Progress Report

on

Impedance Characteristics of Irradiated Thin Films

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Progress Report No. 1
Thin Films Research Laboratory

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Preface

The work described herein was supported primarily by the National Aeronautics and Space Administration under Grant NGR 44-007-006. Some support was provided also by the Department of Electrical Engineering at Southern Methodist University.

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INTRODUCTION

This is the first report of progress toward determination of the effect of electron beam irradiation upon the complex impedance characteristics of thin films.

The principal purpose of initial research efforts has been to attempt to verify and extend previously-observed thin film impedance characteristics. Toward this end eleven sets of four bismuth films each have been prepared by evaporation. The initial resistance values of these films range from 11 ohms to 395 ohms. Infra-red transmission measurements on these films are almost complete, and analytical work which should yield impedance values and equivalent circuits will begin soon.

The effort to establish that these films are similar to those on which previous impedance characteristics were observed has included also a continuing measurement of resistance drift with time. In addition, a preliminary electron microscope study, both of the structure and of the effect of electron beam irradiation, has been carried out. All of these observations tend to indicate that the films and their behavior are similar to the films of previous work.[1,2,3*]

This report will document most of the important details of the research to date, including discussions of the resources acquired for the work, the preparation of films, and the study of film characteristics.

*Superscripts refer to numbered items in the List of References, which may be found on Page 28.

PROJECT RESOURCES

2.1 Personnel

The laboratory has added the following personnel to its staff:

Roy F. Eberline	Research Fellow, PhD. student in Electrical Engineering, 1/2-time.
David S. Glass	Research Assistant, B.S. in Electrical Engineering, 1/5-time.
John H. Lanham	Laboratory Assistant, Undergraduate student in Mechanical Engineering, part-time (supported in part by the Department of Electrical Engineering and in part by the NASA Grant)
W. Stuart Robertson	Laboratory Assistant, Undergraduate student in Electrical Engineering (supported by the Department of Electrical Engineering).

2.2 Literature

A systematic organization of the literature on bismuth films and on the effect of irradiation of films is continuing. Many items are hand-written translations from the principal investigator's files. These have been edited, typed, and filed by year. A cross-referencing index will make them easily available as needed for study of the irradiation and other effects.

The reports from six years of research on conducting thin films, which was sponsored by Air Force Contract AF33(038)-21255, and which dealt particularly with bismuth, have been made available to the project and are being organized similarly.

2.3 Equipment

A Wild Model M5 Stereomicroscope was purchased during this period. It has been very useful in the examination and preparation of film-substrate-holder surfaces. It is also used for evaluation of substrates both before and after coating with bismuth. A special adapter has been designed and built to fit into one of the eye-piece tubes and to receive a Miranda F 1.9 35mm camera loaned to the project by the principal investigator.

The electron microscope facilities of the Southwestern Medical School in Dallas have been generously made available to this project. Doctor W. D. Willis and his assistant, Mrs. J. M. (Venita) Allison, have shared their RCU EMU-3 microscope; and Doctor R. C. Reynolds has made his Hitachi HU-11 B microscope available for demonstration and for appraisal. This project is very grateful to them. Most of the work on the RCA microscope has been routine appraisal and comparison of films of various initial values of resistance. It has included, in addition, however, the first studies on the effects of electron beam irradiation. This will be discussed in Section 4.4.

Results of the preliminary irradiation studies made urgent the search for an adequate electron microscope. For this reason considerable time was given to a study of literature available on current models, to discussion with colleagues and consultants, and to personal inspection of several models. The principal investigator concluded his study with a September trip to the Perkin-Elmer Corporation in Norwalk, Connecticut, where an Hitachi model HU-11B2 microscope was placed at his disposal for a full day. Work with this microscope demonstrated that it had ample capability (at what seems to be the lowest price) for the necessarily-detailed study of irradiation characteristics of thin films. The principal requirement: control of irradiation and the effect of irradiation--without damage to the sample--was met. Preliminary results are given and electron micrographs are shown in Section 4.

This laboratory looks forward to the installation of that Hitachi microscope--currently scheduled by March 1, 1966. The high resolution, the cold stage, and the special cold-trapping facilities, together with a motion-picture camera requested for the irradiation studies of this project, will assist considerably in the research effort.

PREPARATION OF BISMUTH FILMS

3.1 Substrate Holders and Substrates

Previously-reported work[1,2,3] was performed upon films mounted on substrate holders of the type shown in place on the Silver Paint Applicator in Fig. 1 (also shown in place on the mask in the center of Fig. 2). A large number of these holders and the mask shown in Fig. 2 were supplied to this project through the generosity of Doctor Carl E. Drumheller, Manager, Physical Electronics Research, General Dynamics/Electronics, Rochester, New York.

The two sides of this holder[1] are made of lucite; the two ends, of brass. The inside of this "frame" (across which the substrate is mounted, and which is approximately the size of the deposited bismuth film) is 15mm square. (The device seen inside the holder in Fig. 1 is for the purpose of positioning and securing it during the application of silver paint).

Unless otherwise noted, all bismuth films have been, and will in the future be, prepared by evaporated bismuth deposition on a 0.04-micron-thick cellulose nitrate substrate which has been formed by casting on a water surface, and then mounted on one of these holders. After mounting of the substrate, the holder will have silver (Dupont electronic grade No. 4817) bands painted on this substrate at the inside edge of the brass ends, as shown in Fig. 1. The paint will be applied with the applicator shown in the figure. This new applicator was designed and built by laboratory personnel and has several features including a unique mechanical

