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TECHNICAL REPORT ECOM-2573

THIN-FILM PREPARATION

BY

DIETRICH DOBISCHEK

STANLEY CABELL

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THIN-FILM PREPARATION

by

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Electronic Components Department

February 1965

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U. S. ARMY ELECTRONICS LABORATORIES
U. S. ARMY ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY

Abstract

Vacuum deposition techniques for the preparation of thin films were investigated and developed to a point where a study of the usefulness of these structures as tunnel emitters is now feasible. The described experimentation with Al-ZnS-Al, Mg-MgO-Mg, and Al-Al₂O₃-Al structures will eventually lead to a study of the combination Al-Al₂O₃-Au sandwich, with special attention given to the method of forming the oxide film and to the geometry of the structure.

A method of monitoring the thickness of thin films during deposition by means of an oscillating quartz crystal was investigated. Although the results proved promising, a decision on the final capabilities of this method cannot be made until calibration tests are completed and the reproducibility of the results is established.

The usefulness of the electrolytical anodic oxidation technique for the preparation of thin insulating oxide layers was investigated. Preliminary experiments were conducted on various sheet metals. The investigation is presently concentrated on the oxidation of vacuum-deposited films of aluminum and the formation of special patterns using photoresist masking techniques. This work will be continued until the general techniques have been satisfactorily mastered. Thereafter, the work will be extended to metals other than aluminum.

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THIN-FILM PREPARATION

INTRODUCTION

This report covers work on the preparation and fabrication of thin films for use in a study of electron tunnel emission from a metal through an insulator. Vacuum deposition techniques and electrolytical anodic oxidation methods were used in preparing the films.

DISCUSSION

VACUUM DEPOSITION TECHNIQUES

Development of Techniques for Evaporating Materials

Suitable techniques for evaporating zinc sulfide (ZnS), copper (Cu), aluminum (Al), magnesium (Mg), and silicon monoxide (SiO) were investigated. The prime vacuum system used in the experiments consisted of a mechanical fore pump, an oil diffusion pump, a liquid-nitrogen cold trap, a Veeco ionization gauge, and a demountable glass bell jar with metal flanges and copper gaskets. The bottom portion of the bell jar contained ten tungsten pins as feedthroughs; the upper portion of the bell jar was 12 inches high and 4 inches in diameter. In the preliminary experimentation, a commercial evaporator unit (Kinney High Vacuum Evaporator SC-3) was also used.

Initially, a number of problems were encountered. Among these were: (a) Contamination of the films by creepage of oil vapors into the vacuum system; (b) Heater-filament breakdowns; (c) Degassing of the materials during evaporation, and (d) Oxidation of the metal films. All of these problems have been corrected.

Vapor Sources

It was found that the best films were obtained by evaporating the sample material either from resistance-heated refractory metal filaments or wire-heated tantalum crucibles. The use of filaments was found to be most convenient for the evaporation of aluminum. Magnesium and copper were evaporated from wire-heated tantalum crucibles (see Figure 1a). For the evaporation of SiO, a heavier heater and a more efficient heat transfer were needed; Figure 1b depicts the construction of the vapor source used. A quartz boat placed within a heater coil and surrounded by a heat shield proved entirely satisfactory for the evaporation of ZnS (see Figure 1c). It was also found that films of improved quality were obtained by prefiring the ZnS and the Al_2O_3 -coated heater filaments in a separate vacuum system and shielding the substrate by a trapdoor during the early stages of evaporation. The described evaporation techniques eventually produced pinhole-free films when checked on a shadowgraph.

Pressures during evaporation ranged from 10^{-5} to 10^{-6} Torr. The temperature for evaporating SiO was approximately 1350°C , measured at the top of the inside of the crucible. Depending on the pressure in the system, ZnS was evaporated at temperatures between 1150°C and 1250°C , measured at the heater. Copper was evaporated at approximately 1100°C . Considerably lower temperatures were required for the evaporation of Al and especially Mg. Distances between vapor source and substrate were maintained the same in almost all test runs, and were approximately 8.5 centimeters; in exceptional cases, 7.5 centimeters. Substrates were placed in a horizontal position above the vertically mounted vapor source. In a few experiments, different positions of the substrate relative to the vapor source were attempted, but with no apparent advantages.

Preparation of Substrates

The substrates used in the experiments were high-grade glass microscope slides cut in half (1" by 1-1/2"). The slides were thoroughly cleaned by immersion in boiling glass-cleaning solution for 5 minutes. After rinsing under a running water tap for several minutes, the slides were cleaned ultrasonically for 30 minutes, followed by rinsing under running hot and subsequently cold tap water for 5 minutes. The slide surfaces were then rubbed with a soapy sponge. After thorough rinsing under a tap of running cold water, the slides were then rinsed in cold, then boiling distilled water for 10 minutes followed by a rinse in methyl alcohol, and finally placed in a clean, hot drying oven.

In separate test runs in which the commercial evaporator unit, which has no provision for effectively trapping oil vapors, was used, it was established that cleaning of the substrates with a glow discharge in, addition to chemical cleaning, definitely improves the adherence of vacuum-deposited films to the substrates. As a simple adherence test, the "tape method" was used, i.e., scotch tape was pressed firmly against the surface of the films and then removed. Films of insufficient adherence stick partly or entirely to the tape.

After mounting a substrate inside the vacuum system and following the regular bake-out of the system (at 200°C to 250°C), an additional degassing of the substrate was carried out by means of a hotplate. The rectangular hotplate was slightly larger than the substrate and consisted of several rows of a molybdenum helix wound around and spaced by three ceramic rods and mounted in front of a metal plate which served as a heat reflector. The hotplate was placed behind the substrate at a distance of approximately 4 millimeters and heated to approximately 750°C (brightness of the helix).

In substrate preparation, it should be mentioned that preventing the substrates and also all the other parts of the final setup from contamination during assembly is as important as the initial cleaning of the components. In preparing a test run it was, therefore, standard procedure to detach the entire bell jar from the vacuum system and to assemble the parts in the Techniques Branch controlled environment room (the "clean room"). The closed bell jar was then taken back to the pump room and sealed to the vacuum system. Recently the construction of an ultrahigh vacuum system has been completed within Techniques Branch. This system uses Vac-Ion and VacSorb pumps and provides an extremely clean, oil-vapor-free vacuum. Except for the bell-jar dome, the system is all-metal and the base of the bell jar is not removable from the system. The assembly procedure described will be changed when the new system goes into operation. In order to maintain the advantage of performing the entire assembly work in the "clean room", a special interchangeable support structure was made which plugs into a socket built into the stationary base of the bell jar and makes the electrical connections to the feedthroughs of the vacuum system. With the use of the interchangeable support structure, the desired mount can be assembled in the "clean room", after which it can be transferred under a protective cover to the pump station. There the structure can be plugged into the stationary socket and the temporary cover replaced by the bell-jar dome. By this procedure, the finished mount will be exposed to the less-clean atmosphere of the pump room for a minimum of time. Fabrication of the interchangeable support structure is presently underway.

Fabricating and Testing of a Thin-Film Monitoring Device

Information on two basic quantities is of immediate importance in the development of thin films for tunnel devices. These quantities are (1) film thickness and (2) the deposition rate. A study was made in an attempt to obtain reliable data on the thickness of thin films.

For use in the study, a device was built in the laboratory which uses an oscillating quartz crystal for monitoring the film thickness. The principle of operation of this crystal oscillator is simply to measure the frequency change of a quartz crystal as its mass is increased by the deposition of material onto one crystal face. The frequency of the monitoring crystal (megacycle range) is beat against a standard frequency provided by a second fixed-frequency crystal. The low frequency output (kilocycle range) is then fed directly into an electronic counter.

