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ELECTRON BEAM EVAPORATED HIGH MOBILITY
THIN FILMS OF INDIUM ANTIMONIDE

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Final Report

EE-191(71)NASA-028

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INTRODUCTION

Indium antimonide thin films prepared by electron-beam evaporation have been polycrystalline in structure and have electrical properties which are inferior to those of the bulk material. Correlation between mobility and crystalline size suggests that scattering at grain boundaries is important in limiting the electron mobility to about one quarter that of single crystal bulk InSb (References 1, 2, and 3). Long annealing cycles at temperature below the melting point of the compound have not succeeded in promoting extensive crystal growth in such polar semiconductor films. However, poly-dendritic films consisting of an array of crystals which are large in relation to the electron mean free path have been prepared by remelting vacuum deposited films under a protective In_2O_3 cover layer (References 4 and 5).

Clawson and Wieder (Reference 6) have reported electron mobilities of 5.56×10^4 cm^2/V-sec in thin single-crystal dendrite isolated from polydendritic films prepared by this method.

Teede (Reference 7) recrystallized InSb films from the molten state by electron-beam micro-zone melting. He obtained large single-crystal areas in InSb films on glass substrate which have electron mobilities and conductivities approaching 5 percent of their values in single-crystal bulk material having a similar net donor concentration.

It appears that evaporation and recrystallization of InSb films by the electron-beam process yields high mobilities compared to other processes. A systematic study, therefore, was undertaken at The University of New Mexico. Following are the results of some preliminary experiments.

EXPERIMENTAL SETUP

ELECTRON BEAM GUN

The CVC vacuum system, CVI-18, was modified. The electron beam source Model TIH-270, manufactured by the Air Reduction Company, was installed in the vacuum chamber of the CVC system. The electron beam heated vapor source with 270 degrees magnetic deflection is water cooled and is operated with a high-voltage source. Figure 1 shows the setup for the electron beam in the CVC.

PRINCIPLES FOR ELECTRON BEAM

The electron beam filament operates at a negative high-voltage potential, and the electrons are accelerated toward the crucible which is at ground potential. The emission in the tungsten filament is controlled by varying filament current. The filament is set in a cavity bounded by cathode blocks and a beam former, all at cathode potential. Space charges are formed by the emitted electrons at the back, bottom, and top of the cavity, forcing electrons emitted in these directions to return to the filament. Only electrons emitted at the front of the cavity escape. These are accelerated by
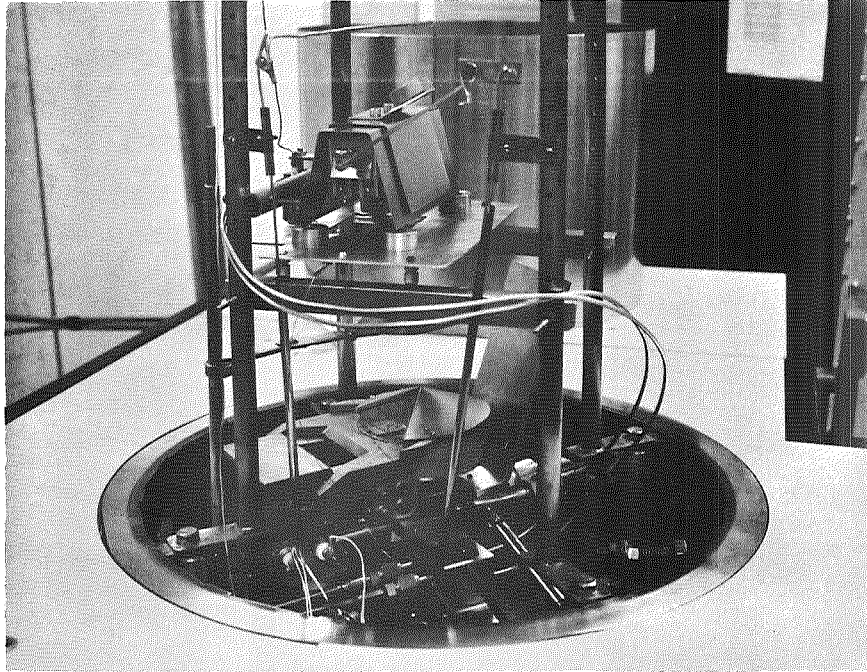
Figure 1. Electron Beam Source in CVC System

the anode potential through a hole in the anode plate. During acceleration they are also focused, the plate operating somewhat as a single aperture lens. Beyond the anode plate, the electron beam is both deflected and further focused by a magnetic field onto a small spot on the evaporant metal in the crucible. The beam position controls vary the position of the electron beam on the crucible, and the dither controls allow the beam to be swept back and forth longitudinally across the crucible. The sawtooth dither waveform is superimposed on the quiescent DC beam position setting.

This electron gun has the capability of sweeping in the x-y direction. The actual beam spot is triangular in shape and has an area of approximately 10 mm^2.

The electron beam has significant advantages. Most of the kinetic particle energy is converted into heat and high

temperatures such as 3000°C can be achieved. Also it can be concentrated on the evaporating surface maintaining other portions at considerably lower temperatures, thus reducing the interaction between evaporant and the support materials. Electron-bombardment heating is versatile and used to evaporate elements as well as compounds, provided they do not decompose upon heating. Finally it is simple in construction giving more directional heat supply and less stirring of the melt.

OPERATION

The electron-beam gun is operated only when the pressure in the CVC system is 10^{-5} torr or lower. The water is turned on before switching the high voltage. After the high voltage is turned on, the emission current is slowly increased, indicating a blue-spot on the evaporant until the evaporant is melted but not evaporated. It is increased further to obtain the most desirable rate of evaporation. The position of the beam is adjusted at the center of the evaporant by the position control.

