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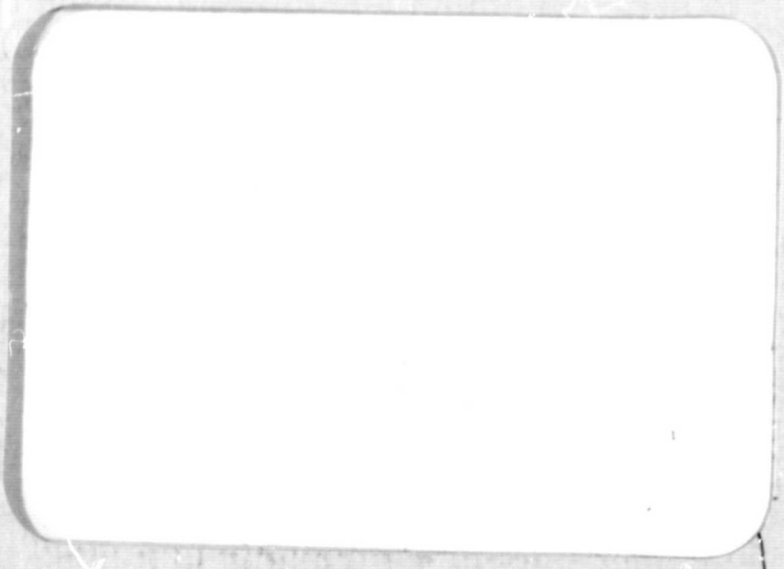

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VACUUM DEPOSITION OF III - V SEMICONDUCTOR MATERIALS BY THE THREE-TEMPERATURE DEPOSITION METHOD

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Vacuum Deposition of III-V Semiconductor Materials

By The Three - Temperature Method

SUMMARY

The work reported herewith was conducted as a part of the 1967 Summer Faculty Fellowship Program. Preliminary evaluation films of InSb have been formed by simultaneous vacuum deposition of indium and antimony. Mobility values of 300 cm^2/volt-second were measured. This represents an improvement over the CdSe films currently under study for thin film device applications. Experimental procedures are detailed together with recommendations for future work.

INTRODUCTION

In order to improve the frequency response of thin-film field-effect transistors, the source drain spacing may be reduced, the gate width may be made smaller, or the mobility of the semiconductor may be made as high as possible. Of these methods, the latter seems to be the most logical approach because closer spacings are becoming more difficult to acheieve, and the improvement that can be realized by changing them is relatively small. The mobilities of the semiconductors that have been used most frequently in thin-film transistors have been in the range of 10^2 $cm^2/v\text{-}sec.$ and these mobilities, together with the spacings that can be obtained, presently limit the applications of these devices to frequencies below 100 mHz. Some of the III-V compounds have much higher mobilities in bulk form, and their use in thin-film transistors could possibly increase the frequency range by several orders of magnitude. The main reason that these materials have not been used to date is because their preparation is difficult and has not moved beyond the experimental stage into commercial applications. The purpose of this study is to experimentally determine the vacuum deposition parameters to be used in the formation of high mobility semiconducting films from some of these III-V materials. The parameters to be determined are the temperatures of the two elements being evaporated as well as the temperature of the substrate where the vapors condense; hence, the name, the Three-Temperature Method.

BACKGROUND

The difficulty encountered in preparing some of the high mobility III-V compounds is that, at temperatures of evaporation, they disassociate into components of different vapor pressures. The result is nonstoichiometric films. To produce films of the exact stoichiometric ratio, the vapor densities of the components, as well as the condensation conditions, are extremely critical. The proper vapor densities of the components can be obtained by the temperature control of the evaporation of the two components from separate sources. The condensation conditions may be controlled by adjusting the temperature of the substrate so that the components will, as they arrive in the proper ratio in the vapor state, react and form a semiconductor film. Since there is no significant reaction of components in the vapor state, the formation of the film is highly dependent on the temperature of the condensation on the surface. The overall conditions that are desired are described by Gunther* as follows:

> "The less volatile component is maintained at a temperature, T_A, which is necessary for the desired impinging rate, M_{+A}, and growth velocity of the film. Now, the temperature, T_B, is chosen in such a manner that the more volatile component B possesses a certain excess in the vapor phase compared with component A ($M_{+B} = C \times M_{+A}$, with C = 2 to 10). Finally, the temperature, T_K, of the condensation surface is maintained at a value which permits the selection of that

*Gunther, K. G., "Vaporization and Reaction of the Elements in Compound Semiconductors", Vol. 1, Preparation of III-V Compounds, Ed. by Willardson, R. K. and Goering, H. L. Reinhold, New York, New York, 1962.

amount of component B which is necessary for the desired compound AB, while the excessive amount (of B) is re-emitted in the vapor phase."

