectively, while the vapor pressure of In at the same temperatures is well below  $10^{-14}$  Torr (10). Assuming a stoichiometric vapor from the melt, the vapor pressure of each element during deposition would be of the order of  $10^{-2}$  Torr. Thus, re-evaporation from the substrate during deposition should not be significant. If, however, the film contained an excess of Sb, annealing for 24 hours at  $200^{\circ}$  C might alter the properties of the film by re-evaporating some of

EXPLANATION OF PLATE VIII

Fig. 10. Conductivity vs annealing time in hours for films H-46 and H-48. H-46 is p-type and H-48 is n-type.

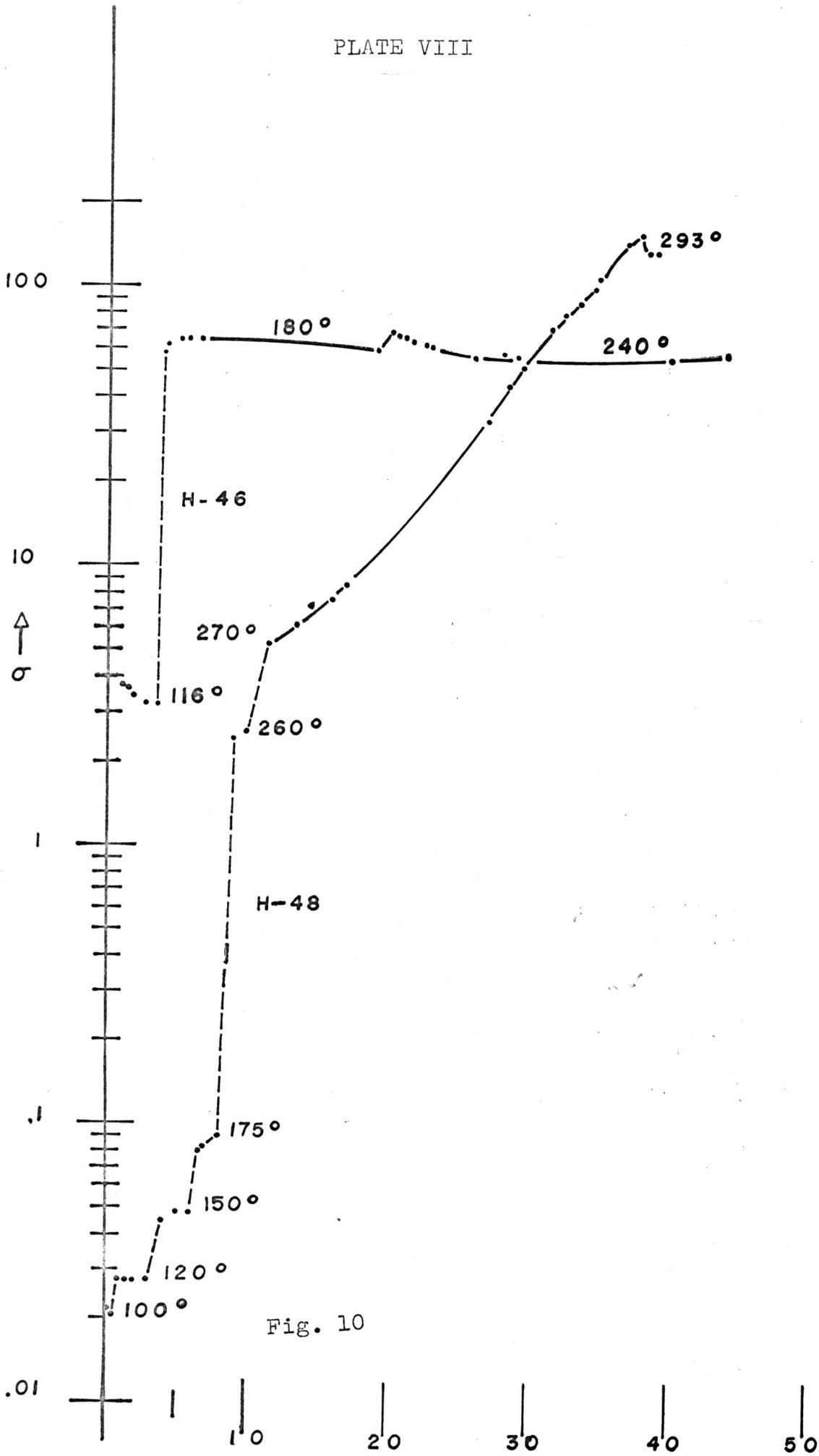


Fig. 10

EXPLANATION OF PLATE IX

Fig. 11. Conductivity, mobility and Hall coefficient vs annealing time in hours for film H-58. H-58 is n-type.