MASK AND SUBSTRATE

For our experiments the five-probe geometry of the samples was chosen as shown in Figure 2(a). Separate masks were cut for the metallization as shown in Figure 2(b). The masks were cut out of very thin copper plate with dimensions as shown. These masks were cleaned first ultrasonically, and later with acetone, isopropyl alcohol before each use. Our

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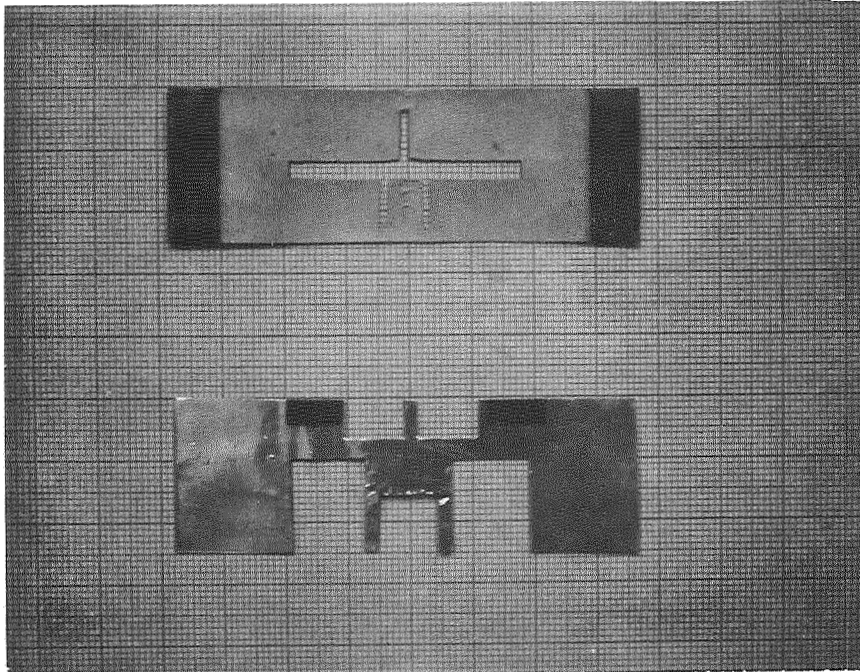
Figure 2.   Deposition and Metallization Masks

substrates were microscopic glass slides 1.0 x 3.0 inches in
size.   They were cleaned with isopropyl alcohol and were kept
in Transene 100 until use.

SUBSTRATE HEATER

In order to obtain a homogeneous temperature over the
sample, an array of quartz iodine lamps is used.   The sub-
strate heater assembly, Model HA-2, manufactured by Air Re-
duction Co. (Temescal) consists of two 500-watt iodine quartz
lamps, one polished molybdenum reflector, and a stainless
steel holder.   The dimensions of the heater assembly are 5.75
x 2.82 x 2.68 inches.

The assembly is heat shielded to focus the heat on the
substrates and minimize heating of the rest of the vacuum
system.   The lamps and the molybdenum reflector can be easily

removed for cleaning or replacement. A Variac is used for better control and more flexibility of operation.

THICKNESS MEASUREMENT

A thickness monitor, Model DTM-3, from Sloan Instruments was installed in our CVC for accurate measurement of the thickness of the deposited films.

The DTM-3 is designed for the measurement of mass of the deposit rather than measurement of second effect parameters such as reflectivity, resistance, etc. Mass is measured by evaluating the change in frequency of a resonating quartz crystal as a deposit builds up on a surface.

Normal reproducible accuracy is of the order of ± 2 percent but an absolute accuracy of the order of ± 50 Å units of aluminum (or mass equivalent) is possible using special techniques.

The thickness monitor was kept as near as possible to the substrates thus giving maximum accuracy. The thickness monitor and substrates were shielded from the evaporant by a shutter which was opened only when the desired rate of deposition was built up.

Thickness of the deposited films was calculated by using the equation

$$t = \frac{2\Delta f}{\rho}$$

where

t = thickness of a film in Å

Δf = frequency shift in Hertz

ρ = bulk density of the material in gms/cm^3

The rate of evaporation was calculated by noting the duration of deposition and the change of frequency.

THERMOCOUPLE

For the measurement of substrate temperatures a thermocouple (iron-constantan) was kept in contact with the bottom surface of the substrates.

METALLIZATION

For metallization of the deposited InSb films another CVC vacuum system was used. A liquid nitrogen cold-trap was used to attain pressures for metallization ranging from 3 x 10^{-7} to 5 x 10^{-7} torr. Aluminum metallization was the primary function but in some cases In, Cu, and Ag were also evaporated.

OXIDATION

All films were oxidized before recrystallization. This was necessary to prevent balling up or rupture of the liquid film due to surface tension during recrystallization. The oxide layer can be formed in the following manner.

1. Allowing a small quantity of O_2 to enter the furnace along with the argon during recrystallization.

2. Heating the sample in air before recrystallization.

3. Opening the vacuum system when the temperature of the substrate drops to 250°C.

In our experiments most samples were oxidized in a Forma-Vac oven heated to 250°C for about 10 minutes, although some films were oxidized by opening the vacuum system when the temperature of the substrate was 250°C.

RECRYSTALLIZATION

Elements in a compound film are always recrystallized to get the proper stoichiometric proportion. Our InSb films were recrystallized in a tube kept in a furnace with a constant temperature zone of 5 inches, through which argon was passed at the rate of 2 to 3.5 liters/min. The temperature was varied from run to run--in most cases it was between 520 and 530°C.

The quartz boat on which the samples were kept in the furnace was cleaned with 10 percent hydrofluoric acid (HF) for 10 to 15 minutes and then kept in deionized water until use. Before putting the sample on the boat, the boat was kept at the end of the heated furnace for 10 minutes to allow the water to evaporate. Then the sample was placed on the boat and slid in exactly at the center of the furnace. A thermocouple was positioned to touch the sample in such a way as to register accurate recrystallization temperature.

In some experiments films were suddenly cooled after recrystallization but in others the furnace was shut off after 5 minutes of heating and the films were removed when the temperature dropped to about 450°C.

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EXPERIMENT, MEASUREMENT, AND RESULTS

EXPERIMENTAL PROCEDURE

For our experiments InSb-8n obtained from Ohio Semitron-ics, Inc., was used. It was cut into pieces using a wire saw, clearned afterward ultrasonically, and put into the crucible. Sometimes InSb in powder form was also used. The masks and substrates were cleaned ultrasonically and then with trichlor-oethylene, isopropyl alcohol, and were positioned above the crucible at a distance of 7 inches. A thermocouple was placed touching the surface of the substrates and was con-nected to a microvoltmeter. The substrate heater was at a distance of 2.5 to 3 inches from the substrates, heating them uniformly. A crystal monitor was arranged as near to the sub-strates as possible. The system was pumped to 3 to 5×10^{-7} torr.

When the substrate temperature was 275°C and the pres-sure around 3 to 5×10^{-7} torr, the crystal monitor was switched on and heating of the evaporant with an electron beam was started. The shutter was opened when the desired evaporation rate was attained. Many experiments were done at an evaporation rate of 3500 Å/min and some were done at 10,000 Å/min. The samples were allowed to cool to room temperature.

