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Studies of Primary Electron Sources

W. G. Shepherd, Chief Investigator

Report Prepared by D. E. Anderson

Electron Tube Research Laboratory

University of Minnesota

Institute of Technology

Contract No. AF 19(604)-8381

Project 4619

Task 46190



Scientific Report No. 1

March 1, 1961 to June 1, 1961

January 1962

Prepared for

**ELECTRONICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
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I. Abstract

An experimental system for studying the controlled activation and deactivation of alkaline-earth metal oxide cathodes is described. In this system the activation rate can be controlled by the addition or removal of carbon as a reducing agent, while the cathode is independently exposed to a deactivating gas.

Preliminary results of studies of long-pulse and dc emission changes from oxide-cathodes are presented, and the measurement system for such studies is described.

Photoelectric measurements on a BaO coated cathode in conjunction with thermionic pulse emission measurements are described. The data obtained thus far indicate a relationship between the thermionic and photoelectric emission. Experiments investigating the enhancement of thermionic emission by ultraviolet light are reported. The procedure used to produce BaO thin films on the standard cathode base structure is outlined and photoelectric yield curves are presented for these cathodes.

A study of electron tunneling through thin insulating films has been initiated. Methods for preparing experimental samples suitable for the measurements have been developed, and preliminary measurements have been made. Non-linear I-V characteristics for such samples have been observed. The Ta-Ta₂O₅-Al samples and Al-Al₂O₃-Al samples studied exhibit hysteresis in the I-V characteristics at a particular bias polarity; and rectification with reversal of the polarity.

II. Studies of Thermionic Cathodes

1. Introduction

The studies to be reported in this section are all directed to obtaining an understanding of the alkaline-earth metal oxides as thermionic cathodes. While other systems will be investigated later, it is felt that the present understanding of the oxide cathode is such as to make specific studies of this system most fruitful at the start.

The purpose of this introduction then is to review the groundwork on which these researches are based, to summarize briefly the important results of our previous work,* and to present the general outline of the plan by which the particular objectives of the research are being approached. We hope that such a resume will serve to relate the individual experiments to the program as a whole.

There is general agreement that the oxide cathode is an n-type semiconductor and that an excess of alkaline-earth metal in the coating is essential for high emission. It is not necessary to assume that this excess metal must occur in the grains of the coating in order to provide donors, but only that the presence of free metal in the pores is necessary for the production of donors. This excess metal is believed to result largely from the action of reducing impurities incorporated in the base nickel. It might reasonably be expected that the evaporation rate of free

* Bureau of Ships, Contract NObsr-63172, Air Force Cambridge Research Laboratories, Contract No. AF-19(604)-3890.

alkaline-earth metal from the oxide coating would serve as an indication of the rate at which this free metal is being produced by chemical reduction. Thus, the evaporation rates of such free metal might be correlated with the emission capabilities of the cathode.

As a convenient and accurate means for measuring the rate at which the alkaline-earth metal is evolved from the coating, radioactive tracers of Ba or Sr can be incorporated in the oxide coating. This method allows one to monitor the total amount of alkaline-earth metal being evolved from the coating, either as the oxide or as the free metal. Although the total amount of Ba evaporated (Ba and BaO) is larger than that of Sr (Sr and SrO), our observation is that the metal-to-oxide ratio is more favorable for the detection of Sr metal than for Ba metal in the presence of the background of oxide evaporation.

Subsequent experiments were designed to determine whether a correlation existed between the Sr evaporation and the emission from oxide-coated cathodes. For these experiments cathodes based on single additive nickel alloys and on pure nickel doped with carbon have been used. A correlation between Sr evaporation and the development of emission has been observed for both types of cathode base. This correlation has been qualitatively explained using a model in which the strontium evolution follows the rate at which the reducing agent arrives by diffusion at the base nickel-oxide interface. The emission is taken as being controlled by the donor concentration in the oxide particles, with the

generation of additional donors at the surface of each particle being a function of the pressure of free alkaline-earth metal in the pores of the coating.

It has been found that, for the concentrations studied, single additive alloys of Al, Mn, W, Mg, and Si in Ni lead to a rate of coating reduction which is limited by the diffusion of the reducing element to the oxide coating-base metal interface. In these cases the rate of reduction is proportional to $t^{-1/2}$ where t is the total operating time. Quantitative agreement with observed data can be obtained when the diffusion coefficient of each additive in nickel is known; these values have been determined. Early studies of the pulse emission from cathodes based on these alloys indicated that, following an initial activation, the emission declined monotonically with cathode life. It is postulated that this decline is a consequence of competing processes and that, under ideal conditions, stable emission levels should be maintained even for the systems with declining rates of chemical reduction. This "stable donor" behavior has been observed with cathodes based on Mg-Ni and Al-Ni alloys.

