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THE PREPARATION AND CHARACTERIZATION OF ELECTRON
BEAM, VAPOR DEPOSITED, GERMANIUM FILMS

Charles Sterling Portwood III
(M. S. Thesis)

April 1970

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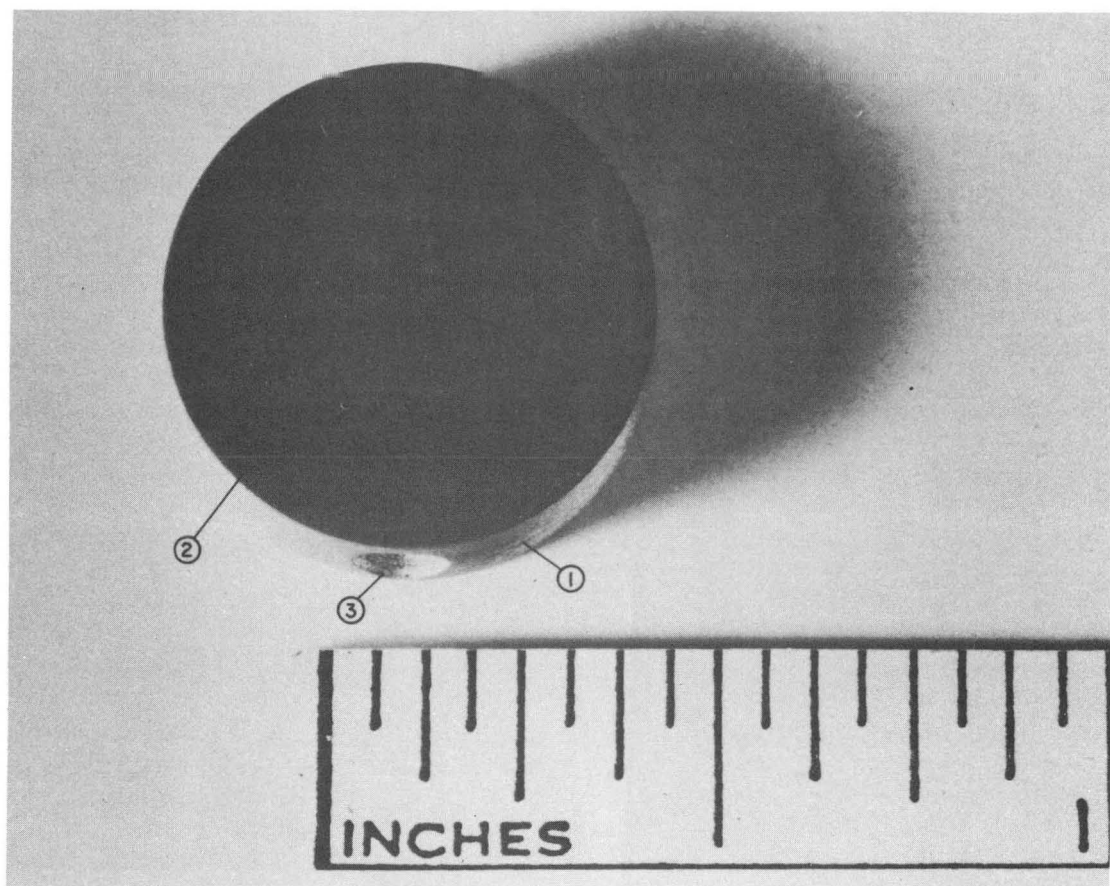
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ERRATA

TO: All recipients of UCRL-19164
FROM: Technical Information Division
SUBJECT: UCRL-19164, "The Preparation and Characterization of
Electron Beam, Vapor Deposited, Germanium Films," by
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Please correct the title on the cover and the abstract
page to read as listed above.

Please replace page 17 with attached corrected figure.



XBB 6910-6538A

Fig. 7. Germanium coated molybdenum substrate.

DESCRIPTION OF FIGURE 7

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(7-1)	Molybdenum substrate	To hold germanium film
(7-2)	Germanium film	One of the end products of this study.
(7-3)	Set screw socket	To accept set screw

TABLE OF CONTENTS

NOMENCIATURE-----	v
LIST OF FIGURES-----	viii
ABSTRACT-----	ix
I. INTRODUCTION-----	1
II. PURPOSE-----	5
III. BACKGROUND-----	6
IV. APPARATUS-----	8
V. PROCEDURE-----	28
A. Procedure for Deposition Runs-----	28
B. Procedure for Vaporization Runs-----	31
C. Procedures for X-ray Diffraction and Electron Microprobe Techniques-----	32
VI. DATA ANALYSIS-----	36
A. Theoretical Calculation of the Germanium Film Thickness Produced During a Deposition Run-----	36
1. Determination of the True Temperature of the Germanium Sample-----	38
2. Derivation of the Effective Temperature, T_e , for a Deposition Run-----	41
B. Vaporization Experiments-----	43
C. Calculation of the Minimum Permissible Thickness of a Germanium Film-----	44
D. Determination of Germanium Removal Rate Due to Oxidation for Both Deposition and Vaporization Runs-----	44

VII.	RESULTS AND DISCUSSION-----	46
A.	Results of the Production Step -----	46
B.	Results of the Vaporization Rate Step-----	49
C.	Results of the Integrity Check-----	51
D.	Results of Contamination Check-----	55
VIII.	CONCLUSIONS-----	57
IX.	RECOMMENDATIONS FOR FUTURE CONSIDERATIONS-----	58
X.	ACKNOWLEDGEMENT-----	60
XI.	REFERENCES-----	61

NOMENCLATURE

α	the increase in transmissivity of the inside mirror due to a germanium coating one cm thick, $[\text{cm}^{-1} - ^\circ\text{K}^{-1}]$.
A	an empirically determined constant, [torr]
A_B	the transmissivity of the bell jar, $[\text{cm}^{-1} - ^\circ\text{K}^{-1}]$
$A_M(t)$	the transmissivity of the germanium coated mirror, $[\text{cm}^{-1} - ^\circ\text{K}^{-1}]$
b	transmissivity of the inside mirror with no germanium coating, $[\text{cm}^{-1} - ^\circ\text{K}^{-1}]$
B	an empirically determined constant, $[\text{cm}^{-1} - ^\circ\text{K}^{-1}]$
h	the distance between the germanium sample and the substrate, [cm]
$I(t)$	the current of germanium atoms impinging on the substrate surface, $[\text{atoms}/\text{cm}^2\text{-sec}]$.
K	a constant, $[\text{cm} \text{ } ^\circ\text{K}^{1/2}/\text{torr-sec}]$
M_{Ge}	the molecular weight of germanium, [grams/gram mole]
M_{O_2}	the molecular weight of molecular oxygen, [grams/gram mole]
N_{Av}	Avagadro's number, [molecules/gram mole]
p°	the vapor pressure of germanium, [torr]
p_{O_2}	the partial pressure of oxygen, [torr]
r_s	the radius of the germanium sample, [cm]
r	the radius of the substrate disk, [cm]
$R(t)$	the evaporation rate of germanium per cm^2 of germanium sample surface, $[\text{atoms}/\text{cm}^2\text{-sec}]$
$\bar{R}$	the average vaporization rate per cm^2 determined from the measured thickness of the deposition film, $[\text{atoms}/\text{cm}^2\text{-sec}]$
t	time, [sec]
t_R	the duration (or total time) of a run, [sec]

t_s	the period of time that a coated substrate (target) must least in the molecular beam machine under run conditions, [sec]
$T(t)$	the germanium temperature at time t , [$^{\circ}\text{K}$]
T_a	the ambient temperature of oxygen inside the bell jar, [$^{\circ}\text{K}$]
T_A	the apparent germanium temperature measured outside the bell jar (see Fig. 16), [$^{\circ}\text{K}$]
T_B	the apparent germanium temperature measured between the bell jar and the inside mirror (see Fig. 16), [$^{\circ}\text{K}$]
T_{BM}	the apparent germanium temperature measured between the inside mirror and the germanium sample (see Fig. 16), [$^{\circ}\text{K}$]
T_e	the effective germanium temperature of the run, [$^{\circ}\text{K}$]
T_T	the true germanium temperature (see Fig. 16), [$^{\circ}\text{K}$]
$\bar{v}$	the theoretical vaporization rate of germanium per cm^2 determined from literature data, [grams/ cm^2 -sec]
$\bar{v}_D$	the average germanium vaporization rate per cm^2 determined from the measurement of the thickness of the deposition film, [grams/ cm^2 -sec]
v_{O_2}	the removal of germanium per cm^2 due to reaction with oxygen, [grams/ cm^2 -sec]
$\bar{v}_V$	the average vaporization rate of germanium per cm^2 determined from the weight loss of the coated substrate during a vaporization run, [grams/ cm^2 -sec]
ΔW	the weight loss of the coated substrate during a vaporization run, [grams]
α_{O_2}	the probability that an oxygen atom, striking a germanium surface, will react with a germanium atom
ϵ	the emissivity of a germanium surface at the wave length measured by the optical pyrometer ($6550\text{\AA}$)

ρ_{Ge}	the density of germanium, [grams/cm ³]
$\psi(t)$	the thickness of the germanium film on the inside mirror, [cm]
ψ^*	the maximum thickness of the germanium film on the inside mirror, [cm]
τ	the theoretical substrate film thickness based on literature data, [cm]
τ_D	the measured thickness of the germanium film deposited on the sur- face of a substrate during a deposition run, [cm]
τ_E	the germanium film thickness calculated from the weight loss of the germanium sample, [cm]
τ_F	the germanium film thickness calculated from the Freeman-Searcy ⁶ data, [cm]
τ_m	the minimum substrate film thickness which is acceptable for an operational target, [cm]
τ_R	the germanium film thickness calculated from the Davydov ⁷ data, [cm]

LIST OF FIGURES

- Fig. 1. Present configuration of the molecular beam machine.
- Fig. 2. Non-horizonta1 beam configuration of the molecular beam machine.
- Fig. 3. Experimental layout.
- Fig. 4. Electron beam heater, configured for deposition run.
- Fig. 5. Substrate preheater.
- Fig. 6. Germanium sample in thermal insulators.
- Fig. 7. Germanium coated molybdenum substrate.
- Fig. 8. Experimental stand, arranged for deposition run.
- Fig. 9. Experimental stand, arranged for vaporization run.
- Fig.10. Electron beam heater, configured for vaporization run.
- Fig.11. Experimental shield (bottom, wide angle view).
- Fig.12. Experimental stand, arranged for a deposition run (close up).
- Fig.13. Experimental system, ready for deposition run.
- Fig.14. Cross section of coated substrate, mounted for electron microprobe.
- Fig.15. A diagramtic representation of the origins of the data used in this study.
- Fig.16. A representation of the observation of germanium sample temperature for a deposition run
- Fig.17. Vaporization rate vs. temperature for germanium.
- Fig.18. Photomicrograph of cross-section of coated substrate.
- Fig.19. Elemental composition of the target film, after a vaporization run.
- Fig.20. Heat sink target.

THE PREPARATION AND CHARACTERIZATION OF ELECTRON
BEAM, VAPOR DEPOSITED, GERMANIUM FILMS

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ABSTRACT

The origin of this study lies in the desire of other experimenters to investigate the chemistry of a liquid (germanium)-vapor (iodine) system using a molecular beam machine.¹ The purpose of the study discussed here was to determine the feasibility of using a liquid germanium film, plated on the surface of a graphite or molybdenum substrate, as a target in the molecular beam machine. It was concluded that neither graphite nor molybdenum is a suitable substrate material.

I. INTRODUCTION

The origin of this study lies in the desire of other experimenters to investigate the chemistry of a liquid-gas system using a molecular beam machine.¹ It was decided that the liquid would be germanium and the vapor would be iodine. Figure 1 shows a top view of the three fundamental elements of the molecular beam machine as it is now arranged. Each element exists in its own, separate vacuum chamber.

The element numbered 1 in Fig. 1 is a knudsen cell from which the reactant gas effuses. The horizontal molecular beam of reactant gas (1-4)* passes through an orifice and strikes the vertically held target (1-2) which is electron bombardment heated. The material of which the target is made is the second reaction component. In the past this second reaction component has always been a solid.

Some of the gas molecules in the molecular beam react with the target material. The reaction products leave the surface and a fraction pass through another orifice and into the quadrupole mass spectrometer (1-3). The mass spectrometer mass analyzes the reaction products and, from this, it is possible to determine the chemical composition and quantities of various reaction products.

The problem with studying a liquid-gas reaction in such a system is that the liquid must be held vertically to interact with the horizontal molecular beam. One solution to the problem is, of course, to change the attitude of the molecular beam from the horizontal, as shown in Fig. 2.

* When a numbered object, say number A, in a figure, say Figure B, is referred to it will be denoted by "(B-A)". (B-A) is called the object number. In the present case object 4 of Figure 1 is denoted by (1-4).

Then, the vapor beam (2-1) could have a vertical component and be directed downward onto a horizontal puddle (2-2) of liquid germanium.

However, the molecular beam machine is already constructed in the horizontal molecular beam configuration of Fig. 1. Therefore, the use of a non-horizontal beam arrangement would require either alteration of the existing machine or construction of a new machine. Rather than undertaking either of these extensive steps initially, it was decided that an effort should be made to find a simpler solution. The proposal was made that the horizontal beam configuration be retained, but the target consist of a liquid germanium film adhering to the surface of a solid substrate.

II. PURPOSE

The purpose of this study was to determine the feasibility of using a liquid germanium film, plated on the surface of a graphite or molybdenum substrate, as a target in the molecular beam machine. This purpose can be accomplished in four steps.

The first step, the target production step, is to perfect a method for producing germanium films on both graphite and molybdenum substrates. The second step, the vaporization rate step, is to determine the vaporization rate and hence the lifetime of liquid germanium films. This step gives us the data from which we can estimate the film thickness necessary for a reaction run of reasonable duration, say two hours. The next step, the integrity check step, is to determine the surface integrity of the liquid germanium film. This indicates whether or not a liquid film of the required thickness can be held vertically on the substrate surface without flowing off. The last step, the contamination check step, is to determine the extent to which the substrate material would contaminate the liquid germanium film through chemical reaction or dissolution. If a significant amount of the substrate material were to contaminate the germanium film, the apparent reaction characteristics of the germanium-iodine system would be affected.

III. BACKGROUND

In this section we will discuss past works which are relevant to this experiment. In doing so we will group these works according to their contributions to the various steps in accomplishing the purpose.

