THE PREPARATION OF THIN FILMS OF InSb
BY VACUUM DEPOSITION TECHNIQUE

by

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INTRODUCTION

Thin films of different materials are often required in such fields of semiconductor research as (1) the measurement of surface recombination rate (6), (2) optical absorption (6), (3) electron diffraction study (7), (4) photoconductivity and photo-voltaic effect (1), and (5) field effect (1).

For monatomic semiconductors such as silicon and germanium, thin films can be obtained very readily by the ordinary vacuum deposition technique in which the bulk material is evaporated in vacuum and is deposited on a suitable substrate. However, an obvious difficulty exists in applying this technique to the binary alloy semiconductors, of which InSb is one. Preferential evaporation of the more volatile constituent of the alloy takes place upon heating the charge to the evaporation temperature. Holland (5) gives a semiquantitative method for isolating metals likely to form binary alloys which will then evaporate without component separation. In the following, a brief discussion on Holland's criteria will be given and the result will be applied to the case of InSb.

Langmuir's (5) equation for the evaporation rate of a solid is given as

$$E = kP \sqrt{\frac{M}{T}} \tag{1}$$

where E is the mass evaporated per unit emitting area per unit time, P is the vapor pressure at $T^{\circ}K$, M is the molecular weight of the substance evaporated, and k is a constant. If two or more

elements are combined in the form of an alloy or solid solution, the evaporation rate of each component can be calculated by applying equation (1) separately to each type of atom. In such a case, E will stand for the evaporation rate of the particular element in question, M will be its atomic weight, and P will be the partial vapor pressure, which is in general lower than the vapor pressure of the same element when existing in a pure form. The partial vapor pressure of an alloy can be obtained experimentally, but the procedures used are so involved that it cannot be determined readily in a short period of time. Moreover, the information concerning the partial vapor pressure of alloys is limited to a few well known alloys, and then within a small range of temperature. This information is not available for InSb.

However, the partial vapor pressure can be estimated by the use of Raoult's law, which is exactly applicable only to a dilute chemical solution. Raoult's law states that the vapor pressure of a chemical solution is lower than that of a pure solvent by an amount proportional to the concentration of solute. If P_V and P_S designate the vapor pressures of solvent and solution, and X_V and X_L designate the mol-fraction of the solvent and solute, respectively, then Raoult's law is given by

$$\frac{P_V - P_S}{P_V} = X_L = \frac{N_L}{N_L + N_V} \tag{2}$$

where N_L is the number of moles of solute and N_V is the number of moles of solvent. Since

$$1 - X_L = 1 - \frac{N_L}{N_L + N_V} = \frac{N_V}{N_L + N_V} = X_V$$

and also since

$$1 - \frac{P_V - P_S}{P_V} = \frac{P_S}{P_V} = 1 - X_L = X_V$$

equation (2) can be written as

$$\frac{P_S}{P_V} = X_V = a_V \tag{3}$$

where a_V is known as the activity of the solvent in solution and
it is equal to X_V only in an ideal solution.

To find a partial vapor pressure of one of the components
of an alloy, the component in question is treated as a solvent
which combined with the second component forms a solution, or,
in this case, an alloy. The partial vapor pressure can then be
found from the vapor pressure of the component in pure form and
by the use of equation (3).

If A and B designate two components of an alloy, then the
ratio of the evaporation rates of the components A and B at a
given temperature is obtained from equation (1), as

$$\frac{E_A}{E_B} = \frac{P_A \sqrt{M_A}}{P_B \sqrt{M_B}} \tag{4}$$

If w_A and w_B designate the concentration by weight of the com-
ponents A and B in the film, and $\triangle t$ designates the evaporation
time, then

$$\frac{w_A}{w_B} = \frac{E_A \triangle t}{E_B \triangle t} \tag{5}$$

If w_A and w_B in the film are to remain the same as in the bulk

material, then the following must be satisfied:

$$\frac{w_A}{w_B} = \frac{W_A}{W_B} \tag{6}$$

where W_A and W_B designate the concentration by weight of the components A and B, respectively, in the bulk material. From equations (5) and (6), there results

$$\frac{w_A}{w_B} = \frac{E_A \triangle t}{E_B \triangle t} = \frac{W_A}{W_B} \tag{7}$$

and therefore
$$\frac{E_A}{E_B} = \frac{W_A}{W_B} \tag{8}$$

Hence if the binary alloy is not to undergo a preferential evaporation, equation (8) must be satisfied.

If P_A and P_B are the partial vapor pressures of the components A and B, and P_1 and P_2 are the vapor pressures of the component A and B existing in pure form, P_A and P_B can be expressed in terms of P_1 and P_2 through equation (3), as

$$P_A = P_1 X_A \tag{9}$$

$$P_B = P_2 X_B \tag{10}$$

Substituting P_A and P_B of equation (9) into equation (4), the ratio of the evaporation rate is found to be

$$\frac{E_A}{E_B} = \frac{X_A \, P_1 \sqrt{M_A}}{X_B \, P_2 \sqrt{M_B}} \tag{10}$$

Now, since the concentration by weight W_A and W_B can be expressed as,

$$W_A = \frac{N_A M_A}{N_A M_A + N_B M_B}$$

$$W_B = \frac{N_B M_B}{N_A M_A + N_B M_B}$$

(11)

the ratio $\frac{W_A}{W_B}$ can be written as

$$\frac{W_A}{W_B} = \frac{\dfrac{N_A M_A}{N_A M_A + N_B M_B}}{\dfrac{N_B M_B}{N_A M_A + N_B M_B}} = \frac{N_A}{N_B}\frac{M_A}{M_B}$$

(12)

and since

$$\frac{X_A}{X_B} = \frac{\dfrac{N_A}{N_A + N_A}}{\dfrac{N_B}{N_A + N_A}} = \frac{N_A}{N_B}$$

(13)

then

$$\frac{W_A}{W_B} = \frac{X_A}{X_B}\frac{M_A}{M_B}$$

(13')

Solving equation (13') for X_A/X_B and substituting the result into equation (10), gives

$$\frac{E_A}{E_B} = \frac{W_A M_B P_1 \sqrt{M_A}}{W_B M_A P_2 \sqrt{M_B}} = \frac{W_A}{W_B}\frac{P_1}{P_2}\frac{\sqrt{M_B}}{\sqrt{M_A}}$$

(14)

For depositing a film, the composition of which is similar to the parent bulk alloy, the condition stated in equation (8) must be satisfied. This can be satisfied in equation (14) only if

$$\frac{P_1 \sqrt{M_B}}{P_2 \sqrt{M_A}}$$ is equal to unity.