It is possible to devise a cathode base from which carbon can be dispensed to the coating at a rate which is constant over extended periods of time. The Sr evolution from coatings based on such a dispenser is found to be constant. This system is of considerable interest because of the possibility of producing chemical reduction of the coating at a constant and controllable rate.

All of the foregoing studies have been made with the cathode in thermal equilibrium at a fixed temperature. A complete understanding of the factors affecting chemical activation demands information as to their temperature dependence. An experimental investigation of the response of oxide cathodes to step changes in temperature has been made which shows both short-term and long-term changes, corresponding respectively to (1) the fraction of the donors thermally ionized and (2) changes in the equilibrium concentration of donors.

Anode poisoning of an oxide cathode, caused by drawing current to an electrode which has accumulated evaporation products from the cathode, has been studied with respect to the change in activity during such poisoning and to subsequent recovery. The pulse emission under these conditions may drop from amps/cm^2 to milliamps/cm^2 with an apparent exponential decay having a time constant of a few minutes. It is known from other studies made in these laboratories that there is a low-voltage threshold for the dissociation of anode deposits or desorption of gas layers. If the anode bombardment is stopped when the emission has fallen to a stable level, the pulse emission then recovers in a manner very closely resembling the initial chemical activation of the cathode. It has been shown that the material which dissociates under electron bombardment is an impurity, rather than the oxides, related to the bakeout of the envelope of the structure.

Two major processes can contribute to the activation of the oxide cathode. These are chemical activation due to reducing agents incorporated in the base metal and electrolytic activation

of the coating. The effect of chemical activation has been studied by operating the cathodes without current drain during life. Early attempts to produce simple electrolytic activation by drawing a continuous current from an oxide cathode based on a passive nickel led to activity levels which were much lower than could be achieved from cathodes based on active nickels in which chemical activation played a role. The results of studies of bombardment-induced poisoning suggested that this competing process limited the development of electrolytic activation. Accordingly, a structure was developed which permits the drawing of a continuous current to a positive grid located so close to the cathode that the threshold for anode poisoning would not be exceeded. Under these conditions, a very pronounced activation of the cathode occurred when continuous current was drawn through the coating. It was found that the cathode activated with a time constant of the order of 10 minutes at 1119°K, and also that a continuation of current drain for several hours resulted in the development of a stable level of activity which then persisted even when current drain was discontinued.

These results have been interpreted in terms of a model in which the donors are not volatile and are thus stable in the absence of competing processes. A continuous current drain leads to a field-enhanced preferential evolution of anions from the coating with a corresponding increase in donor concentration, and emission capability, at the surface of the individual oxide grains. The permanent activation is viewed as the result of a

saturation of the bulk of the oxide particles by the presence of this excess donor concentration at the surface.

The apparent emission measured from an oxide cathode by a method dependent on the deviation from a three-halves power law is influenced by the resistive drop in the oxide coating. This drop can develop across a resistance appearing at the interface between the oxide coating and the base metal and also across a resistance occurring in the bulk oxide. Studies of the formation of resistive interface layers for various reducing impurities have shown that only in the case of silicon is a significant resistive interface layer developed. The bulk resistive effects can be compensated by suitable measuring instrumentation and thereby an accurate determination of the saturation pulse emission and of the coating resistance can be made. The necessary instrumentation to permit this has been developed in this laboratory. The deviation of a plot of (i) vs $(v - ki)$ is observed with k adjusted to fit a $3/2$ power space-charge curve. As a measure of the saturation emission, either J_{20} (the current at which the I-V trace has fallen 20% below the space-charge law) or J_d (the current at which deviation begins) can be determined.

2. Controlled Activation and Deactivation of Oxide Cathodes

R. Springer

In a previous study* it was demonstrated that the steady-state rate of reduction of the oxide coating by carbon can be controlled such that two or three different carbon diffusion rates can be maintained before cathode depletion becomes evident. The

* Final Report, Studies on Base Nickels for Oxide-Coated Cathodes, University of Minnesota, Air Force Cambridge Research Laboratories, Contract No. AF 19(604)-3890.

reduction of the oxide by carbon at a constant rate generates a constant partial pressure of free metal in the oxide coating and presumably a constant chemical activity. The geometry of the tubes used in this study is such that gases admitted to the tube would not react with either the carbon source or the cathode heating system. Thus we have the possibility of examining the pulse emission activation-deactivation time constants as a function of oxygen pressure in the tube from a cathode subjected to a constant level of chemical activation.

A preliminary examination of the effects of oxygen admission was reported earlier.* This experiment was carried on late in cathode life and resulted in only limited data, but it demonstrated the practicality of oxygen admission to this system.

A tube has been constructed for oxygen admission and is shown in Fig. 1. This is a double-envelope tube with two separate vacuum enclosures joined together at a 0.005 inch Kovar partition. The cathode base consists of a Ni disc 1/2 inch in diameter and 0.010 inches thick, which is welded to the top of the Kovar partition. The oxide coating, which incorporates radioactive Sr^{89} as a tracer, is applied to this disc and remains in the environment of the top enclosure, independent of environmental changes in the bottom enclosure.