There are three papers which contain information relevant to the target production step. Airco Temescal, a division of Air Reduction Co., Inc., makes electron beam heaters for, among other purposes, vapor depositing films. They have published an elementary booklet² which discusses electron beam vaporization. Schiller and Wenzel³ have described various techniques for viewing vacuum processes. Among other things, they discuss the subject of viewing ports for use in high rate, vapor deposition studies. Smith⁴ has written a useful paper entitled, "Conditions and Considerations in High-Rate Thick-Film Vacuum Deposition Processes". In it he discusses (1) factors that control the maximum permissible deposition rate, (2) techniques for vacuum depositing thick films, and (3) conditions for obtaining improved adhesion. Experimental evaporation rate data for various materials are also given.

Three major experimental studies which either give directly or imply vaporization rate vs. temperature information for germanium have been reported. Searcy⁵ and Freeman and Searcy⁶ report vapor pressure of liquid germanium vs. temperature data, which can be converted by Eq. 10 to vaporization rate vs. temperature information. Davydov⁷ in his book, Germanium, reports vaporization rate vs. temperature data, but the experimenter who obtained the data is not named. Unfortunately, these three studies are in very poor agreement. The predicted vaporization rates differ from each other by as much as two orders of magnitude.

A paper by Taylor⁸ gives some insights into the various factors which affect the surface integrity of liquid metal films.

An x-ray diffraction unit and an electron microprobe were used to determine the extent to which the germanium film was contaminated by substrate material. X-ray diffraction is a well known technique; therefore, no discussion of it is deemed necessary.

The electron microprobe is designed to determine the elemental composition (the relative amounts of various elements) of a piece of material. Electrons are directed at a point on the surface. When electrons strike the various atoms, characteristic x-rays are produced. Each element produces a different spectrum of characteristic x-rays and can, therefore, be identified by it. If the experimenter desires to determine the elemental composition as a function of position (as is the case in this study), the point at which the electrons strike the surface can be moved in two micron steps. Heinrich⁹ has edited a book on electron microprobe analysis.

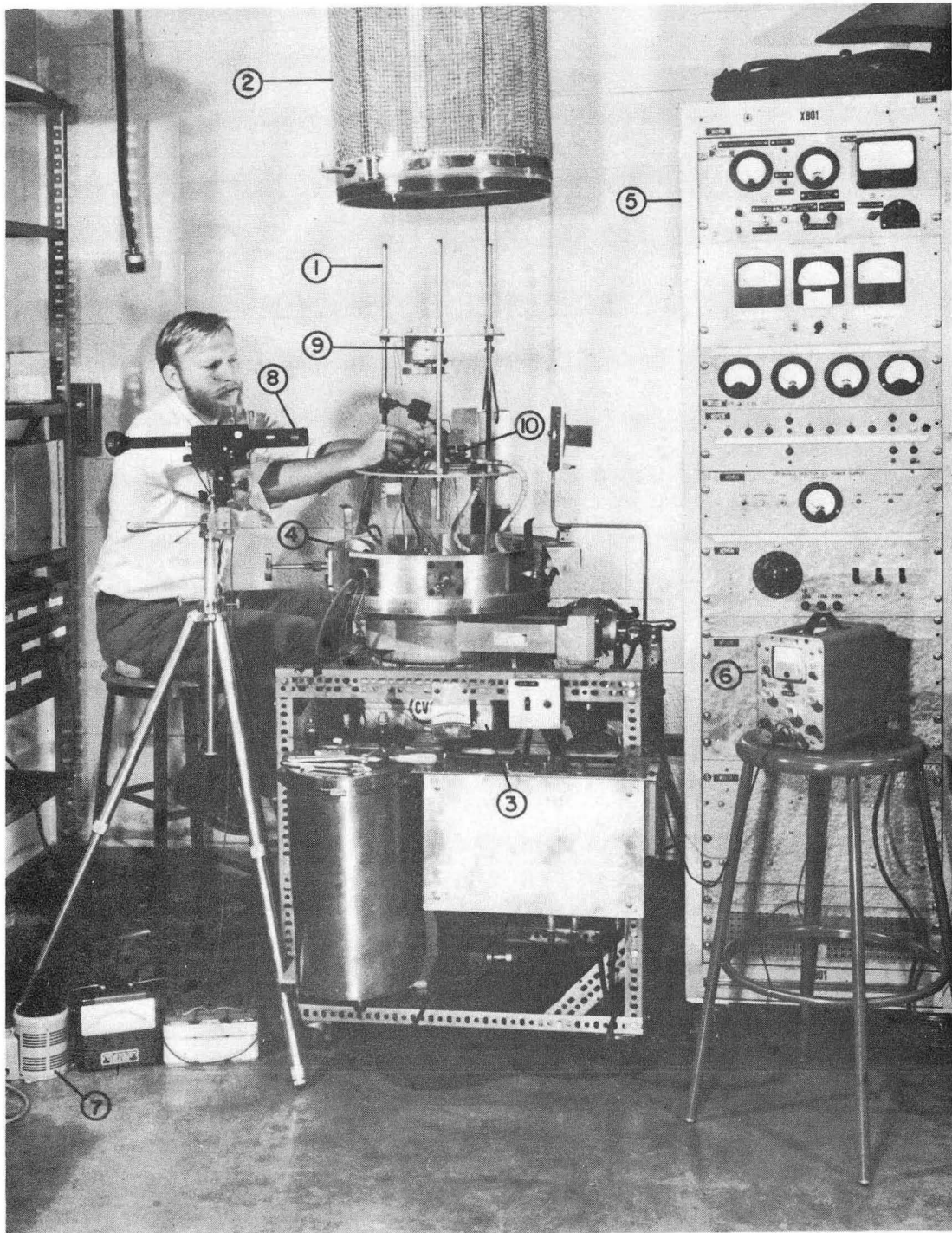
IV. APPARATUS

In this section the apparatus will be described by the use of photographs and descriptions of these photographs. Numbers on a photograph are associated with various pieces of equipment. The left hand column of the associated description contains some or all of these numbers. The center column gives the name of the associated piece of equipment and the right hand column indicates the functions, and specifications where applicable, of this piece of equipment.

Figure 3 is a picture of the overall experimental layout. The electron beam heater, Fig. 4 (see also (3-10, 8-1, 9-7, 10-1)), is the heart of the experimental apparatus. The tungston filament (4-3) is heated by an alternating electric current and is floated at a high negative voltage (3-5). The extraction plate (4-4), which is at ground potential, draws electrons from the area of the filament and imparts to them an energy, in electron volts, equal to the negative voltage of the filament. The electron beam is then bent by the electromagnet (4-5) so that the electrons strike the germanium sample (4-6). There the electrons impart their energy to the germanium, causing heating and evaporation. The electron beam heater was constructed by Mr. Harry Braun of the Nuclear Engineering Department, University of California, Berkeley, California.

The substrate preheater is pictured in Fig. 5. This preheater is nothing more than a customized hot plate.

Figure 6 is a close-up picture of the germanium sample (4-6) in its double crucible, ceramic insulator. And Fig. 7 is a close-up of a germanium coated molybdenum substrate.

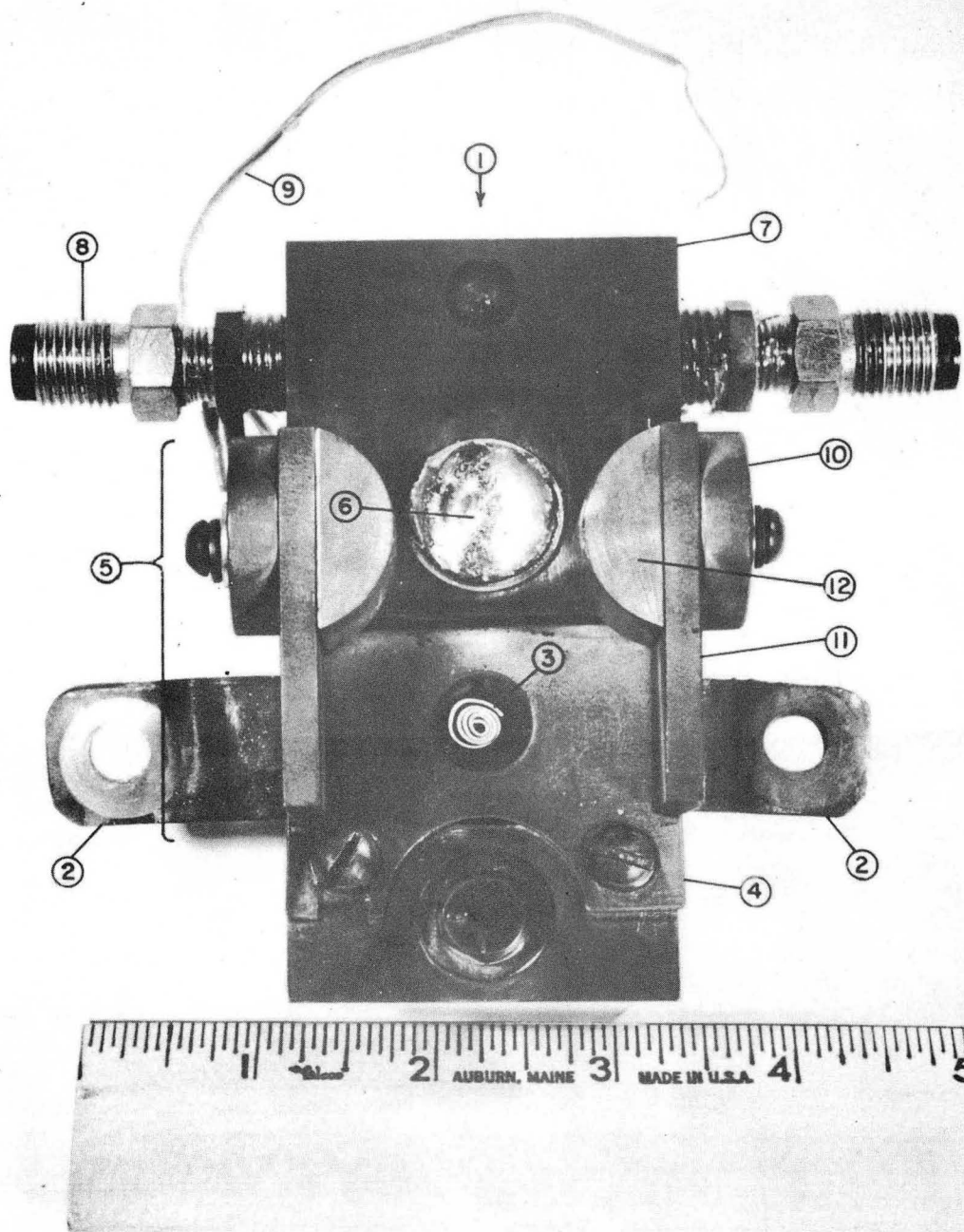


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Fig. 3. Experimental layout

DESCRIPTION OF FIGURE 3

Objects Number	Name of Piece of Equipment	Function and Specifications of Piece of Equipment
(3-1)	Experimental stand	To support various pieces of the experimental apparatus inside the vacuum chamber (3-2).
(3-2)	Bell jar	To be lowered over the experimental stand (3-1) and maintain a vacuum within. (The area inside the bell jar, when it is in place, is referred to as the vacuum chamber).
(3-3)	Vacuum equipment (includes forepump and 500 litre/second oil diffusion pump)	To maintain a vacuum (down to about 10^{-6} mm) in the vacuum chamber (3-2).
(3-4)	Vacuum feedthrough ring	To supply electricity, water, and mechanical motion to the vacuum system while maintaining the integrity of the vacuum.
(3-5)	Electron beam power supply	To deliver 0 to 40 amps at 0 to 3.8 KV to the filament (4-3) of the electron beam heater (4-1).
(3-6)	Constant current source	To deliver 0 to 1.5 amps to the electromagnet (4-5) of the electron beam heater.
(3-7)	Variable transformer	To deliver 0 to 120 a.c. volts to the substrate preheater (5-1).
(3-8)	Pyrometer	To read temperatures (800 to 3000°C) inside vacuum system.

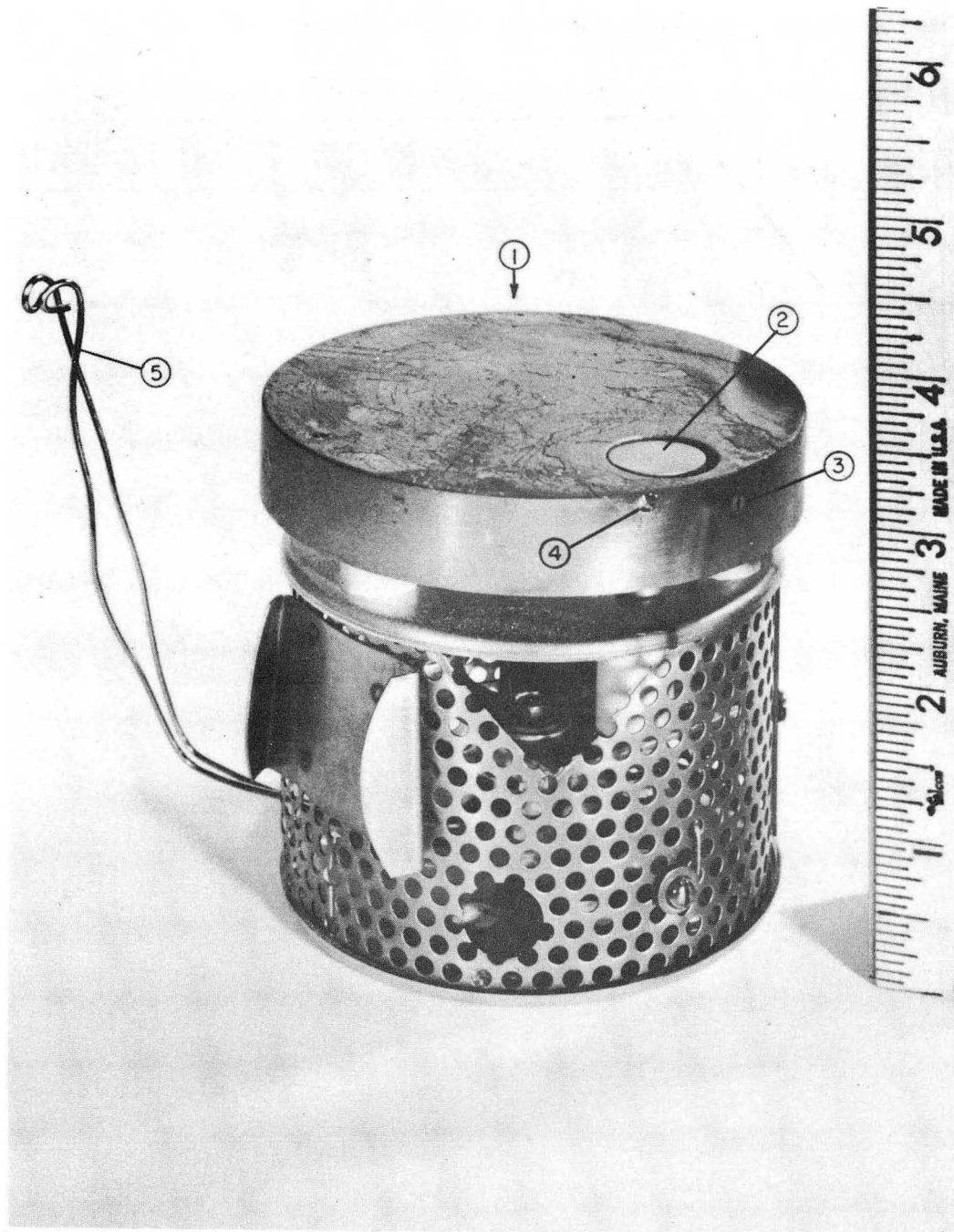


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Fig. 4. Electron beam heater, configured for deposition run.