Commercial quartz crystals which were available in these Laboratories were used in the early experiments. However, a number of difficulties were encountered, primarily as a result of crystal deficiencies. The crystals, as received, were encapsulated. Upon removal of the capsule, some of the crystals performed erratically. Also, when operated at atmospheric pressure or at temperatures slightly above room temperature, most of the crystals failed to operate. In addition, the performance of the crystals while being coated in vacuum was not satisfactory because of lack of reproducibility of results. Problems also arose with loose electrical connections and crystal electrode shorts. Better results were obtained with crystals which were made to order* according to specifications indicated in a report by RCA. These crystals are approximately 1/2 inch in diameter and 7.14 mils thick, have a shear mode of oscillation, and the surfaces have not been polished after grinding. A number of evaporation experiments in which these crystals were used indicated that the crystals operated with satisfactory reliability. These experiments were conducted with a substrate and a properly masked crystal mounted side-by-side in a bell jar. A removable metal shield protected both the crystal and substrate during degassing of the vapor source. The material was then evaporated, covering simultaneously the exposed part of the crystal and the substrate, and the change in frequency was observed on the electronic counter.

Magnesium Evaporations (Heater Voltage Varied)

Figure 2 gives the results of an experiment in which a series of magnesium evaporations were made at various heater voltages (i.e., at various temperatures). The figure represents a plot of observed frequency change versus time. During the initial stages of the experiment, the vapor source was degassed by raising the heater voltage in steps from 3 volts to a maximum of 4 volts, as indicated in Figure 2. Pressure readings during the experiment were as listed in Figure 2. At a heater voltage of 3.6 volts and 4 volts, evaporation of the magnesium was noticed, but since the substrate and the monitoring crystal were shielded from the vapor source during the degassing period, no change in frequency occurred, as can be seen from Figure 2. After a total degassing time of 34 minutes, the heater voltage was turned off and the system pumped for approximately 85 minutes. The vapor source was then heated again for 10 minutes with the heater voltage set at 3 volts and with the shield still applied. The same frequency reading as before was obtained and no change in frequency occurred during this heating period. After turning off the heater filament and cooling the vapor source for 15 minutes, the shield was dropped and the evaporation of magnesium initiated by setting the heater voltage at 3.5 volts where it was held for 20 minutes. As can be seen from Figure 2, a linear change of frequency with time occurred, indicating the deposition of magnesium on the monitoring crystal. Two more magnesium evaporations were conducted; one with 3.8 volts, the other with 4.2 volts heater voltage. The time

*by the Piezoelectric Crystal and Circuitry Branch, Solid State and Frequency Control Division, U. S. Army Electronics Laboratories

of evaporation was again 20 minutes in both cases. Between the evaporations, the vapor source was always cooled for 15 minutes. Figure 2 shows that the slope of the lines representing the frequency change versus time during each evaporation changes as the heater voltage, and hence the temperature of the vapor source is increased. The slope of the line obtained with a heater voltage of 3.8 volts was slightly steeper than that obtained during the evaporation with 3.5 volts applied to the heater. The increase in heater voltage from 3.8 volts to 4.2 volts resulted in a pronounced increase in steepness of the slope. The increased steepness of the slope indicated an increased evaporation rate and consequently the formation of a thicker film on the crystal, as was to be expected from the increase in the vapor-source temperature. It should also be noted that no appreciable drift in the frequency readings occurred during the cooling of the vapor source inbetween the evaporations. After a three-day interval, the experiment was continued. Two evaporations were performed with heater voltages of 4.5 volts and 4 volts respectively. The time of evaporation was 10 minutes and 24 minutes respectively. Inbetween the two evaporations, the vapor source was cooled for 15 minutes. These results are also included in Figure 2 and are similar to the results obtained prior to the three-day interval. The deviation from a straight line observed toward the end of the evaporation with a heater voltage of 4 volts may be explained by final exhaustion of the magnesium supply.

Magnesium Evaporations (Heater Voltage Constant)

To verify the reproducibility of the measurements obtained in Figure 2, two experiments were performed, each consisting of three magnesium evaporations. The mount and the conditions under which the evaporations were conducted were kept as identical as possible. The heater voltage used was 4.2 volts, and was applied for 10 minutes. In each experiment, the vapor source was cooled inbetween evaporations for 10 minutes. The monitoring crystal was the same in both experiments, but different from the crystal used in the experiment previously described. The results of the two experiments are shown in Figures 3 and 4. It can be observed from these figures that the slopes of the frequency-versus-time plots indicating evaporation rates varied considerably from evaporation to evaporation. The results shown in Figure 4 indicate that the evaporation rate observed in this experiment gradually decreased with the number of evaporations. In the experiment represented by Figure 3, the lowest evaporation rate was also obtained in the last evaporation. This tendency of the evaporation rate to decrease with the number of evaporations possibly may be attributed to gradual alloying of the magnesium with the container material (tantalum) and to progressive oxidation of the magnesium in the container.

How severely the observed variations in the slopes of the frequency-versus-time plots of Figures 3 and 4 will affect the accuracy of determining the thickness of the deposited films can hardly be judged as long as the relationship between frequency change and actual film thickness has not been established. This relationship may be determined by measuring various film thicknesses with an interferometer and plotting the film-thickness data versus the associated changes in frequency observed on the monitoring crystal. In this manner, a calibration curve can be obtained which, for the particular geometry of the experimental setup, will permit determination of film thickness directly from the change in frequency. Calibration with an interferometer will be conducted as soon as the instrument, which is on order, has been received.

Crystal Mounting Difficulties

In the experiments described in the preceding paragraphs, it was observed that the monitoring crystal ceased to oscillate during the bake-out of the vacuum system before the final bake-out temperature was reached. When the system was cooled after the bake-out, the monitoring crystal began to operate as soon as the temperature had decreased to a certain value. This behavior of the monitoring crystal is represented in Figures 5 and 6. Figures 5 and 6 give the results, with respect to temperature and frequency, of two experiments in which the monitoring crystal was mounted in the bell jar using a conventional ceramic holder with two metallic contacts into which the two pins of the crystal base were plugged. Two different crystals were used in the experiments. A regular bake-out of the bell jar was carried out, and the temperature near the bell jar and the frequency readings on the electronic counter were recorded in certain time intervals. The observed changes of temperature and frequency versus time are plotted in Figures 5 and 6. The gap in the frequency curve of the two figures denotes the time period during which the crystal ceased to operate (zero reading on the counter). The temperature range during this period can be seen from the temperature-versus-time curve. In the first experiment (Figure 5), the monitoring crystal was nonoperating between approximately 200°C and 180°C. The monitoring crystal of the second experiment (Figure 6) did not oscillate between approximately 275°C and 250°C.

Because it was thought that contact degeneration in the crystal holder due to elevated temperature could account for the failure of the monitoring crystals to operate, an experiment was conducted in which the conventional ceramic crystal holder was eliminated and the pins of the monitoring crystal were welded directly to the support wires of the crystal. The same crystal was used as in the first experiment (Figure 5) and the same experimental procedure was followed.

No breakdown of the crystal oscillations occurred at higher temperatures, as can be seen from Figure 7. This appears to confirm the assumption that poor contacts developed in the experiments with conventional crystal holders at higher temperatures.

The dependence of the frequency readings on temperature is shown in Figure 8. The data obtained with the monitoring crystal welded to the support wires and the data obtained with the monitoring crystal mounted in the conventional ceramic holder are presented. As long as the monitoring crystal mounted in the conventional ceramic holder was operable, the observed frequency readings did not change appreciably from the data which resulted from the monitoring crystal welded to the support wires.