EXPERIMENTAL METHODS

The Vacuum System:

The vacuum equipment used for this study was manufactured by Consolidated Vacuum Corporation, CVC. It has a four-inch vacuum system, and consists of a 12-inch glass bell jar pumped by a liquid nitrogen trapped oil diffusion pump. The base pressure of the unit is 10^{-7} torr with the nitrogen trap in operation; however, most depositions are made in the 1 to 4 X 10^{-6} torr range.

Evaporation Assembly:

A schematic of the apparatus for preparation of the films is shown in Fig. I.

The substrate heater consists of three quartz infrared lamps and is capable of producing substrate temperatures in excess of 500°C. The source heaters are selected according to the materials to be evaporated. The materials used for this study were an R. D. Mathis, ME 21 tungsten boat for the indium and a ME 22 tantalum boat for the antimony. A layer of Al_2O_3 paper (Fiberfrax paper, 970-AFJ, the Carborundum Company) is used in conjunction with a 100-mesh tantalum wire screen as the boat cover to prevent "spitting" of the antimony during evaporation. The indium boat was not covered.

Source to substrate distance was 26 cm and the separation between sources, on center, was 2.5 cm. A glass barrier approximately 1.3 cm

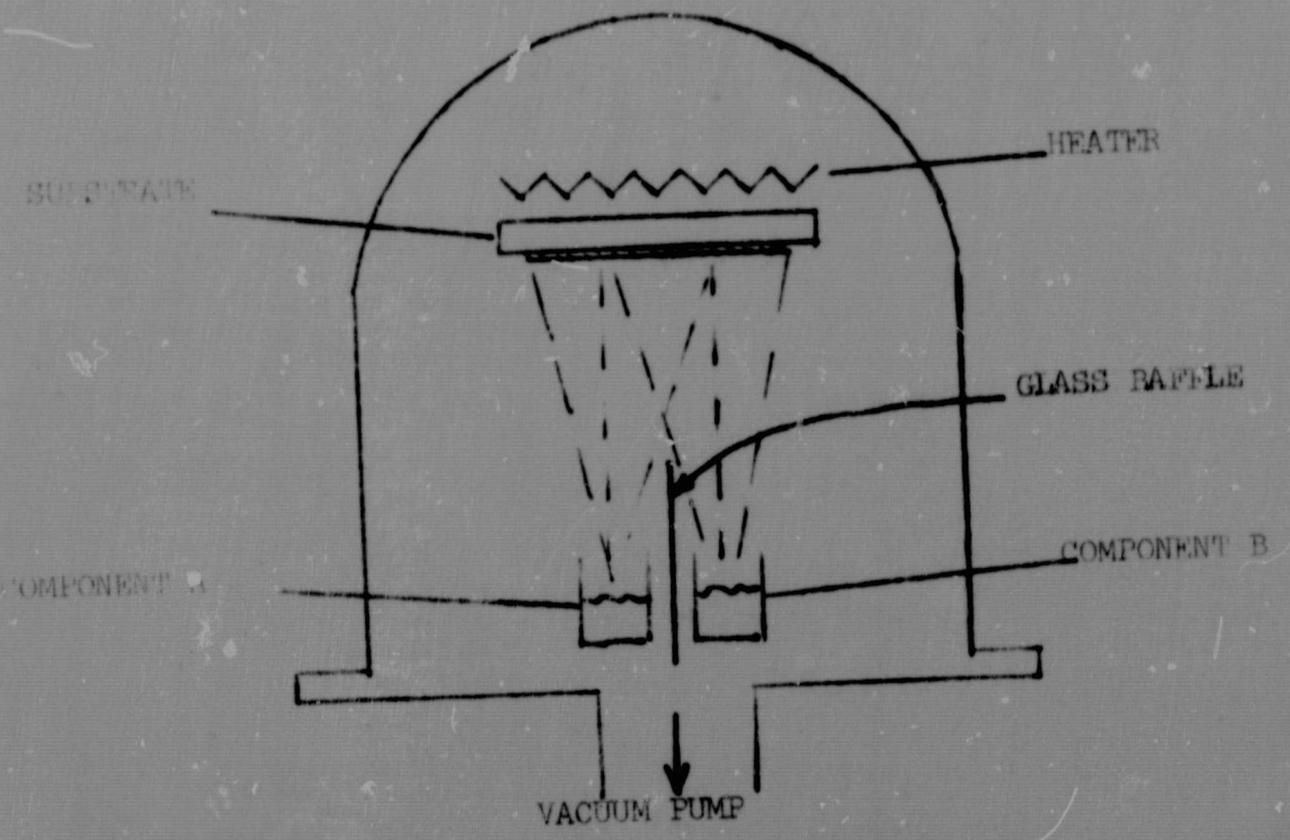

HEATER
SUBSTRATE
GLASS BAFFLE
COMPONENT B
COMPONENT A
VACUUM PUMP

Fig. 1

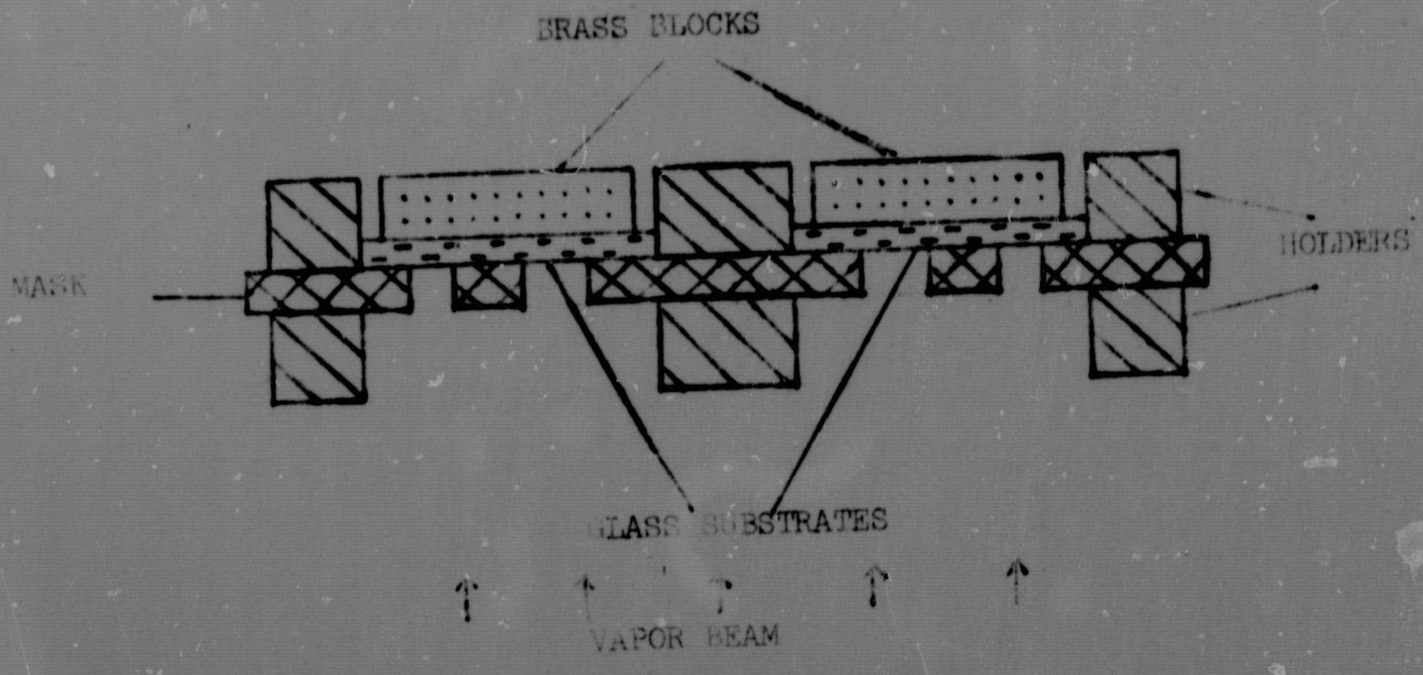

BRASS BLOCKS
HOLDERS
MASK
GLASS SUBSTRATES
VAPOR BEAM

Fig. 2

higher than the top of the boats was placed between the sources to prevent the materials from being mixed at this point.