DESCRIPTION OF FIGURE 4

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(4-1)	Electron beam heater	In this configuration, to heat germanium to high temperatures (up to 2000°C) by electron bombardment. (See (10-1) for alternative configuration. The differences between Figs. 4 and 10 are in the poles (4-5) and the sample (4-6).)
(4-2)	Filament terminals	To act as electric power terminals for the filament (4-3).
(4-3)	Filament	To supply electrons at a high negative potential (up to -3.8 KV) for the electron bombardment process.
(4-4)	Electron extraction plate	To extract electrons from the area of the filament (4-3) and accelerate, them through a ground potential.
(4-5)	Pole of electromagnet (consists of (4-10, 4-11, and 4-12).	To bend and focus the electron beam so that the beam impinges on germanium sample (4-6).
(4-6)	Germanium sample (6-1)	To, upon heating, vaporize and form germanium film on the substrate (5-2).
(4-7)	Copper block	To hold germanium sample (4-6) and to conduct electrons and heat away from germanium sample.
(4-8)	Water connection	To convey cooling water (8-8) through copper block (4-7).
(4-9)	Electromagnet current wire	To conduct electricity to the coils of the electromagnet. (The other end of the coil is grounded).
(4-10)	Magnetic field transmission element	To guide the lines of magnetic force from the electric coil, which runs through the copper block (4-7) to the collecting and bending element (4-11) and focusing element (4-12).
(4-11)	Collecting and bending elements	To capture electrons as they are accelerate through the hole in the extracting plate (4-4) and bend their path upon the germanium sample.
(4-12)	Focusing element	To focus the electron beam upon the germanium sample.

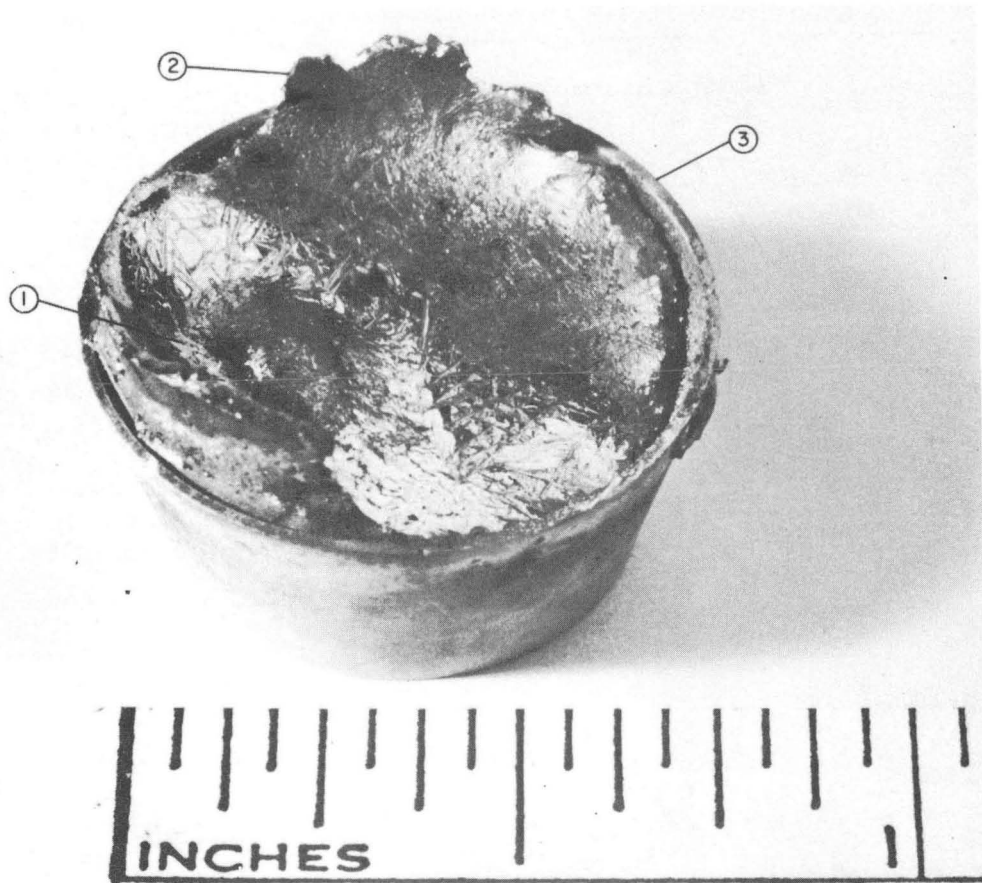


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Fig. 5. Substrate preheater

DESCRIPTION OF FIGURE 5

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(5-1)	Substrate preheater	To preheat substrate and maintain a certain minimum temperature
(5-2)	Substrate	To hold the germanium film
(5-3)	Substrate set screw	To hold the substrate in place. (Sometimes a wrinkley molybdenum foil was placed on the side of the substrate opposite the set screw to hold the substrate in place during thermal distortion.)
(5-4)	Thermocouple hole	To hold the substrate thermocouple (9-6)
(5-5)	Preheater power wires	To conduct electric power to the preheater.

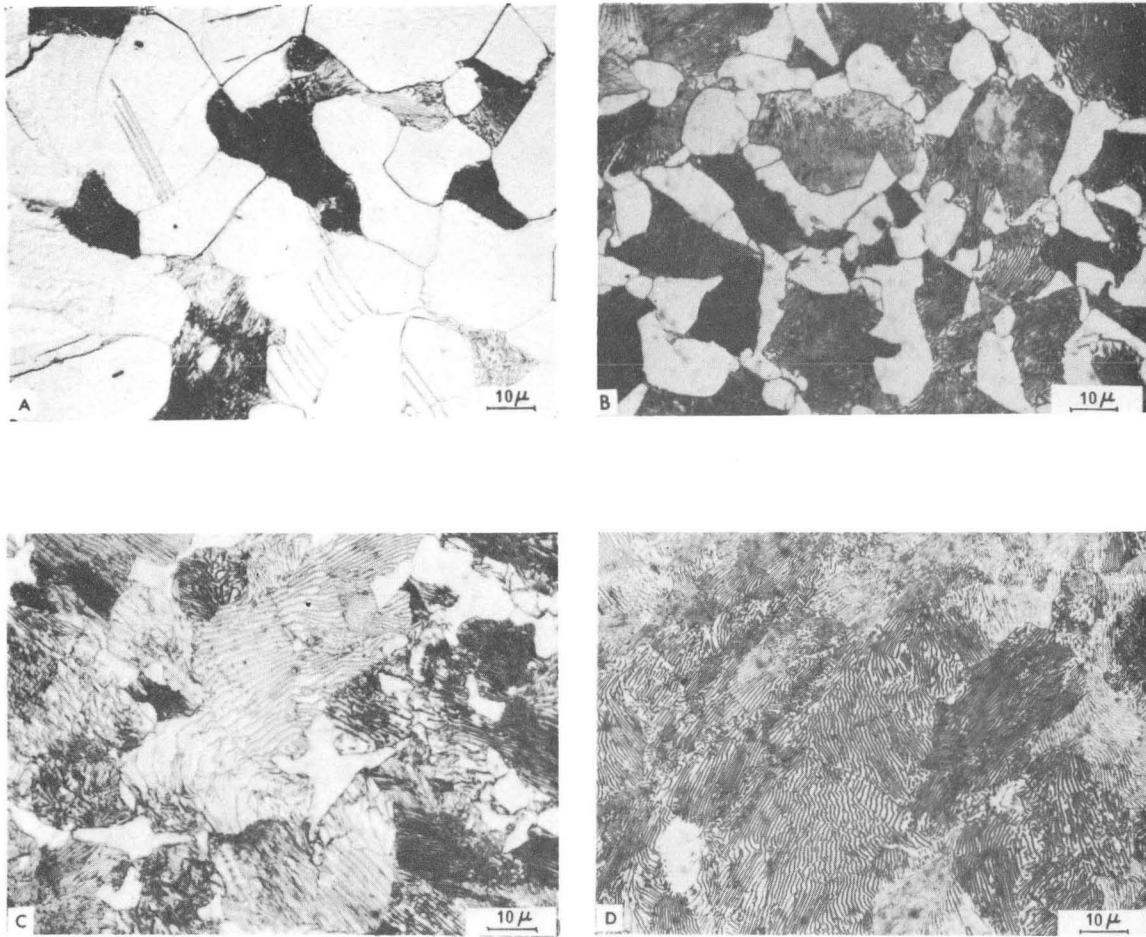


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Fig. 6. Germanium sample in thermal insulators

DESCRIPTION OF FIGURE 6

Object Number	Name of Piece of Equipment	Function and Specifications of Piece of Equipment
(6-1)	Germanium sample (4-6)	To be vaporized by the electron beam heater and form a germanium film. (Supplied from Electronic Space Products Inc. Los Angeles Ca. 90035) (Purity: 99.999% germanium). (The germanium was procured in the form of a polycrystalline ingot.)
(6-2)	Inside crucible (barely visible due to germanium coating)	To form the first stage of thermal insulation of the germanium sample. Made of alumina.
(6-3)	Outside crucible	To further lower the thermal energy escaping from the germanium samples. Made of boron nitride.



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Fig. 7. Germanium coated molybdenum substrate.

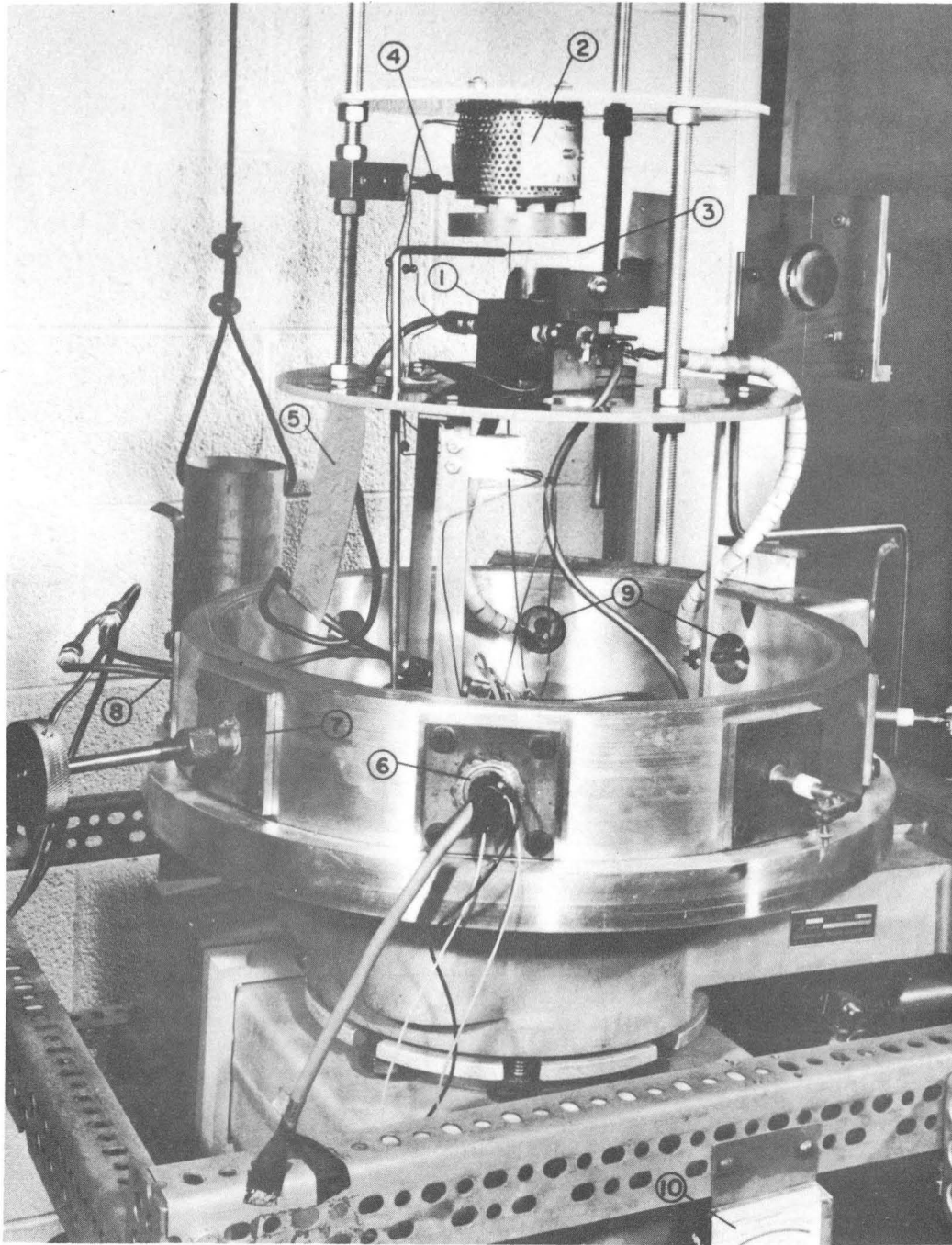
DESCRIPTION OF FIGURE 7

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(7-1)	Molybdenum substrate	To hold germanium film
(7-2)	Germanium film	One of the end products of this study.
(7-3)	Set screw socket	To accept set screw

Figures 8 and 9 are both pictures of the experimental stand (3-1). The equipment is arranged for a deposition experiment in Fig. 8 and for a vaporization experiment in Fig. 9. During "deposition runs" germanium is vapor deposited on a preheated substrate (5-2) (see Section II). "Vaporization runs" are designed to heat the germanium coated substrate and determine both the vaporization rate and the surface integrity of the germanium film (see Section II).