Multilayer Films

Due to the extensive effort spent on the establishment of the basic technique for the vapor deposition of thin films including thickness monitoring methods, work directed toward the preparation of metal-insulator-metal sandwiches suitable for studying tunneling characteristics must still be considered to be in the early stages. The arrangement of the films used in the initial experiments is shown in Figure 9. Three dumbbell-shaped metal layers were deposited through a suitable mask onto a glass substrate. After shielding the portions of the substrate where the circular areas of the metal layers are located, a thin insulating layer was evaporated onto the substrate to cover the small rectangular areas of the metal layer. The circular areas of these layers were left uncoated to serve as electrical contact areas. Two narrow metal strips approximately as wide as the narrow part of the base metal layers (approximately 3 millimeters) were then deposited onto the insulating layer in a direction perpendicular to the base metal layer. The active parts of the structures were the intersections of the top and base metal layers with the insulator inbetween. Pressure-adjustable probe wires were used for making electrical contacts to the metal layers.

The first structures prepared and tested were Al-ZnS-Al sandwiches. However, the electrical breakdown strength proved to be too low for observing electron tunneling. Mg-MgO-Mg and Al-Al₂O₃-Al structures were next selected for experimentation. The insulating oxide layers of these structures were formed by exposing the base metal layer for several hours to air of atmospheric pressure at room temperature or by heating them in air at approximately 200°C. To reduce the danger of electrical breakdown or shorts along the edges of the active areas, attempts were made to enhance the thickness of the thin insulating layers along these edges. This can be achieved by first evaporating SiO onto the oxidized base metal layers through a mask as shown in Figure 10a. A second deposition of SiO is then performed after the mask used during the first deposition is replaced by the mask shown in

Figure 10b. After removal of this mask, the top metal strips are deposited, using the mask shown in Figure 10c. Thus far, enhancement of the insulator thickness along the edges of the active areas has been carried out in one direction only, i.e., only the mask shown in Figure 10a was used during the deposition of SiO. The finished structure was a Mg-MgO-Mg sandwich. Difficulties were encountered inasmuch as part of the base metal layer deteriorated during the bake-out which was carried out after the oxidation of the base metal surface. It is planned to repeat the experiment using Al-Al₂O₃-Al instead of Mg-MgO-Mg.

ELECTROLYTICAL ANODIC OXIDATION TECHNIQUE, INCLUDING PHOTOMASKING

The preparation of thin insulating layers for tunnel-cathode use by electrolytical anodic oxidation rather than by vacuum deposition techniques is also under investigation. Initially, the same anodization method was utilized that another group within the Techniques Branch had used in the past. Unpolished and polished tungsten and aluminum strips or discs were anodized using various electrolytes. Initially, diluted H₂SO₄ (15%) was used as electrolyte. Later, an aqueous solution of 3% ammonium tartrate and 2% ammonium hydroxide was used. This mixture was eventually replaced by an aqueous solution of 3% tartaric acid buffered with ammonium hydroxide to a pH value of 5.5. The pH value must be accurate to within ± 0.1 . For meeting this requirement, a Taylor slide comparator was used for measuring the pH value.

After satisfactory results were obtained with sheet-metal samples, the experiments were extended to include the anodic oxidation of evaporated aluminum layers. Starting with a heavy aluminum layer evaporated onto a microscope slide, the layer was oxidized to a depth of approximately 1000 Å except for two strips at the ends of the slide and several circular spots, which were protected against oxidation by a hardened Kodak photoresist layer. The dots form the active area of the finished device, and the two strips permit making electrical contact to the unoxidized aluminum base layer. After removal of the photoresist, the sample was anodized again, but only lightly, to produce an oxide layer of approximately 100 Å on the formerly protected spots. Following this, aluminum was deposited onto the sample through a suitable mask to form individual layers which covered the dots and served as a top electrode.

The electrolytical anodic oxidation and photoresist techniques created problems inasmuch as some of the aluminum layers developed holes during removal of the hardened photoresist masks. Excessive hardening was assumed to have prevented the photoresist layers from loosening in the proper time. The developer started to penetrate the layers at weaker spots, thus damaging the aluminum layer. Closer control of the hardening procedure will be exercised in future experimentation. In some experiments, insufficient oxide growth occurred during anodization. This failure was indicated by the fact that the anodizing current did not drop as expected. The reason for this behavior is not fully understood, although it is possible that electrical leakage of the oxide layer hindered the buildup of the high electric field which is supposed to exist across the oxide and to play an essential role in the mechanism of the electrolytical anodic oxidation process. The experiments are being continued to resolve the described problems. Since it is felt that, in general, the aluminum films currently used are too thin, much heavier films will be used as base layers in the future experiments. Further improvement of the experimental techniques is also expected from the use of higher-grade microscope slides as substrates and of high-purity aluminum for the base metal layer.

CONCLUSIONS

Vacuum deposition techniques for the preparation of thin films were investigated and developed to a point where a study of the usefulness of these structures as tunnel emitters can be attempted. After completion of the present experiment with an Al-Al₂O₃-Al structure, a study of the combination Al-Al₂O₃-Au will be made with special attention given to the method of forming the oxide film and to the geometry of the structures. After sufficient experience with these structures, other metal-insulator-metal combinations will be investigated.

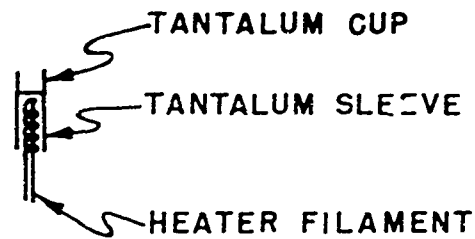
Upon completion of the interchangeable support structure, the recently built Vac-Ion pump station will be utilized in future thin-film experiments. A considerable benefit is expected from the use of this ultrahigh and ultraclean vacuum system.

The method of monitoring the thickness of thin films during deposition by means of an oscillating quartz crystal was investigated. Although the results proved promising, a decision on the final capabilities of this method cannot be made until calibration tests are performed, more quantitative data are collected, and the reproducibility of the results is established after receipt of the interferometer now on order.

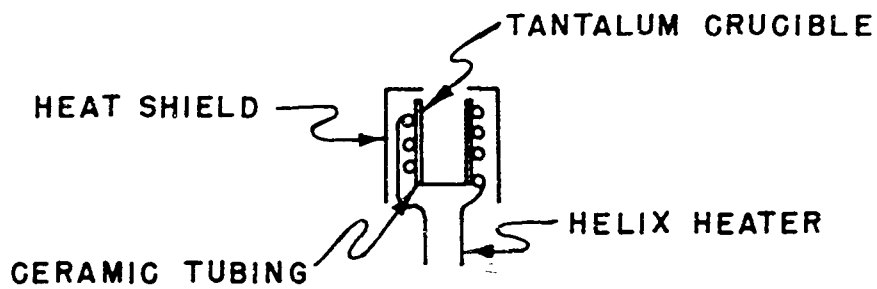
The usefulness of the electrolytical anodic oxidation technique for the preparation of thin insulating oxide layers was investigated. Preliminary experiments were conducted on various sheet metals. The investigation is now concentrating on the oxidation of vacuum-deposited films of aluminum and the formation of special patterns using photo-resist masking techniques. This work will be continued until the general techniques have been satisfactorily mastered. Thereafter, the work will be extended to metals other than aluminum.