A similar Ni disc is welded to the bottom of the Kovar partition directly below the oxide cathode base. This disc has four Ni tabs welded around the edge. Control of the carbon diffusion is achieved by painting carbon on the ends of the Ni tabs to increase the reduction rate, and cutting off the tabs to reduce

* Final Report, Studies on Base Nickels for Oxide-Coated Cathodes, University of Minnesota, Air Force Cambridge Research Laboratories, Contract No. AF 19(604)-3890.

the rate. Progressively higher reduction rates are achieved as the Ni tabs are shortened and the carbon source is placed closer to the oxide coating.

The cathode assembly is heated by electron bombardment from an auxiliary oxide cathode situated under the Kovar partition in the bottom vacuum enclosure. Both the upper and lower enclosures are pumped continuously during life by separate titanium sputter pumps. There are separate Ti anodes for Sr evolution and pulse emission measurements. The temperature of the cathode is measured by a Pt-Pt+10% Rh thermocouple welded to the side of the upper Ni disc. A 0.0015 inch Kovar window is provided in a side arm to measure the radioactivity of a given anode, and hence the Sr evolution rate, with an external Geiger-Mueller tube.

A valve and oxygen flask are incorporated to permit controlled oxygen admission, and an omegatron-type mass-spectrometer is attached for gas analysis. One tube of this type, KK8BB, has been processed and is being operated; the data are insufficient for presentation at this time.

3. Long Pulse and DC Performance of Oxide Cathodes

D. A. Campbell

Studies of changes in the properties of oxide cathodes under long pulse and dc operation can provide information which will augment the basic understanding of the oxide-coated cathode. To this end techniques were devised under a previous contract* for

* Contract No. AF 19(604)-3890, Electronics Research Directorate of the Air Force Cambridge Research Laboratories.

observing transients occurring with periods between 0.1 and 0.5 milliseconds. The observations made using these techniques were explained qualitatively on the basis of temperature changes that occur in the oxide coating which result from evaporative ($J\phi$) cooling at the emitting surface and Joule ($J^2\rho$) heating in the bulk oxide. The time constants and the nature of the changes in the I-V characteristics observed experimentally were in accord with those predicted on the basis of a transient solution of the heat equation subject to appropriate boundary conditions.*

During the interval covered by this report a technique was devised for measuring the I-V characteristics of an oxide cathode during and after dc current drain. The technique used** measures the I-V characteristic by applying 3 μ sec ramp to the diode under test, as shown in block diagram form in Fig. 2. This ramp is adjusted in peak amplitude, from 0 to 9000 volts, to sweep into the saturation region of the diode under test. A signal proportional to the current is detected at SW 3 and passed through SW-2 to the vertical input of a Tektronix type 536 X-Y oscilloscope.

A signal proportional to the voltage across the diode under test is selected by SW 4 and passed through SW 2 to the horizontal input of the oscilloscope. To correct for resistive voltdrops in the oxide coating and the sampling resistances, a differential preamplifier is used before the horizontal amplifier of the

* For details of these studies see Scientific Reports Nos. 8-11 of the previous contract.

** Details of the method of measuring I-V characteristics are presented in Scientific Report No. 4 of the previous contract.

oscilloscope. The circuit shown in Fig. 2 then permits an oscilloscope presentation of i versus $(v - ki)$, where k can be adjusted to present the Childs' Law trace of an ideal diode until saturation is reached.

To permit direct read-out of the values of v and i , SW 2 can be changed to select calibrated marker pulses which directly indicate the coordinates of a selected point on the oscilloscope trace.

The dc power supply used to obtain a continuous current drain is connected in parallel with the pulse emission tracer across the diode under test. A blocking capacitor is inserted to prevent a dc path through the pulse emission tracer, while an inductance prevents pulse current from flowing through the dc power supply.

The arrangement permits a series of pulsed I-V characteristics to be recorded at any desired times following application, or removal, of dc current drain. A Polaroid camera mounted on the oscilloscope can then record a family of characteristics obtained by applying single pulses to the diode at each desired instant of time.

A direct tracing of one such photograph is shown in Fig. 3. In this case the characteristics are those observed immediately subsequent to the application of a dc current drain of 3.1 ma. The cathode in this instance was equimolar (BaSr)O deposited as the carbonate on a 0.27% Mg-Ni alloy base, and had operated 2000 hours at 1053°K prior to the measurement (at 948°K).

A normalized semilog plot of the current at a fixed voltage in the temperature limited region is shown in Fig. 4. It is noted that the points can be fitted by a single straight line if the initial point is not considered. The first point is ignored because of an instantaneous shift in the characteristic that occurs when the dc is switched on. The time constant for the decay observed for this case was about 3.3 seconds. Similar results can be obtained for the recovery process by recording the I-V characteristics after cessation of dc current drain.