Figure 10 shows the electrons beam heater arranged for a vaporization run. Note that the configuration of the magnetic poles (10-2) in Fig. 10 differs from their configuration in Fig. 4, which depicts the deposition arrangement. The focusing elements (4-12) are removed for vaporization runs because there is no room for these elements during vaporization runs (see Fig. 9) and also because such a high degree of focusing is not necessary.

Figure 11 is a wide angle picture of the experimental shield (13-1) which encloses most of the experimental stand (3-1) during a run. (See Fig. 13 for an undistorted view of the experimental shield.) The purpose of the experimental shield is to prevent stray electrons and germanium molecules from striking the bell jar.

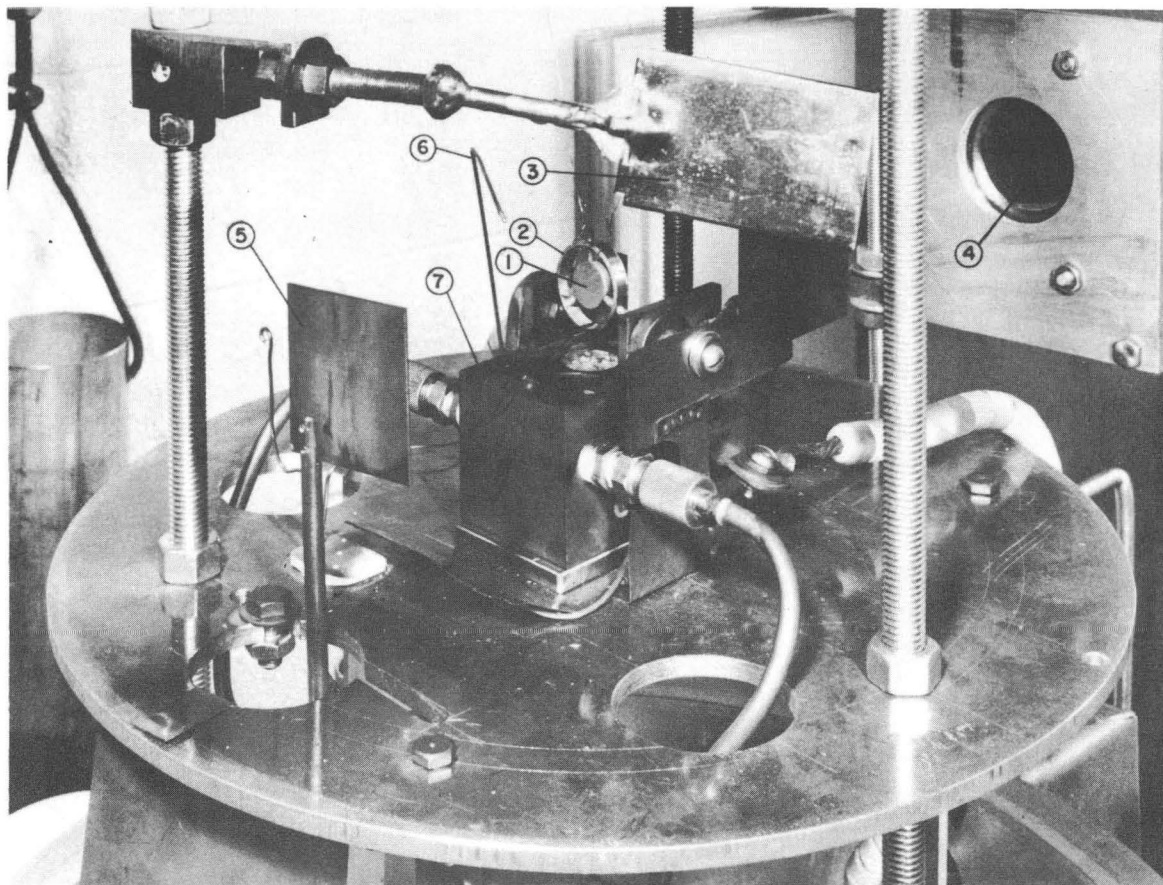


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Fig. 8. Experimental stand, arranged for deposition run.

DESCRIPTION OF FIGURE 8

Object Number	Name of Piece of Equipment	Function and Specifications of Piece of Equipment
(8-1)	Electron beam heater (4-1)	To vaporize germanium which plates out on the preheated substrate (5-2) above.
(8-2)	Substrate preheater(5-1)	To preheat substrate.
(8-3)	Deposition shutter (12-1)	To precisely control the deposition time.
(8-4)	Inside mirror (largely obscured in this view) (12-2)	In this configuration the inside mirror is used for viewing the germanium sample (4-6) during a run, when the experimental stand is covered by the experimental shield (11-1, 13-1).
(8-5)	Electron shield	To prevent stray electrons from the electron beam heater from striking the bell jar (3-2).
(8-6)	Electric feedthrough	To convey electricity to the substrate preheater (5-1) and the electromagnet (4-5) of the electron beam heater. To transmit the temperature reading from the substrate thermocouple (9-6) to the substrate temperature guage (8-10).
(8-7)	Mechanical feedthrough	To transmit mechanical motion into the vacuum system to move the deposition shutter (8-3) or the vaporization shutter (9-5).
(8-8)	Water feedthrough	To transport cooling water to and from the electron beam heater.
(8-9)	High voltage feedthrough	To transport the necessary electrical energy (3-5) to the electron beam heater.
(8-10)	Substrate temperature gauge	To indicate the temperature of the substrate (5-2).

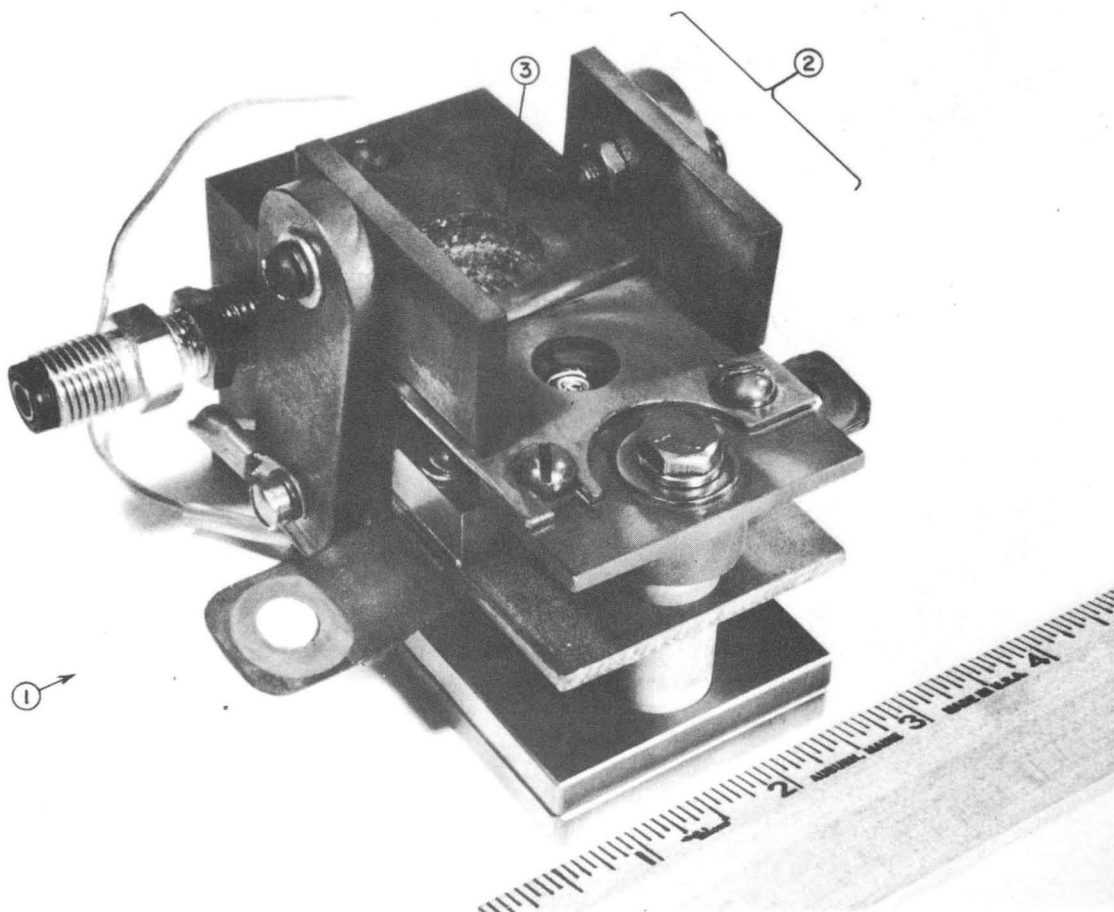


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Fig. 9. Experimental stand, arranged for vaporization run.

DESCRIPTION OF FIGURE 9

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(9-1)	Germanium coated substrate (5-2).	In this configuration, to be heated by electron bombardment to determine the vaporization rate of germanium and to test the surface integrity of the germanium film.
(9-2)	Substrate holder	To hold substrate during vaporization run.
(9-3)	Inside mirror (back view)	In this configuration, to view the integrity of the germanium film.
(9-4)	Outside mirror	To view the back of the substrate.
(9-5)	Vaporization shutter	To prevent electrons and germanium vapor from striking the bell jar when experimenter is not viewing the germanium film.
(9-6)	Substrate thermocouple	To measure the substrate temperature during deposition runs. No function during vaporization runs.

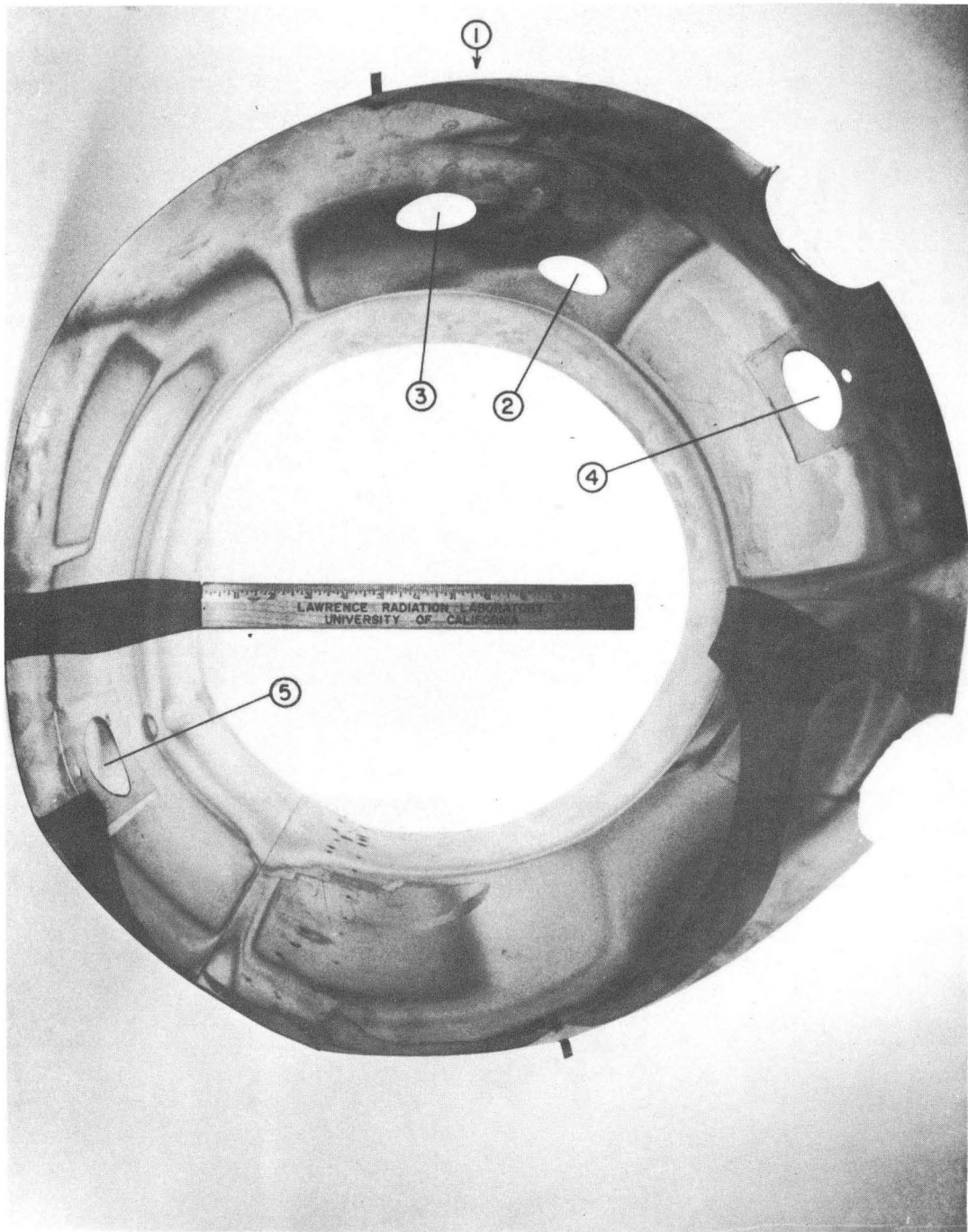


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Fig. 10. Electron beam heater, configured for vaporization run.

DESCRIPTION OF FIGURE 10

Object Number	Name of Piece of Equipment	Function and Specifications of Piece of Equipment
(10-1)	Electron beam heater	In this configuration, to heat a germanium coated substrate which hangs between the poles during a vaporization run (See Fig. 9 for a more complete vaporization configuration). (See Fig. 4 for deposition configuration of electron beam heater).
(10-2)	Electromagnet pole, in vaporization run configuration	To collect electrons and bend them upon the coated substrate. (The focusing elements (4-12) are omitted for vaporization runs).



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Fig. 11. Experimental shield (bottom, wide angle view).