The vapor pressures of indium and antimony in pure state at 1200 degrees C were calculated from an equation given by

Dushman (3).

$$\text{Log } P = A - B/T \tag{15}$$

where A and B are constants which are also given by Dushman.
The values of the vapor pressure for indium and antimony as cal-
culated at 1200 degrees C from equation (13) are:

Indium --- 4.75×10^{-1} mm of Hg

Antimony --- 50.2 mm of Hg

Substituting these values into equation (4), the ratio of $\dfrac{P_1 \sqrt{M_B}}{P_2 \sqrt{M_B}}$
for indium to antimony was calculated to be approximately
0.01, which is far less than unity. Hence it can be concluded
that the InSb alloy will undergo component separation upon evap-
oration, with the antimony evaporating approximately 100 times
faster than the indium.

One way of avoiding such preferential vaporization is the
use of a multi-source evaporation technique in which component
elements are evaporated from separate crucibles simultaneously.
The temperature of each crucible is separately adjusted to the
proper values calculated from the desired composition of the de-
posit and evaporation rate of each element. The difficulty of
controlling the relative evaporation rate of each source often
results in a non-uniform, stoichiometrically unsatisfactory
deposition of film.

An alternative technique to the above is to evaporate the
components in sequence and form a multi-layer coating, which on
heating produces a homogenous layer through diffusion. Brentan
and Richards (2) have obtained the film of InSb in this manner.
Obviously, here again the difficulty of controlling the

stoichiometry of the deposit is encountered. Moreover, Brentan and Richards report that the formation of thin InSb on the interfaces between the layers prevents further formation of InSb within the layers, when the thickness of the individual layers is more than two atoms. Thus this method requires an extreme precision in controlling evaporation rate and such complexity is rather prohibitive.

The purpose of this investigation was to explore tha possibility of using the first-mentioned method to prepare InSb films with satisfactory composition from the bulk InSb.

EQUIPMENT AND PROCEDURE

Plate I, Fig. 1, shows the pumping arrangement and electrical wiring of the vacuum evaporation plant employed for this investigation. The pumping combination consists of an oil diffusion pump backed by a rotary mechanical oil pump. An ionization vacuum gauge was used to measure the gas pressure of the chamber. A ring of polystyrene sheet cut to fit the bottom rimface of the bell jar sealed the vacuum chamber. The crucible was made of graphite according to the specifications on Fig. 2, Plate I, and it was attached to copper electrode plates, one inch by two inches by one-eighth inch in dimensions, by screws. A very tight fit between the crucible and the electrodes was necessary. A current surge of the order of 200 amperes would produce a localized very intense heat at any gap or loose contact. This would almost instantaneously destroy the copper electrodes and

EXPLANATION OF PLATE I

Fig. 1. Pumping arrangement and electrical wiring of the vacuum evaporation plant.