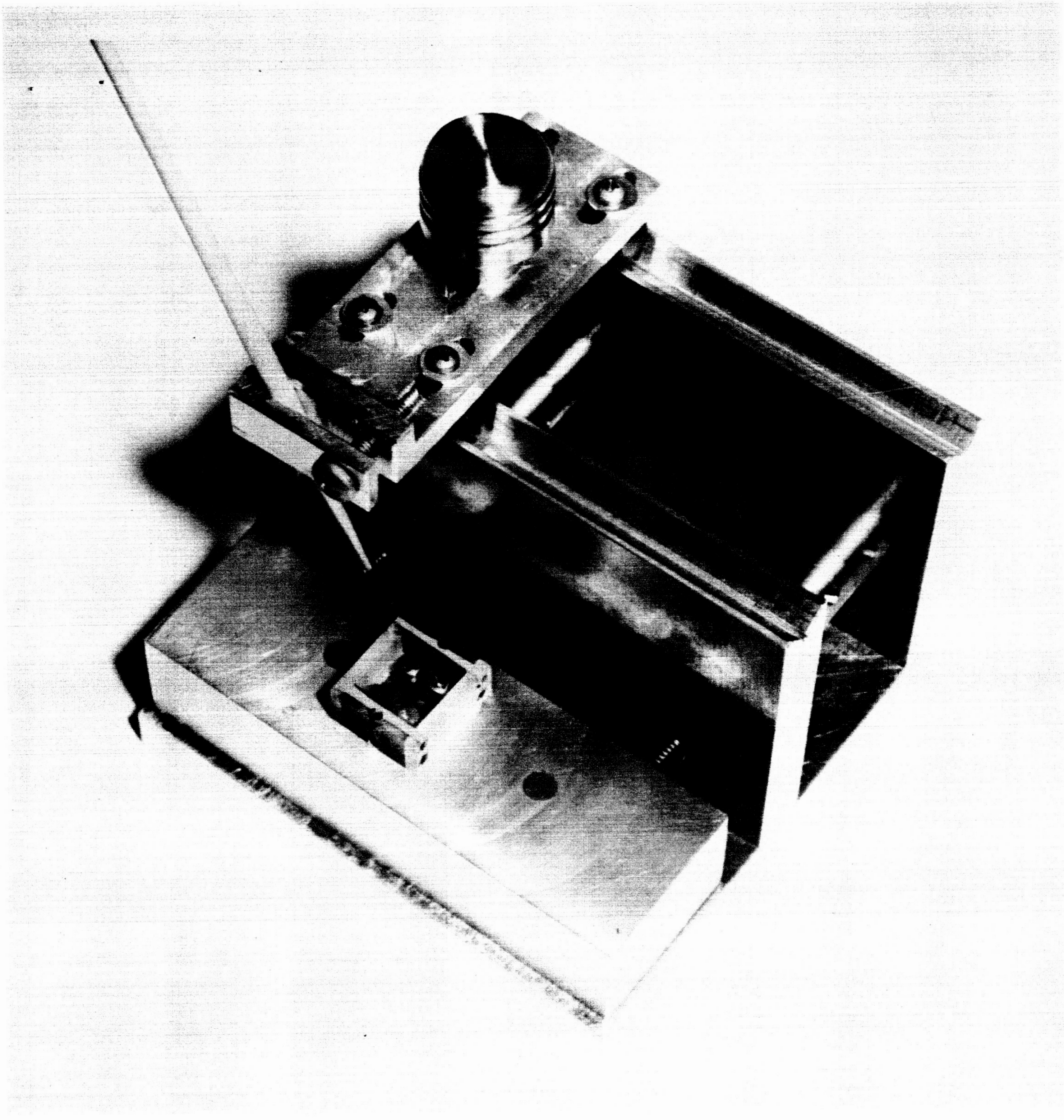


Fig. 1. Silver Paint Applicator

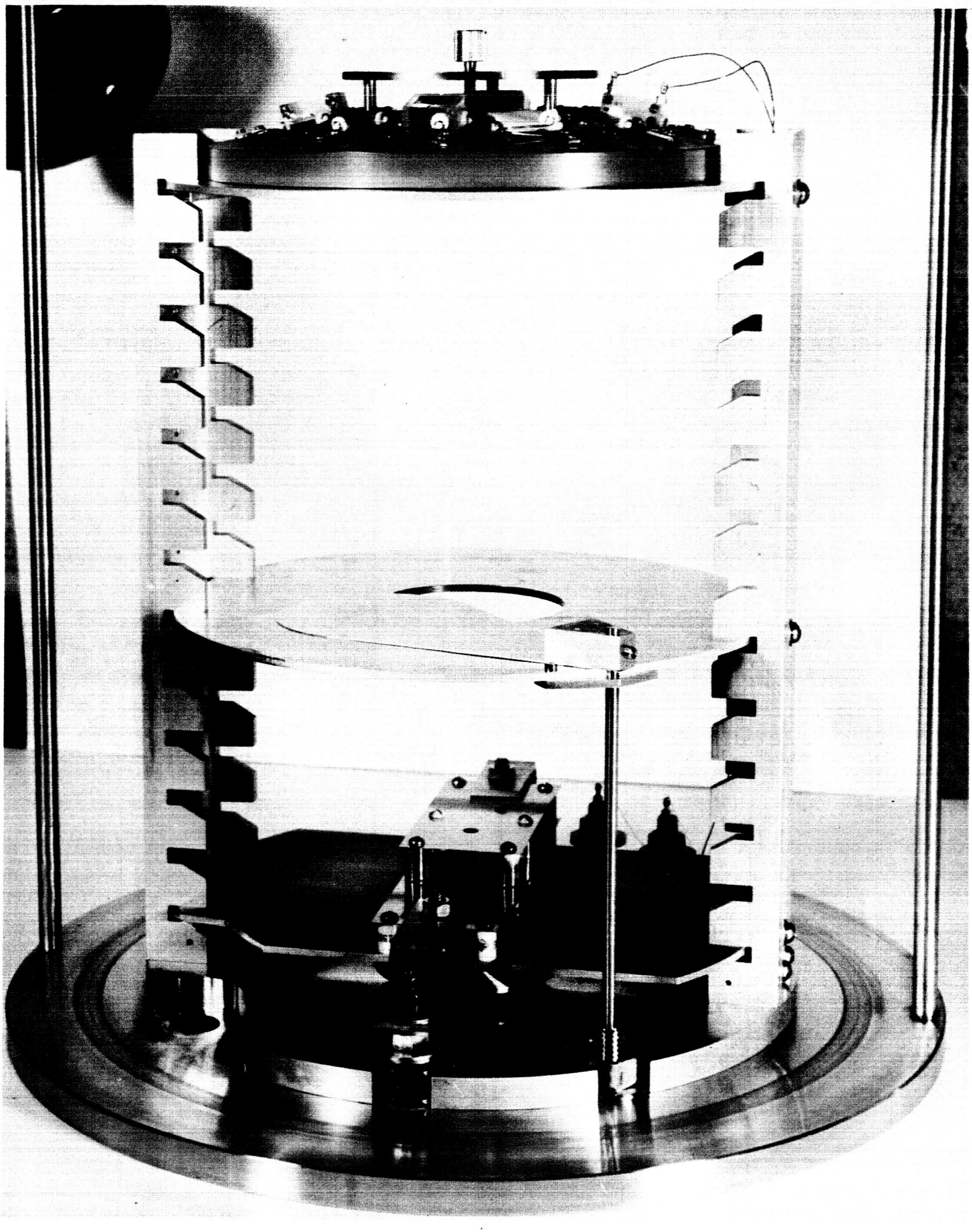


Fig. 2. Bell-Jar Apparatus for Positioning of Substrates, Mask, Shutter, and Source

linkage under the substrate holder support which will make it possible to control the size and location of the silver band better than was possible with previous methods.

3.2 Bismuth Film Deposition Apparatus

Shown in Fig. 2 is the apparatus essential for deposition of the bismuth films. At the bottom is a vacuum-system base-plate of 15-inch diameter. Two guide rods for the vacuum-system belljar rise from the right and left edges. The central source-, shutter-, and mask-support system with the notched cast-aluminum channels on the side is a design similar to one developed in the Physical Electronics Research Laboratory at General Dynamics/Electronics, Rochester, New York. The system shown is a modified version designed by SMU Thin Films Laboratory personnel. Several major parts of it were fabricated for the Laboratory without charge by the machine shop facility of the Graduate Research Center of the Southwest. The machining was well done, and this laboratory is grateful for that contribution to its progress.

At the top of the support-system is the mask (and support) for the film substrate holders. It is shown in detail in Fig. 3. In the center of the support-system is a magnetically-controlled shutter. It is closed except for a measured interval during evaporation. At the bottom is a specially-designed bismuth evaporation source, shown in further detail in Fig. 4. Wire leads may be seen coming from two feed-through insulators running up the right-hand channel, and coming out to connect to a substrate holder (for resistance monitoring during evaporation) at the top.