DESCRIPTION OF FIGURE 11

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(11-1)	Experimental Shield (13-1)	To shield bell jar from germanium vapor and electrons.
(11-2)	Viewing port No. 2	To view, by reflection from inside mirror (8-4), the germanium sample during deposition run.
(11-3)	Viewing port No. 3	To view, by reflection from inside mirror (9-3), the integrity of the germanium film during vaporization runs.
(11-4)	Viewing port No. 4	To view, by reflection from outside mirror (9-4), the back of the substrate during a vaporization run. Closed during deposition runs.
(11-5)	Viewing port No. 5	To view the germanium film during a vaporization run. Closed during deposition runs.

V. PROCEDURE

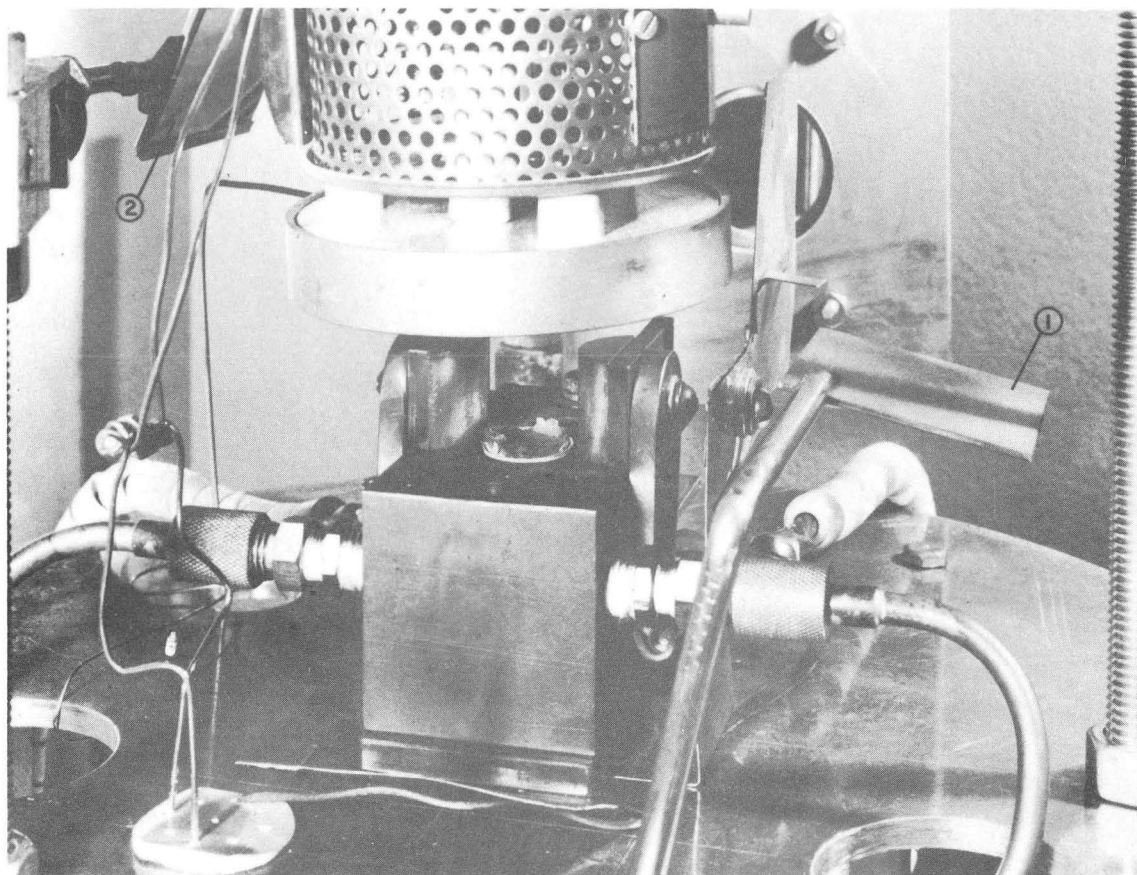
As noted in Section IV, two types of experiments were conducted in this study, deposition and vaporization. Also, in checking for contamination in the germanium film x-ray diffraction and electron microprobe analytical techniques were utilized. The procedure for deposition, vaporization, x-ray diffraction, and electron microprobe runs will be presented in that order.

A. Procedure for Deposition Runs

Deposition runs were necessary to produce germanium coated substrates. Vaporization rate data is a by-product of deposition runs.

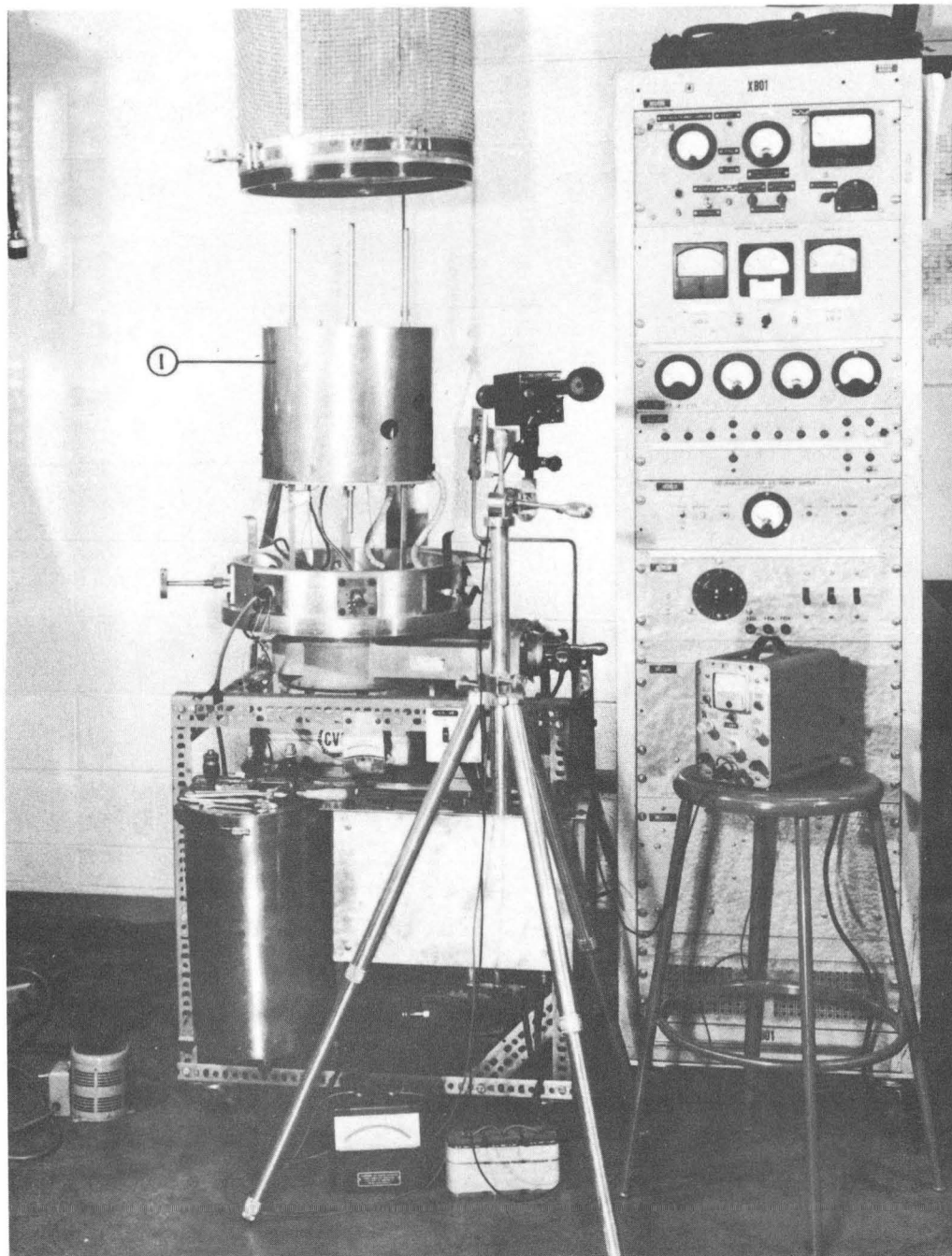
The first step in a deposition run was to chemically clean the molybdenum substrate in a 50% HCl solution at 180°F for 1.5 minutes. Graphite substrates were not cleaned. Then, the substrate and the germanium sample (plus crucibles) were weighed. The equipment on the experimental stand (3-1) was arranged as shown in Figs. 8 and 12, except that the deposition shutter (8-3) was positioned between the germanium sample (4-6) and the substrate (5-2), not as shown in Fig. 12. The glass part of the inside mirror (8-4) was replaced. Port holes No. 4 and 5 of the experimental shield (11-1) were then closed off and the shield lowered over the experimental stand, as picture in Fig. 13.

The start up procedure was then begun. The bell jar (3-2) was lowered to the feedthrough ring (3-4) and the system evacuated to about 10^{-5} torr. The electron beam heater cooling water, the substrate preheater, and the electromagnet current were then turned on. At this point the electron beam heater was turned on and the electromagnet



XBB6910-6546A

Fig. 12. Experimental stand, arranged for a deposition run (close up).



XBB6910-6541A

Fig. 13. Experimental system, ready for deposition run.

current adjusted to guide the beam into the germanium sample. When the germanium sample and the substrate reached the desired temperatures the deposition shutter (12-1) was moved to the position shown in Fig. 12 to allow vaporizing germanium to plate the surface of the preheated substrate.

During the run the germanium sample could be viewed with the aid of the inside mirror through viewing port No. 2 (11-2) and the pyrometer was positioned, as in Fig. 13, to determine the temperature of the germanium sample.

When it was felt that the film was thick enough, the deposition shutter was closed and the system shut down. When shut down was completed, the coated substrate and the germanium sample plus crucibles were removed and weighed.

B. Procedure for Vaporization Runs

In vaporization runs, a coated substrate was heated to about 1000°C. The vaporization rate of germanium was measured and the surface integrity of the liquid germanium film was noted.

The first step in a vaporization run was to weigh the coated substrate. Figure 9 shows the experimental stand arranged for a vaporization run. Once the equipment was arranged in this manner and the glass part of the inside mirror replaced, viewing ports 4 (11-4) and 5 (11-5) of the experimental shield were opened and the shield lowered over the experimental stand. The bell jar was lowered and the vacuum chamber evacuated.

Then the cooling water, the electromagnet, and the electron beam heater were turned on. The electromagnetic current was adjusted until

the electrons deflected by the magnetic field struck the back of the coated substrate.

By use of the pyrometer, positioned as shown in Fig. 3, the apparent film temperature was recorded through viewing port 5. The temperature of the black body hole on the back of the substrate was measured through viewing port 4, with the aid of the outside mirror (9-4). The observed black body temperature in combination with the apparent temperature of the liquid germanium film, was used to determine the emissivity of liquid germanium.

To check the surface integrity of the film, the germanium surface was viewed through viewing port 3, with the aid of the inside mirror.

Following shut down the coated substrate was removed from the system and weighed to determine the weight loss.

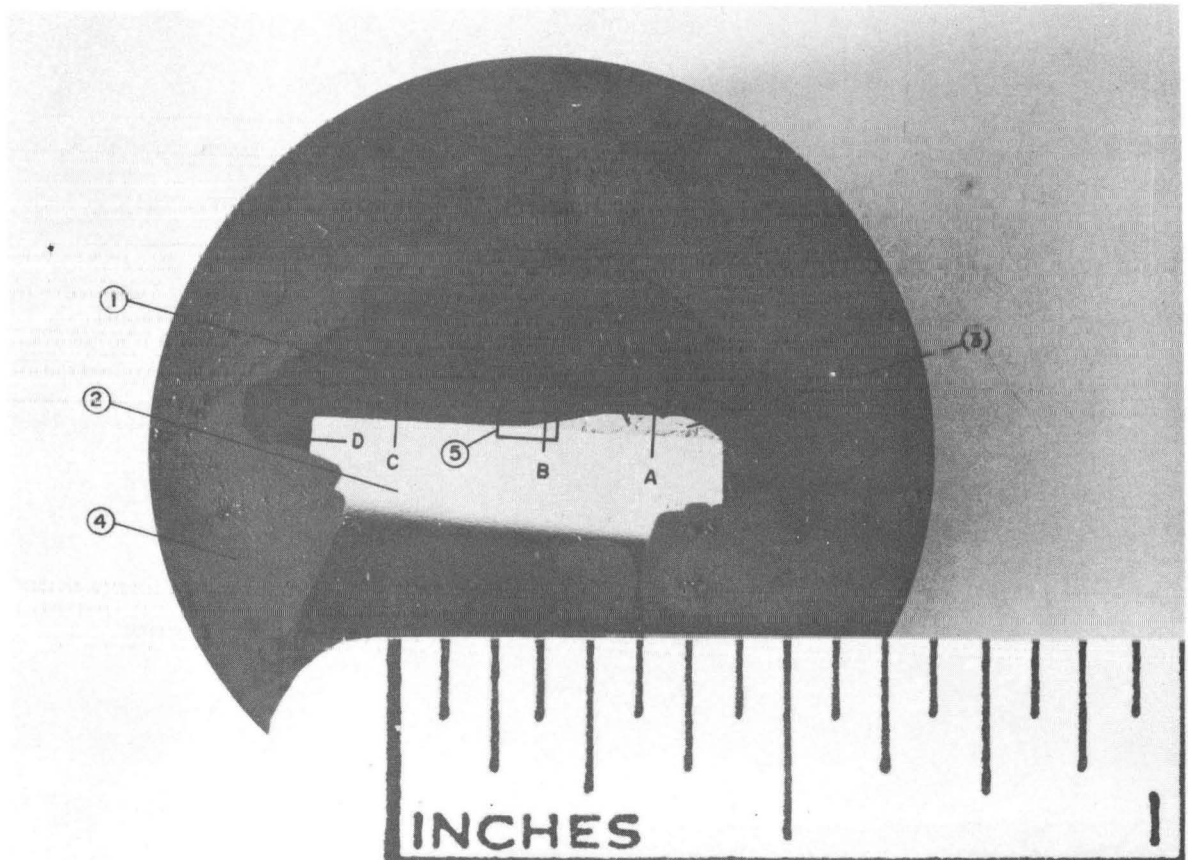
C. Procedures for X-ray Diffraction and Electron Microprobe Techniques

To determine the degree of contamination of the germanium, X-ray diffraction and the electron microprobe techniques were employed. Both of these processes were carried out at the University of California, Lawrence Radiation Laboratory in Berkeley.