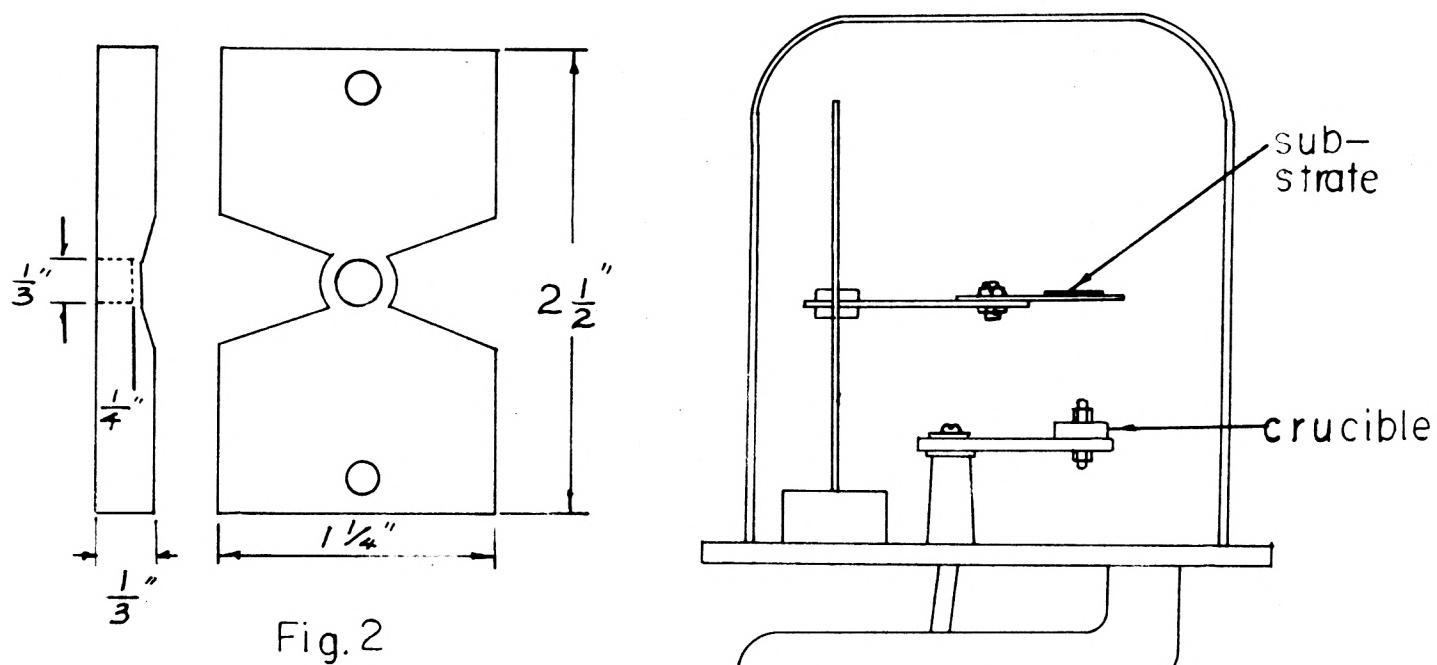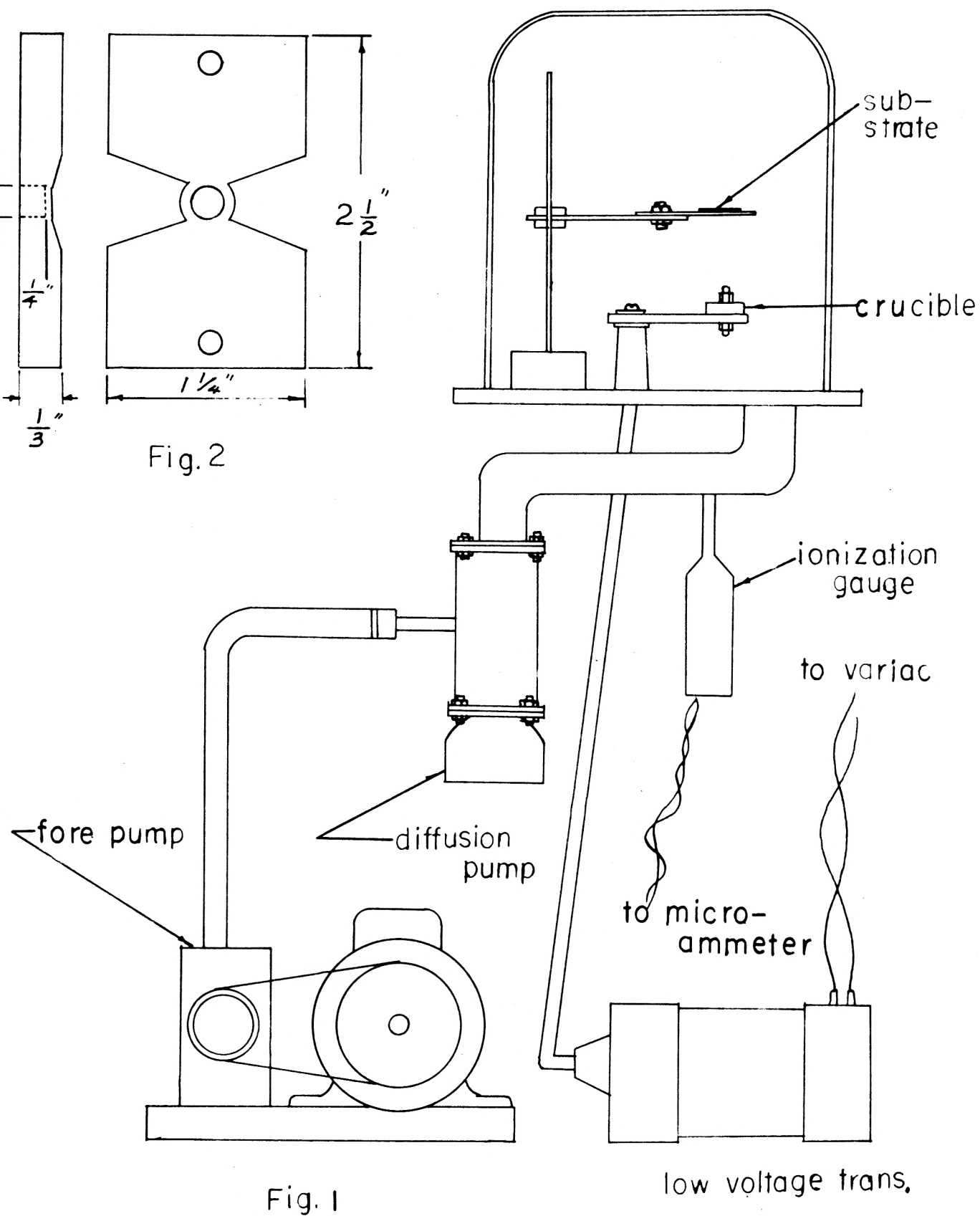Fig. 2. Specification of graphite crucible in which alloy was heated.

PLATE I

Fig. 2

Fig. I

the crucible. The transformer for heating the crucible is rated at 0.97 kva and has a voltage ratio of 110/5 volts. A variac inserted in the primary of the transformer regulates the secondary voltage. An ammeter connected in series with the primary is calibrated to read the secondary current. The leads connecting the transformer secondary to the electrodes are copper tubing 3/4 inch in diameter and 1/8 inch in wall thickness. The temperature of the crucible when heated was measured with an optical pyrometer.

The substrates on which the films would form were placed on a platform which was clamped to a ring stand. The distance of the substrates from the heated crucible was varied to study the effect on the composition of the deposited film. Slide glass cut to 3/8 inch by one inch was used as substrate. In order to make an electron-diffraction study of the films, a stainless steel, 200-mesh screen coated with a parlodion film was placed with the glass substrates in the evaporator. It was assumed that the composition of the film deposited on the screen was identical to that of the film deposited on the glass substrates which were placed in close proximity and at the same distance from the crucible. The variac was set at a predetermined position and when sufficient gas was pumped out of the bell jar, the switch was turned on. It takes from one to two seconds for the crucible to become white hot, a temperature of approximately 2500 degrees C. Timing was done by means of a stop watch.

The evaporation time was varied from two to 10 seconds. After the evaporation was completed, the pressure in the bell

jar of 3.5 microns was maintained for 10 to 20 minutes, or until the temperature of the film was at room temperature. This was done to avoid the possibility of oxidizing the film.

Plate II shows the cross section of the device for measuring resistance of thin films at various temperatures. The space between the inner and outer tubes was evacuated to about 3.5 microns. A copper plate was soldered onto the bottom end of metal-to-glass seal attached to the inner tube. The heating element consisted of nichrome wire wound around a thin mica sheet which is sandwiched between thicker mica sheets. The heating element was pasted with silver paint to the copper plate, and for a reinforcement the two ends were clamped with copper sheets and soldered onto the same copper plate. Ohmic contacts to the sample film were provided by means of silver paint. Thin copper wires were pasted to these contacts and soldered on the other ends to larger wires leading to a Wheatstone bridge. The thermocouple test junction was also pasted to one end of the sample film and its emf was read on a Rubicon potentiometer. The heating element was connected through a tungsten glass-to-metal seal to a variac which controlled the voltage applied to the element. The temperature of the sample was varied in the low temperature region by first cooling it down to -190 degrees C by pouring liquid nitrogen into the inner tube and letting the nitrogen evaporate slowly. The temperature above room temperature was obtained by means of the above-mentioned heating element. The variation of temperature with time was very gradual at all temperatures. The taking of data then virtually corresponded to

EXPLANATION OF PLATE II

Apparatus used for measuring resistance
at various temperatures.