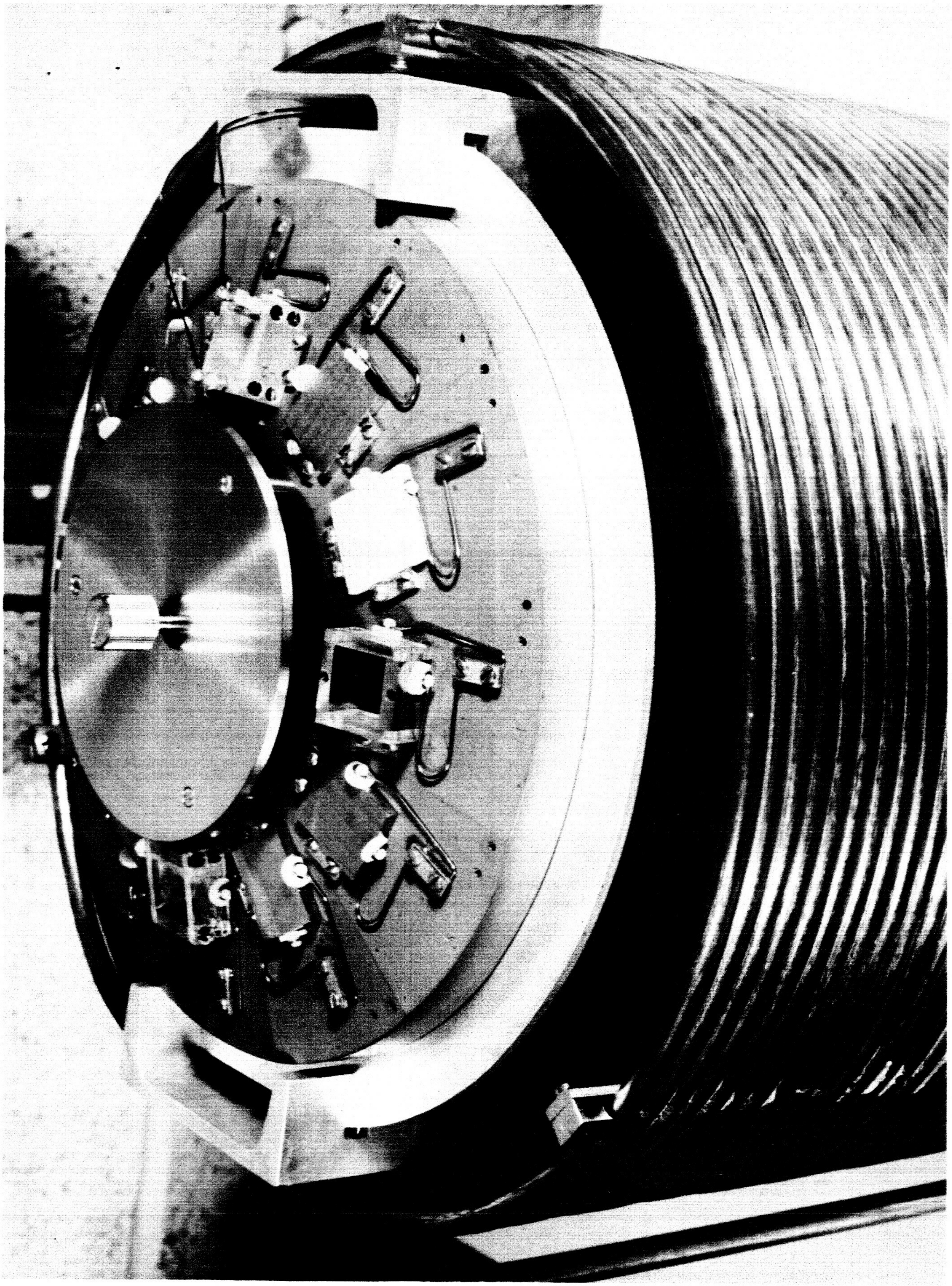


Fig. 3. Substrate Holder and Mask Detail

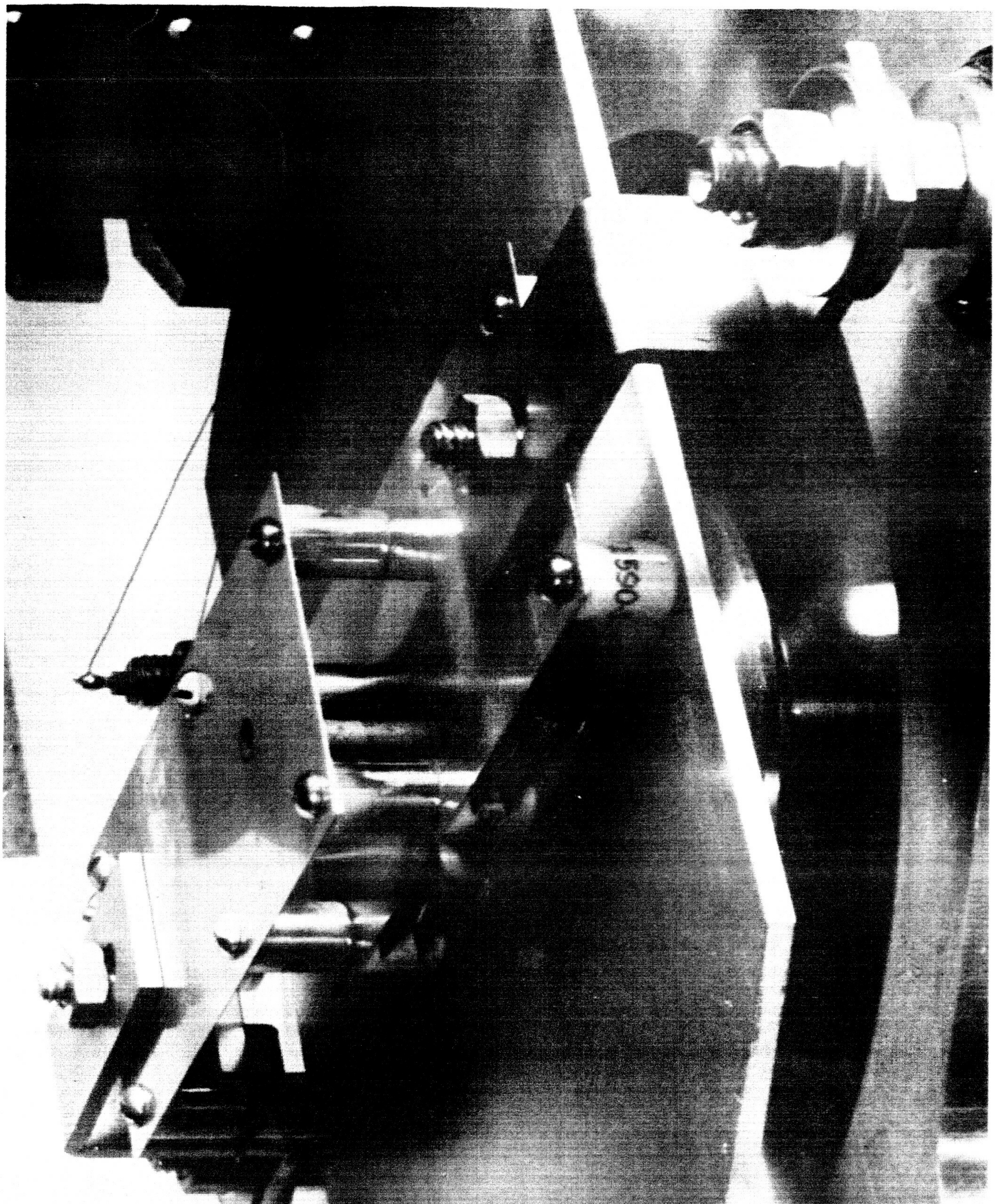


Fig. 4. Special Source for Bismuth Evaporation

A liquid nitrogen "shroud" surrounds the support system during normal operation. This is shown in the top view given by Fig. 3. This shroud, made of copper tubing, supplied liquid nitrogen continuously and vented to atmosphere during evaporations, has improved pressures by more than an order of magnitude.

Also, in Fig. 3 the mask and substrate holder support can be seen to provide space for up to twelve holders. In a normal evaporation, however, only four are in place. Stainless steel or microy blanks fill other openings. Stainless steel mask insulates the brass in the holders from the steel. Holders are shown upside down. The laboratory is very grateful to Doctor Carl E. Drumheller for the loan of this expensive device.

The bismuth evaporation source shown in Fig. 4 is a modification of an earlier design that is noteworthy for its uniform vapor emission pattern, but which frequently fails by arcing at the carbon crucible in the center. The present design is improved so that now many (more than fifteen on the source shown) cycles of heavy (100 amperes or more) current can be obtained without failure. The carbon-rod crucible in the center operates at reddish-yellow heat during bismuth evaporations.