In the x-ray diffraction measurements, x-rays were directed upon the surface of the germanium film. By measuring the angle and intensity at which the x-rays were diffracted, the chemical compounds in the film were identified.

After x-ray diffraction the coated substrate was prepared for the electron microprobe. First, the substrate was cut in half, from front to back, with a spark cutter. One half was mounted in a bakelite holder,

as shown in Fig. 14, and then polished. The holder was placed into the electron microprobe and the elementary composition (amount of various elements) determined as a function of position along lines A, B, C, and D of Fig. 14. See Section III or Heinrich⁹ for a discussion of the operation of the electron microprobe.



XBB6910-6539A

Fig. 14. Cross section of coated substrate, mounted for electron microprobe.

DESCRIPTION OF FIGURE 14

<u>Object Number</u>	<u>Name of Piece of Equipment</u>	<u>Function and Specifications of Piece of Equipment</u>
(14-1)	Bakelite mount	To hold the spark cut piece of coated substrate for electron microprobe analysis
(14-2)	Substrate cross-section (spark cut in half from front to back). (The front of the substrate is facing up and the back facing down).	
(14-3)	Germanium film cross-section (after germanium droplet was formed during vaporization run)	
(14-4)	Carbon film	Was spread over surfaces of bakelite and part of substrate cross-section to conduct electrons away from the coated substrate during electron microprobe analysis.
(14-5)	Photomicrograph area	This area is pictured in the photomicrograph, Fig. 18.
(14-A, B, C, D)	Probe lines	Lines along which electron microprobe measurements were taken.

VI. DATA ANALYSIS

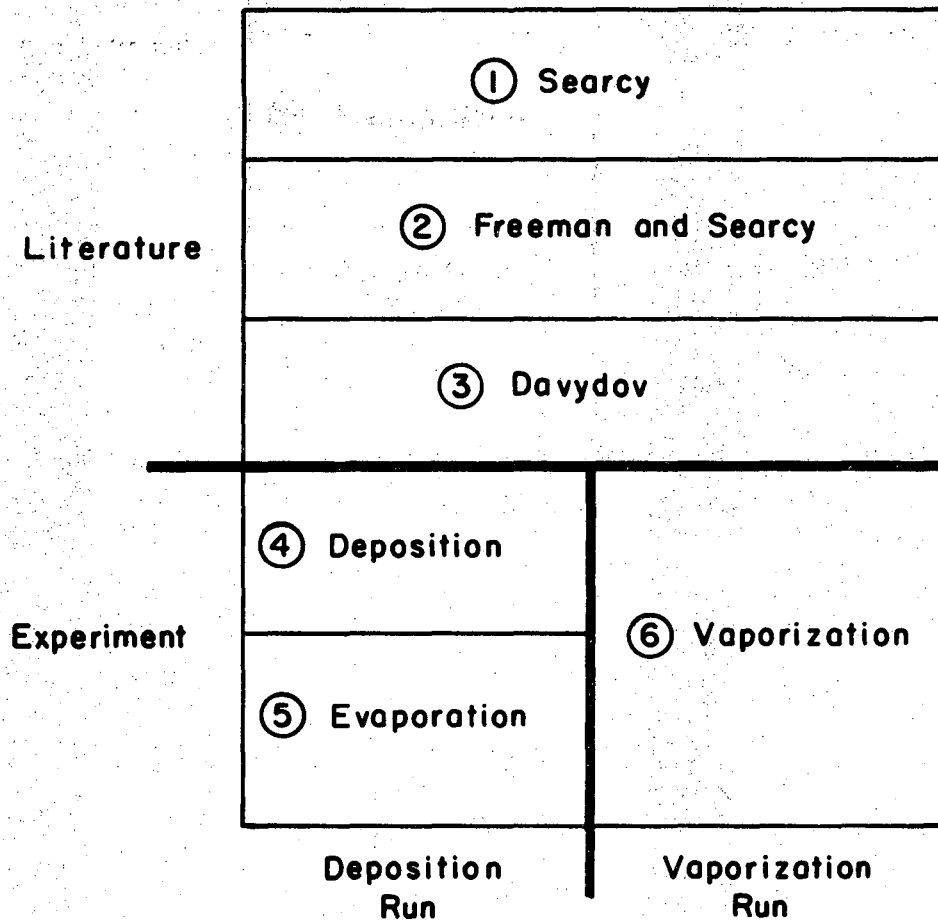
In this section the various mathematical formulas necessary for analyzing the data are derived. All symbols used in the body of this paper are defined and their units given in the Nomenclature.

Before discussing the methods of data analysis, it will be helpful to investigate the origins of the data employed. Figure 15 gives a diagrammatic representation of these origins. The left hand margins of the table gives the ultimate source of the data, the literature or this experiment. The bottom margin gives the types of runs in which the experimental data was taken, deposition or vaporization runs.

Areas 1, 2, and 3 of the table represent the data obtained from the Searcy paper,⁵ the Freeman and Searcy paper,⁶ and Davydov.⁷ Area 4 contains the data based on the amount of germanium deposited on the substrate during a deposition run. Area 5 holds the data based on the amount of germanium evaporated or lost from the germanium sample (6-1) during a deposition run. Area 6 represents the data based on the amount of germanium vaporized or lost from the coated substrate (9-1) during a vaporization run.

A. Theoretical Calculation of the Germanium Film Thickness Produced During a Deposition Run

This derivation, although simple in concept, requires many corrections to the experimental data. First, the apparent (observed) temperatures must be corrected for the transmissivity of the bell jar, the mirror, the germanium coating on the mirror and the emissivity of liquid germanium. Second, a formula for the effective temperature of the germanium puddle, T_e , is derived. Third, a formula for predicting the film thickness,



XBL 702-312

Fig. 15. A diagrammatic representation of the origins of the data used in this study.

τ , from the effective temperature is developed.

In calculating τ it is assumed that all germanium atoms incident upon the coated substrate surface stick to the surface and that no germanium atoms are evaporated from the film once they have condensed.

1. Determination of the True Temperature of the Germanium Sample

Figure 16 gives a diagrammatic representation of the relationship between the apparent temperature, T_A , and the true temperature, T_T , for a deposition run.

The pyrex bell jar causes an apparent temperature decline given by¹⁰

$$\frac{1}{T_A} = \frac{1}{T_B} + A_B \quad (1)$$

where A_B is the transmissivity of the glass.

In a similar manner the correction for the mirror is

$$\frac{1}{T_B} = \frac{1}{T_{BM}} + A_M(t) \quad (2)$$

The transmissivity of the mirror is time dependent because of the progressive coating of the mirror surface with germanium.

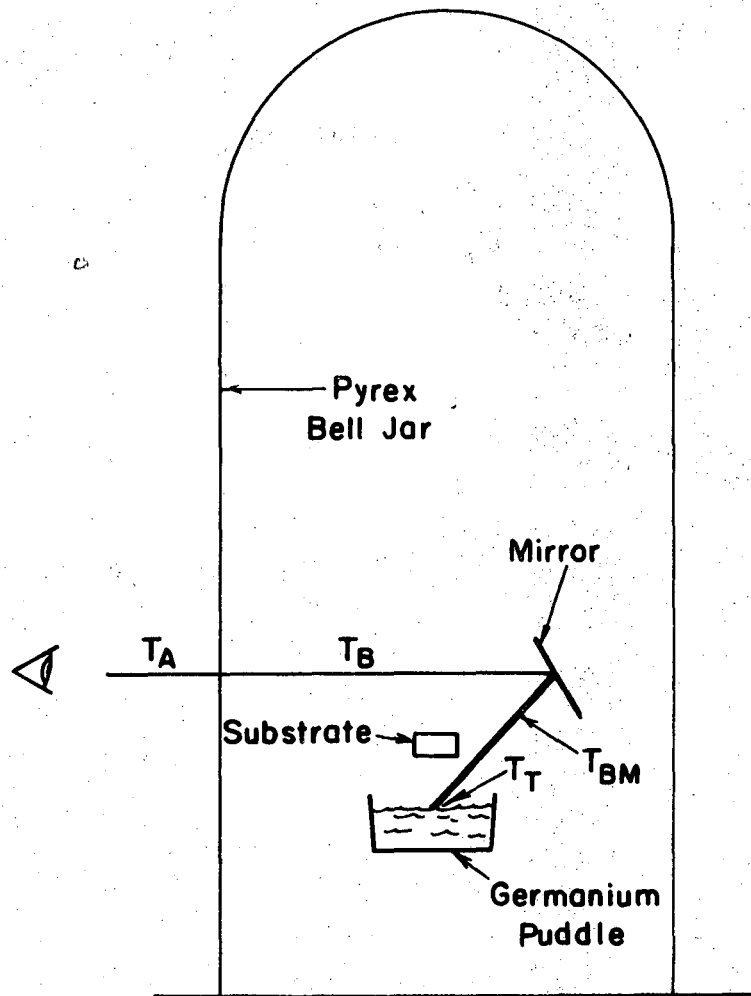
Finally, the true temperature of the germanium surface, T_T , is given by¹⁰

$$\frac{1}{T_{BM}} - \frac{1}{T_T} = - \frac{\log_{10} \epsilon}{9588} \quad (3)$$

when ϵ is the emissivity of the germanium surface at the wave length of optical pyrometer (6550Å). Adding Eqs. (1)-(3) yields

$$T_T(t) = \left[\frac{1}{T_A(t)} - A_B - A_M(t) + \frac{\log_{10} \epsilon}{9588} \right]^{-1} \quad (4)$$

The transmissivity of the bell jar was determined by measuring the temperature of a hot filament with and without the bell jar interposed. This procedure yielded $A_B = 2.1 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$. The emissivity of



XBL 702-313

Fig. 16. A representation of the observation of germanium sample temperature for a deposition run.

liquid germanium was estimated by simultaneous measurement of the rear black body hole temperature and the apparent front germanium film temperature during a vaporization run. From the data and Eq. (3), the emissivity was found to be 0.7.

The mirror transmissivity, $A_M(t)$, is derived as follows. The correction due to the clean mirror is denoted by b . To this is added a term proportional to the thickness of the germanium film on the mirror.

$$A_M(t) = a\psi(t) + b \quad (5)$$

where $\psi(t)$ is the thickness of the germanium on the mirror.

To determine $\psi(t)$, we assume that the build up rate of germanium is constant in time and that, once the film thickness reaches its maximum value, it maintains that value. The latter assumption is due to the fact that the germanium splinters and begins to flake off the surface of the mirror at a certain maximum thickness, ψ^* . Some splinters spring from the surface immediately, whereupon plating begins again, while others remain on the surface for a time before falling away.

The rate at which the mirror is coated can be related to the rate of germanium deposition on the substrate, which is a measurable quantity. If τ_D is measured film thickness on the substrate after a deposition run of duration t_R , the film thickness on the mirror can be determined by scaling the rate of film growth by the square of the ratio of germanium-to-substrate distance (1.37 inches) and the germanium-to-mirror distance (6 inches). This yields:

$$\psi(t) = \left(\frac{\tau_D}{t_R}\right) \left(\frac{1.37}{6}\right)^2 t, \text{ for } \psi < \psi^*. \quad (6)$$

In Eq. (6), the rate of growth of the germanium film on the substrate has been assumed to be equal to τ_D/t_R at all times during the run.

The clean mirror absorption coefficient, b , was determined in the same manner as was the analagous bell jar term. A value $b = 0.3 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ was found. Another experiment on a mirror which had a known film thickness permitted a value $a = 0.14 \text{ (cm } - ^\circ\text{C)}^{-1}$ to be estimated.

Using the measured values of the constants and Eqs. (5) and (6), Eq. (4) becomes

$$T_T(t) = \left[\frac{1}{T_A(t)} - 3.4 \times 10^{-5} - 7.3 \times 10^{-3} \left(\frac{\tau_D}{t_R} \right) t \right]^{-1}. \quad (7)$$

2. Derivation of the Effective Temperature, T_e , for Deposition Runs

During a deposition run the temperature of the germanium sample varied with time. The range of this variation was often 200 to 300°C .

The effective temperature, T_e , for a deposition run is a constant temperature which can be used in deposition calculations in place of integrating over temperature as a function of time. In order to derive an expression for the effective temperature of a deposition run, it is first necessary to find an expression relating the theoretical film thickness, τ , and, the temperature of the germanium sample as a function of time, $T(t)$.

The rate growth of the film on the substrate is related to the current of atoms impinging on the surface, $I(t)$, by:

$$\frac{d\tau}{dt} = \frac{I(t) M_{\text{Ge}}}{\rho_{\text{Ge}} N_{\text{Av}}} \quad (8)$$

where M_{Ge} is the molecular weight of germanium, N_{Av} is Avogadro's number, and ρ_{Ge} the density of germanium.

In Price¹¹ it is shown that the impingement rate per square cm of substrate surface is related to the evaporation rate per square cm of source surface $R(t)$ by

$$I(t) = R(t) \left[\frac{r^2}{r^2 + h^2} \right] \quad (9)$$

where r is the radius of the vaporizing germanium surface and h is the distance between the germanium sample and the substrate.

Assuming unit condensation coefficient, the germanium vaporization rate into vacuum is related to the equilibrium vapor pressure by:

$$R(t) = \frac{3.5 \times 10^{22} p^0 [T(t)]}{\sqrt{M_{\text{Ge}}} T(t)} \quad (10)$$

where the vapor pressure (in torr) is given by

$$p^0 = A e^{-B/T} \quad (11)$$

The vapor pressure measurements of Searcy⁵ or Freeman and Searcy⁶ or the vacuum vaporization measurements reprinted by Davydov⁷ can be utilized to determine the constants A at B .