PLATE II

to potentiometer

to variac

liquid nitrogen

heater
silver paint
film
thermocouple
junction

to vacuum
pump
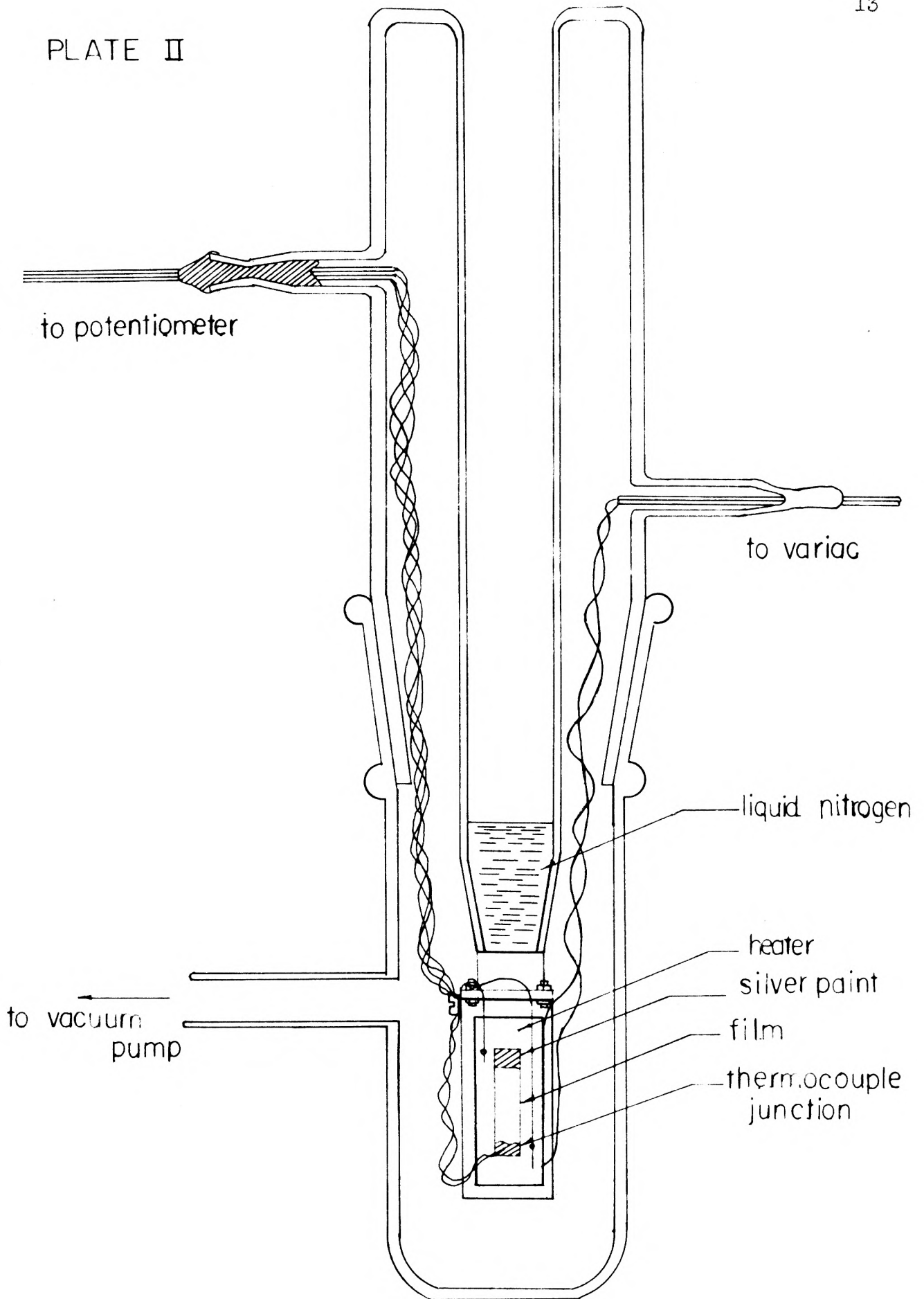
chosen values of temperatures.

EXPERIMENTAL RESULTS AND CONCLUSION

Seven samples were prepared with varied substrate-to-crucible distances and with different times of evaporation. The resistance versus temperature measurements were made on all the samples and R versus 1/T curves were plotted on semi-log paper in Plate III. Since only the magnitude of the slope of the linear portion was of interest for the calculation of the energy gap, the resistance rather than resistivity was plotted against 1/T. For this reason the dimensions of the film were not measured.

As can be seen from Plate III, within a certain range of temperature the curves of log R versus 1/T are almost straight lines, indicating a relationship of the type $R = A \exp(a/T)$, where A and a are constants. The slopes of all samples are almost identical except that for Group III. The energy gaps E_g calculated from these slopes, assuming an expression for the intrinsic conductivity region, namely, $R = A \exp(E_g/2kT)$ where k is the Boltzman's constant, are all in the neighborhood of 0.7 ev which differs less than an order of magnitude from the accepted value of 0.18 ev for pure bulk InSb. It has been suggested by Hannay (4) that the magnitude of the slopes in the steep portion of the resistivity versus 1/T curves increases with the concentration of impurities in InSb. Thus the steep linear portion of curves which are indicated by the solid lines on Plate III,

EXPLANATION OF PLATE III

Resistance versus 1/T for the following groups:

Group I. Evaporated for 5 seconds in a vacuum of 3.5 microns with the distance of substrate from the crucible of 5.5 cm.

Group II. Evaporated for 6 seconds in a vacuum of 3.5 microns with the distance of substrates from the crucible of 5.0 cm.

Group III. Evaporated for 7 seconds in a vacuum of 3.5 microns with the distance of substrates from the crucible of 4.5 cm.

Group IV. Evaporated for 8 seconds in a vacuum of 3.5 microns with the distance of substrates from the crucible of 3.0 cm.

Group V. Evaporated for 5 seconds in a vacuum of 3.5 microns with the distance of substrates from the crucible of 2.5 cm.

Group VI. Evaporated for 5 seconds in a vacuum of 3.5 microns with the distance of substrates from the crucible of 2.0 cm.