Chromel-alumel thermocouples are spot-welded to the bottoms of the boats for temperature monitoring of the sources while the same type thermocouple is pressed on the substrate surface to obtain this measurement. The thermocouple wires are 36 gauge, providing rapid response to changes in temperature. The output of the thermocouples is fed to MiniMite, temperature compensated potentiometers to obtain the temperature values. A cutaway representation of the mask and substrate holder is given in Fig. II.

The thermocouple used to measure the substrate temperature is placed between a brass block and the glass substrate. Four 1 X 1 glass slides are coated during each deposition.

The region between the base of the bell jar and the bottom of the substrate holder is surrounded by a 6-inch diameter pyrex chimney to prevent contamination of the chamber. These chimneys are cleaned after each deposition and the base of the bell chamber is cleaned with a vacuum cleaner.

Film thickness and deposition rates are obtained from a Sloan Deposition Thickness Monitor that is a part of the vacuum system.

Evaporants:

The materials used were indium wire 99.99% pure, by Indium Corp. of America, Utica, New York, and antimony shot 99.9999% pure, by Electronic Space Products, Los Angeles, California. Enough material was used so that evaporation was not complete during each deposition, and "make-up"

material was added to the boats prior to each run. The antimony boat was kept approximately half-full because it was found that this made it easier to maintain a constant temperature during depositions. Approximately 1 gram of indium was added to the boat for each melt.

The substrates used are 25 mm sq. Corning cover glass. They are cleaned by the procedure given in Appendix I.

Vaporization Parameters:

Typical vaporization parameters of each component were observed by separate depositions and examples are given in Tables I and II.

TABLE I

Indium	
Boat Temp. °C	Rate Å/sec.
845	0
920	6
940	15
980	38
1000	50
1025	78
1050	115
1020	50
995	10
980	10

TABLE II

Antimony	
Boat Temp. °C	Rate Å/sec.
515	0
595	10
600	16
640	50
670	110
705	230
617	28

The general base lines determined are that indium would begin to evaporate at approximately 890° to 900°C and antimony would begin to evaporate at approximately 580° to 600°C. Pressures were from 1.4 to 2.0 X 10^{-6} torr. Substrates were at room temperature for the indium and approximately 100°C for the antimony. Antimony would not adhere to the substrate at room temperatures.

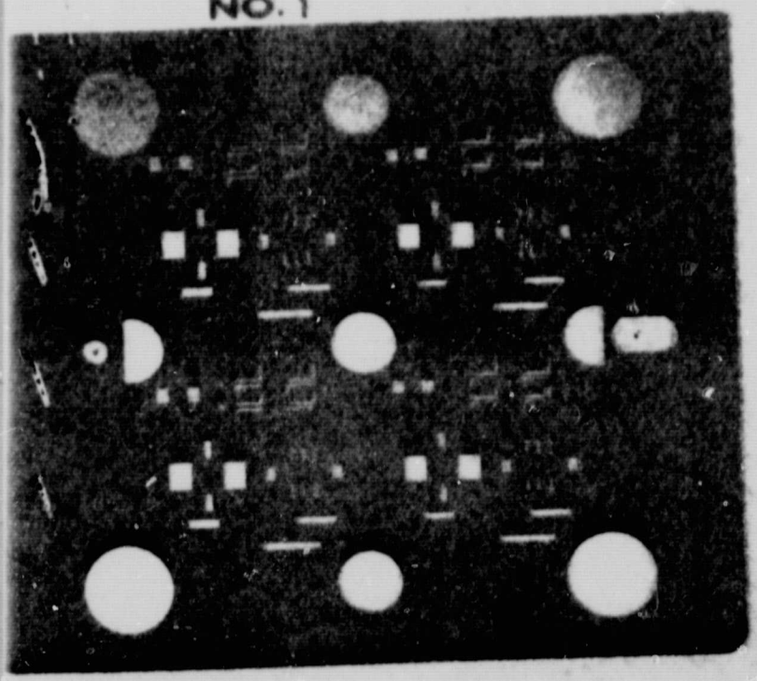
Starting points for the vaporization parameters of compound films were determined by deposition of the components at differing boat and substrate temperatures until films were obtained that had resistivities in the semiconducting range. Source temperatures of approximately 1010° to 1030°C for indium, 650 to 750°C for antimony, and 110° to 170°C for the substrate are possible values to work around.