Horizontal plates (and the radiation shields below them) are made of 10-mil molybdenum. The straps are made of OFHC copper. Insulator screw pockets are vented along the screw axis.

3.3 Control of Film Deposition

The film deposition apparatus was shown and described in the previous section. Its operation is controlled by a monitoring system (see Fig. 5) located nearby. The bell-jar vacuum surrounding the deposition apparatus is monitored with a Varian ionization gauge located on the second panel from the top. The third panel from the top contains instrumentation for source current (and temperature) control and monitoring, shutter control, and digital recording of elapsed time in each phase of the film deposition process. Its circuit is shown in Fig. 6. The bottom panel contains instrumentation for measuring and recording the resistance of a film while it is being deposited. This resistance is obtained (by comparison with the resistance standards shown at the bottom of the figure) from an off-balance bridge output signal after that signal has been amplified by a DC amplifier located at the top of the control panel. The bridge circuit is shown in Fig. 7.

3.31 Resistance Recording During Evaporation

Present practice in the determination of film thickness is to monitor the resistance of a single film in a set while bismuth is being deposited on it, and then to shut off the supply of vapor to all films when the resistance of the monitored film has reached a previously-determined value. The resistance is measured with a low-powered bridge, the circuit of which is shown in Fig. 7. Bridge input in approximately 1 mv under normal conditions. This serves to keep power in the film, R_x, low in order to avoid

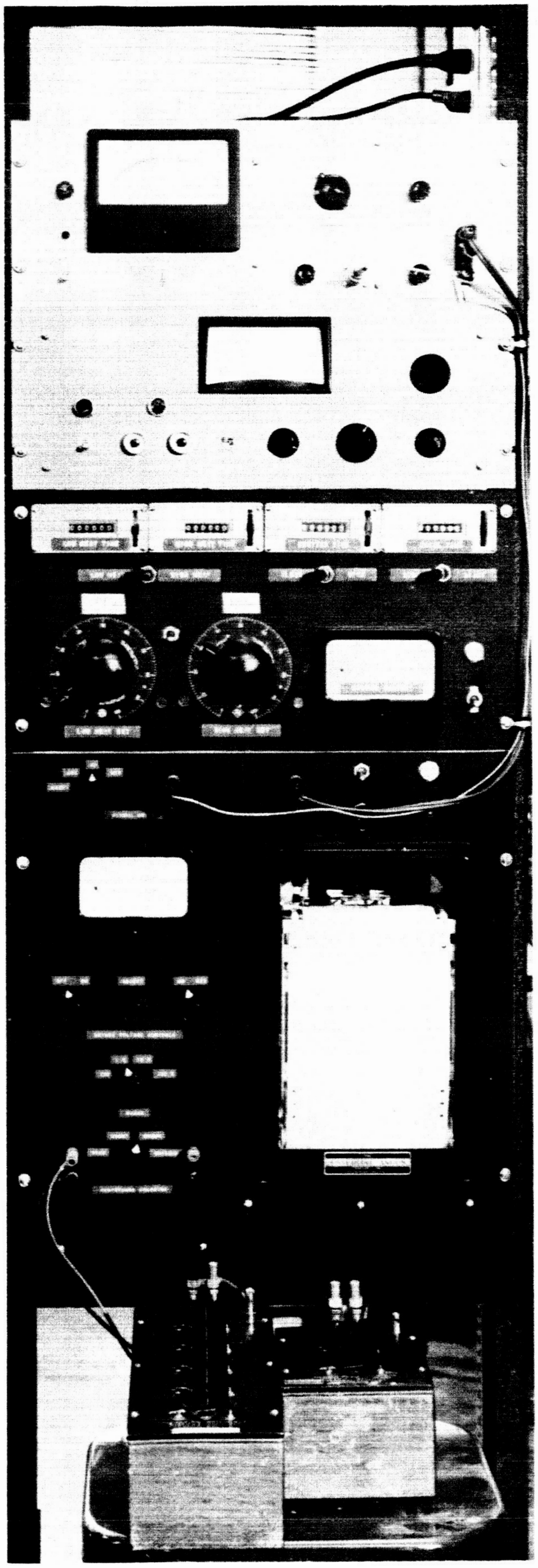
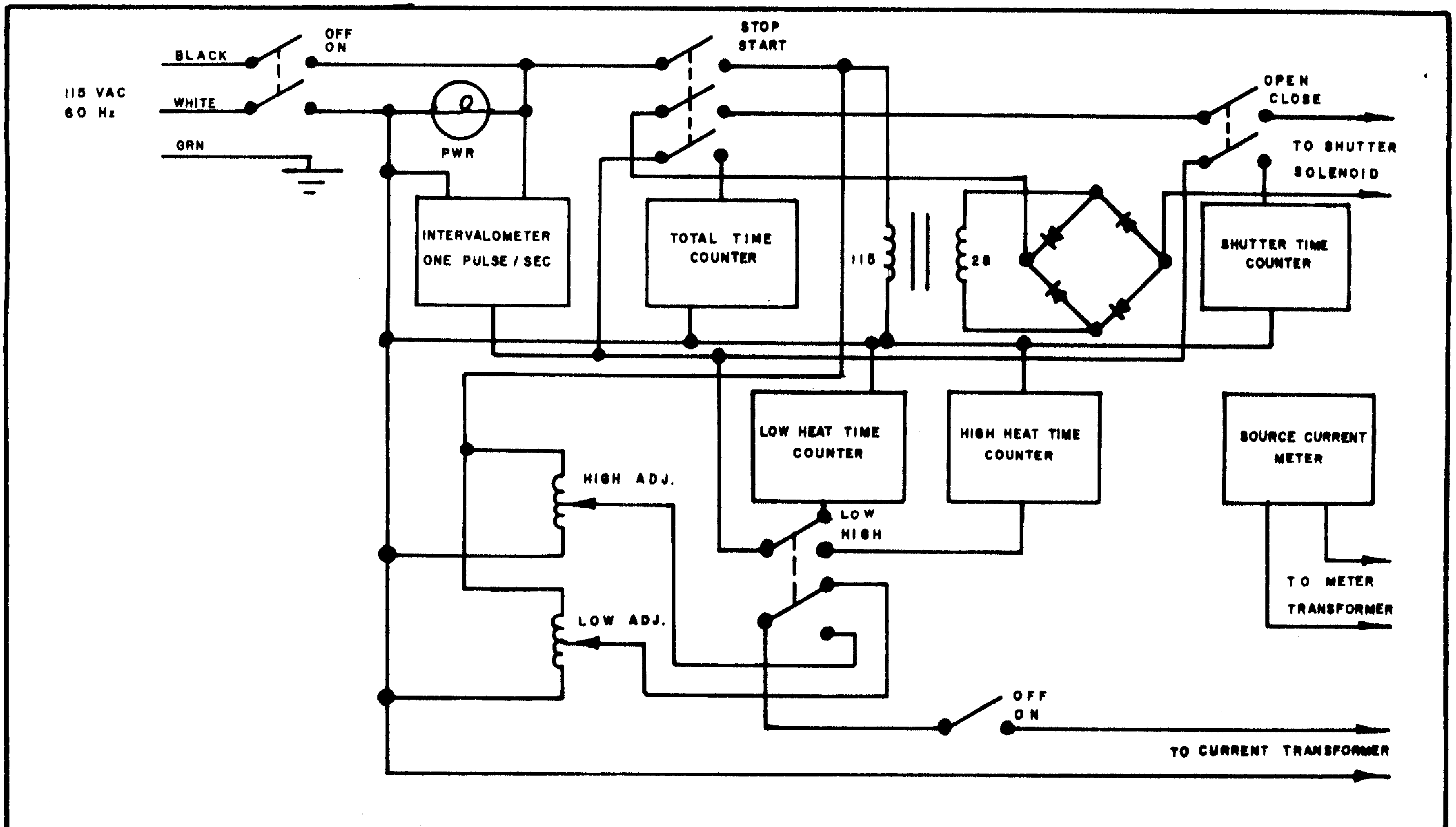