Metallization of the aluminum was done immediately in another CVC system using different masks. In some cases when the oxidation was done in the vacuum system just after the deposition of InSb the metal contacts were deposited before

the deposition of InSb. In other cases the samples, just after metallization, were heated in an oven at 250°C for about 10 minutes.

These oxidized films were recrystallized in a furnace. The sample was kept on a quartz boat and then slowly slid into the center of the furnace. Argon was passed over the sample at the rate of 2 to 3.5 liters/min. The temperature of the furnace was maintained between 520 and 530°C and measured with a thermocouple touching the surface of the sample. Recrystallization at this temperature was done for 3 to 5 minutes, varying from run to run. Some samples were cooled down immediately but some were allowed to cool slowly in the furnace. When the temperature reached 450°C they were pulled out very slowly. These samples were then examined in the microscope and microphotographs were taken before measurement.

MAGNET AND SAMPLE HOLDER

The electromagnet, Varian Associated type V2901, was used for the measurement. It is a medium-size magnet with a reasonably uniform magnetic field within 3 inches. The diameter of the pole pieces having flat faces is 2 inches. The distance between the pole pieces is adjusted by a two-way knobbed wheel pole device. The necessary current to energize the coils is supplied from a regulated power supply. The polarity of these pole pieces can be changed manually. Further, the intensity of the field can be changed either by changing the current passing through the coil or by changing the distance between the pole pieces.

Intensity of the magnetic field with variation of current as well as with pole gap was calibrated with the help of a gaussmeter, Empire Model 900. Figure 3 shows the variation of magnetic fields vs. current passed through electromagnetic coils for different pole gaps.

The sample holder consists of a copper tube with copper and bakelite plates at the end as shown in Figure 4. The sample was held firmly against the bakelite with two copper strips at the end. Copper blocks 3/16 x 1/4 x 3/8 inch were used as the pressure contacts for the sample. They were connected with flexible wire to the main circuit.

ELECTRICAL CIRCUIT AND V_H MEASUREMENT

Figure 5 shows the electrical circuit used in the measurement of Hall voltage.

For the measurement of the Hall voltage, V_H, a current of 1 ma magnitude was passed through the sample. A potential drop between points a and b which is V_{ab} was balanced with a potentiometer thus giving initial zero Hall voltage (with no magnetic field). Then the magnetic field was applied and the Hall voltage was measured for different magnetic fields and different current passed through the sample. V_{ab} was also measured. Hall mobility was calculated by using the formula (Reference 8)

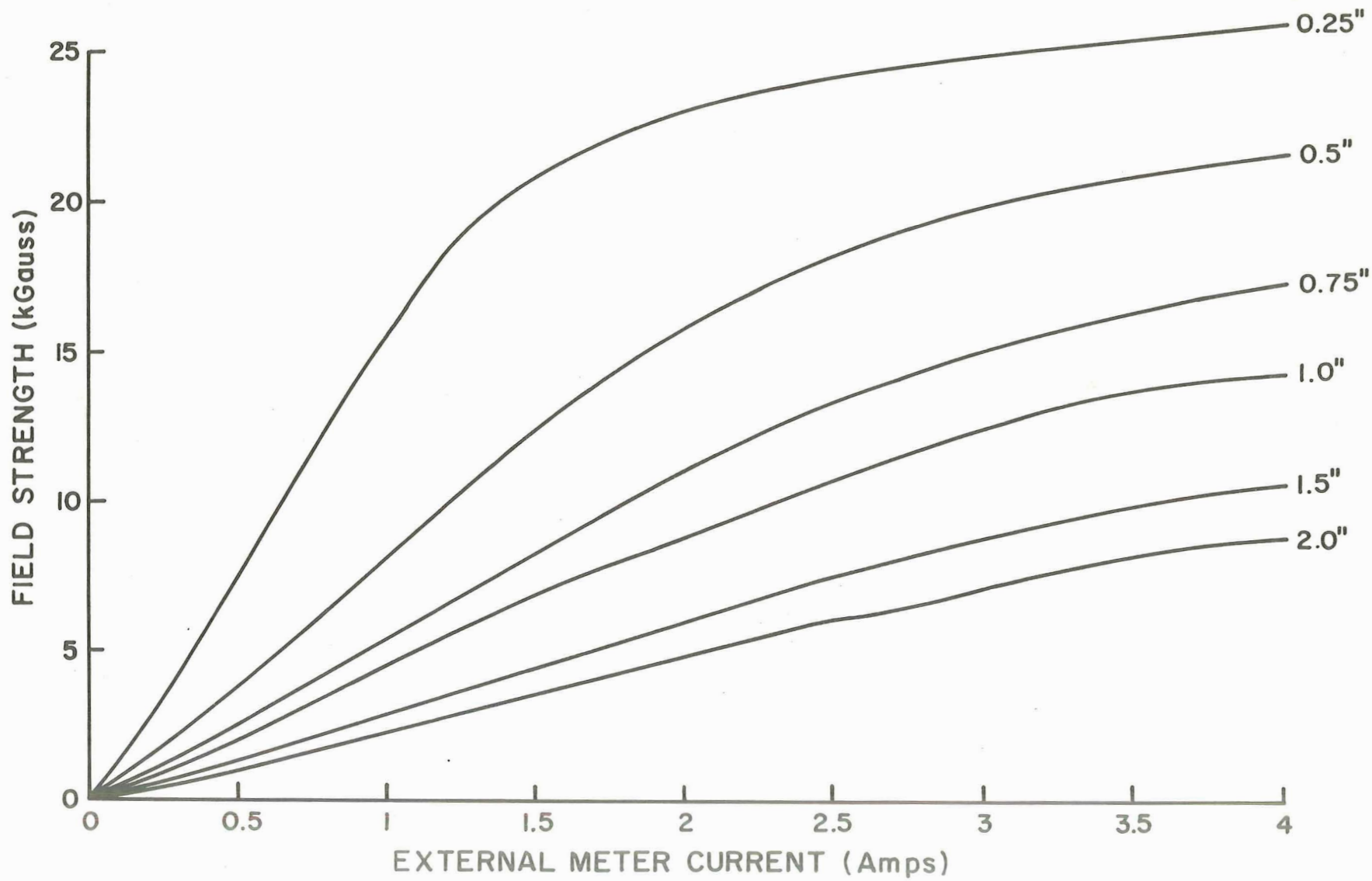$$\mu_H = \frac{V_H}{V_{ab} \times B_z} \frac{\ell}{b} \ m^2/volt\text{-}sec$$