Group VII. Evaporated for 5 seconds in a vacuum of 3.5 microns with the distance of substrates from the crucible of 1.5 cm.

PLATE III

Group V

Group VI

Group IV

Group II

Group VII

Group III

Group I

$\dfrac{1}{T}$
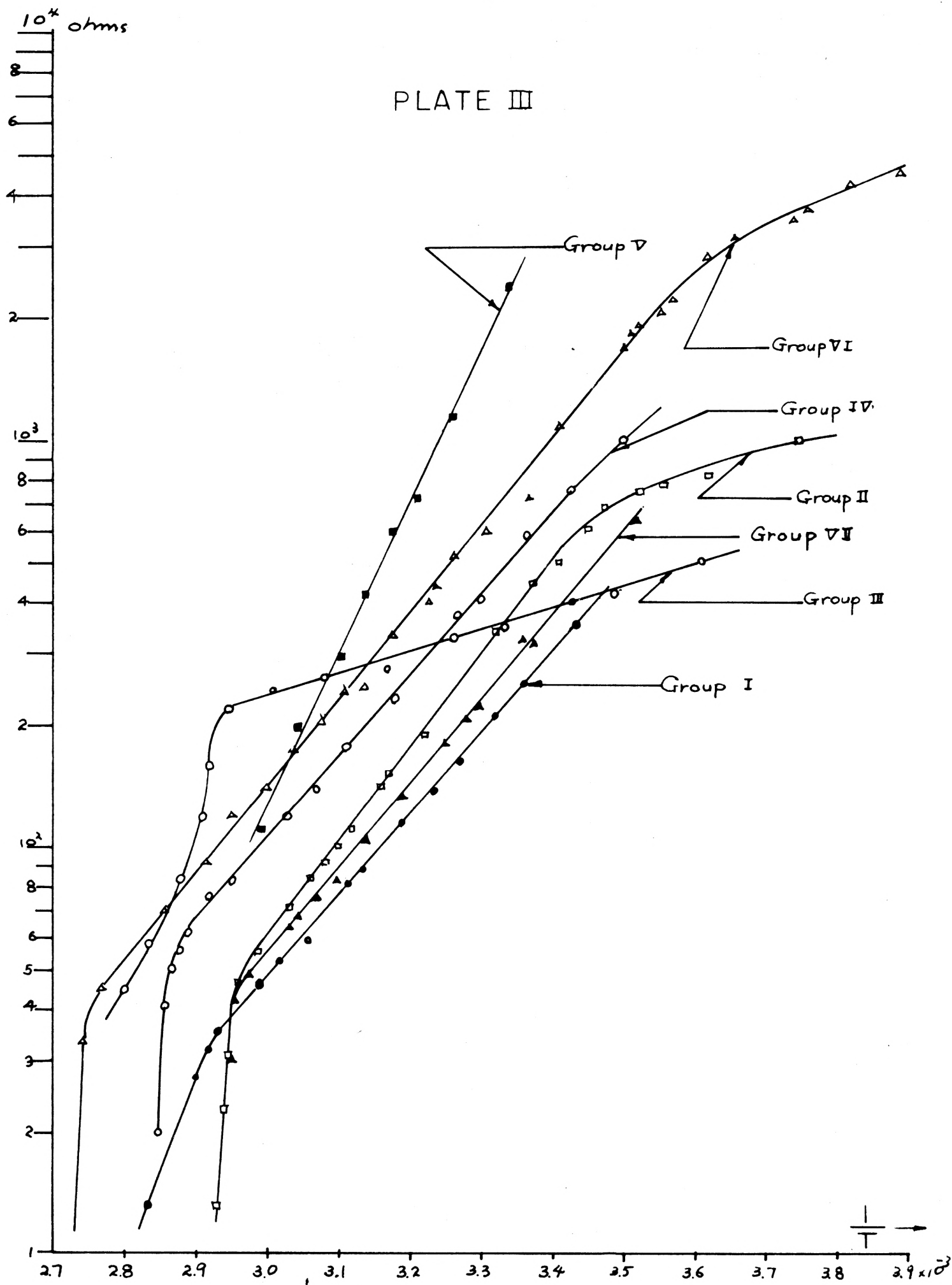
was at first interpreted to be the intrinsic conductivity region
of the InSb film with a rather high impurity concentration.
Sudden sharp drop of resistance observed for all samples at a
high temperature--in the neighborhood of 100 degrees C--has been
believed to be due either to the diffusion of silver from the
ohmic contacts on the ends or to the oxidation process in the
film. For this reason the resistance measurement was not made
beyond this transition temperature. These sharp changes of re-
sistance have been observed to be irreversible. The resistance
change is reversible before the samples were heated beyond this
"critical temperature". However, in the process of the electron
diffraction study, evidence was brought forth that the sample
was initially in an amorphous state rather than in crystalline
form. The diffused broad ring pattern obtained with a weak elec-
tron beam for a sample which was freshly made, indicated an amor-
phous material. However, when the electron beam intensity was
increased to a maximum value, the ring patterns changed at a
detectable high rate to those of a crystalline material. The
photographs of the ring patterns for the same section of a sample
before and after the exposure to a strong electron beam are
shown in Plate IV, Fig. 1 and Fig. 2, respectively. Evidently
the electron bombardment of the initially amorphous material re-
sulted in the formation of crystals. From the diffraction pat-
tern identical to the one shown in Fig. 2 of Plate IV, the diam-
eters of rings were measured and d-spacings of the crystal were
calculated. The results obtained for the sample of Group I are
tabulated in Table 1 along with the value of d-spacings obtained

EXPLANATION OF PLATE IV

Electron diffraction pattern of an InSb film.