Fig. 5. Film Deposition Monitoring System



MATERIAL LIST

2—DPST SWITCHES	4—6-DIGIT COUNTERS, 115 VAC
1—SPST SWITCH	2—VARIACS, 115 VAC, 10 a
1—3PST SWITCH	1—AMMETER, 150 a AC
1—DPDT SWITCH	1—PILOT LIGHT 115 VAC
1—INTERVALOMETER, 1 PULSE / SEC, 115 VAC	
1—BRIDGE RECTIFIER 115 VAC 28V DC	

EVAPORATION CONTROL PANEL
THIN FILM RESEARCH LABORATORY

SMU, DR. L. L. HOWARD

NOV. 1, 1965 BY D. S. GLASS

Fig. 6. Evaporation Control Panel Circuit

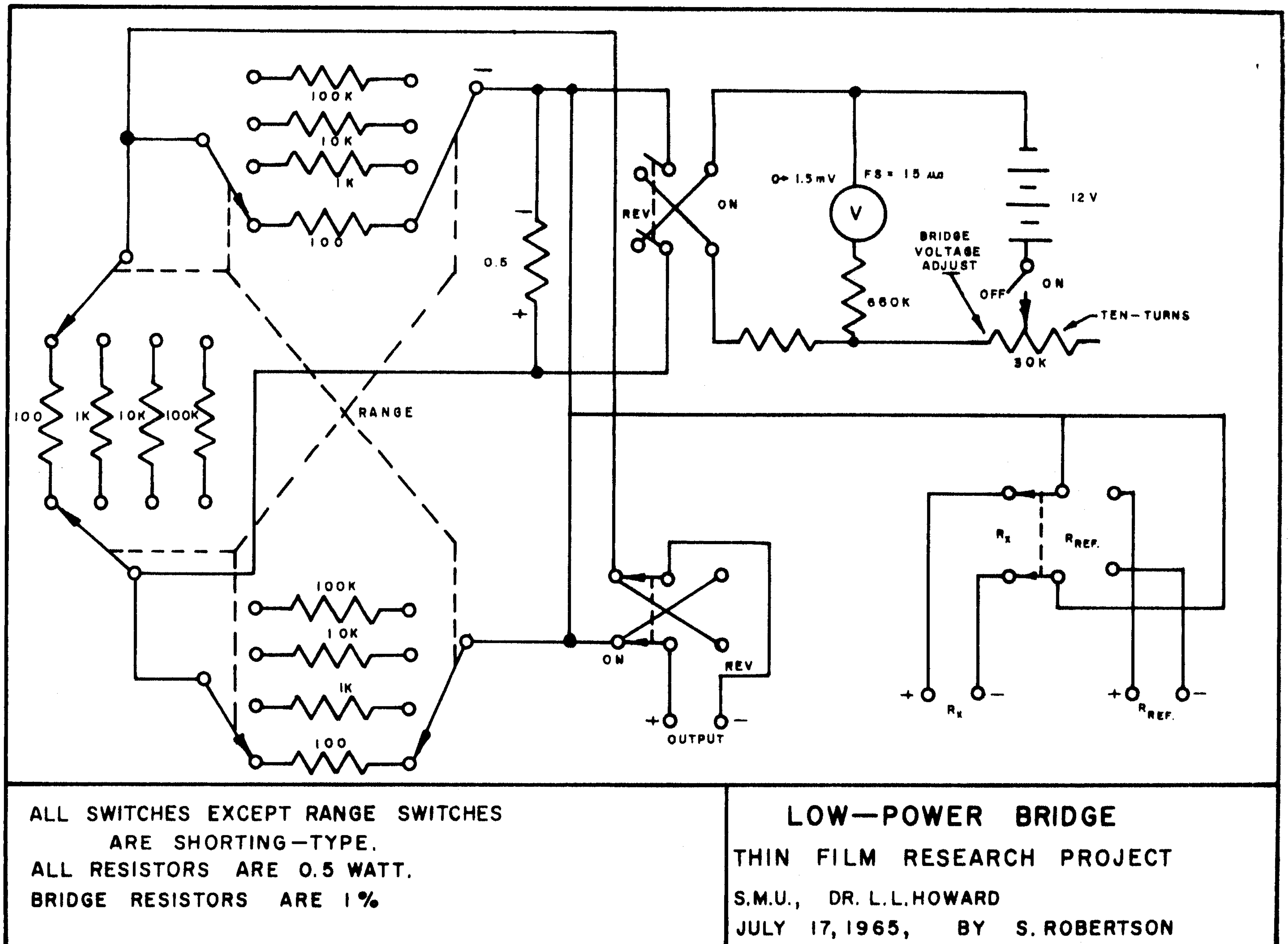


Fig. 7. Low-Power Bridge Circuit

permanent changes. At this input level, the power dissipated during resistance measurement is less than that normally received due to radiation from the surrounding walls.

The bridge has four available ranges that enable its operation about balance points corresponding to R_x equal to 100, 1000, 10,000, or 100,000 ohms. By means of the bias circuit this balance point can be moved to the center of the recording scale so that a range of values on each side of the balance point can be recorded. In preparation for an evaporation, one of the balance points above is chosen and set at the center of the bridge-output recording scale. The rest of the scale is then calibrated against a standard resistance box.

Film resistance changes during evaporation (for all of the evaporations performed thus far) have been obtained as shown in Fig. 8. (Numbers, e.g. 11L-42, refer to film numbers.) Note that in each evaporation most of the resistance change has occurred before 1.6 minutes have elapsed. This is a relatively slow evaporation time; however, it corresponds with that of previous work, and will be continued. An effort will be made to choose and to continue to use a simple evaporation rate. It is expected that film deposition rate control apparatus currently scheduled for engineering evaluation in the laboratory will make this possible.

3.32 Control of the Source Current and the Shutter

The Evaporation Control Panel and circuit are designed to provide easy control of the shutter and the source current, and to provide timing of each step in the film deposition program.