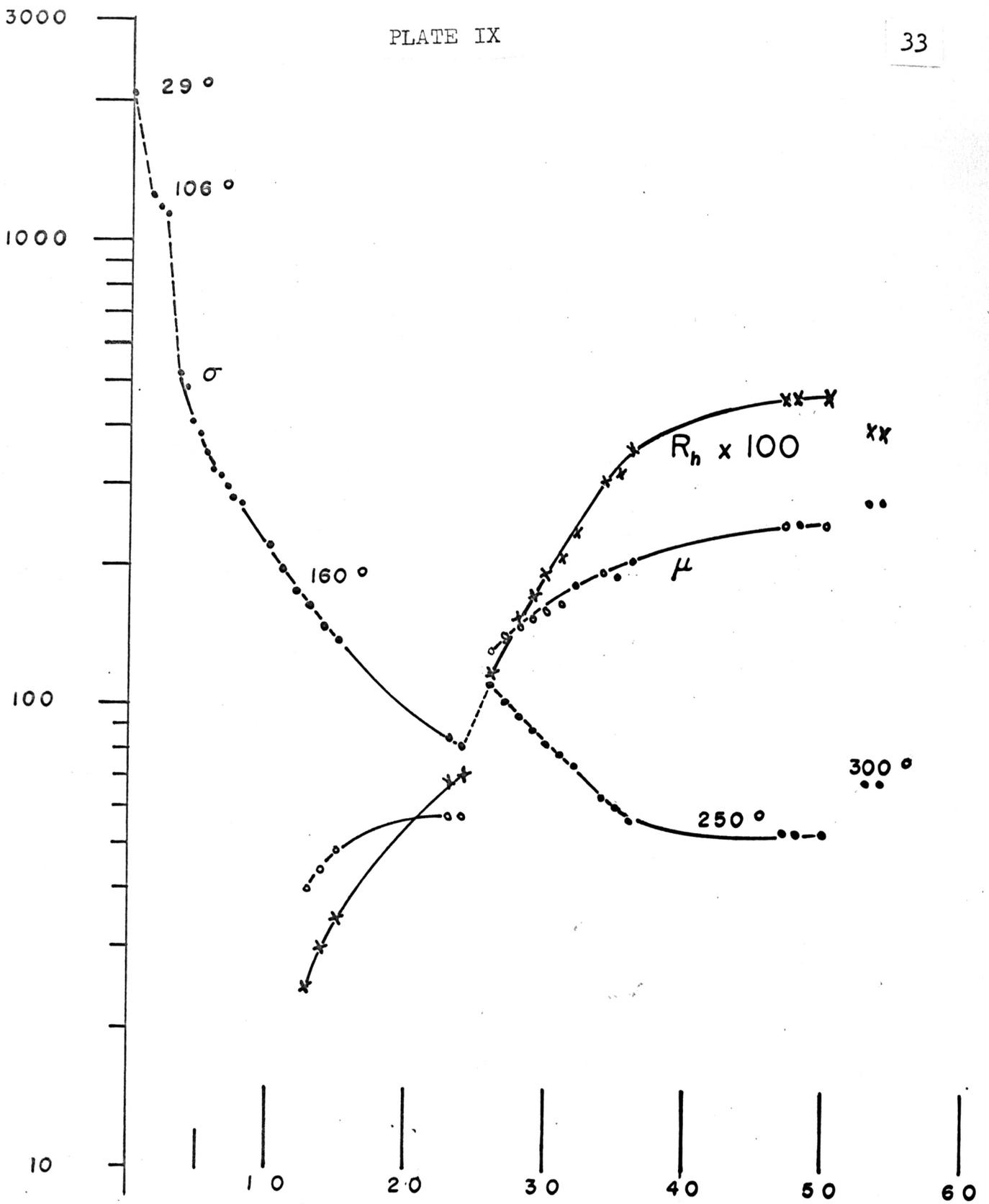


Fig. 11

this excess Sb. For example, a 1000 Å film would contain approximately  $3 \cdot 10^{-5}$  gm/cm<sup>2</sup> of Sb. Eqn. 2 gives a value of approximately  $3 \cdot 10^{-8}$  gm/cm<sup>2</sup> as the maximum amount of Sb that could be evaporated at 200° C in 24 hours. The same computation for In gives a figure that is smaller by a factor of at least  $10^{-3}$ . The amount of Sb re-evaporated would be one part per thousand parts originally deposited, while for In the figure would be of the order of one part per million. These computations assume that not all the material evaporated has formed InSb, as the elements, once formed into the compound, would be much more difficult to evaporate. Senecal (15) looked for evidence of re-evaporation from the substrate during annealing, and concluded that very little, if any, occurred.

A more plausible explanation of the difference between properties of the films deposited on room temperature and heated substrates is suggested by Appleyard (1).

The latent heat of evaporation of the atom from the surface will then be the energy required to remove an atom from its lowest vibrational level to infinity. But in order to move freely over the surface an atom needs much less kinetic energy than  $L$ . In fact, if the atom is given sufficient kinetic energy  $A$  for it to surmount the potential barrier between one pocket and the next, it may (so long as it retains the energy) move freely over the surface. Thus since  $A$  is less than  $L$ , free motions of the atoms on the surface occurs at temperatures far below those needed to evaporate the atoms from the surface; a well-known experimental fact.

Thus it is suggested that a substrate temperature of 200° C would assist in the formation of atoms of InSb. That is, the higher temperature would aid the movement of atoms and hence the formation of the compound.

In the second series of films, the results seem at first to negate Raoult's Law, at least in this situation. However, it is obvious that one cannot first add 1.7 mg of InSb to pure In and then remove 5.2 mg of InSb. Also, Raoult's Law deals with saturated vapor pressures. Since the elements condense on the sides of the glass bell jar, and on other room temperature surfaces present in the evaporator, the vapor does not become saturated.