The above described data indicate that the method used can give a description of the dc performance of oxide cathodes. It is hoped that further measurements using this method will yield a coherent picture of the behavior of oxide-coated cathodes under dc current drain.

4. Optical Measurements of Oxide Cathodes C. A. Stolte

The method for preparing thin film BaO coatings on nickel alloy bases, developed under the previous contract,* has been used to produce two coatings. The system used, shown in Fig. 5, includes an evaporator which deposits Ba from a getter onto the nickel alloy base, in the standard cathode assembly used in these laboratories, and at the same time onto a nickel control tab which is used to determine the thickness of the film. The oxidation of the Ba is done in a side arm by flowing reagent grade oxygen over the sample. The photoelectric yield of the sample can be monitored during the oxidation process to assure complete

* Scientific Report No. 10, Studies on Base Nickels for Oxide-Coated Cathodes, University of Minnesota, Air Force Cambridge Research Laboratories Contract No. AF 19(604)-3890.

oxidation of the Ba. The entire "preparation" structure is isolated from the "measurements" structure by a 20 mm glass bubble. This isolation is necessary to eliminate Ba migration which can take place during the bakeout schedule used to outgas the "measurements" structure.

To clarify the procedure used to produce the BaO thin coating the process used will be outlined below. The "preparation" structure (which includes the Ba evaporator structure, the oxidation section, the omegatron, sample disks and control tabs) was sealed to the main Ti sputter pump and evacuated. The entire structure was baked at 400°C for 8 hrs. The getters were outgassed by heating to approximately 800°C.

The "measurements" structure which included a Ti sputter pump, a pure nickel cathode base, a 0.02% Mg-Ni cathode base, and the anode and cathode trolley system was sealed to the "preparation" structure. The cathode assemblies were constructed so that they could be placed on the trolley wires under the anodes. The cathode could be moved under the Ni screen for photoemission measurements, under a Ti anode for pulse emission measurements or under the Ti life anode. The cathode assemblies could be removed from the trolley and moved through the entire tube structure for the evaporation and oxidation process.

The "preparation" and "measurement" structures were baked at 250°C for 8 hrs. and the anodes in the "measurements" structure heated to 800°C to outgas them. The cathode bases were outgassed by heating to 1000°C. The getters in the evaporation section were again outgassed by heating to 700°C. The 20 mm

bubble was then broken and the pure nickel base cathode assembly moved into position over the evaporation structure. A nickel control tab was placed in position and the getter heated to 760°C. The pressure increased to 4×10^{-9} mmHg and then decreased during the 7 hours the getters were held at 760°C. After the evaporation the cathode base and control tab had a light metallic coating. The cathode and tab were moved to the oxidation section of the "preparation" structure and the tab placed on the trolley for a photoemission measurement. The photoelectric yield curve obtained on the tab is shown by Curve No. 1 of Fig. 6. The threshold energy is seen to be about 2.4 ev; a Fowler plot of these data yielded a threshold of 2.42 ev. The side arm was then heated to 200°C during which time the pressure increased to 5×10^{-9} mmHg. Curve No. 2 of Fig. 6, taken with the side arm at 200°C, demonstrates the stability of the Ba deposit. After the side arm had been at a temperature of 200°C for 20 minutes the oxygen valve was opened to increase the pressure in the system to 7×10^{-6} mmHg. Curve No. 3 of Fig. 6 was taken after 15 minutes exposure to oxygen. The omegatron spectra showed mainly O_2 with small amounts of CO, CO_2 and A. The CO and CO_2 are believed to be a consequence of carbon in the system or in the omegatron filament. Argon was probably released from the Ti sputter pump as a result of heating caused by these pumping conditions. The oxidation was allowed to continue for 5.5 hours until no change in the photoelectric yield curve was observed. Curve No. 4 of Fig. 6 was taken at the end of the oxidation schedule with the side arm still at 200°C and Curve No. 5 of Fig. 6 was taken with the side arm at room temperature.

The cathode and control tab were observed to determine the thickness of the film produced. The cathode had a light blue color when viewed in room light while the tab had a gradient from a transparent film to a yellow color. The pattern on the mask which held the cathode structure and control tab indicated that the cathode base received more Ba than the tab. The color observed on the cathode base and control tab indicated a film thickness of the order of $1200 \text{ \AA}$.