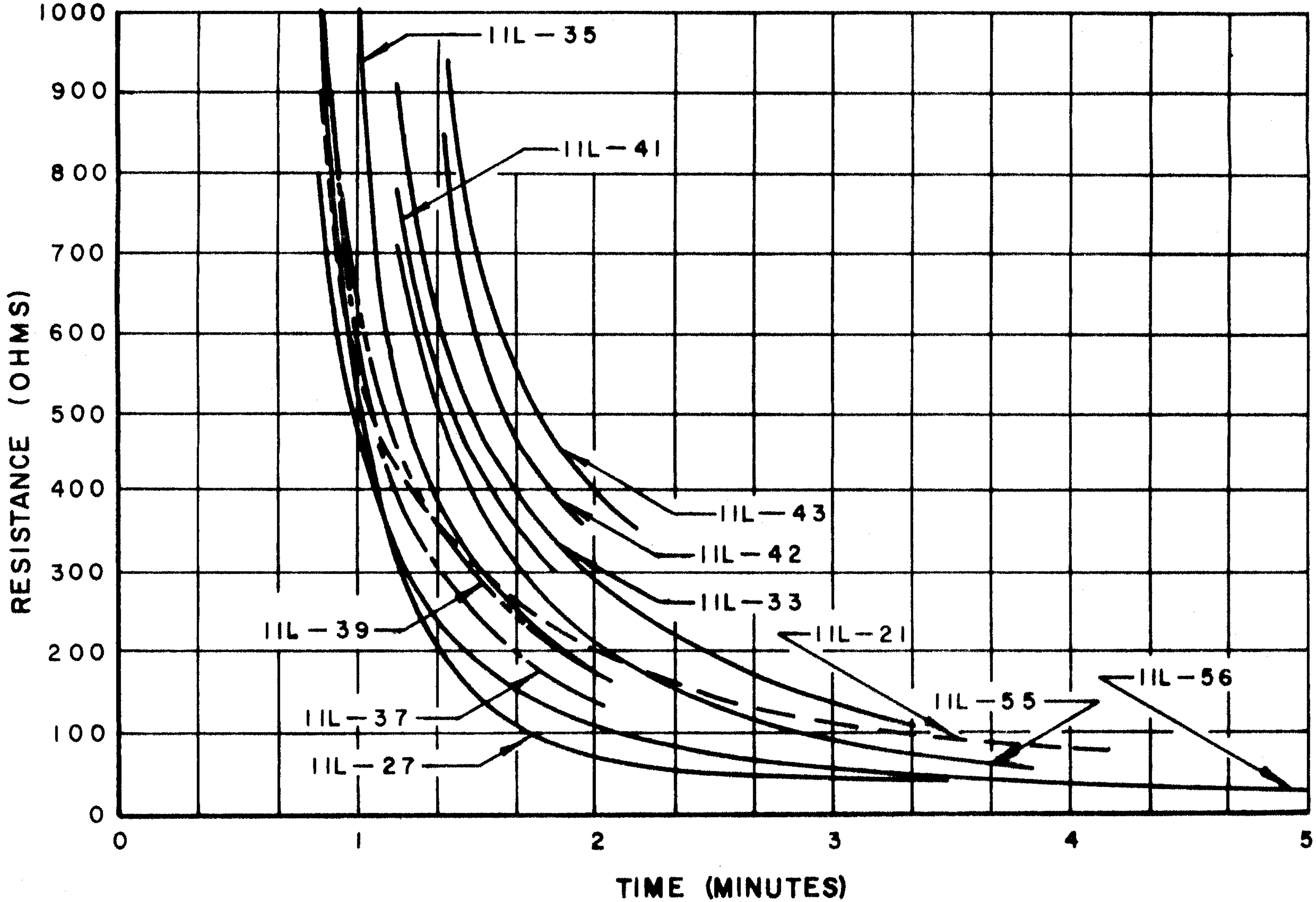


FIG. 8 BISMUTH FILM RESISTANCE CHARACTERISTICS DURING FORMATION (Shutter open at t=0)

When the deposition system is ready for an "evaporation" the Control Panel power switch is energized, and the "stop-start" switch is placed in the "start" position. This energizes a pre-set variable transformer which supplies a source heat just great enough to melt the bismuth charge in the crucible. After a pre-determined period the "low-high" switch (until now in the "low" position) is placed in the "high-heat" position. This energizes another pre-set variable transformer which supplies vaporization heat to the crucible, removing the first heat source simultaneously. The shutter may be "open"-ed at any time thereafter. When the film resistance has reached its desired value, throwing the "stop-start" switch to "stop" halts all functions: the shutter is closed, current to the source is stopped, and timing stops automatically.

The source-current meter provides a constant monitor of the heating current. Time keeping is performed by four digital counters which are driven by an intervalometer operating at one pulse per second. The appropriate counter is sequenced into operation by the current control and shutter switches. (These counters are Veeder-Root units, 115VAC, 6-digit, electrically pulsed. They were on surplus equipment made available by Texas Instruments, Inc.)

Shutter power is supplied by a small bridge rectifier. Shutter power is switched on the DC side in order to prevent the shorting of the solenoid field that would occur when the power supply was removed if AC-side switching were used.

This evaporation control system has helped to give more consistent results and to simplify carrying out the routine associated with film deposition.

BISMUTH FILM CHARACTERISTICS

4.1 Electron Micrographs

A major part of the study of complex impedance characteristics has involved the relation of film structure to equivalent (and probably also to actual) circuits. This structure may be examined using electron micrographs.

Good sharp electron micrographs of bismuth films (particularly of films unchanged by irradiation or evaporation) are not easy to obtain because of bismuth's low melting point and because of its activity in the electron beam; nevertheless, specimens of the films prepared in the laboratory have been examined for structure similarity and for similarity of previously-observed activity in the electron beam, and have been found to have characteristics which appear to be similar to those formerly observed. A constant source of dismay, however, was the inability 1) to get enough film illumination to be able to study the structure in the microscope; 2) to stabilize the activity so that it, too, could be studied in the microscope under variation of various parameters. The decision of NASA to assist Southern Methodist University in the procurement of an electron microscope has made it possible, however, to plan research considering that these problems will be largely resolved. Proof of this came during an appraisal of the Hitachi HU11B2 microscope (the instrument ordered later by the University). At that time the principal investigator was for the first time able to examine a typical bismuth film for long periods under high illumination and high magnification. The electron micrograph in Fig. 9 was made at that time. It is unique; and yet it is considerably below the ultimate capability of the microscope. There is "information" in the grain boundaries which has not been previously displayed or discussed. Analysis of this information and its relevance to bismuth characteristics will be given after more study of it has been carried out on the University's own microscope. (The magnification given is a very rough estimate from imperfect records.)

4.2 Resistance Drift

An outstanding characteristic of bismuth films previously examined has been their drift of resistance with time. This was true of a "first generation" of these films, which were formed at pressures of approximately 3×10^{-5} Torr, and also of a "second generation", formed at approximately 3×10^{-6} Torr. The "third generation", having been formed at approximately 3×10^{-7} Torr, is already displaying the same general characteristics. A plot of these characteristics is shown in Fig. 10. With no longer time experience than that shown, it appears that the break in long-term "change" characteristics will occur at approximately the same values of initial resistance: between 300 and 400 ohms.

4.3 Infra-Red Transmission

Infra-red transmission measurements (at $2\mu < \lambda < 15\mu$) are carried out with the films positioned in special adapters as shown in Fig. 11. These adapters are mounted on the source housing of a Beckman IR-5 spectrophotometer made available to this laboratory through the courtesy of Doctor Harold Jeskey of the Southern Methodist University Department of Chemistry.