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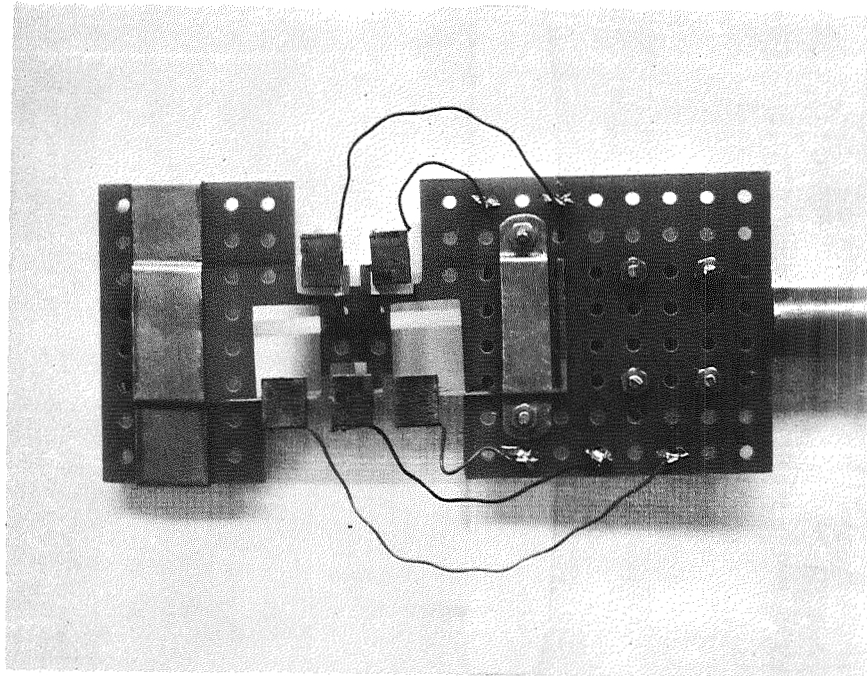Figure 3.   Magnetic Field vs. Current

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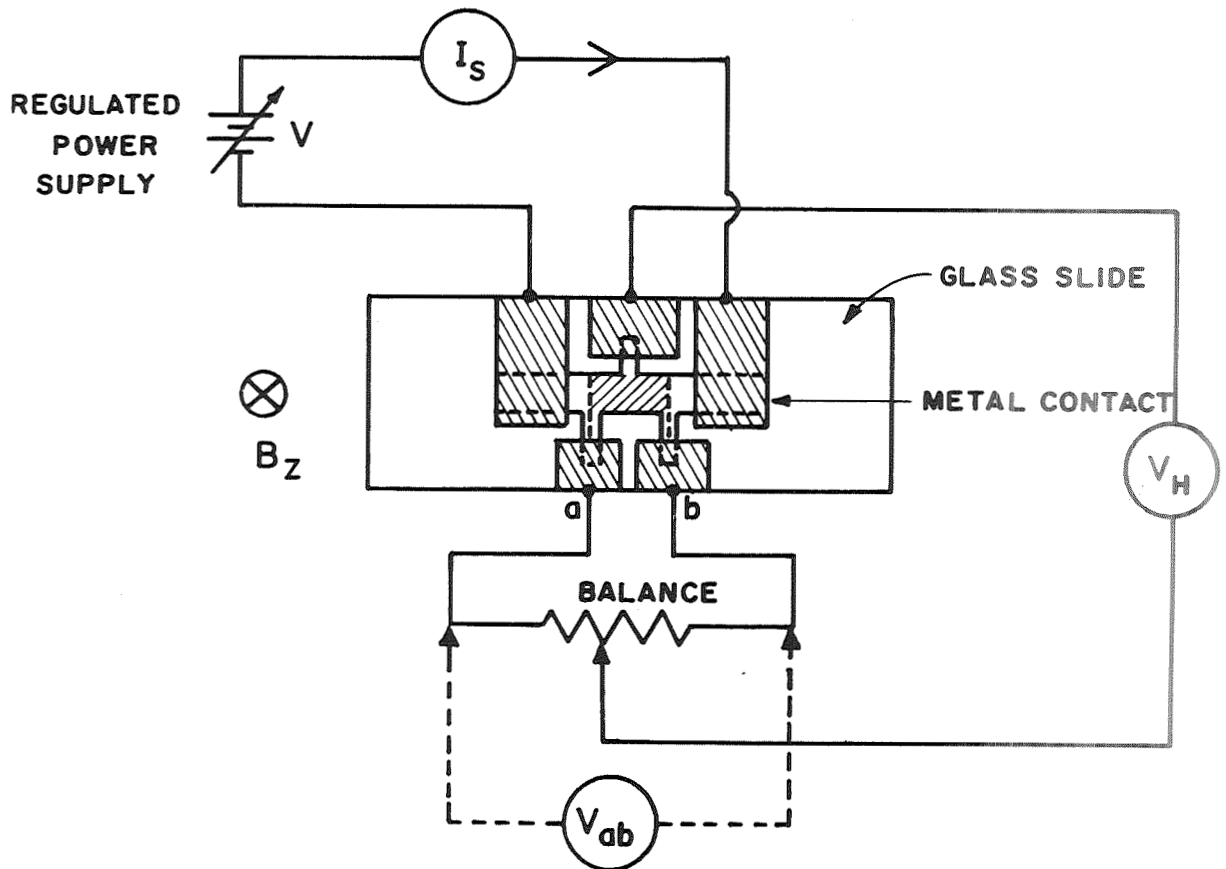Figure 4.   Sample Holder

Figure 5.   Electrical Circuit Used in the
Measurement of Hall Voltage

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where

μ_H = Hall mobility

V_H = Hall voltage

V_{ab} = potential between a and b

B_z = magnetic field

ℓ = distance between a and b

b = width of the film

The resistance of the sample, R_s, was measured.

RESULTS

Figure 6(a) and (b) shows micrographs of a film with 50 and 500 times magnification. This film was deposited at a substrate temperature $\simeq 310°C$ and with an evaporation rate of 2500 Å/min at a pressure of 2 x 10^{-6} torr. The film was annealed at $\simeq 310°C$ for 30 minutes in the vacuum chamber and then allowed to cool. Figure 7 shows the variation of Hall voltage with magnetic field for this film. The calculated Hall mobility was 5300 cm^2/V-sec.