With such a small concentration of Sb, evaporation of equal parts of In and Sb will soon deplete the Sb, causing a higher and higher concentration of In to be evaporated. Thus a higher concentration of Sb will be needed for stoichiometry than the computed value. It should be noted that since the variation of vapor pressure with temperature is almost the same for both elements, the evaporation temperature is not critical. A change in the boat temperature will change the absolute rates of evaporation, but should not change the relative rates.

After the first four films were made in the second run, 8.7 mg more InSb was added to the charge than weight lost from the previous evaporation. Two successive semiconducting films were produced, H-53 and H-54, with H-54 having a higher mobility than H-53. The next two films, H-55 and H-55a obviously had a great excess of In. In order to produce near stoichiometric films, it was found necessary to add more InSb than material lost from the previous evaporation.

Three factors seem significant: the new InSb is placed on top of the melt, the depth of the melt is approximately equal to the diameter of the melt, and the original charge for the second

run was almost pure In. Since evaporation occurs from the surface, if the top of the melt is of the desired composition and the bottom of the melt is almost pure In, some of the Sb that is added after each evaporation will be evaporated during the next evaporation and some of it will diffuse toward the bottom of the melt. Until enough evaporations have been made (and new InSb added) that the melt approaches the desired composition throughout, more new InSb will be required in the charge than material lost in the previous evaporation to produce stoichiometric films.

It is believed that if the process of replacing the weight lost each time with new InSb were repeated enough times, a stoichiometric vapor would be obtained, as was the case in the first series of films.

#### CONCLUSION

The experiment shows that the process of successive dilution yields films that tend toward stoichiometry as the process continues. The present indication is that the composition of the liquid from which In and Sb will evaporate at equal rates is somewhat richer in Sb than predicted by Raoult's Law.

Since semiconductors are very sensitive to impurities, and each evaporation presents the possibility of contamination, it would be desirable to determine the composition of the melt that produces InSb films, and use this composition as the initial charge for a series of films.