The system cracked over a weekend and as a consequence no further data are available. The system was rebuilt and a new cathode base and getter installed. The structure was processed as indicated above. The isolation bubble was broken and the pure nickel cathode base and a control tab placed over the Ba evaporator. The getters were operated at 770°C for 8.5 hours during which time the pressure did not rise above 10^{-8} mmHg. The cathode base and control tab had a light metallic coating after this evaporation. The tab was moved to the oxidation section to measure the photoelectric yield. The press holding the trolley and collector system had a high electrical leakage which made photoelectric yield measurements impossible. The 0.024% Mg-Ni cathode base was moved into the evaporator structure with a control tab and the getter operated at 840°C for 9 hours. The cathode base and tab had a light metallic coating after the Ba evaporation.

The two cathode structures and control tabs were moved to the oxidation section and the side arm heated to 210°C . The samples were exposed to oxygen at a pressure of 7×10^{-6} mmHg

for a period of 4 hours. From the colors observed on the cathode films and control tabs it is believed that the Mg-Ni based film is slightly thicker than the pure nickel-based film. Both films are of the order of $1200 \text{ \AA}$ thick.

The cathodes were moved back through the structure to the "measurements" structure and the photoelectric yield taken on each. During these measurements it became apparent that the glass walls of the envelope were positively charged. The collector current measured appeared to be a combination of the photoelectrons originating from the cathode minus the photoelectrons leaving the Ni screen used as the collector. In the future the yield curves will be taken measuring the cathode current to eliminate the effects of charged glass.

The photoelectric yield curves taken on the BaO films on the 0.024% Mg-Ni base (PM1FF1) and on the pure nickel base (PM1BB1) are shown in Fig. 7. The "measurements" structure was sealed from the "preparation" structure at the 28 mm tubing near the bubble. The sputter pump was turned on and filaments in the cathode structures checked. During the next interval the cathode will be lifed to determine the pulse emission capabilities and attempt to correlate these with the photoelectric yield curve structure and magnitude.

Further measurements have been obtained on a BaO cathode coating prepared by converting BaCO_3 applied in binder and shaved to a thickness of 0.0022". The cathode coating was applied to a 0.1% Mg-Ni disc and converted using the standard schedule, which includes heating the cathode slowly to 800°C and

holding it at that temperature until the pressure decreases below 10^{-7} mmHg. The temperature is then increased to 1050°C in steps of 25°C every 2 minutes. After the cathode temperature had been at 1050°C for two minutes the temperature was reduced to 800°C and a pulse emission measurement taken. The pulse emission level was 0.084 amp/cm^2 . The photoelectric yield, Curve No. 2 of Fig. 8, was taken 43 minutes after the conversion schedule. Data were taken increasing the photon energy up to 5.5 ev and then the curve was retraced as indicated by the arrows. This curve shows hysteresis which was a consequence of activation of the cathode by the ultraviolet light which was observed for photon energies above 3.7 ev. Curve No. 3 of Fig. 8 was taken 70 hours after the conversion schedule, during which time the cathode was at room temperature in a light-tight box. There is a decrease in the yield in the low energy end and only a slight hysteresis effect.

The cathode was operated for 1/2 hour at 800°C during which time the pulse emission rose from 0.084 amp/cm^2 to 0.275 amp/cm^2 . The photoelectric yield curve taken 19 minutes after this life period is shown by Curve No. 4 of Fig. 8. There is observed to be a large increase in the photoelectric yield and additional structure in the yield curve. The measurements taken above 3.7 ev showed a rapid increase in the photoelectric yield as a function of the time the light was on the sample. It was because of this activation that Curve No. 4 was taken only up to 4.0 ev. The dashed curve represents the data taken after the solid curve and

shows the enhancement of the yield as a consequence of the ultraviolet irradiation.

The cathode was left at room temperature in a light-tight box for 144 hours after which time the photoyield, Curve No. 1 of Fig. 9, was taken. There was a large decrease in the yield and the curve shows little structure in the low energy end. The dashed curve again illustrates the enhancement of the yield as a consequence of the ultraviolet irradiation used to obtain the solid curve.

The cathode was lifed at 800°C for 1.5 hours during which time the thermionic pulse emission increased from 0.215 amps/cm² to 0.332 amps/cm². The photoelectric yield curve taken 10 minutes after the life period is shown in Curve No. 2 of Fig. 9. The photoelectric yield curve taken 140 hours after this life period is shown in Curve No. 3 of Fig. 9. These curves show the same general behavior as those of Fig. 8. The cathode was heated to 800°C for 3 minutes to obtain a pulse emission reading; Curve No. 1 of Fig. 10 shows the photoelectric yield after this period.

The cathode was lifed for 2.0 hours at 800°C during which time the pulse emission rose to 0.334 amps/cm². The photoelectric yield taken 15 minutes after this life period is shown by Curve No. 2 of Fig. 10 and that taken 122 hours later by Curve No. 3 of Fig. 10.