In another experiment two films were deposited at 250°C substrate temperature at 2.3 x 10^{-6} torr pressure with an evaporation rate of 3100 Å/min. The substrate heater was shut off immediately after the deposition. After cooling these samples to room temperature one of them was oxidized in the oven at 250°C for 5 minutes (S-11(b)).

Figure 8 shows the micrograph of S-11(b) before annealing. A similar structure was observed for S-11(a) also. The measurements showed a Hall mobility of 2500 cm^2/V-sec for S-11(b) while S-11(a) did not show anything.
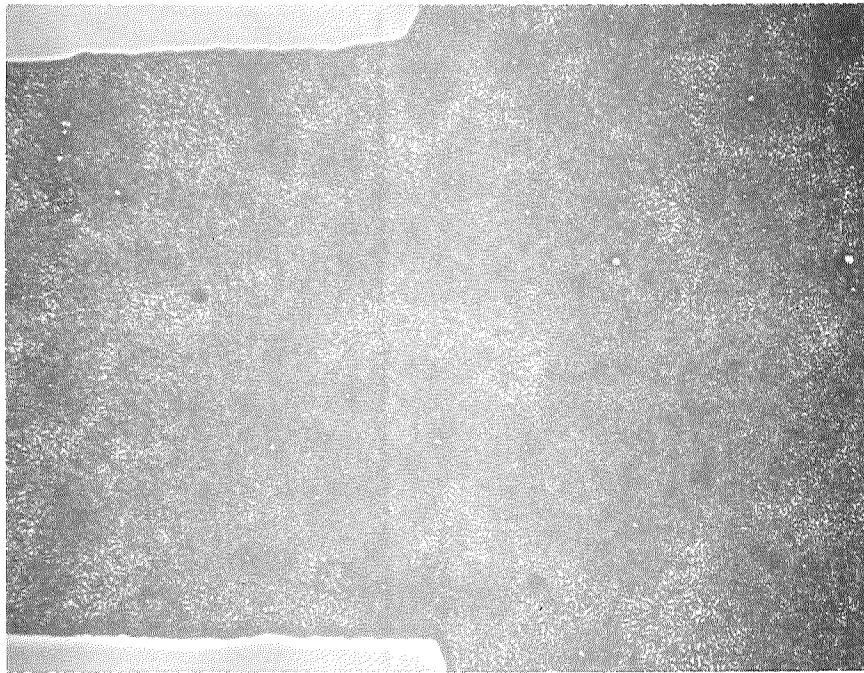
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(b) InSb Film Deposited,
3 μm Thick, 500 Magnification,
ASA 400, T = 1/2 sec
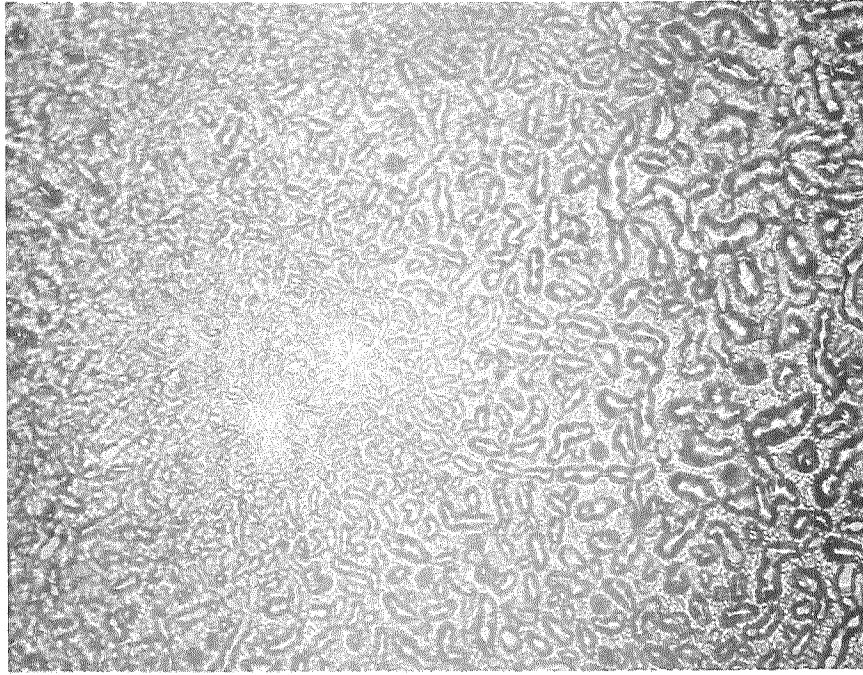
(a) InSb Film Deposited,
3 μm Thick, 50 Magnification,
ASA 400, T = 1/2 sec