## ACKNOWLEDGMENT

The author expresses his gratitude to his major professor, Dr. E. Brook Dale, whose guidance and assistance made this work possible. Indebtedness is acknowledged to Dr. Clifton E. Meloan, for his assistance and to Dr. Basil Curnutte for his helpful guidance with the manuscript.

Appreciation is expressed to the Electronic Research Directorate of the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research, for sponsoring this research under contract AF 19(604)-7218.

## REFERENCES

1. Appleyard, E. T. S., Proc. phys. Soc., London, extra part, 49, 118 (1937).
2. Bate, G., and K. N. R. Taylor, Production and Properties of Thin Layers of InSb, J. Appl. Phys., 31, 991 (1960).
3. Dale, E. B., and G. Senecal, Annealing Effects in Evaporated InSb Films, J. Appl. Phys., 33, 2526 (1962).
4. Dushman, S., and J. M. Lafferty (editor), Scientific Foundations of Vacuum Technique, John Wiley and Sons, New York, 1962.
5. Gunther, K. G., Evaporated Films of Semiconducting III-V Compounds, Z. Naturforschg., 13a, 1081 (1958).
6. Gunther, K. G., and H. Freller, Properties of Evaporated InSb and InAs Films, Z. Naturforschg., 16a, 279 (1961).
7. Hannay, N. B. (editor), Semiconductors, Reinhold, New York, 1959.
8. Hilsum, C., and A. C. Rose-Innes, Semiconducting III-V Compounds, Pergamon Press, New York, 1961.
9. Holland, L., Vacuum Deposition of Thin Films, John Wiley and Sons, New York, 1960.
10. Honig, R. E., Vapor Pressure Data for the Solid and Liquid Elements, RCA Rev., 23, 567, (1962).
11. Kakihana, S., The Preparation of Thin Films of InSb by Vacuum Deposition, Technique, A Master's Thesis (unpublished), Kansas State University, 1959.
12. Lindberg, O., Hall Effect, Proc. IRE, 40, 1414 (1952).
13. Neugebauer, C. A., J. B. Newkirk, and D. A. Vermilyea, (editors), Structure and Properties of Thin Films, John Wiley and Sons, New York, 1959.
14. Putley, E. H., The Hall Effect and Related Phenomena, Butterworths, London, 1960.
15. Senecal, G., The Preparation and Properties of Thin Films of InSb, A Ph D Dissertation (unpublished), Kansas State University, 1963.

THE PREPARATION AND PROPERTIES OF  
NEAR-STOICHIOMETRIC, NON-STRATIFIED, THIN FILMS  
OF INDIUM ANTIMONIDE

by

DAVID HENRY HUEBNER

B. S., Kansas State University, 1958

---

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

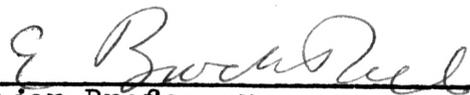
MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1963

Approved by:

  
Major Professor

Studies of thin films of crystalline materials provide much valuable information about the materials. Many semiconductors have been studied in this manner. The production of elemental semiconducting thin films is straightforward, but many of the compound semiconductors present difficulty in their stoichiometry due to the difference in vapor pressure of their component elements. Indium antimonide is such a semiconducting compound. InSb is of great theoretical interest and is the most extensively studied of the compound semiconductors. Many complex methods of producing thin InSb films have been devised, and simpler methods are needed.

The work described is an attempt to produce InSb thin films by vacuum evaporation from a single source, using a process of successive dilution, evaluating the films so produced.

The composition of In and Sb in the melt required to produce a stoichiometric vapor was computed from Raoult's Law. Two series of film were produced, one with an excess of Sb in the melt for the initial evaporation, the other with an excess of In in the initial melt. After each evaporation, the melt was weighed and the weight lost due to evaporation was replaced with new InSb.

The thickness of the films was measured. The conductivity and the Hall coefficient were measured as a function of temperature using a direct current method. The films ranged up to 1800 Å in thickness, and electron mobilities up to  $260 \text{ (ohm-cm)}^{-1}$  were found.

Films deposited on substrates at  $200^{\circ} \text{ C}$  were found to have

properties more similar to bulk material than did those deposited on room temperature substrates.

The experiment indicated that a melt composition somewhat richer in Sb than indicated by Raoult's Law is needed to produce stoichiometric films.