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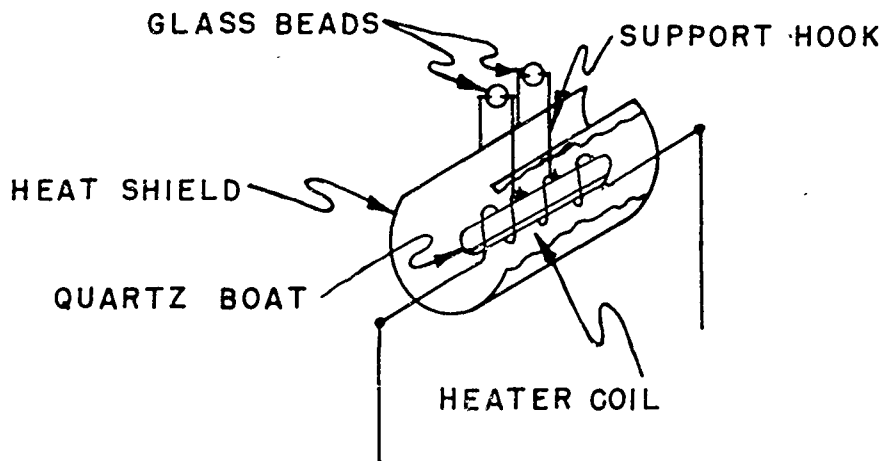
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(a) WIRE-HEATED TANTALUM CRUCIBLE (EVAPORATION OF MAGNESIUM AND COPPER)

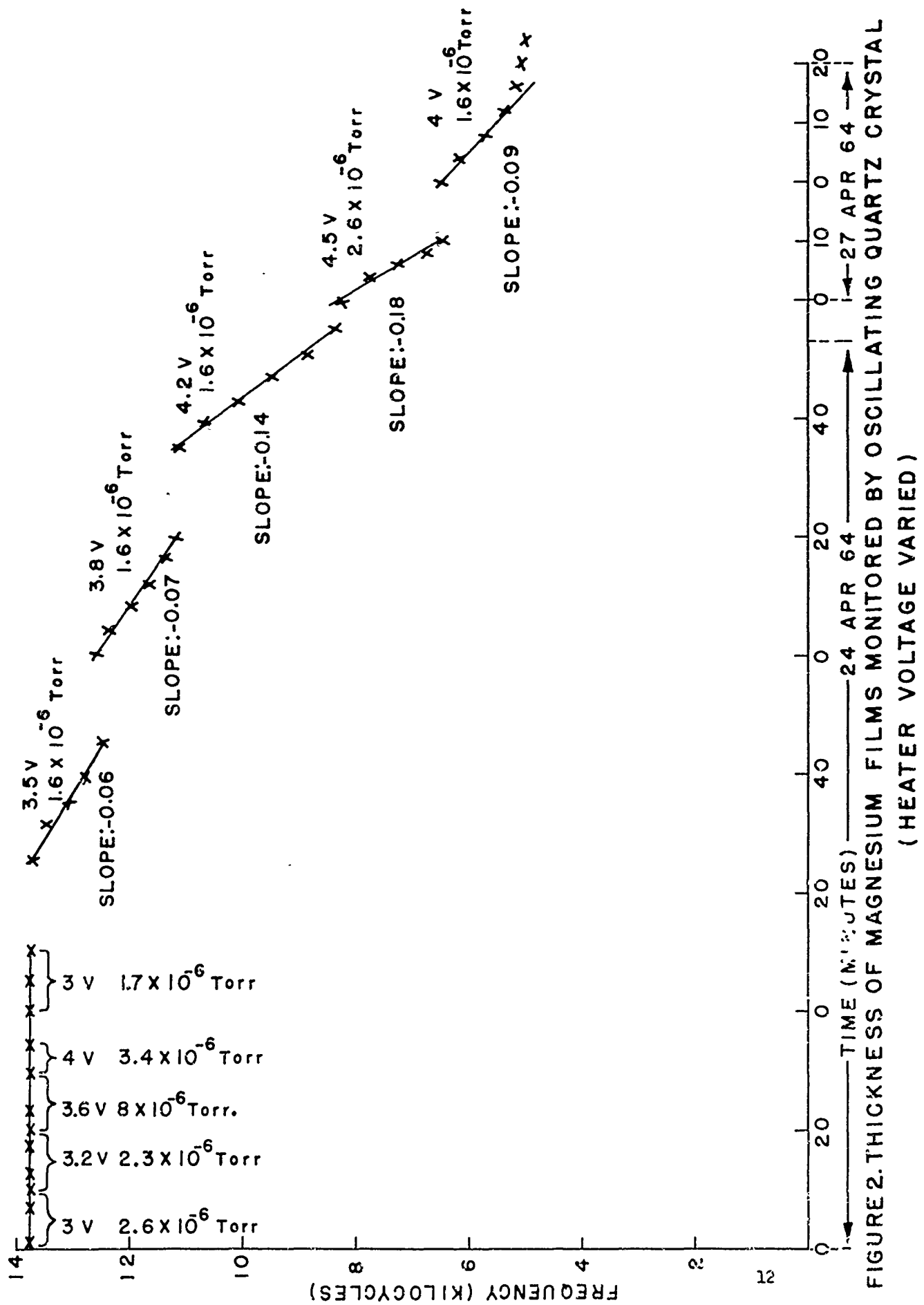


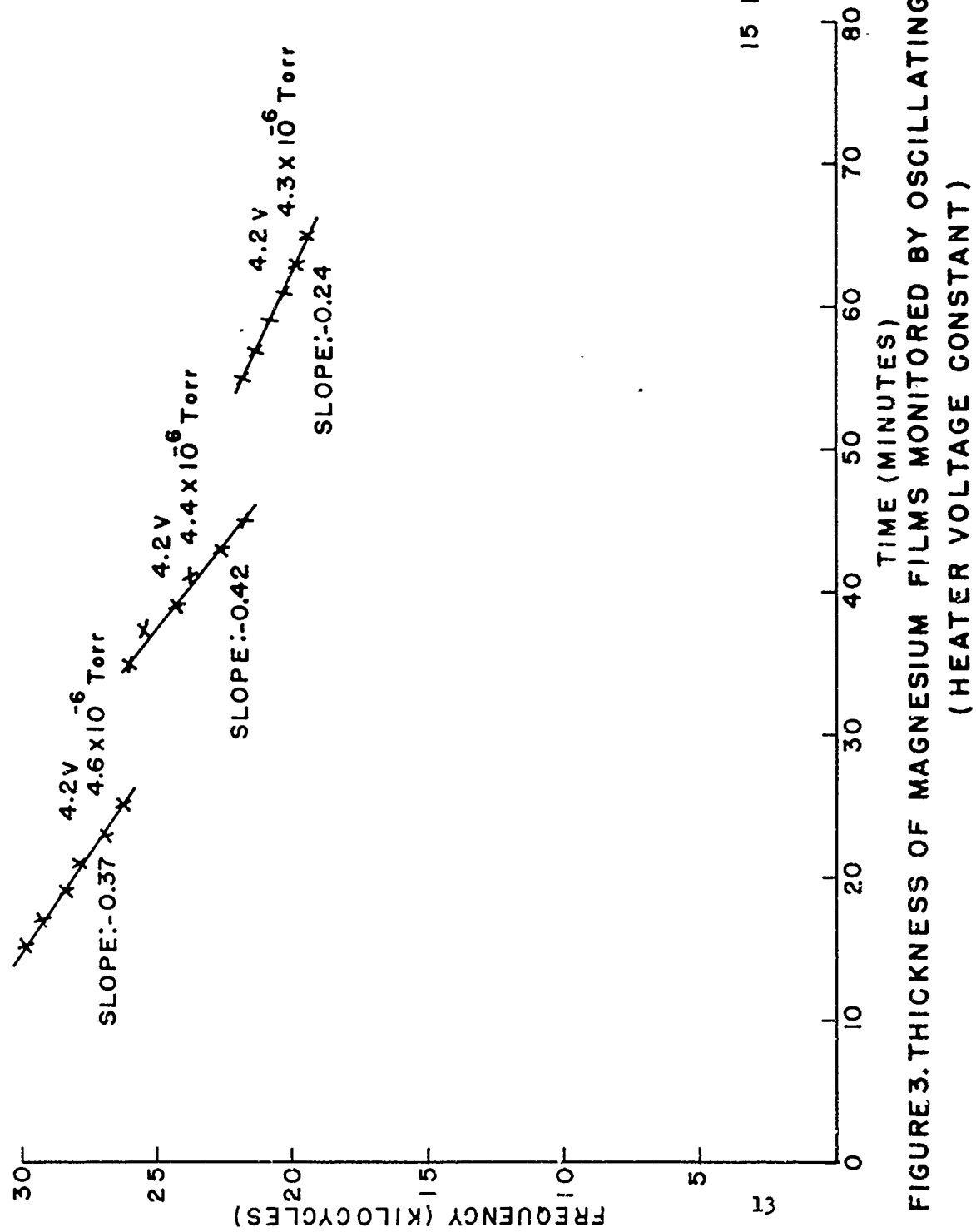
(b) WIRE-HEATED TANTALUM CRUCIBLE WITH CERAMIC INSULATOR AND HEAT SHIELD (EVAPORATION OF SILICON MONOXIDE)