Fig. 1.   Before the electron bombardment.
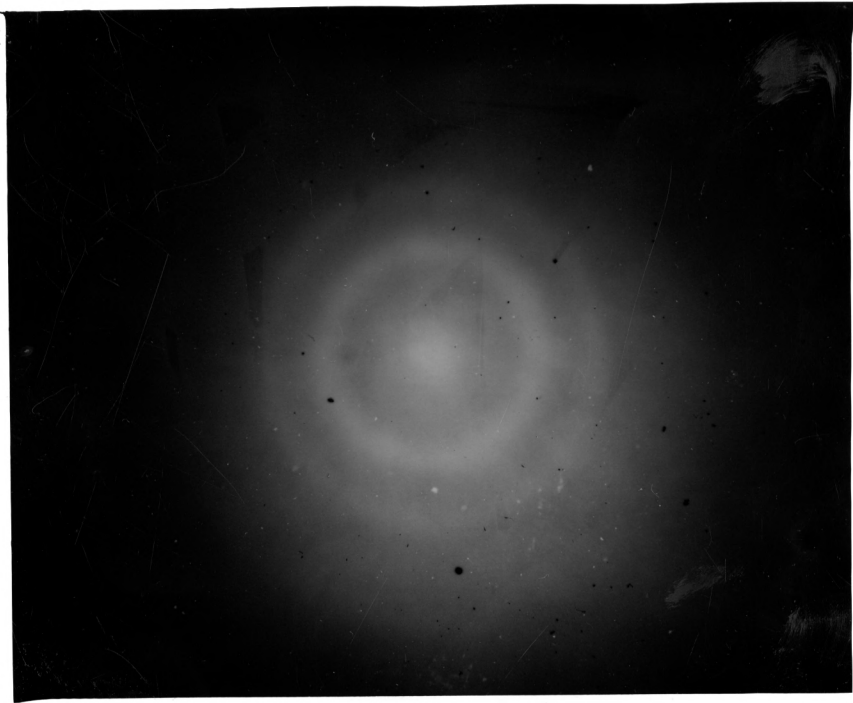
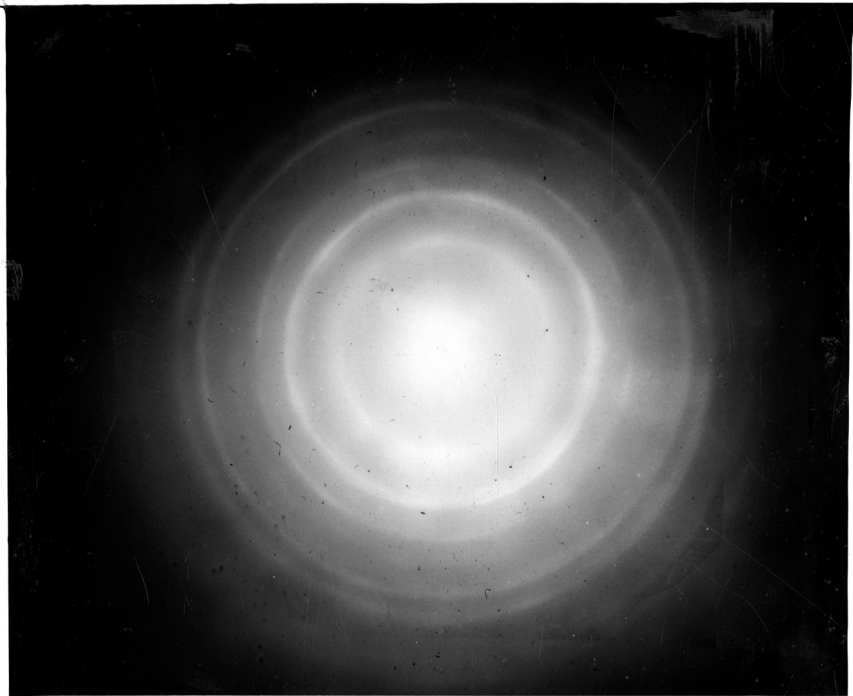Fig. 2.   After the electron bombardment.

PLATE IV

Fig. 1.

Fig. 2.

Table 1.   The results of electron diffraction study on the film of InSb.

Swanson, Fugat, and Ugrinic			The results of this experiment for Sample I	
hkl	d(A)	I/I$_1$	d(A)	Observed relative intensity
111	3.74	100	3.710	Very strong
220	2.290	80	2.330	Very strong
311	1.953	55	1.923	Strong
400	1.620	15		
331	1.486	22	1.482	Strong
422	1.323	25	1.363	Strong
511	1.247	12		
440	1.1453	9	1.173	Weak
531	1.0950	12	1.061	Weak
620	1.0243	9	1.022	Weak
533	0.9880	6		
444	0.9349	7)	0.9127	Very weak
711	0.9071	8)		
642	0.8657	12)	0.8625	Weak
731	0.8434	9)		
800	0.8098	3	0.8046	Very weak

from standard x-ray diffraction powder pattern by Swanson, Fugat, and Ugrinic, of the National Bureau of Standards. Although the 1.620 A, 1.247 A, and 0.9880 A relatively weak lines are missing in the result of this experiment, the agreement in all the rest of the lines is more than adequate to insure that the film after being exposed to electron bombardment is InSb.

This is in direct contradiction to the deduction made from the resistance versus 1/T curves, namely, that the deposited material is already crystalline InSb even before annealing by means of thermal agitation or by means of electron bombardment. To find a reconciliation between these two contradicting evidences,

the investigation of the effect of thermal annealing on the re-
sistance versus 1/T characteristic was carried out. Two more
samples, Groups VIII and IX, were prepared and were enclosed in
two separate glass tubes which were then evacuated to 3.5 microns
and sealed off. The samples were kept free of silver paint so
as to isolate the effect of possible diffusion of silver on the
resistance versus 1/T curves. The sample of Group IX was heated
at 150 degrees C for 20 minutes, and the sample of Group VIII
was heated at 150 degrees C for an hour.

The results of resistance versus temperature measurement on
these samples are plotted on Plate V. On the same plate is plot-
ted a curve of the resistance versus 1/T for a thin slab sliced
from the parent bulk InSb. The energy gap calculated from the
steep linear portion of the bulk InSb curve was found to be
0.243 ev, which is slightly higher than the accepted value of
0.18 ev for pure bulk InSb. The energy gap calculated from the
slope of the curves for the annealed sample for Group IX came
out to be 0.15 ev, which is lower than that from the curve of
parent bulk material and slightly lower than that of the pure
InSb. The energy gap calculated for the slope of the sample of
Group VIII was found to be 0.093 ev, which is even lower than
that for the sample of Group VIII. The reduction of resistance
after annealing was striking. In the sample of Group VIII it
changed from 2.72 megohms to 1430 ohms at 23 degrees C.