The data presented indicate that the operation of this cathode at 800°C introduced structure in the low energy end of the photoelectric yield curve. This enhancement is not stable at room temperature but decreases with time, as does also the thermionic pulse emission. The activation by ultraviolet light,

3.7 to 5.5 ev, is more pronounced when there is structure in the low energy end of the photoelectric yield curve. To summarize the behavior observed, the thermionic pulse emission and the photoelectric yield at 2.5 ev and 3.6 ev are plotted as a function of hours life in Fig. 11. From this plot there appears to be a correlation between the pulse emission, J_s , and the photoelectric yield, η . These results must be considered preliminary since the range of emission is small; however, it does indicate a relationship between the photoelectric yield and the thermionic emission.

The enhancement of the thermionic emission by ultraviolet light was investigated using the cathode described above. The first attempt was made with the cathode temperature at 800°C. There was no observable enhancement of the thermionic emission by 4.0 ev light. The cathode was then operated at 230°C and the dc thermionic emission monitored while ultraviolet light was incident on the cathode. Irradiation with 3.9 ev light for about 0.5 minutes increased the thermionic emission by a factor of ten. With the light off the emission decayed to its original level in about 5 minutes. When irradiated with 3.5 ev light there was only a very slight enhancement of the thermionic emission while 3.6 ev and 317 ev light produced an enhancement. The results do not warrant further discussion at this time; further data will be obtained in the future. The enhancement of the photoelectric yield at low energies by irradiation in the ultraviolet will also be further investigated.

The large increase in the photoelectric yield at 3.7 eV has been observed by other investigators and has been attributed to excitons which give up their energy to an electron in a level close to the vacuum level. To investigate this phenomena and also to aid in the interpretation of the photoelectric yield curves a transverse magnetic field energy analyzer will be constructed. This will allow one to distinguish between a one-step process, in which the energy of the emitted electron is a function of the energy of the incident photon, and a two-step process, such as exciton-induced emission, where the energy of the emitted electron should be relatively independent of the energy of the incident photon.

III. Studies of Non-Thermionic Electron Sources

1. Introduction

Thermionic emitters are characterized in general as those in which the necessary energy required for electron escape at the surface is supplied thermally. The electron energy distribution in the emitter is in thermal equilibrium with the lattice, and only that portion of the electron population having surface-directed energies equal to or greater than the thermionic work function can escape. In addition to thermal excitation, it is possible to supply excess kinetic energy to electrons in a solid so that these "hot electrons" can escape.

To show promise of providing a useful electron source, any non-thermionic emitter should satisfy a number of criteria. These include the following:

- a) The current density, and total current per device, must be adequate.
- b) The excitation energy should not be too difficult to supply, in comparison with thermionic excitation.
- c) The velocity distribution of the emitted electrons must be limited to facilitate focusing, modulation, and other utilization requirements.
- d) Random fluctuations, or noise, must be limited.
- e) Lifetime of the source, in its projected application and environment, must be adequate.

The above list is not exhaustive, and the relative importance of each criterion will of course depend upon the projected application.

In the studies being undertaken by this project, two general means of exciting the electrons are being considered. In both, the excitation energy will be in the form of externally applied electric fields (as in normal field emission). One scheme invokes the possibility of cooperative acceleration of electrons in a superconductor; the studies are too preliminary to be reported here and discussion will be deferred until the next report. The second scheme involves the acceleration of electrons while passing through a thin film insulator; this work is described in the following section.

2. Electron Penetration through Insulating and Conducting Films

E. D. Savoye and O. L. Nelson

A. Preliminary studies

A study of the phenomena of electron penetration through thin insulating and conducting layers has been initiated. Devices utilizing these phenomena hold the promise of providing electron emission into vacuum from a cold source. Such a device would require electron tunneling through a thin insulating film and subsequent penetration of the thin metal overlayer, into vacuum.*

Devices to observe these phenomena consist of a metal base, a thin insulating film (of the order of $100 \text{ \AA}$), and a thin metal overlayer. When a potential of a few volts is applied between the metal layers an electric field of the order of 10^7 volts/cm is established in the insulating film. Fields of this magnitude are large enough to cause field emission of electrons from the negative metal through the potential barrier of the insulator into

* C. A. Mead, Proc. IRE 48, 359, March (1960).

the positive metal film. If now this metal film is thin enough an appreciable fraction of the electrons may be able to reach the metal-vacuum interface with energy greater than the work function and pass into the vacuum. This last requirement implies that the thickness of the insulator be chosen such that a voltage greater than the metal-vacuum work function can be applied before sample damage or breakdown occurs.

During this interval preliminary attempts were made to observe both the tunneling of electrons through an insulator and the emission of electrons into vacuum. Diode devices were fabricated from 1/2" diameter pure Al discs 0.025" thick.* The discs were first electro-polished in a perchloric acid-ethyl alcohol solution.** They were then anodically oxidized in a solution of 3% tartaric acid neutralized to pH 5.5 with NH_4OH .† A 3/16" diameter center portion was oxidized to a desired thickness of the order of $100 \text{ \AA}$, and the surrounding portion was oxidized to $1000 \text{ \AA}$.