(c) HEATER COIL WITH QUARTZ BOAT PLACED INSIDE (EVAPORATION OF ZINC SULFIDE)

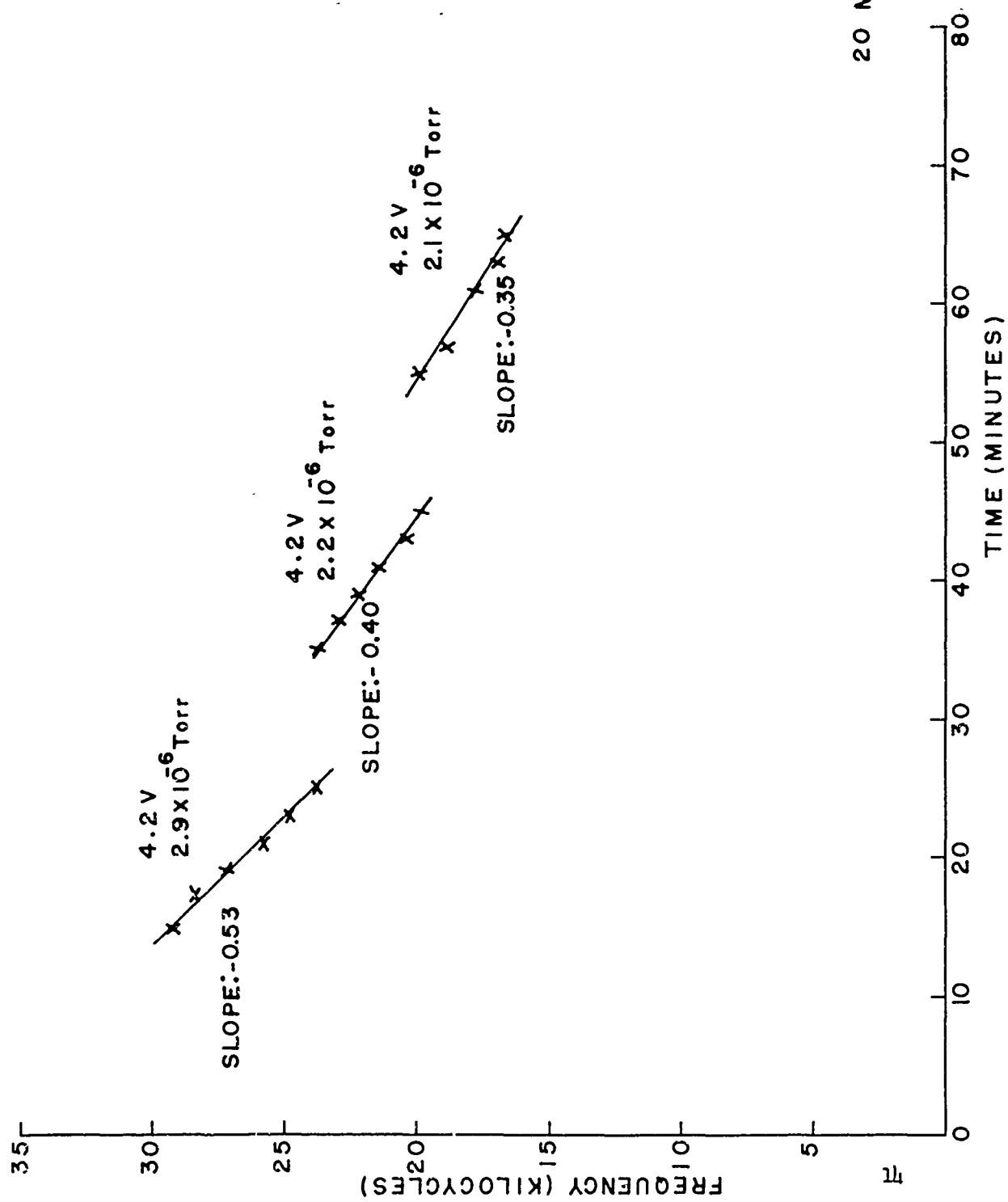
FIGURE 1. VAPOR SOURCES





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FIGURE 3. THICKNESS OF MAGNESIUM FILMS MONITORED BY OSCILLATING QUARTZ CRYSTAL
(HEATER VOLTAGE CONSTANT)



20 MAY 64

FIGURE 4. THICKNESS OF MAGNESIUM FILMS MONITORED BY OSCILLATING QUARTZ CRYSTAL
(HEATER VOLTAGE CONSTANT)