A number of devices were designed to facilitate making the appropriate electrical measurements on the films. The masks required for these devices are illustrated in Fig. 3.

Mask number one is used to make source drain contacts using nichrome as the material. Mask number two is used to make the semiconducting film to be studied. Mask number three is used to make metallic contacts to the semiconductor material. Indium is used for this although other materials would be suitable. Mask number four is used to deposit the dielectric material for a field-effect device. The formation of the Hall voltage test configuration is shown in Figures IV through VII. The Hall mobility test procedure is described in Appendix II.

FIGURE III : DEPOSITION MASKS

NO. 1



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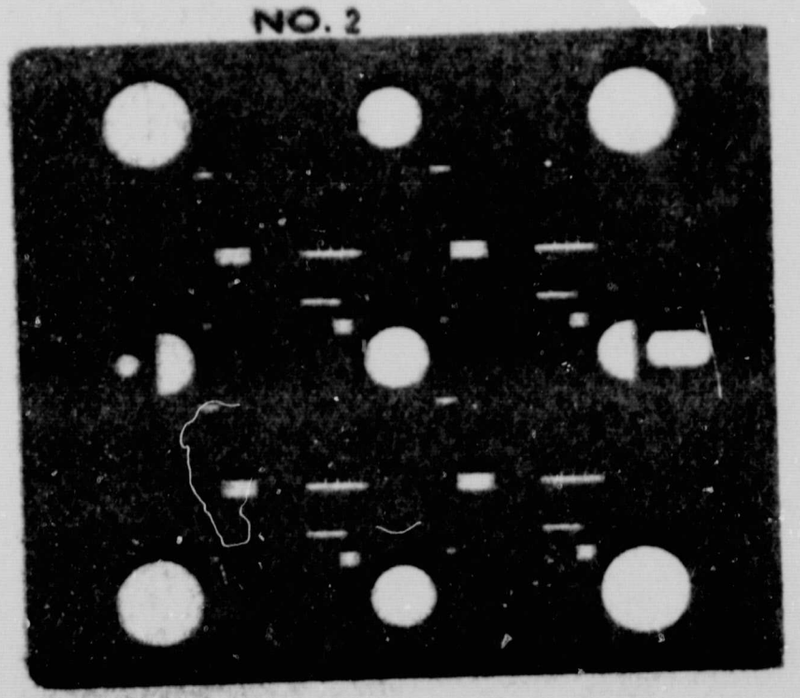

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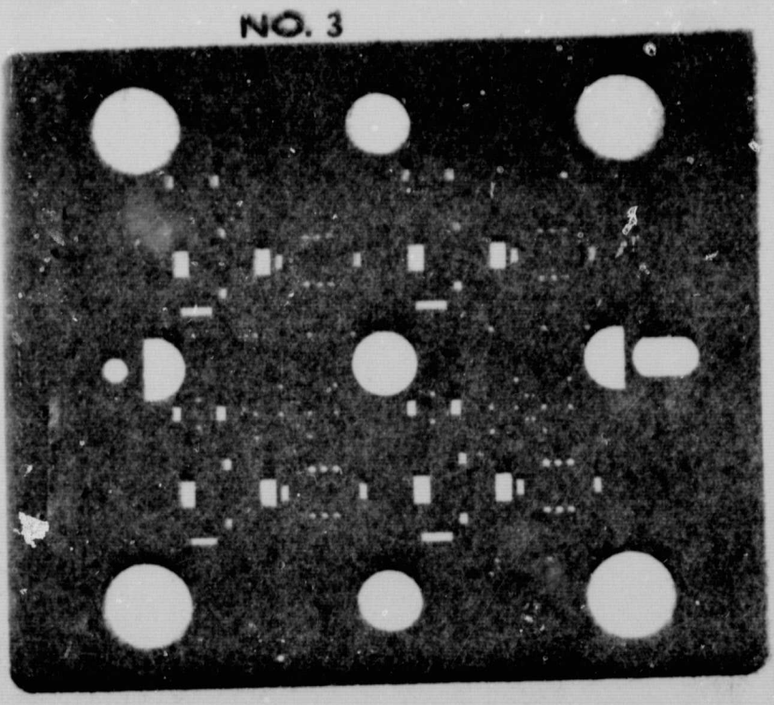