Fig. 9. Electron Micrograph (approximately 400,000X) of Evaporated Bismuth Film

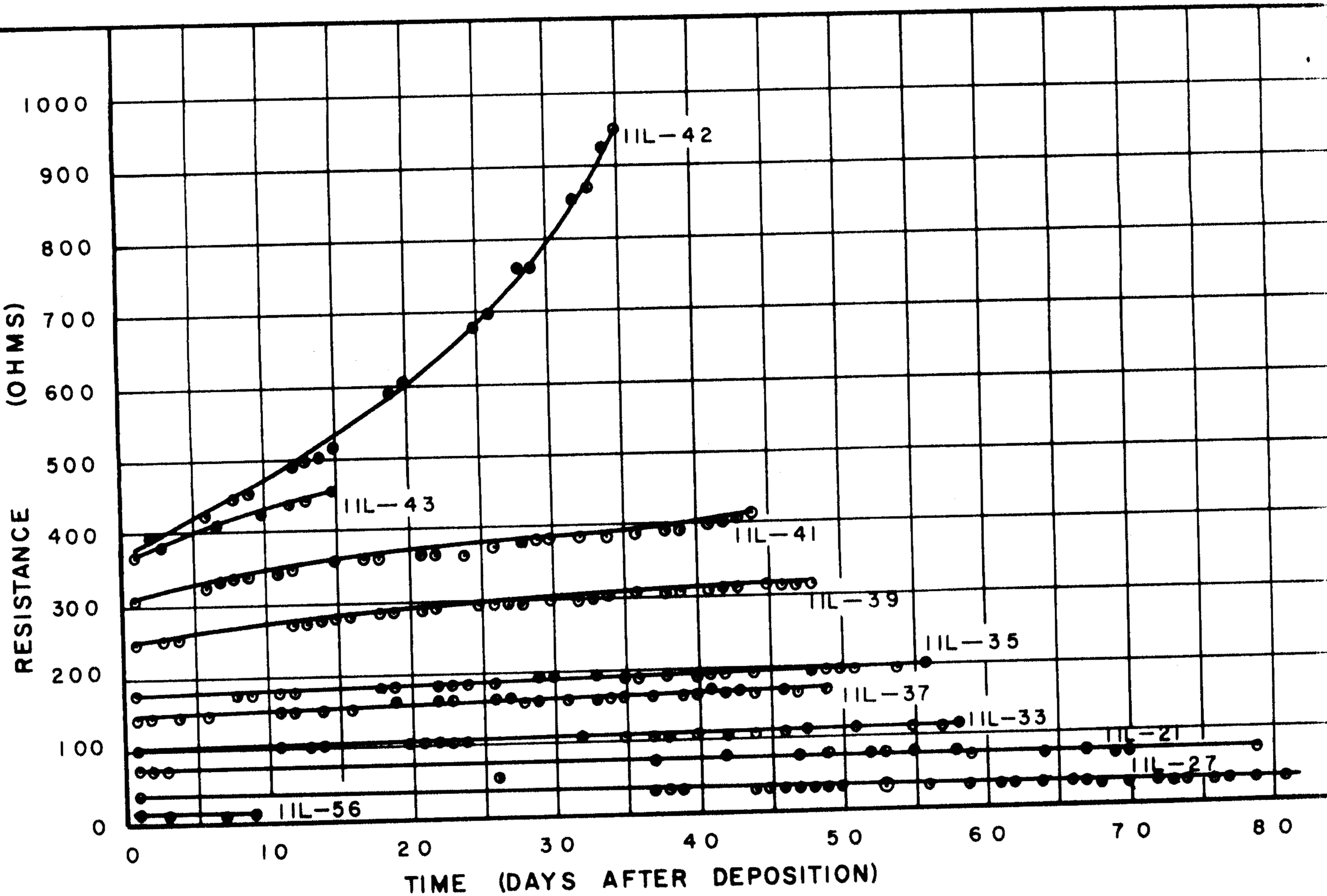


FIG. 10 DRIFT OF BISMUTH FILM RESISTANCE WITH TIME

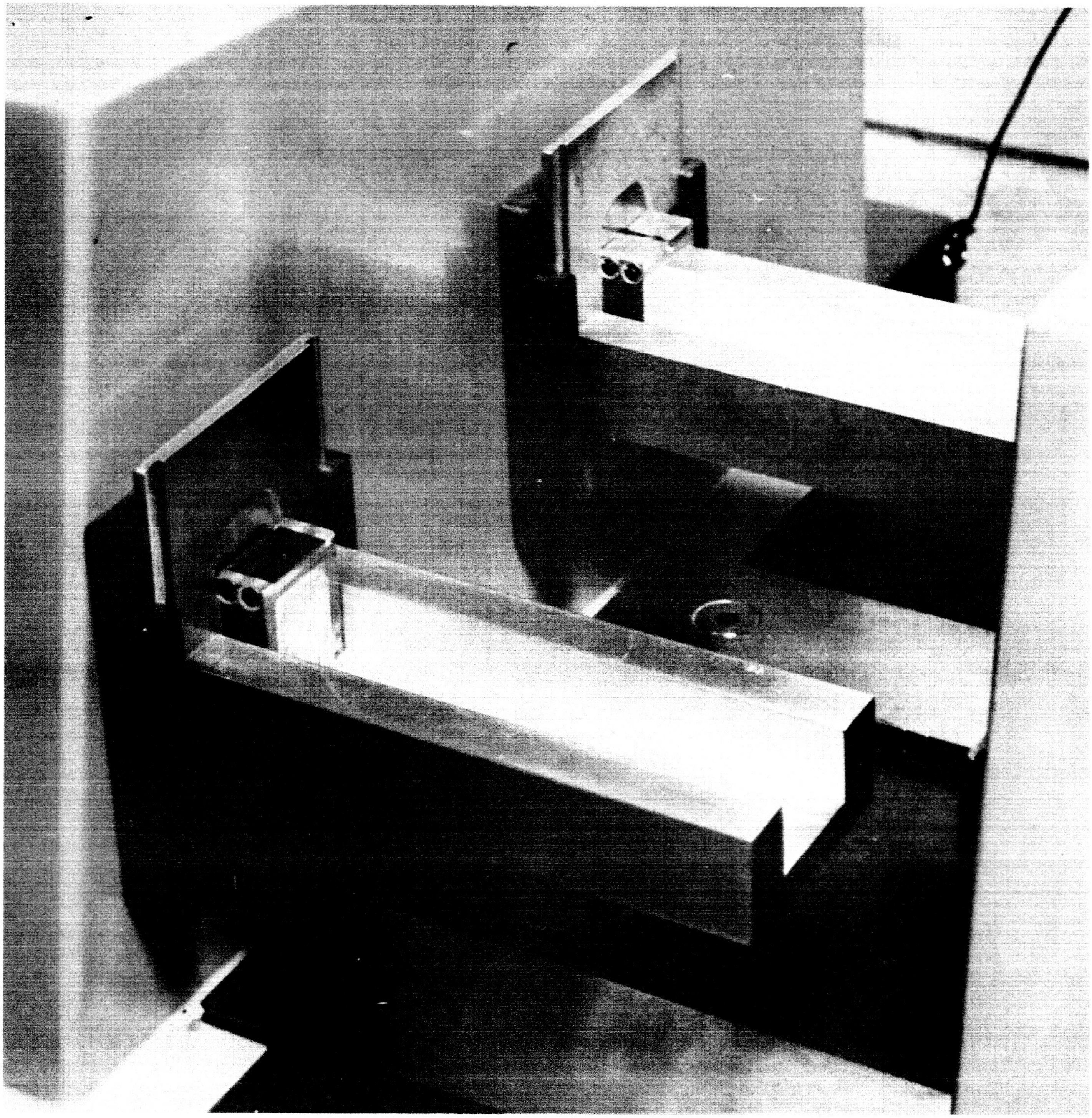


Fig. 11. Bismuth Film and Reference Substrate Positioned in Special Holders for Infra-Red Transmission Measurements

Figure 12 gives a complete set of infra-red transmission characteristics for films in the resistance range of interest. These data are new and are being used to determine complex impedance information. It is expected that perhaps the complex impedance postulation (based upon structure) may be able to explain the shape of these curves.

4.4 Crystallite Change During Irradiation

It has been pointed out (in Section 4.2) that the films described herein are different from those previously deposited in that these films were deposited at a lower pressure, i.e., at approximately 3 x 10^{-7} Torr. They appear to behave in a manner similar to that of previously deposited films, however, in that electron beam irradiation excites considerable activity in them.

This activity was observed when a specimen was examined in the RCU EMU-3 electron microscope, but was difficult to control adequately. When a specimen was placed on the cold stage in the Hitachi microscope, however, it was possible to exercise considerable control over the activity. Control was so good, in fact, that the change of crystallite orientation could be stopped essentially at any stage. Figure 13 is an example of this control. The left-hand view was made first; then irradiation was allowed to take effect; then finally, the right-hand picture was made.