The temperature in the denominator of Eq. (10) has but a slight effect on the vaporization rate, and $T(t)$ in this term will be approximated by the effective temperature of the run, T_e . Substituting Eqs. (9)-(11) into (8) and integrating yields:

$$\tau = \frac{K}{\sqrt{T_e}} A \int_0^{t_R} e^{-B/T(t)} dt \quad (12)$$

with the $M_{\text{Ge}} = 72.6$, $\rho_{\text{Ge}} = 5.32$, $r = 0.87$ cm and $h = 3.5$ cm. The constant K is

$$K = \frac{3.5 \times 10^{22} \sqrt{M_{\text{Ge}}}}{\rho_{\text{Ge}} N_{\text{Av}}} \left[\frac{r^2}{r^2 + h^2} \right] = 5.4 \times 10^{-3} \quad (13)$$

The effective temperature T_e is defined as the constant temperature which gives the same film thickness as Eq. (12); therefore,

$$T_e = - \frac{B}{\ln \left[(1/t_R) \int_0^{t_R} e^{-B/T(t)} dt \right]} \quad (14)$$

The deposited film thickness, τ_D , is used to obtain $T(t)$ from the pyrometer reading by Eq. (7). The theoretical film thickness is then

$$\tau = \frac{KA}{\sqrt{T_e}} e^{-B/T_e} t_R. \quad (15)$$

Alternatively, an average germanium vaporization rate can be computed from the deposition film thickness by using time-average values in Eqs. (8) and (9):

$$\bar{v}_D = \frac{\bar{R} M_{\text{Ge}}}{N_{\text{Av}}} = \rho_{\text{Ge}} \left(\frac{r^2 + h^2}{r^2} \right) \frac{\tau_D}{t_R}. \quad (16)$$

B. Vaporization Experiments

The temperature of the liquid film of germanium during the vaporization tests is related to the pyrometer temperature by an equation of the form of Eq. (4). However, since no mirror is present, the term $A_M(t)$ in this relation is omitted. The effective temperature averaged over the duration of the run was determined by Eq. (14).

The experimental average vaporization rate, $\bar{v}_V$, for a vaporization run was calculated from the weight loss of the coated substrate.

$$\bar{v}_V = \frac{\Delta W}{\pi r_s^2 \times t_R}, \quad (17)$$

where ΔW is the weight loss of the germanium film during the vaporization run and r_s is the radius of the substrate disk (0.8 cm).

The theoretical vaporization rate for vaporization runs, $\bar{v}$, is given by Eq. (11) and the time-average of Eq. (10)

$$\bar{v} = \frac{3.5 \times 10^{22} A e^{-B/T_e} \sqrt{M_{Ge}}}{N_{Av} \sqrt{T_e}} \quad (18)$$

C. Calculation of the Minimum Permissible Thickness for a Germanium Film

One of the specifications of this study is that the germanium-coated target must last for a significant period of time in the molecular beam apparatus described in Section I. If the germanium film completely evaporates, in a short time at run temperatures (about 1000°C), the target would not be suitable. Here, a significant period of time, t_s , is taken to be two hours.

If the average vaporization rate is $\bar{v}$, the minimum permissible film thickness is

$$r_m = \frac{\bar{v} t_s}{\rho_{Ge}} \quad (19)$$

D. Determination of Germanium Removal Rate

Due to Oxidation for Both Deposition and Vaporization Rate

Since germanium forms an oxide (GeO), volatile at the temperatures investigated here, part of the observed average experimental vaporization rate may be due to removal of germanium by oxidation. For both types of runs, the removal rate of germanium due to oxidation may be determined from Eq. (18) as follows:

$$v_{O_2} = 2 \alpha_{O_2} \frac{3.5 \times 10^{22} p_{O_2} \sqrt{M_{Ge}}}{\sqrt{T_a} M_{O_2} N_{Av}} \quad (20)$$

where α_{O_2} ($\alpha_{O_2} = 3.5 \times 10^{-2}$ for germanium at $1203^\circ K$)¹² is the probability that an oxygen atom, striking a germanium surface, will react with a germanium atom; p_{O_2} is the partial pressure of oxygen in the vacuum system; M_{Ge} is the molecular weight of germanium; and T_a is the ambient temperature of the oxygen.

VII. RESULTS AND DISCUSSION

The results of this study and conclusions drawn from these results will be discussed in four parts, one for each step in accomplishing the purpose.

A. Results of the Production Step

The intention of the production step was to perfect a method for producing germanium films on both graphite and molybdenum substrates.

As prescribed two high melting point substrates, graphite and molybdenum, were used. Four deposition runs were made using pyrolytic graphite with the basal planes exposed. In each case no special surface preparation was performed, but each substrate was preheated to 210°C or more.

In three of the runs the germanium film was formed but did not adhere well to the graphite and fell off of the substrate during or immediately following the deposition run. In the fourth run a film, .023 cm in thickness, adhered to a graphite substrate which had been preheated to 230°C . When the coated substrate was removed from the vacuum system it was cracked and its adherence to the graphite surface appeared to be rather tenuous.

These runs placed in doubt the usefulness of graphite as a substrate material. But its performance during a vaporization run, which will be discussed later, sealed its fate.

Molybdenum substrates were used in about 15 deposition runs. The substrate surface was chemically cleaned (see Section VA) before all runs and substrates were preheated to between 210 and 340°C . Unlike the graphite substrates, the molybdenum substrates held the germanium films rather well. One film reached a thickness of .035 cm.

For preheat temperatures used in this experiment, 210-340°C, a trend was observed for the molybdenum substrates. The higher the preheat temperature the better the adhesion of the germanium film to the molybdenum surface.

From these observations, it was concluded that molybdenum was a feasible substrate material from the standpoint of target production.

Table 1 is a summary of the deposition runs. It tabulates the measured thickness of the germanium film, τ_D ; the film thickness calculated from the weight loss of the germanium sample (6-1), τ_E ; the film thickness calculated from Freeman-Searcy⁶ data, τ_F ; and the film thickness calculated from Davydov⁷ data, τ_R . The deviations of the three predicted film thicknesses from the measured thicknesses are large. The deviation of τ_E from the measured germanium film thickness, τ_D , ranges between a factor of 1.02 and 1.8. τ_F is by far the most deviant; it ranges between a factor of 10 and 1000 less than τ_D . The deviations of τ_R from τ_D ranges between a factor of 1.0 and 10.

Various explanations of the large and consistent deviation of τ_F from τ_D were considered. One explanation was that ambient oxygen reacted with the hot germanium forming GeO . The GeO then vaporized and a fraction was deposited on the substrate. But x-ray diffraction studies showed that no oxide of germanium was present in the film.

It was then hypothesized that the oxide might have dissociated into oxygen gas and elementary germanium upon striking the substrate. But it was shown by use of Eq. (20), that if indeed this oxidation and subsequent reduction process had occurred, its contribution to the experimental thickness would be negligibly small. A typical value of $\bar{v}$

TABLE I

Run No.	T_e (°K)	t_R (sec)	τ_D (cm) $\times 10^3$	τ_E (cm) $\times 10^3$	τ_F (cm) $\times 10^3$	τ_R (cm) $\times 10^3$
1	1618	240	1.2	---	.015	1.2
2	1559	549	3.0	---	.014	1.2
3	1413	705	1.5	---	.0015	.15
4	1534	780	0.90	---	.013	1.15
5	1700	1060	35	---	.20	16.
6	1878	944	17	---	1.4	87
7	1566	1336	5.0	4.9	.038	3.3
8	1943	840	26	14.7	2.3	134
9	1919	780	23	14.7	1.7	99
10	1440	970	1.5	.96	.0035	.34
11	1462	720	.62	.75	.0038	.37

might be 8.26×10^{-4} g/cm²-sec, while a typical value of v_{O_2} might be 4.37×10^{-8} g/cm²-sec.

Another possible explanation was then considered. It might be possible that the temperature of the germanium sample was consistently underestimated by as much as 40°C, due to maladjustment of the measuring apparatus. But calculations showed that an error in temperature measurement of about 150°C would be necessary to cause an error in τ of even one order of magnitude. Therefore, the discrepancy between the predicted and experimental germanium film thicknesses remains unexplained.

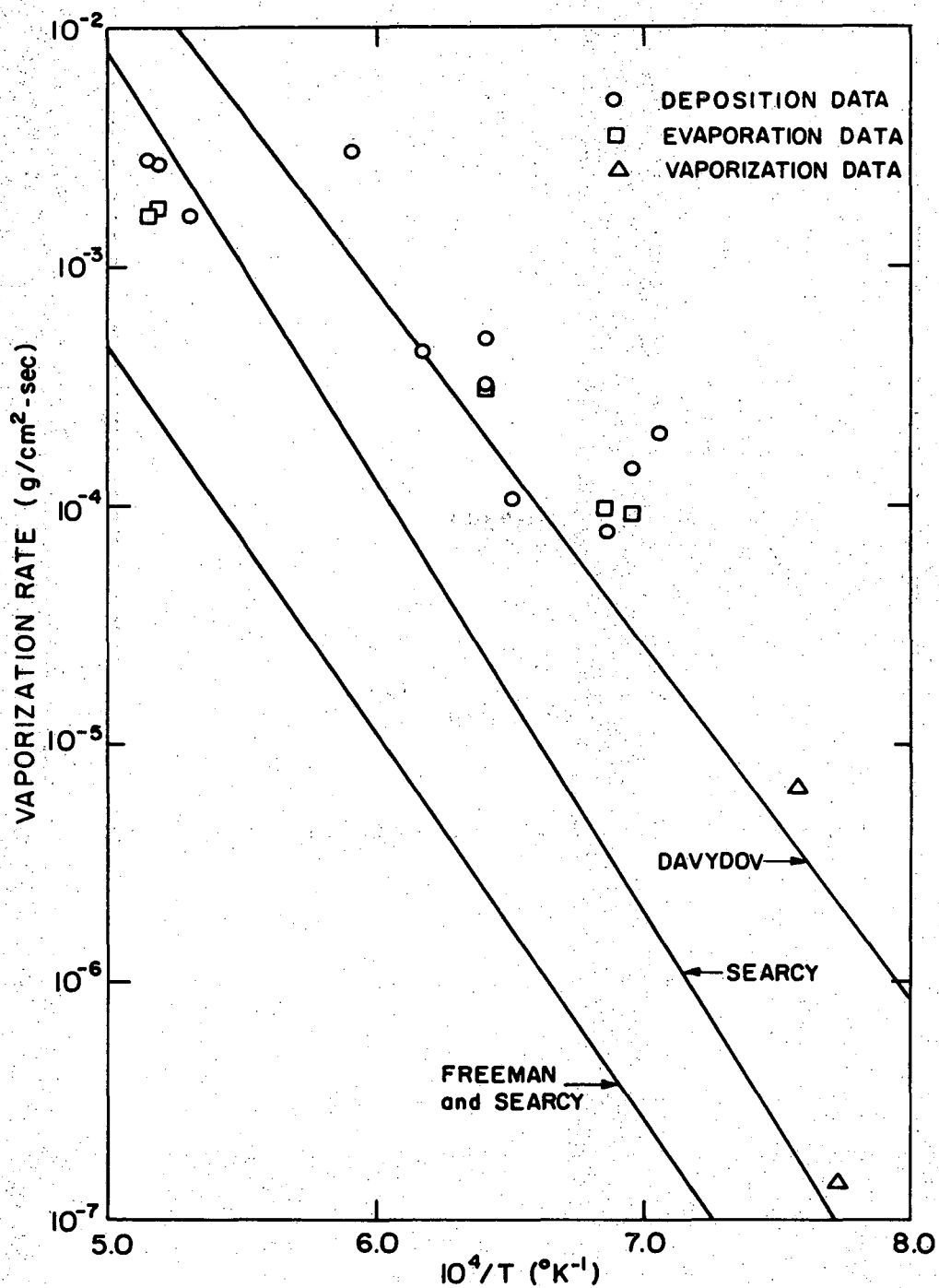
B. Results of the Vaporization Rate Step

The purpose of the vaporization rate step was to determine vaporization rate vs. temperature information for germanium. This information was then to be used to calculate the minimum acceptable substrate thickness.

Figure 17 shows plots of vaporization rate of germanium vs. temperature from four sources. Three sources are from the literature; Searcy,⁵ Freeman and Searcy,⁶ and Davydov⁷ (Searcy plus Freeman and Searcy data are converted from partial pressure to vaporization rate data). The fourth source is this study; deposition, evaporation, and vaporization data (see Fig. 15) were plotted.

Although the variance of the data within each literature study is small, the variance between the studies is very large. The Freeman and Searcy⁶ study reports vaporization rates almost two orders of magnitude lower than the Davydov⁷ data. There is no known explanation for this large discrepancy.

Likewise, the variation in the experimental data is also very large. But, it should be noted that obtaining vaporization rate data is not the



XBL 702-309

Fig. 17. Vaporization rate vs. temperature for germanium.

major purpose of this experiment. Vaporization rate data are only a by-product and the techniques used here to obtain these data are far from optimal.

To calculate the minimum permissible germanium film thickness, τ_m , we employ Eq. (19). If we set t_s equal to two hours, set T_e equal to 1000°C , and calculated τ_m using each of the four sets of data given in Fig. 17; we obtain the results given in Table 2.

C. Results of the Integrity Check

The integrity check was designed to determine the surface integrity of the liquid germanium film.

The only graphite substrate which retained its germanium film was subjected to a vaporization run. The substrate was electron bombardment heated on the back surface to about 1100°C , but the film remained relatively cool, about 750°C . Obviously, the thermal conductivity from the back of the substrate to the film was low. First, there was a significant temperature gradient between the back and the front of the substrate, which decreased with time. This gradient was due to the low thermal conductivity perpendicular to the basal plane of pyrolytic graphite. Second, the temperature difference between the front of the substrate and the film was excessive, up to 300°C . This differential was due to the poor physical contact between the germanium and the graphite.