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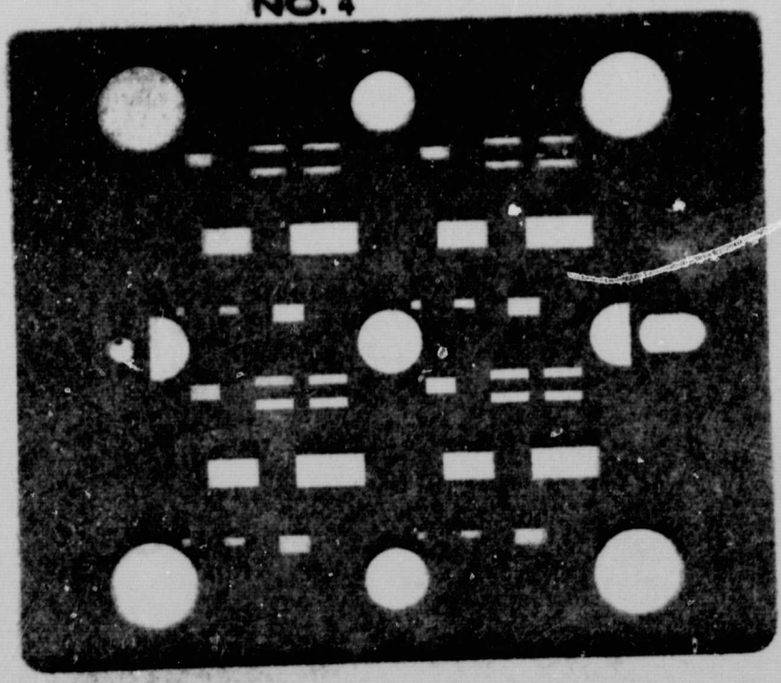