In order to study the change in the surface due to thermal
annealing, a Leitz microscope was used. For this purpose a new

EXPLANATION OF PLATE V

R versus 1/T curves for the following groups:

Group VIII. Sample 1, annealed for 20 minutes at 150 degrees C; sample 2, unannealed.

Group IX. Sample 1, annealed for one hour at 150 degrees C; sample 2, unannealed.
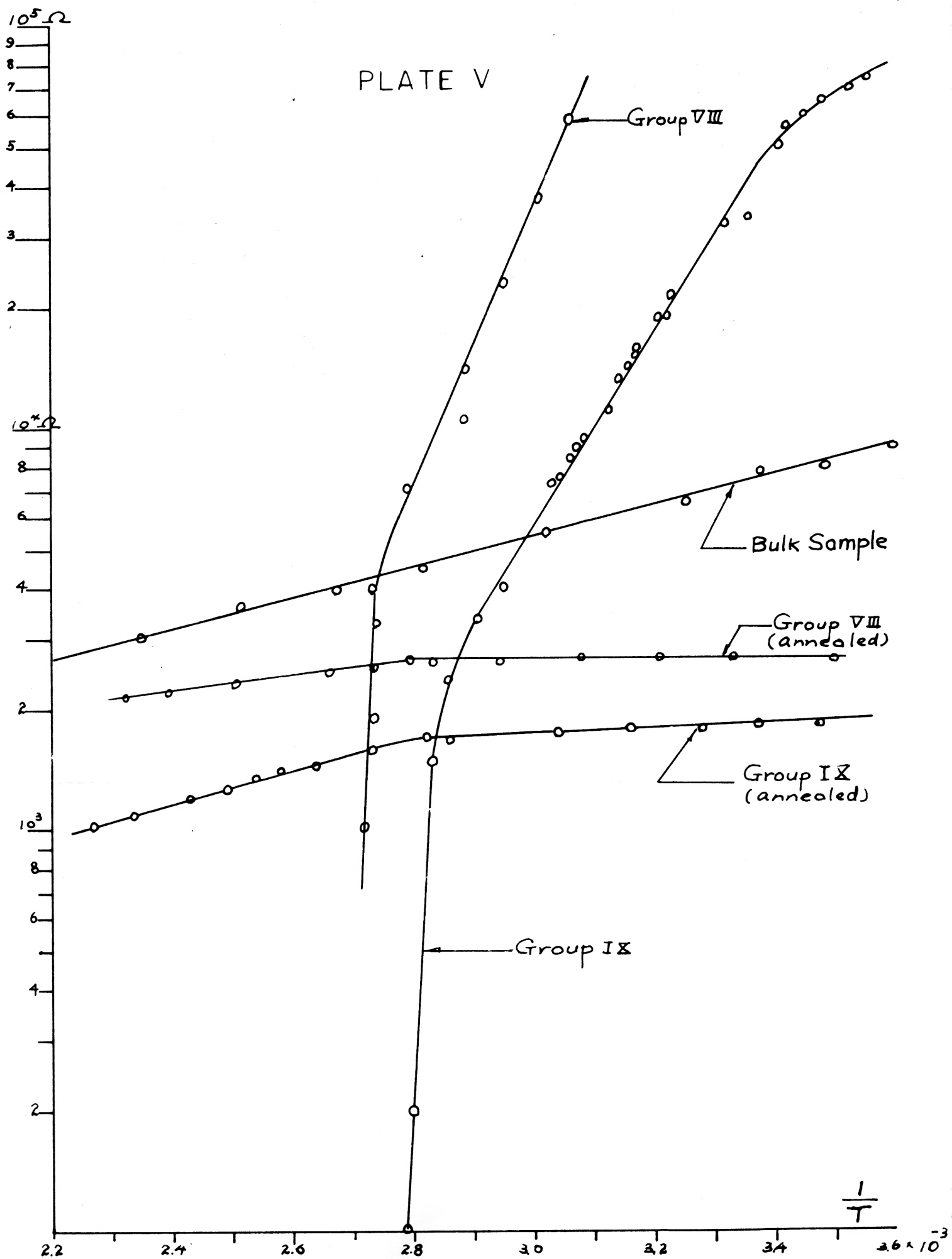
PLATE V

sample was made. The photographs taken of this sample before and after the annealing at 120 degrees C for 24 minutes are shown on Plate VI. The magnification used was approximately 600X. The lower half of Fig. 1, Plate VI, where white spots are distributed without an apparent order, is representative of the major portion of the surface of this Group before annealing. Approximately 20 per cent of the surface was covered with large fragments as seen on the upper section of the figure. These large fragments may be crystalline InSb powder particles which were evaporated from the charge and deposited on the glass face without decomposing into molecular particles. The smaller white spots are believed to be dislocations. Figure 2, Plate VI, is the photograph of the surface of the sample of the same group after annealing. As can be seen, there is a distinct line of etch pits running diagonally across the photograph. There are also a few lines of less brightness parallel to this line on the lower right-hand corner of the photograph. These lines are probably etch pits developed along the [110] direction of the InSb crystals. Also there are innumerable vertical lines, which are thought to be in the [100] direction. A dark vertical line slightly to the left of the center of the photograph must be an absence of strain. From the photograph of Fig. 1, Plate VI, alone, it cannot be inferred that the film before annealing is not in a crystalline form, but it can be safely said that the photograph of Fig. 2 is definitely indicative of crystalline material.

EXPLANATION OF PLATE VI

Optical micrographs of InSb film surfaces
by reflected light.

Fig. 1. The surface of the sample III before an-
nealing, magnification 600X.