After 13 minutes of the vaporization run the germanium film fell from the graphite substrate. Upon later inspection of the film, it was noted that a small area on the edge had melted and formed into a small ball. Assuming that this melt occurred before the film fell from

TABLE 2

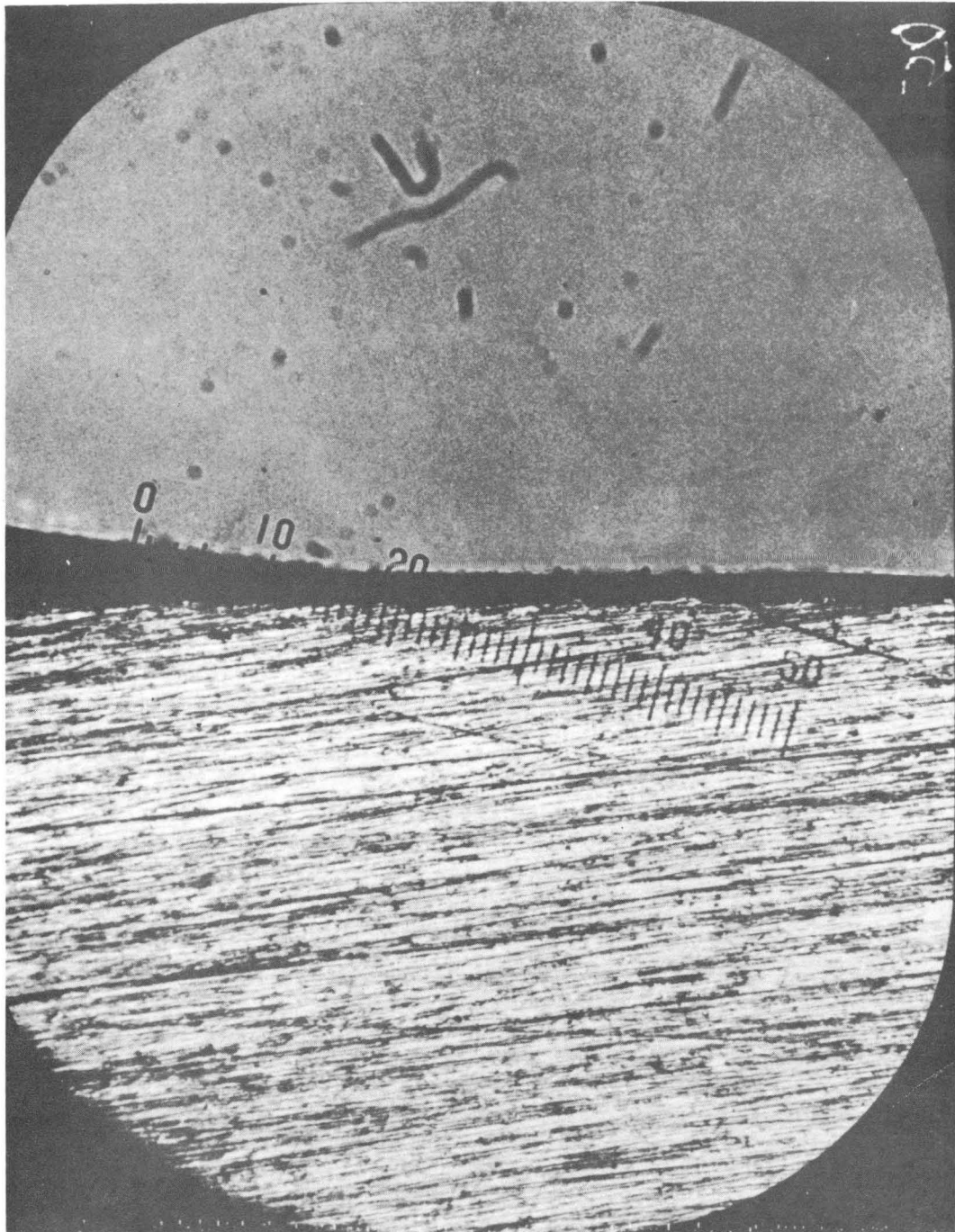
Source of data	$\tau_m \text{ (cm)} \times 10^3$
Searcy	.082
Freeman-Searcy	.015
Davydov	2.0
Experimental	2.7

the substrate, this indicates that germanium does not wet graphite. If germanium did wet graphite, one would expect that melted germanium would spread out on the graphite surface rather than ball up. Wetting is a necessary condition for the integrity of the liquid germanium film. At this point we can safely conclude that, under the conditions tested, graphite is not a suitable substrate material.

Two 1000°C, vaporization runs were made using molybdenum substrates. The first run utilized a coated substrate with a germanium film thickness of .035 cm. When the film became liquid it immediately began to slump to the bottom of the substrate. Obviously, a liquid germanium film of this thickness could not support itself.

Both Figs. 14 and 18 show cross-sections of this substrate, cut vertically through the center, from front to back. The part of the cross-section shown in Fig. 18 is (14-5) in Fig. 14. Note that in Fig. 18 the part of the film to the left of the droplet is relatively constant in thickness. This thickness averages about .0035 cm. It was felt, therefore, that this was the maximum liquid germanium film thickness that could support itself. Note that this thickness is greater than any of the τ_m 's listed in Table 2.

Another vaporization run was carried out using a coated molybdenum substrate with a film thickness of .0015 cm. No slippage of the liquid film was observed during this run. It was concluded, therefore, that the surface integrity and life expectancy of the molybdenum-germanium target were satisfactory. The molybdenum-germanium target configuration had only one additional requirement to meet.



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Fig. 18. Photomicrograph of cross-section (14-5) of coated substrate.

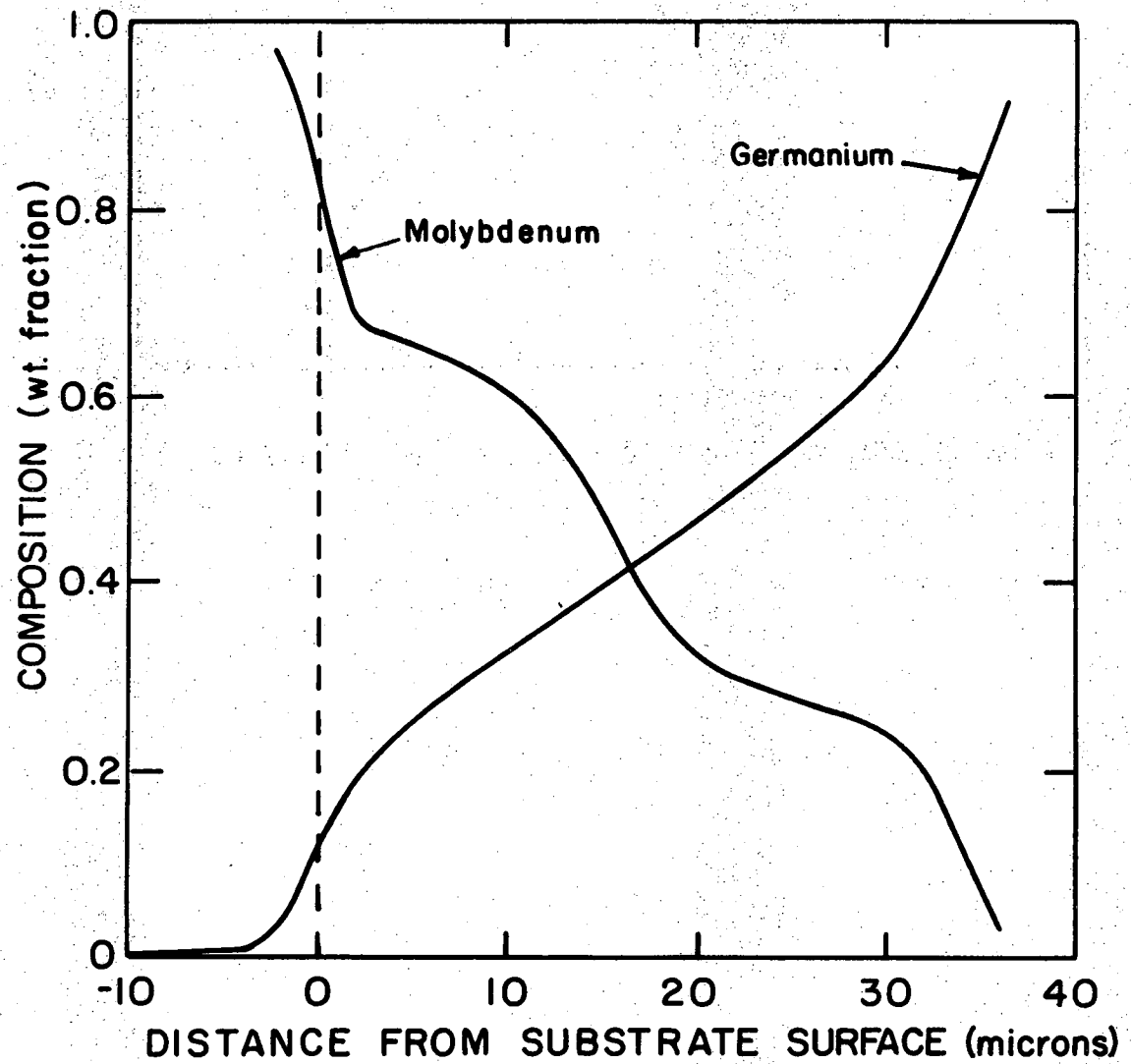
D. Results of Contamination Check

The contamination check was to determine the extent to which the germanium film might be poisoned by impurities. Ambient oxygen might have reacted with the germanium at some point in the deposition process and been incorporated into the film. Or, the substrate material might have diffused (through chemical reaction or dissolution) into the germanium films.

As was stated earlier (in Section VII A), germanium films were subjected to x-ray diffraction and no oxides of germanium were found. Therefore, it was concluded that germanium oxide contamination was not a problem.

After deposition the film of a coated molybdenum substrate was analyzed by x-ray diffraction and no impurities were found. But later a coated molybdenum substrate was analyzed after a vaporization run at 1000°C. The results of this x-ray diffraction study showed that a substantial quantity of MoGe_2 (β -phase) was present in the germanium film. This indicates that a drift of molybdenum into the germanium film occurs at temperatures comparable to those attained during molecular beam machine runs.

The electron microprobe was employed to investigate a cross-section of the same target. Figure 19 shows the results of that investigation along line A of Fig. 14. A substantial quantity of molybdenum has diffused into the germanium. Therefore, molybdenum is also unacceptable as a substrate material.



XBL 702-308

Fig. 19. Elemental composition of the target film, after a vaporization run.

VIII. CONCLUSIONS

The purpose of this study was to determine the feasibility of using a liquid germanium film, plated on a graphite or molybdenum substrate, as a target in the molecular beam machine. This purpose was accomplished. It was concluded that neither graphite nor molybdenum is a suitable substrate material and, therefore, the proposed targets are infeasible.

IX. RECOMMENDATIONS FOR FUTURE CONSIDERATIONS

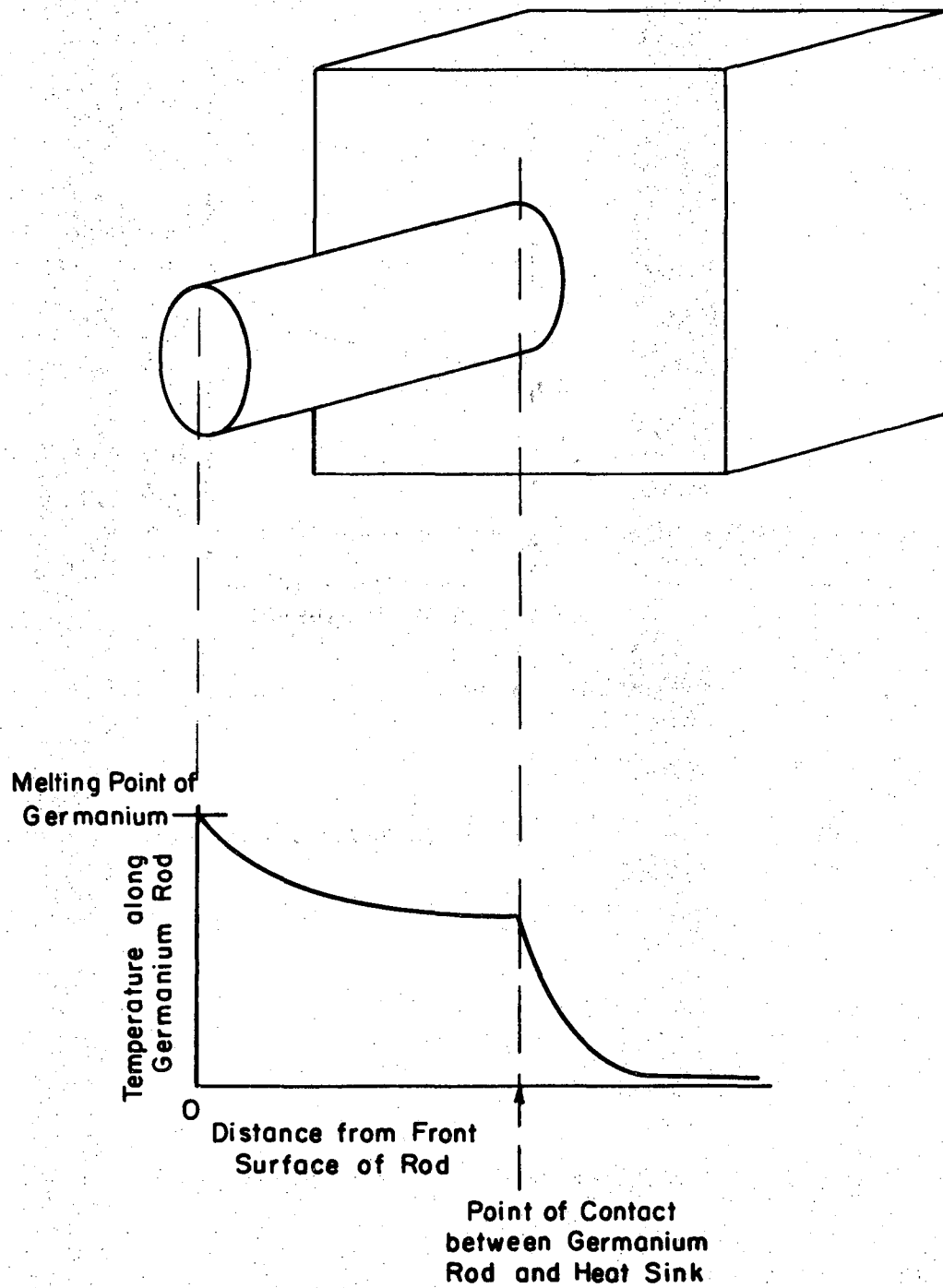
Even though the first concerted attempt to develop a target to study a gas-liquid reaction in the molecular beam machine was not successful, there remain many other possible approaches.

The most obvious approach would be to test other materials for use as substrates. For example, various ceramics might be suitable for this application.

Instead of a solid substrate, it might be desirable to employ a porous substrate. The voids in such a substrate could be filled with germanium. During a reaction run the target would be heated. As the germanium left the surface of the substrate, liquid germanium held within the pores could creep to the surface to maintain the film.

It might be possible to use a germanium rod as a target. See Fig. 20. The rod could be heated by electron bombardment, by a laser beam, by an electric current, or by induction. If the back of the rod were connected to a heat sink a thermal gradient would be set up as depicted by the graph in Fig. 20. If the shape of the rod were chosen correctly and the heating controlled properly, it should be possible to maintain a thin liquid film on the front surface of the germanium rod.

Another possibility is that the molecular beam machine could be altered or that a new molecular beam machine could be built to accommodate horizontal targets. This would necessitate raising the molecular beam from the horizontal, but might be the simplest alternative.



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Fig. 20. Heat sink target.

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