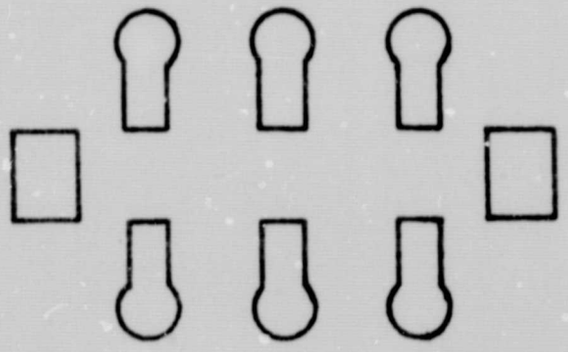

Figure IV:
Nichrome Electrode
Deposition

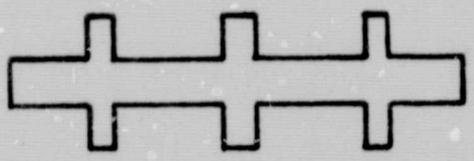

Figure V:
Indium Antimonide
Semiconductor
Deposition

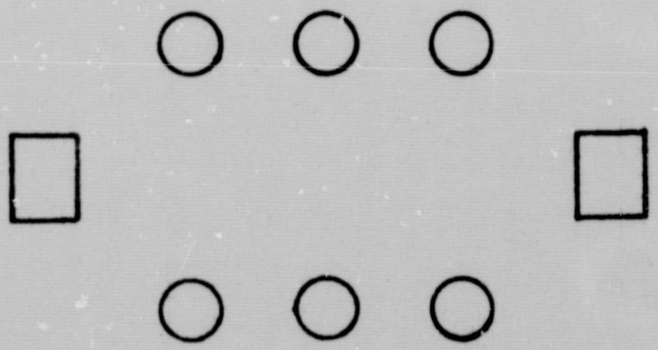

Figure VI:
Indium Contact
Pads

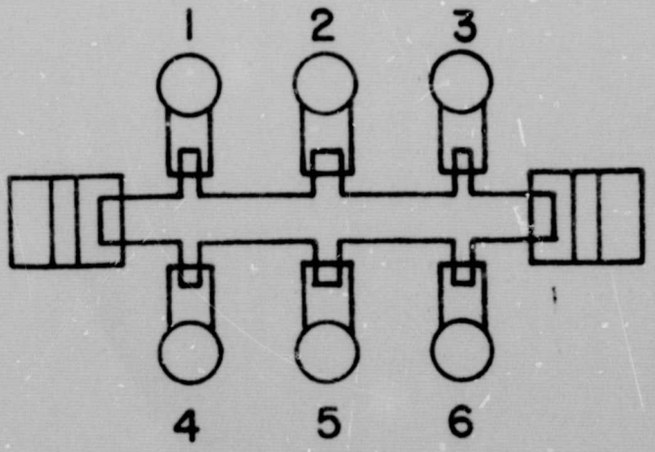

Figure VII:
3 Depositions
for Hall Effect
Measurements

EXPERIMENTAL RESULTS

Successful films having a Hall mobility of approximately 300 cm^2/v-sec. were formed at the following temperatures: In at 1020 - 1035°C, Sb at 700° - 740°C, and the substrate at 120°C. This is a fraction of the 15,000 and 20,000 cm^2/v-sec. reported by Juhasz and Anderson,* and Gunther, respectively. Their source temperatures were comparable, but the substrate temperatures were in the 400 to 500°C range on mica. Depositions made at these temperatures on glass substrates resulted in oxidized films of little value leading to a questioning of the accuracy of the temperature measurement at this point, or the need for use of mica substrates.

*Juhasz, C. and Anderson, J. C., "Preparation of High Mobility Thin Films of Indium Antimonide," Transactions of the Third International Vacuum Congress, Vol. 2, p. 333, Pergamon Press, 1965.

FUTURE WORK

This study has shown some of the difficulties with the three-temperature method.

One difficulty is holding the temperature of the antimony boat constant during evaporation. As the antimony evaporates, the temperature of the boat fluctuates as much as 100°C. This fluctuation may be due to the antimony not wetting the boat and the antimony moves about in the boat. Possible solutions are different boat materials or a heavier boat.

Another problem is determining the substrate temperature. There appears to be a discrepancy between the results obtained here and those of another worker. The problem of determining the temperature of the substrate is not as simple as it may seem. The substrates are transparent, while the thermal couple is opaque. The source of heat is from infrared lamps. Further, some workers have pointed out that the temperature difference between the front side and the back side of the substrate can differ by 100°F. There is also some question as to whether the temperature is uniform across the substrate where there are holes in the mask.

Another area of study is the effect of depositing a dielectric on the semiconductor. When a dielectric was deposited on properly heat-treated CdSe, the resistance across the source-drain spacing decreased. If the resistance did not decrease, there was no field-effect, and no TFT devices.

The annealing process may also have to be optimized to produce satisfactory field effects. That is, the resistivity of the semiconductor should change when a potential is applied to an electric field plate on the dielectric layer. The semiconductor should not only have a high field effect, but also a high mobility. Temperatures of the substrates and boats will be varied for maximum mobility of carriers. In addition, mobilities may be improved by post-deposition treatment of films by using such techniques as the shielded recrystallization method discussed by Johaz and Anderson.

Further improvements could possibly be realized by investigating the effect of the oblique incidence of the vapor beam on the substrate. This suggestion is made because the properties of thin-film magnetic materials are influenced by a "self-shadowing" mechanism that occurs during this process. It is believed that an improved crystalline structure and a resultant increase in mobility could be obtained by this method.

APPENDIX I

SUBSTRATE CLEANING PROCEDURE

a. Wash each substrate in detergent water using abrasive action.

b. Rinse under running water 3 minutes.

c. Ultrasonically clean twice in trichloroethylene, 10 minutes each cleaning.

d. Ultrasonically clean twice in acetone, 10 minutes each cleaning.

e. Ultrasonically clean three times in demineralized water, 10 minutes each cleaning.

f. Ultrasonically clean in 10 to 20% boiling HNO_3, 10 minutes (delete this setp on alumina).

g. Wash substrates in demineralized water from 30 to 45 seconds, five times by hand agitation of container.

h. Ultrasonically clean substrates once in demineralized water for 10 minutes.

i. Ultrasonically clean in methanol twice for 10 minutes each cleaning.

j. Pour off and store dry.

Note: Delete steps (f), (g), and (h) for glazed alumina and Corning code 7059 glass.