Fig. 2. The surface of sample III after anneal-
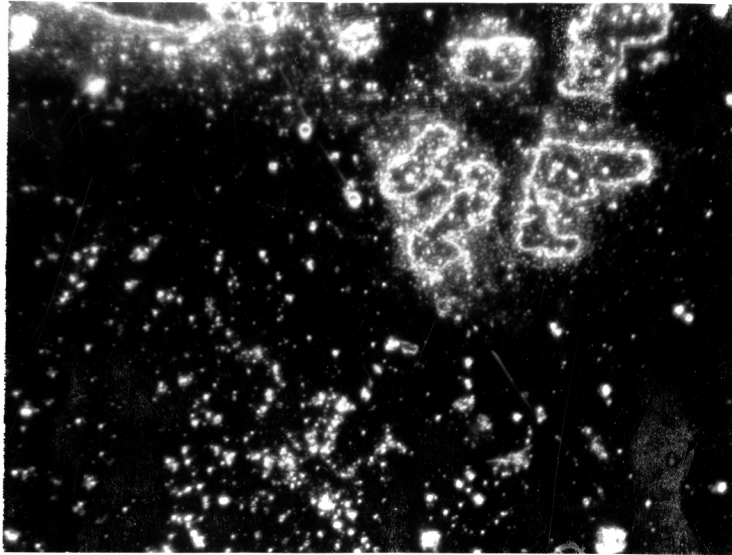ing, magnification 600X.
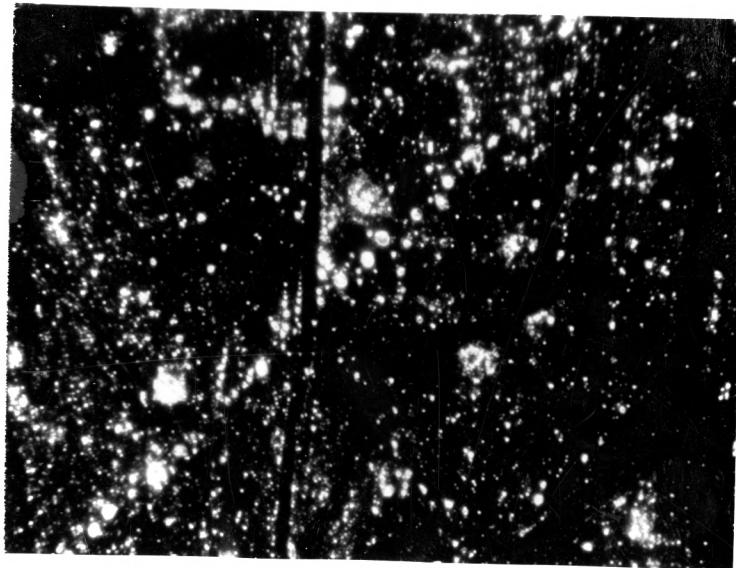
PLATE VI

Fig. 1.

Fig. 2.

SUMMARY

Summarizing the evidence obtained from the electron diffraction study, from the resistance versus 1/T curves, and also from the metallographic study of the surface before and after the annealing, the following conclusions have been drawn:

1. As predicted by the criteria given by Holland, component separation does take place during the rapid evaporation of the InSb powder charge. Some portion of the charge may be evaporated and deposited without component separation as evidenced from the metallographic study.

2. However, contrary to the common belief that the film of this binary alloy could not be made by the ordinary technique, there is a definite evidence that it can be done. The composition of the amorphous film obtained by a rapid evaporation is not greatly different from that of the parent bulk material as crystalline InSb can be formed by thermally annealing the film.

FUTURE STUDY

With thin films of InSb available, the following studies can be made:

1. Optical absorption. This has been carried out by Kaiser and Fan (9). However, the range of wavelength used by them was limited because the thickness of their InSb slab could not be reduced below 10 microns. Interesting phenomena should

be observed beyond the wavelengths which have been covered by these people.

2. Hall coefficient measurement on the films before and after thermal annealing may reveal transition from n-type to p-type. Before the annealing it is very likely that the film is rich in antimony for the reason that antimony evaporates almost 100 times faster than indium, thus making the film n-type. Then, after annealing, preferential evaporation of antimony may again take place and if annealing is carried out at a high temperature for a longer period of time, it may eventually become indium-rich or p-type.

3. Photoconductivity measurement may reveal very interesting results for InSb has one of the lowest energy gaps and one of the highest mobilities. It may be a promising infrared detector if properly constructed.

4. Field effect studies can be carried out with more convenience as this effect becomes more pronounced as the thickness of the sample is reduced.

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Thin films of different materials are required in many fields of semiconductor research. Preparing thin films of monatomic semiconductors, i.e., silicon and germanium, can be easily done by evaporating the bulk material in vacuum and depositing on suitable substrates. However, as the semi-quantitative criteria discussed by Holland shows, in the case of evaporating binary alloys a preferential evaporation of the more volatile component is apt to take place. From this criteria it was found in the case of InSb that the preferential evaporation is unavoidable, if ordinary evaporation at slow rate is employed. It was shown that antimony would evaporate approximately 100 times faster than indium.

To avoid such preferential evaporation, a technique of evaporating from multi-sources can be employed. Another method is to evaporate thin layers of indium and antimony alternately and produce films of InSb by annealing. The above two methods are costly in set-up and unnecessarily complicated in procedure. Thus in this investigation a possibility of preparing InSb films by evaporating powdered InSb at a very rapid rate has been explored.

In total, 10 samples have been made following the above procedure. Along with the glass substrates, 200-mesh stainless steel screens coated with a film of parlodion were placed to receive the evaporated alloy. This was done to study the structure of the substance deposited by means of electron diffraction techniques. The resistance versus temperature measurement on the samples with glass substrates were made and $\log_e R$ versus

1/T curves were plotted. The energy gaps were calculated from the slope of the steep linear portion of the curves for both annealed and unannealed samples. For unannealed samples the energy gaps calculated were found to be in the neighborhood of 0.7 ev, while the energy gaps calculated for the annealed samples were 0.15 ev. For comparison the energy gap for the parent bulk InSb was calculated and found to be 0.243 ev. The accepted value of the energy gap for pure bulk InSb at 100 degrees C is 0.18 ev.

Around 100 degrees C the resistance of unannealed samples dropped very sharply. The change was irreversible. These transitions were interpreted to be the points of formation of InSb crystals. The electron diffraction study shows that the samples were largely amorphous before annealing but after exposure to electron bombardment, which is equivalent to thermal annealing, the material changed to a crystalline solid. Calculations of d-spacings from the ring diffraction pattern of the crystalline sample are in close agreement with the data obtained by Swanson, Fugat, and Ugrinic, of the National Bureau of Standards.

Metallographic studies made on the sample before and after annealing also indicate that the films were originally without an apparent order, which is characteristic of amorphous material, but after annealing exhibited orderly arrangements of etch pit lines characteristic of crystals.

From these evidences it was concluded that decomposition

of InSb upon evaporation does take place. The composition of the amorphous films is such that when they are thermally annealed, InSb crystalline films of a composition resembling the parent bulk can be formed.