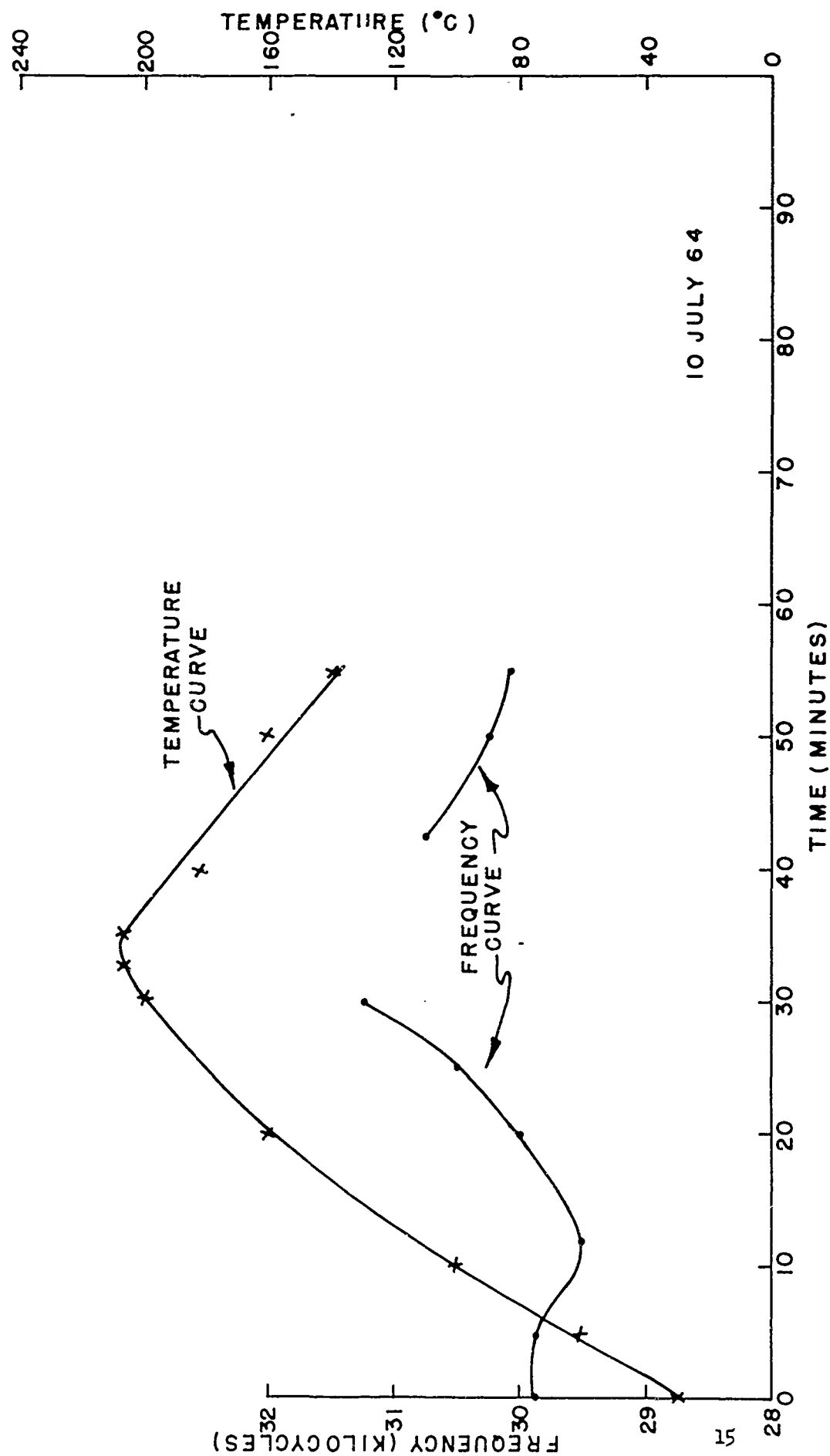


FIGURE 5. TEST RESULTS FOR MONITORING CRYSTAL MOUNTED IN CONVENTIONAL CERAMIC HOLDER

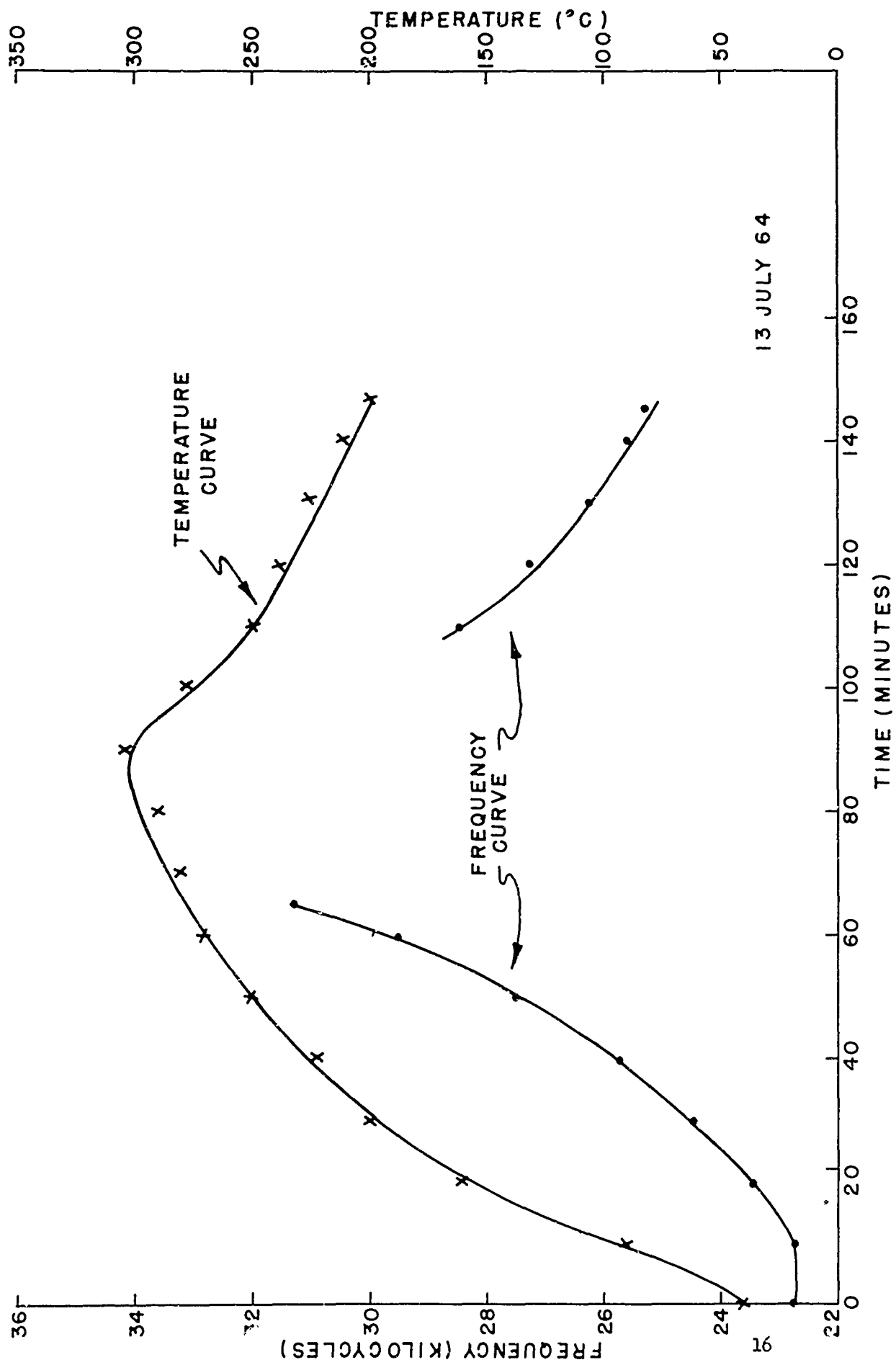


FIGURE 6. TEST RESULTS FOR MONITORING