Two methods were tried to accomplish this oxidation to different thicknesses. One method involved the anodizing of the entire disc to the desired center thickness, e.g., $100 \text{ \AA}$. The center 3/16" portion was then masked with ethyl cellulose and the outer portion again anodized, to $1000 \text{ \AA}$. The second method consisted of partial immersion of the disc into the anodizing

* Alcoa #1199H19.

** H. M. Tomlinson, Phil. Mag. 3, 867 (1958).

† G. Haas, J. Opt. Soc. Am. 39, 532 (1949).

solution. The disc was rotated slowly so that only the outer portion was oxidized to $1000 \text{ \AA}$. The disc was then totally immersed and the center portion anodized to the desired thickness.

A number of these samples were mounted on a trolley in a tube constructed so that a thin controlled film of Al could be evaporated over the whole sample, and a heavy Al layer could be evaporated onto the outside of the disc by suitable masking, where the oxide was thicker. Contact was made to the heavy Al layer by means of a platinum contact on a spring which could be drawn up or down with a magnet.

The I-V characteristics from the devices were very erratic. The samples tended to short out at low-current levels, of the order of microamperes, and the characteristics showed sudden random changes of voltage and current levels. In some cases currents as high as a few milliamps were observed, but these were not reproducible, and could be changed by changing the contact pressure or position. It is believed that the samples were shorted through the oxide layer and that the I-V characteristics were produced by the overlayer-contact junction. In no case was any indication of emission into vacuum observed with these devices.

In view of the above inconclusive results, it was felt that an investigation of the tunneling process of electrons through the insulator was required. To facilitate this study a more simple configuration, shown in Fig. 12, was employed. The samples consist of a metal strip 0.10" wide evaporated onto a 1" long fire-polished glass substrate. The outer surface of the

metal is oxidized to the desired thickness and metal overlayers are evaporated at right angles to the underlayer. The regions where the metal layers cross thus form a metal-oxide-metal diode suitable for tunnel current measurements. These samples can contain many diode regions on one substrate, and are suitable for four-terminal measurements which eliminate resistive errors. In addition a vacuum enclosure is not required.

Two metals were chosen for the initial experiments, Al and Ta. These were chosen because they both can be anodized in a non-solvent electrolyte to yield a dense unbroken oxide layer of uniform and reproducible thickness. Also, both oxides have large band gaps, of the order of 10 ev, so that complications from electronic conduction and avalanche breakdown are minimized. Preliminary results from samples using these materials are presented below.

B. Ta-Ta₂O₅-Al system

E. D. Savoye

Experimental devices were prepared with Ta-Ta₂O₅ in the following way. With reference to Fig. 12, a narrow strip of Ta metal was vacuum deposited through a suitable mask onto a fire-polished glass slide. The strip of Ta metal was then anodized in ammonium tartrate solution to form an oxide layer of the desired thickness.* A number of Al strips were then vacuum-deposited at right angles to the oxidized Ta strip. The regions in which the strips cross thus form the active areas, consisting of Ta metal-Ta₂O₅-Al metal sandwiches. Electrical

* The relationship between the voltage applied in the anodic bath and the oxide thickness produced is reported as 16 Å per volt in L. Holland, "Vacuum Deposition of Thin Films," Chapman and Hall Ltd., 1956, p. 517.

contact was made by means of In solder connections to both ends of each strip. Electrical measurements could then be made using a four-probe technique as illustrated, in order to eliminate errors caused by contact resistance or the bulk resistance in the films.

Samples were prepared with this technique with oxide thicknesses ranging from $32 \text{ \AA}$ to $192 \text{ \AA}$, as determined by the voltage applied to the sample during anodizing. Electrical measurements were made using the four-probe-technique shown in Fig. 12. The I-V characteristics obtained for samples Ta-4 through Ta-7, traced directly from the X-Y recorder charts, are shown in Figs. 13 through 16 respectively. Each of these samples had 5 Al strips deposited as overlayers, and consequently there are 5 active areas on each sample. There are small variations in the geometrical area of the overlap regions, and of course it is not known whether the entire overlap region is active in each case.

It is seen that some of the active areas were shorted out when measurements were first made. In other cases, for example, area #3 of Sample Ta-5, electrical breakdown was observed during the course of the measurements. In that particular case, breakdown occurred as a transition to a new I-V characteristic; in other cases breakdown has resulted in the sample becoming shorted out.

It will be noted that all the I-V characteristics display positive curvature, indicating a non-linear dependence of current on voltage. Comparison of the sets of curves obtained for the

various oxide thicknesses shows that the I-V curves are displaced toward higher voltages and lower currents as the oxide thickness increases. Thus, for example, the curves for sample Ta-4, 32 Å oxide thickness, extend to levels as high as 4 ma, over a range of voltages at which no current was detected for samples Ta-7 of 192 Å oxide thickness. One would expect such behavior in the case of tunneling currents, where the magnitude of the current density depends upon the magnitude of the electric field.