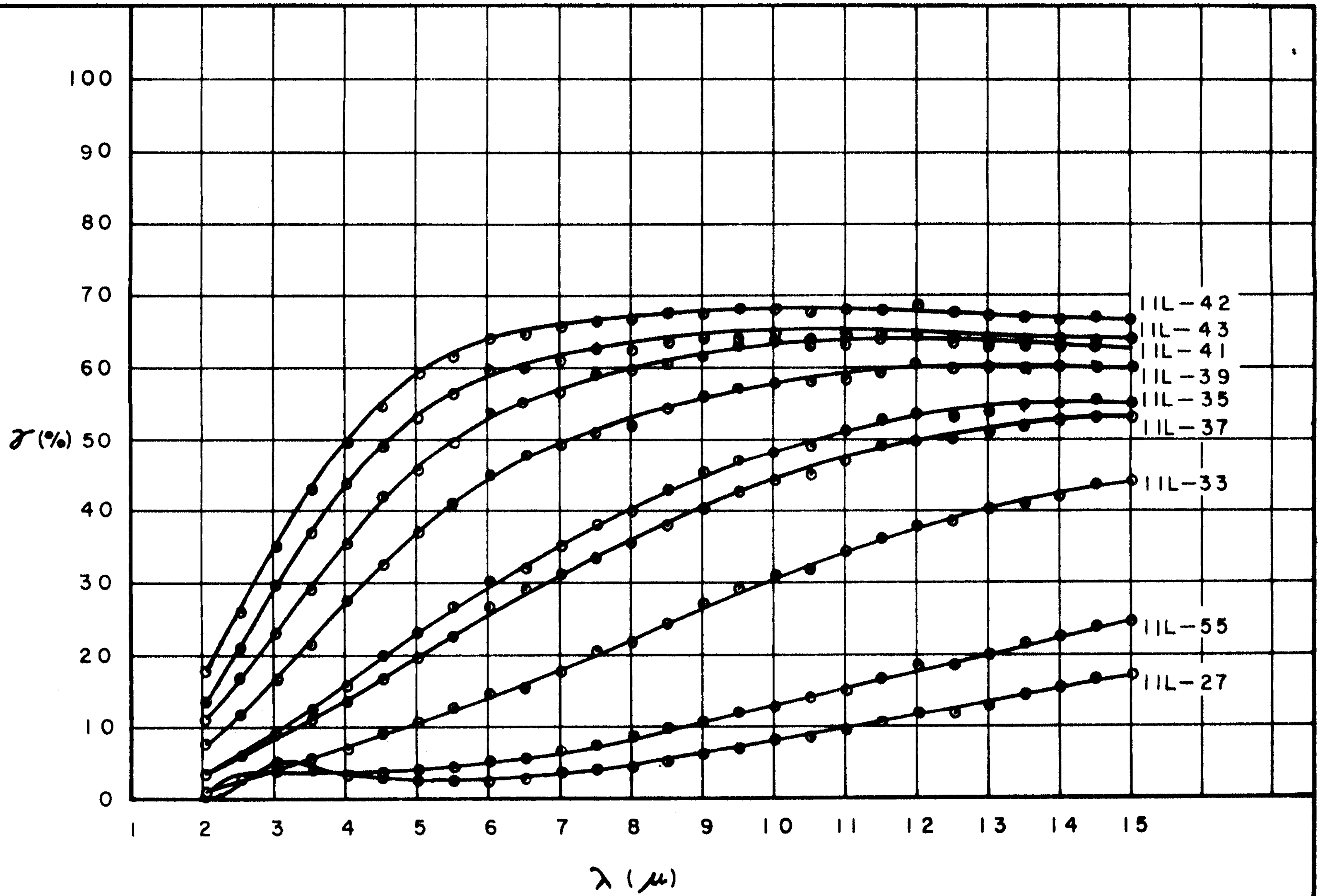
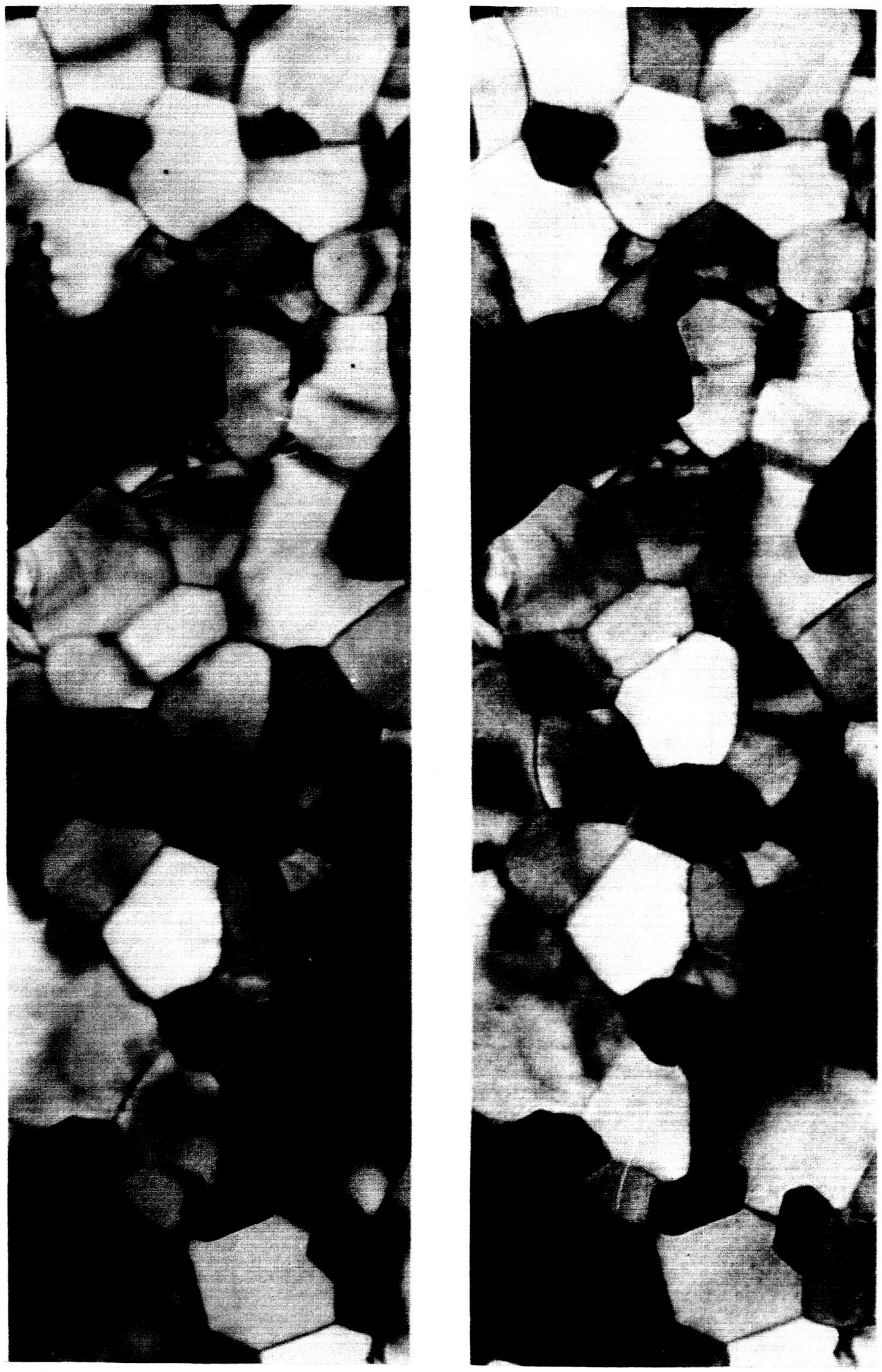


FIG.12 INFRA-RED TRANSMISSION CHARACTERISTICS OF EVAPORATED BISMUTH FILMS



(a) (b)

Fig. 13. Electron Micrograph (approximately 210,000X) of Evaporated Bismuth Film, 70 Ohms Initial Resistance

(a) Before Electron Beam Irradiation
(b) After Electron Beam Irradiation

There are many changes in the crystallite structures. Some of the most obvious are: the band in the crystallite in the upper left corner has disappeared in the "after" view; the grey crystallite in the center has turned white in the "after" picture; next to it the bands in the crystallite have changed markedly between pictures. The most unusual thing is the fact that only very isolated radical changes (all white to all black, and vice versa) have occurred. Usually there is a predominance of radical change. Temperature control of a cold stage should make it possible to obtain the amount of change desired.

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