CRYSTAL MOUNTED IN CONVENTIONAL CERAMIC HOLDER

FIGURE 7. TEST RESULTS FOR MONITORING CRYSTAL WELDED TO SUPPORT WIRES

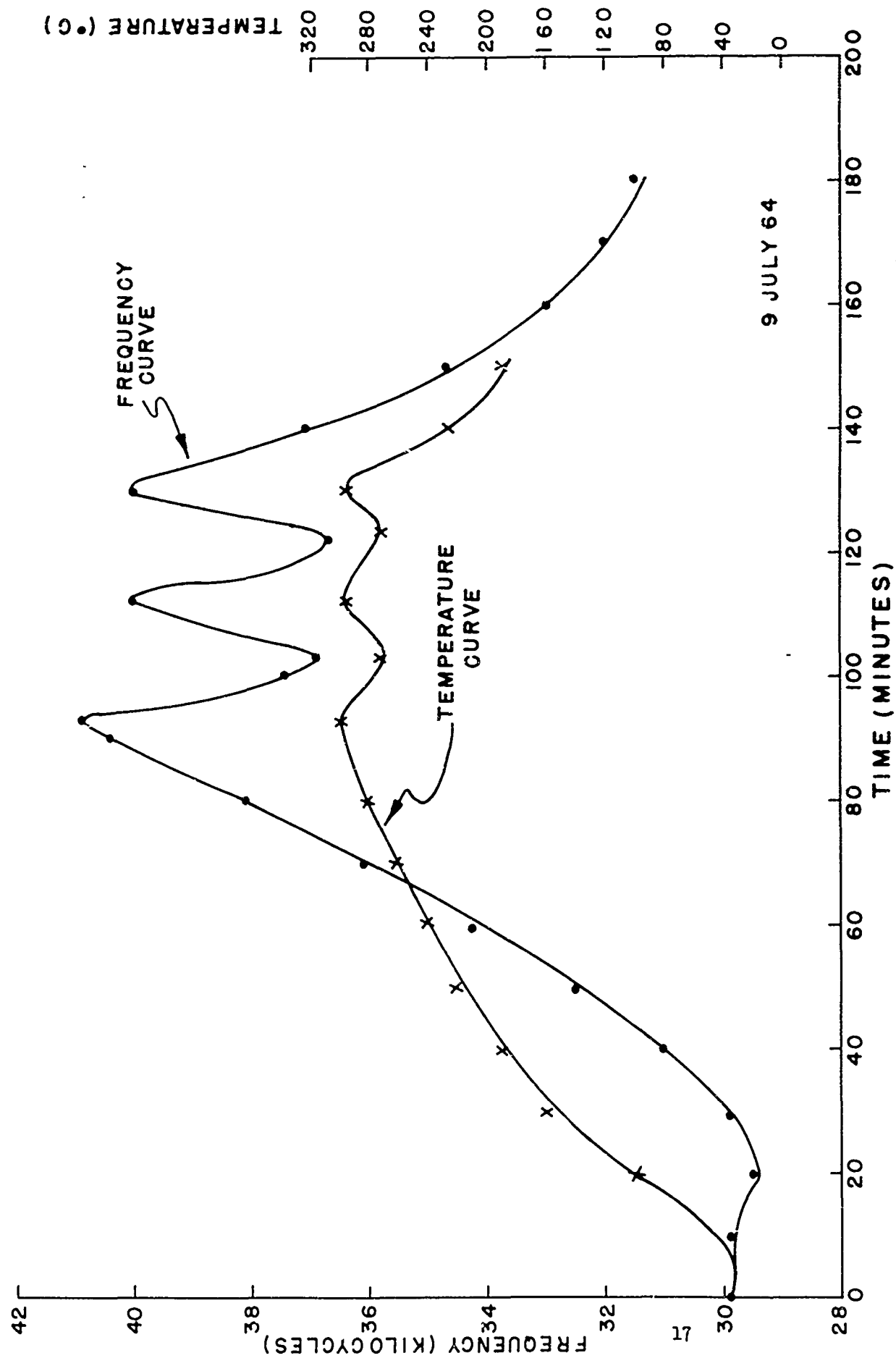
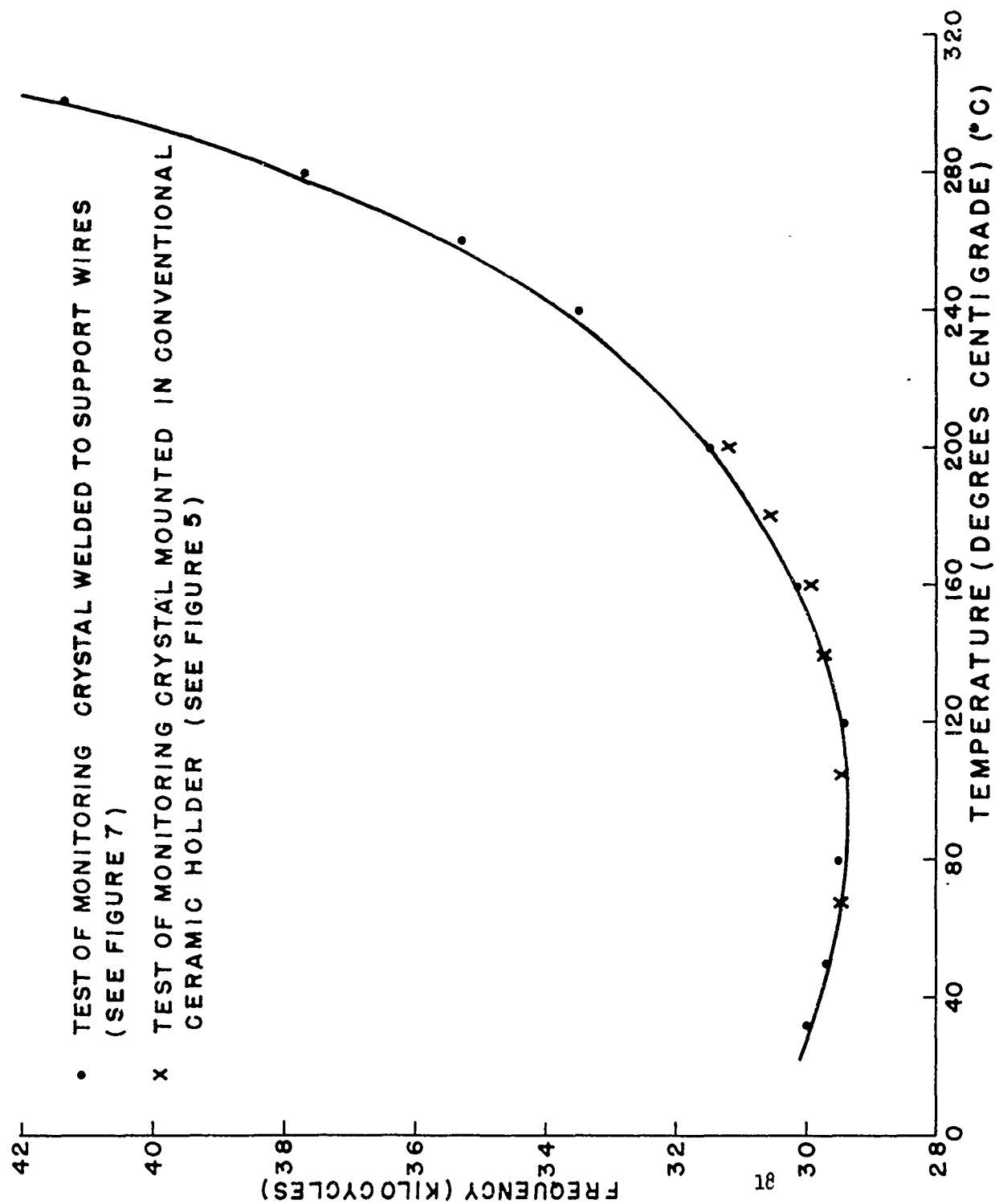