APPENDIX II

HALL MOBILITY MEASURING TECHNIQUE

The Hall voltage is measured across contacts 2 and 5 (see Figure VIII). Contacts 1 and 3, or 4 and 6 are used to measure conductivity. Two sets of contacts are employed to determine if the sample is homogenous along the width. That is, the resistance from 1 to 3 should be the same as from 4 to 6.

The Hall voltage is given as

$$R_H = \frac{V_y}{I_x} \frac{t}{B_z} 10^8 \left(\frac{C_m^3}{C}\right)$$

where V_y is the voltage across the contacts 2 and 5, I_x is the current in amperes through the sample, B_z is the magnetic field (in Gauss) applied perpendicular to I_x, and V_y. The subscripts x, y, z, refer to the right-handed coordinate system x, y, z. The thickness of the sample is given as t(cm).

The conductivity (σ) is given by

$$\sigma = \frac{I_x}{V_x} \frac{L}{WT} \quad (mho\text{-}cm^{-1})$$

The voltage V_x is measured from contacts 1 and 3, or 4 and 6. The length L (units of cm) is the distance from contacts 1 to 3, or 4 to 6. The width of the sample is given by W (cm).

The Hall mobility (μ_H) is given by

$$\mu_H = \sigma R_H \left(\frac{cm^2}{V\text{-}sec}\right)$$

The term Hall mobility means that the mobility is determined from the Hall coefficient whereas drift mobility means that the mobility was determined from application of an electric field. Because of various scattering mechanisms in the semiconductor, there is some variation between the two mobilities. The mobility is the average velocity that the charged carrier (holes or electrons) will have per unit of electric field. An electron (or hole) will accelerate in an electric field until it is scattered by the prevailing scattering mechanism.

Hence, a high mobility would imply a long mean free path and a long relaxation time, and a high frequency response. For a high frequency response in a thin-film transistor, the gain-bandwidth product ($G \cdot BW$) is given by

$$G \cdot B_w \approx \frac{\mu_d \ V_d}{2\pi \ L^2}$$

Where μ_d is drift mobility, V_d is the voltage across the source-drain spacing, and L is the source-drain spacing. Since the source-drain spacing (L) has been decreased as far as practical, it is desirable to increase the mobility in order to increase the frequency response.

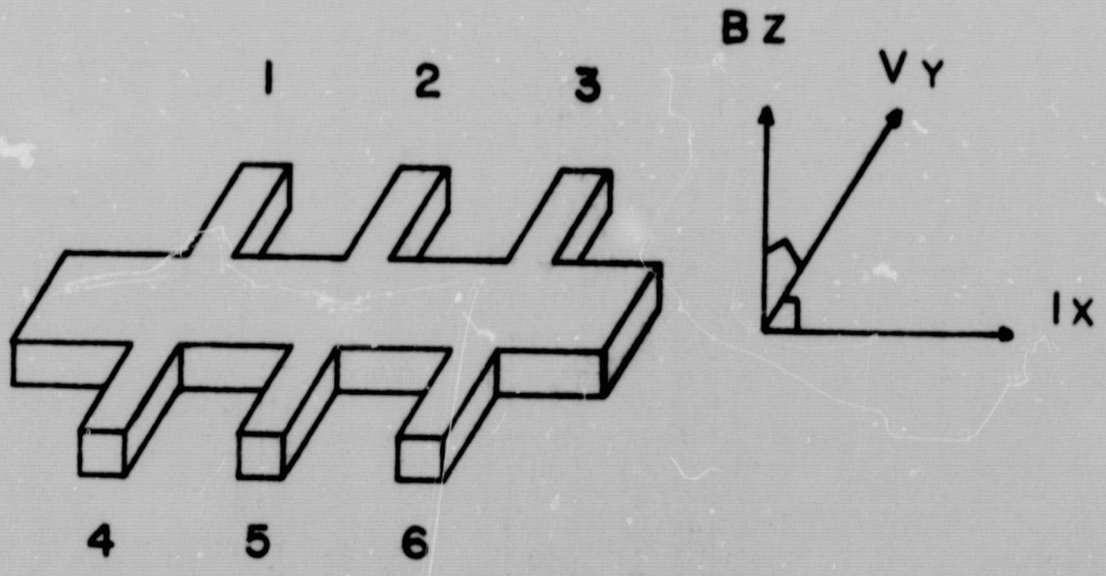

FIGURE VIII: Hall Voltage Test Configuration