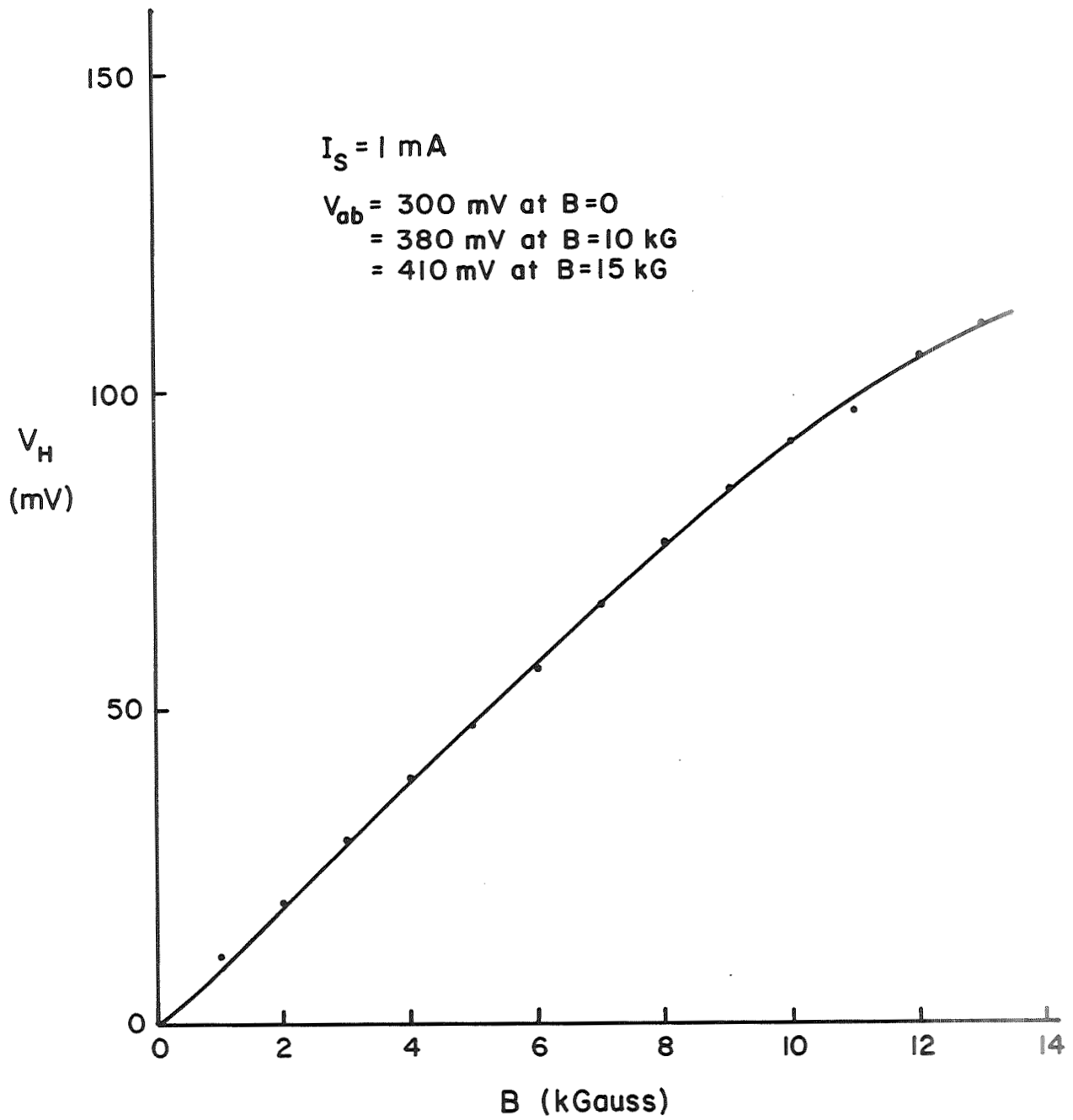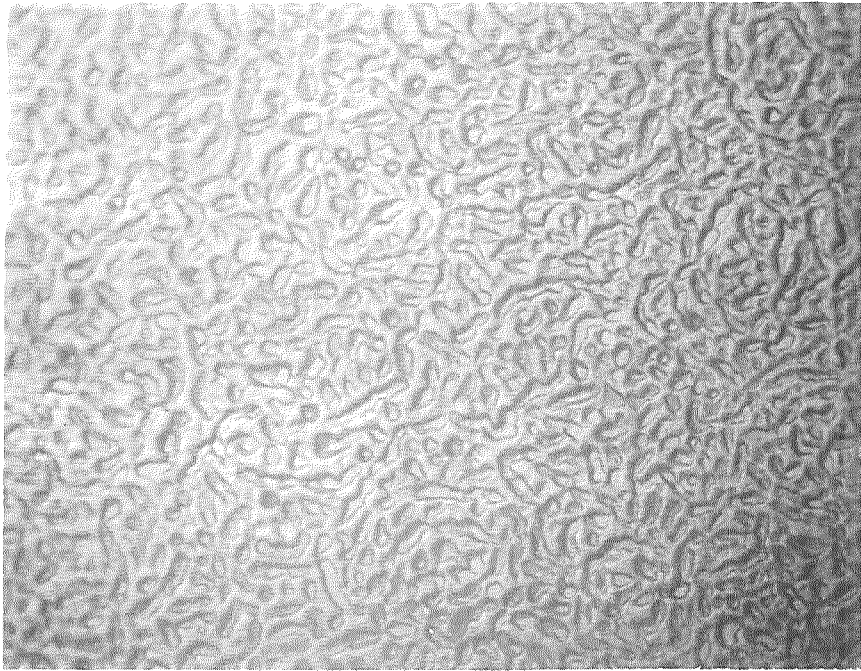Figure 6. Micrographs of a Film with 50 and 500 Times Magnification

Figure 7. Hall Voltage vs. Magnetic Field

In the figure:

$I_S = 1$ mA

$V_{ab} = 300$ mV at B = 0
$= 380$ mV at B = 10 kG
$= 410$ mV at B = 15 kG

Axis labels: V_H (mV) on the vertical axis, B (kGauss) on the horizontal axis.

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InSb Film Before Annealing, 3.5 μm Thick,
500 Magnification, ASA 400, T = 1/2 sec

Figure 8. Micrograph of S-11(b) Before Annealing

S-11(a) was annealed at 530°C for about 2.5 minutes in a furnace in argon gas which produced a mobility of 12,700 cm^2/V-sec. The same film was annealed again at 545°C for 1.5 minutes which produced a mobility of 13,300 cm^2/V-sec. Figure 9 shows the variation of Hall voltage vs. magnetic field, although this film showed a reduction in the value of Hall mobility (10,250 cm^2/V-sec) when it was annealed at 560°C for 1.5 minutes. Figure 10 is a micrograph of S-11(a) after annealing with 50 and 500 times magnification.