FIGURE 8. THERMAL CHARACTERISTICS OF TWO CRYSTAL MOUNTINGS COMPARED



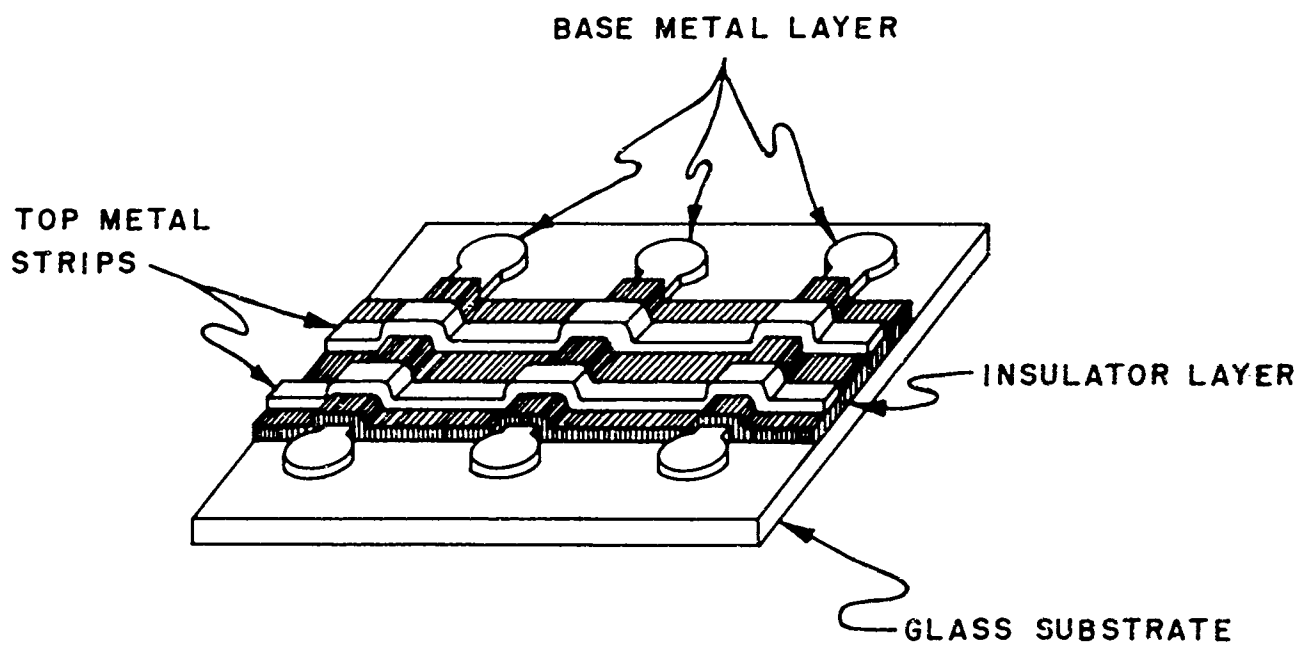


FIGURE 9. METAL-INSULATOR-METAL STRUCTURE INITIALLY USED

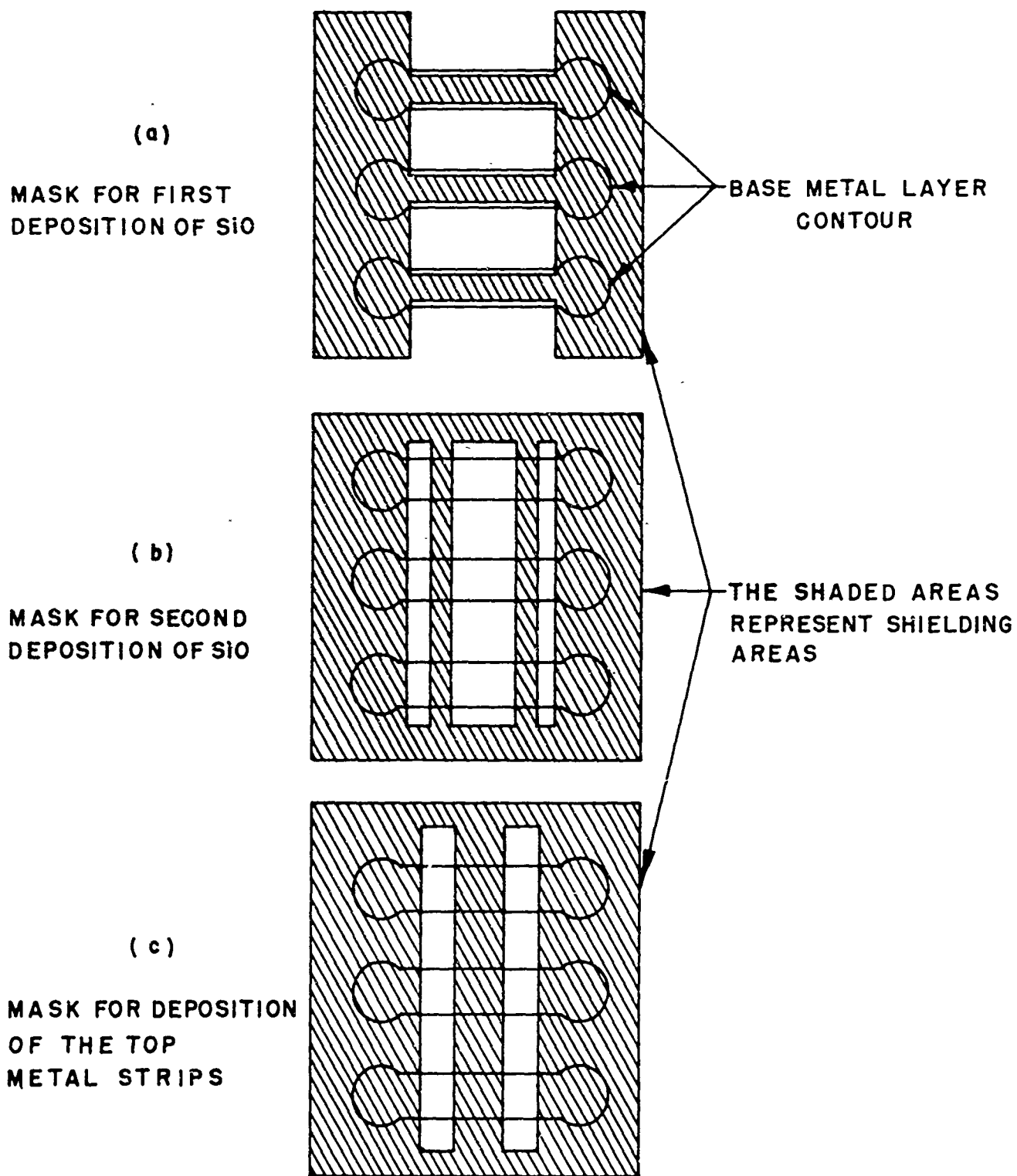


FIGURE 10. MASKS FOR FABRICATING MULTILAYER STRUCTURES
WITH ENHANCED INSULATOR THICKNESS ALONG THE
EDGES OF THE ACTIVE AREAS.

Unclassified

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| 13. ABSTRACT Vacuum deposition techniques for the preparation of thin films were investigated and developed to a point where a study of the usefulness of these structures as tunnel emitters is now feasible. The described experimentation with Al-ZnS-Al, Mg-MgO-Mg, and Al-Al ₂ O ₃ -Al structures will eventually lead to a study of the combination Al-Al ₂ O ₃ -Au sandwich, with special attention given to the method of forming the oxide film and to the geometry of the structure. A method of monitoring the thickness of thin films during deposition by means of an oscillating quartz crystal was investigated. Although the results proved promising, a decision on the final capabilities of this method cannot be made until calibration tests are completed and the reproducibility of the results is established. The usefulness of the electrolytical anodic oxidation technique for the preparation of thin insulating oxide layers was investigated. Preliminary experiments were conducted on various sheet metals. The investigation is presently concentrated on the oxidation of vacuum-deposited films of aluminum and the formation of special patterns using photoresist masking techniques. This work will be continued until the general techniques have been satisfactorily mastered. Thereafter, the work will be extended to metals other than aluminum. (D. Dobischek, S. Cabell) | | |

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| 12 KEY WORDS | LINK A | | LINK B | | LINK C | |
|----------------------------------|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Thin Films | | | | | | |
| Vacuum Deposition Techniques | | | | | | |
| Thin Oxide Films | | | | | | |
| Magnesium Films | | | | | | |
| Multilayer Films | | | | | | |
| Sandwich (Metal-Insulator-Metal) | | | | | | |
| Electron Tunnel Emitters | | | | | | |
| Oscillating Quartz Crystal | | | | | | |
| Thin-Film Monitoring Device | | | | | | |
| Vapor Sources | | | | | | |
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| Electrolytical Anodic Oxidation | | | | | | |
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