S-11(b) was annealed at 545°C for 3 minutes which resulted in a mobility of 6000 cm^2/V-sec. Figure 11 shows micrographs of S-11(b) at 50 and 500 times magnification. It
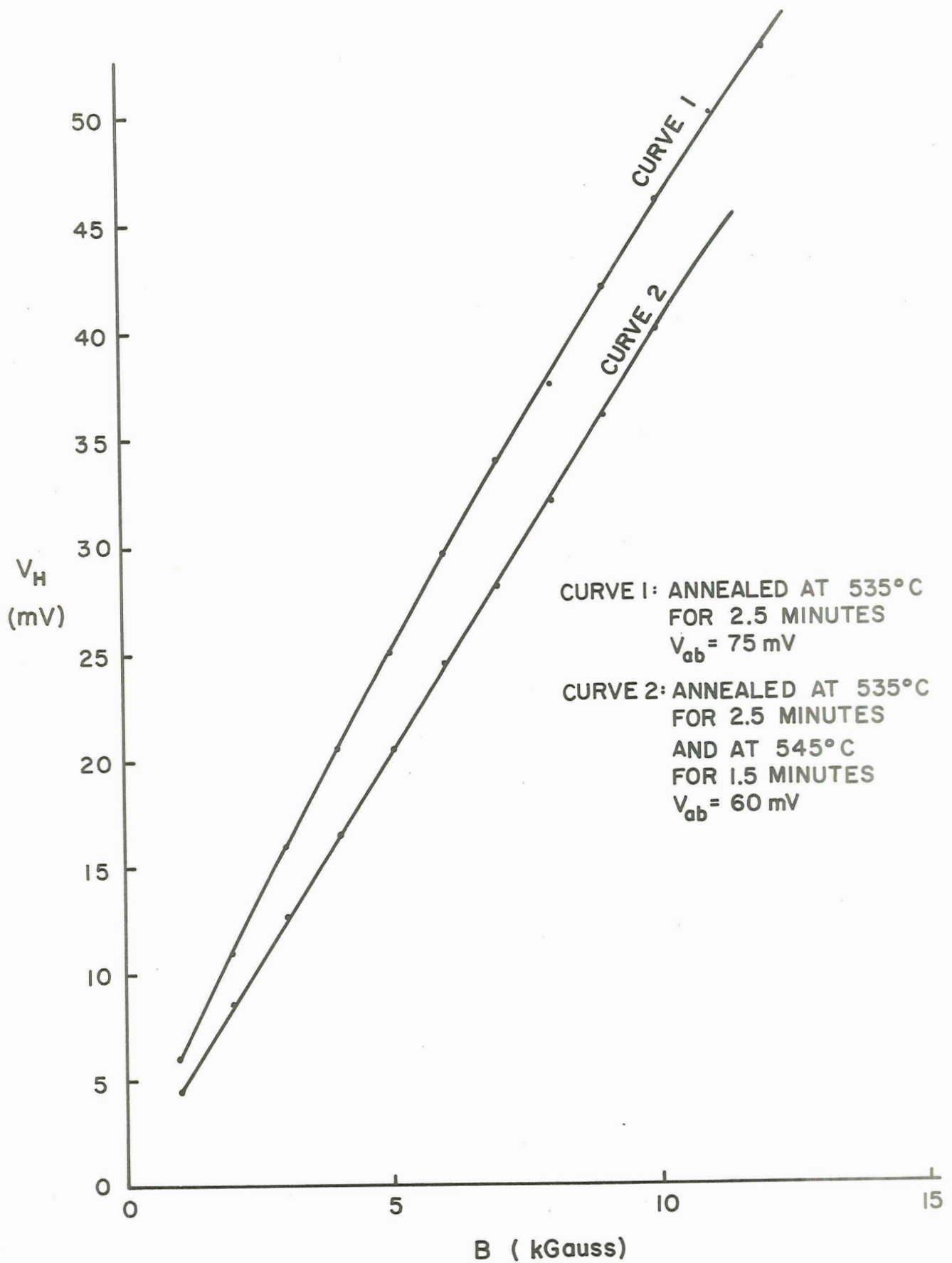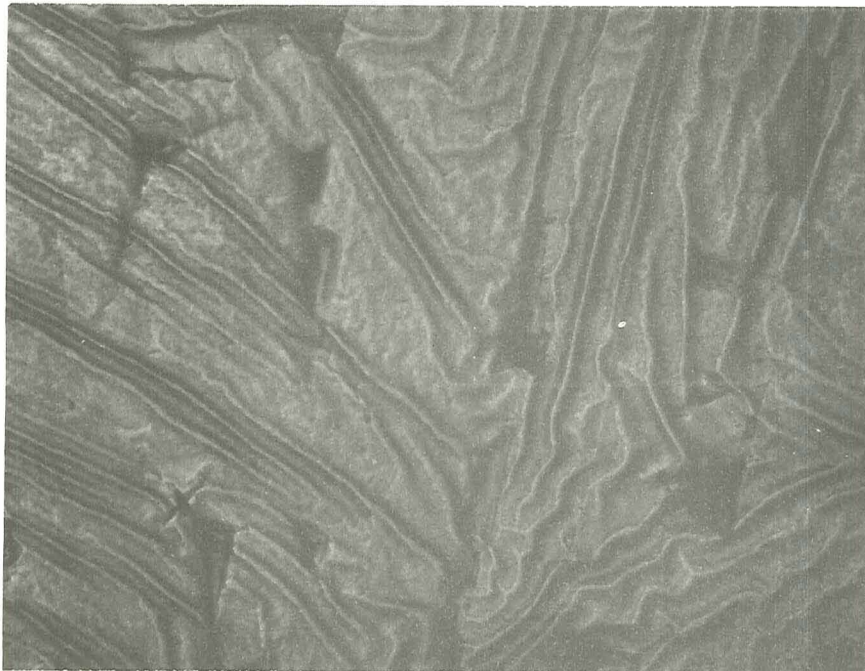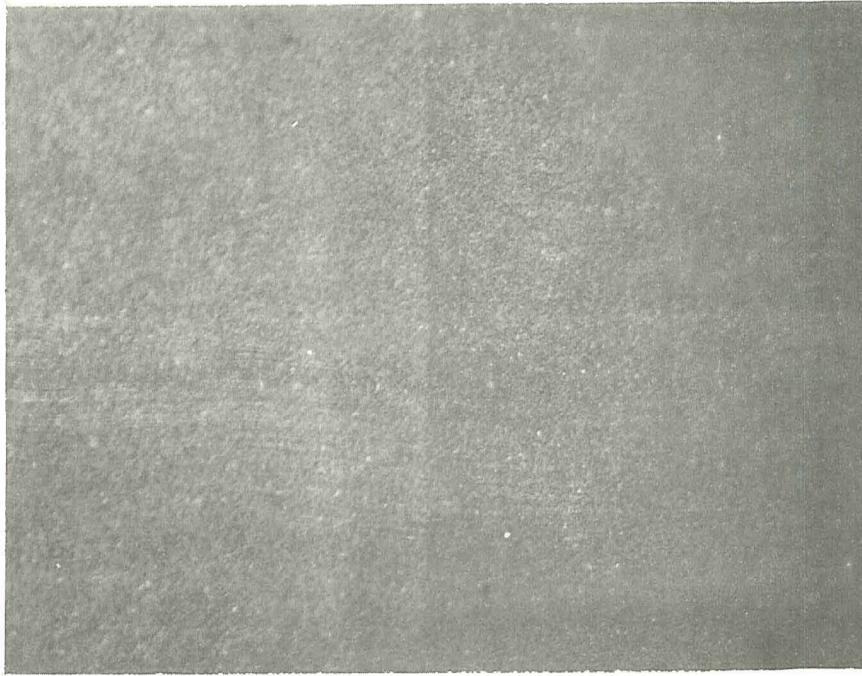
Figure 9.   Hall Voltage vs. Magnetic Field (S-11(a))

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(a) S-11(a), InSb Film Annealed at 535°C for 2-1/2 Min, 3.5 μm Thick, 50 Magnification
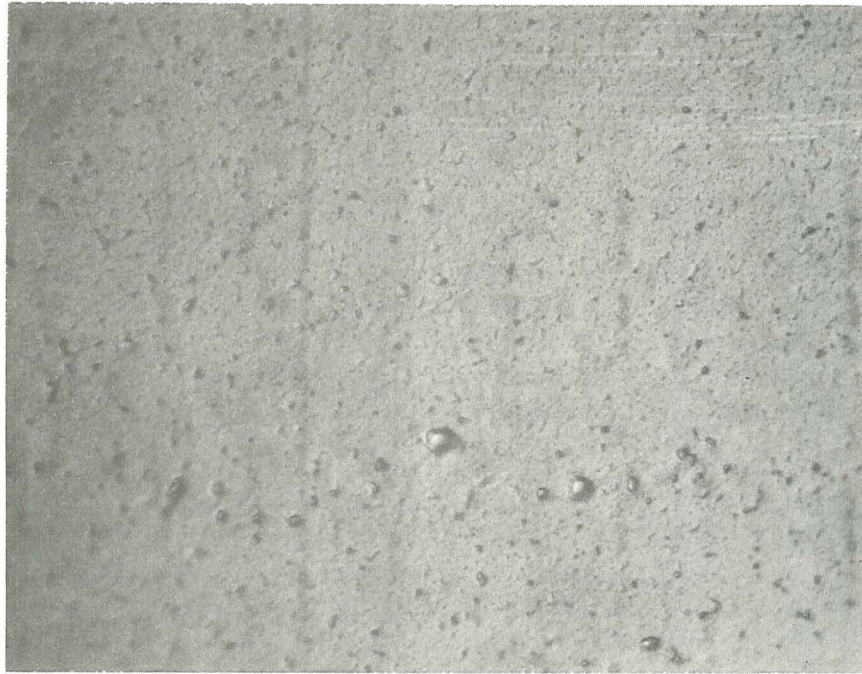
(b) S-11(a), InSb Film Annealed at 535°C for 2-1/2 Min, 3.5 μm Thick, 500 Magnification

Figure 10. Micrographs of S-11(a) After Annealing (50 and 500 Times)

(a) S-11(b), InSb Film Annealed at 540°C
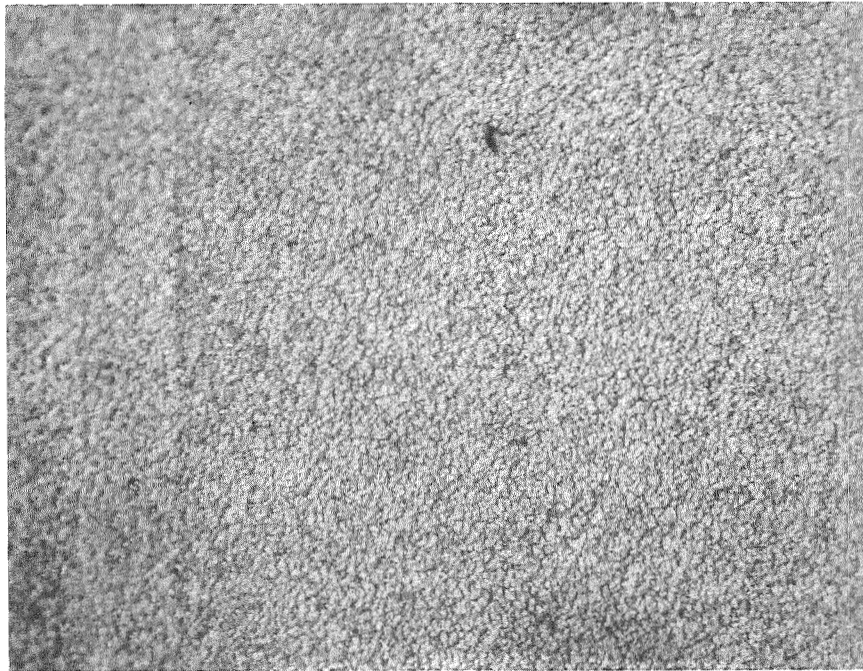for 3 min, 3.5 μm Thick,
50 Magnification

(b) S-11(b), InSb Film Annealed at 540°C
for 3 min, 3.5 μm Thick,
500 Magnification

Figure 11. Micrographs of S-11(b) After Annealing

is obvious that annealing produced a dendritic structure; however, mobilities were low.

Figure 12 is a micrograph of S-2. This sort of structure never yielded any mobility.

S-2, InSb Film Before Annealing,
3.5 µm Thick, 500 Magnification

Figure 12. Micrograph of S-2 InSb Film

Some experiments with fast evaporation rates such as 10,000 Å/min to 12,000 Å/min were also carried out, but they showed Hall mobilities of the order of 11,000 cm^2/V-sec and 5700 cm^2/V-sec.

DISCUSSION OF THE RESULTS AND CONCLUSIONS

Carrol and Spivak (Reference 5) and Wieder and Clawson (Reference 4) mentioned in their papers that the fastest

evaporation rates resulted in high mobilities; however, in this laboratory better mobilities were obtained with comparatively slow rates of evaporation. This may be due to the re-evaporation of volatile antimony which produces a non-stoichiometric film.

Those films deposited at high substrate temperatures between 280 and 350°C were not good even in appearance. Many pinholes were observed. Films deposited at 250°C with rather slow rates of evaporation had a very milky-white appearance and were quite uniform. After oxidation the color of these films changed from milky white to grey. Annealing in a furnace at 535°C gave a dendritic structure with a golden color. Annealing of the same film at 545°C increased Hall mobility but further annealing resulted in the reduction of the μ_H value, indicating re-evaporation of the film. It is certain that the oxide layer formed before recrystallization prevented rupture and balling up of the evaporated film during recrystallization.

Electron-beam evaporation appears to yield higher mobilities based on the experiments completed. With proper rates of evaporation and recrystallization by the electron beam gun, higher mobilities are expected.

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