The preceding results were obtained with the Al overlayer biased positively. Measurements were also made with the reverse bias. In Fig. 17 is shown a comparison of two of the curves obtained for a particular sample, Ta-5. The upper curve was obtained with the Al layer negative, and the lower curve with the Al layer positive, with respect to the Ta underlayer. These results show that there is a rectification effect, with the Al negative as the forward direction. The results are typical of those observed with these samples.

As can be seen from the figures, there is a hysteresis effect in these measurements. The re-trace characteristically lies below the trace, for Al negative bias, and re-trace characteristically lies above the trace for Al positive bias. In addition an aging effect has been noted. That is, during the application of a bias of either polarity to the samples, the I-V characteristic of the sample is observed to shift, along the load line of the system. The direction of the shift is characteristically toward higher currents, lower voltages, for samples

biased with the Al positive, and in the opposite direction for negative bias. These shifts are consistent with the hysteresis in the curves which was noted above.

In view of the preliminary nature of these experiments, no attempts at analysis of the results will be made at this time. The experiments with the Ta-Ta₂O₅ system will be continued during the next interval. It is anticipated that measurements will be extended to lower temperatures in order to determine whether the processes of importance are temperature dependent.

C. Al-Al₂O₃-Al system

O. L. Nelson

Al-Al₂O₃-Al samples were prepared by vacuum depositing 0.10" strips of Al on fire-polished glass and anodically oxidizing the strips to the desired thickness. Al overlayer strips were then deposited at right angles to the base having widths of 0.02", 0.04", 0.06", 0.08" and 0.10". (See Fig. 12.) Connections were made to both ends of each strip with indium solder.

The first three samples constructed contained three base strips on a single 1" x 1" glass slide. These were unsatisfactory for detailed measurements because several shorted active areas could form closed paths which could effect measurements taken at another active area. Subsequent samples contained a single underlayer on a 1" x 1/2" glass slide, again with the five overlayers of varied widths. Measurements have been obtained from two such samples, Al-4 which was anodized at 6 volts yielding a nominal 75 Å oxide layer, and Al-5, anodized at 3 volts corresponding to a 38 Å thick oxide layer. The resistance of all layers was less than 5 ohms.

Measurements were made using a four-terminal method as shown in Fig. 12. The I-V characteristics were recorded on an X-Y recorder. Characteristics from the 0.06" overlayer of Al-4 and Al-5 are shown in Fig. 18. Notice that a hysteresis effect was observed for some of the traces, and that Al-4 showed a marked voltage shift when the overlayer polarity was reversed, while Al-5 showed a slight shift in the opposite direction. Note also that the maximum current drawn was about 30 μ a. Other active areas were broken down at current levels less than this value, and no sample has withstood more than 50 μ a of current. The breakdown is sudden, with no noticeable current increase prior to breakdown.

The high field tunnel emission formula as given by Fowler and Nordheim is*

$$J/J_0 = (E/E_0)^2 e^{-E_0/E} ,$$

where E is the field strength and E_0 and J_0 are parameters dependent on the material. To compare the results from Al-4 and Al-5 with this expression, plots of $\log I/V^2$ versus I/V were prepared, and are shown in Figs. 19 and 20. As can be seen, the data from each sample cannot be fit by a single straight line, because of the hysteresis effect. Nevertheless each set of points was assigned a straight line, which was used to calculate an experimental value for E_0 . The slope of the lines gives values of V_0 , from which $E_0 = V_0/d$, where d is the oxide thickness, can be calculated. From the theoretical expression for

* R. H. Fowler and L. Nordheim, Proc. Roy. Soc. (London) A119, 173 (1928).

E_0^*

$$E_0 = \frac{8\pi}{3} \frac{2m^* \phi^{3/2}}{he} = 6.8 \times 10^7 (\phi)^{3/2} \text{ v/cm} ,$$

the potential barrier height ϕ , in ev, can be found. For the data presented, using the straight line fits, the computed values of E_0 and ϕ are shown in Table I.

Table I

Sample	Oxide Thickness	Overlayer Polarity	Voltage Sweep	E_0 , v/cm	ϕ , ev
Al-4	75 Å	+	increase	8.6×10^7	1.17
		+	decrease	9.7	1.27
		-	increase	12.5	1.48
		-	decrease	12.6	1.50
Al-5	38 Å	+	increase	15.5	1.73
		+	decrease	11.8	1.45
		-	increase	9.0	1.20
		-	decrease	14.0	1.62

From the variations of E_0 and ϕ for the same sample and polarity it is concluded that the Fowler-Nordheim formulation is too simple to describe the observed data. The hysteresis effect superimposes a time-current dependent variation. The widely separated characteristics from Al-4 for several polarities

* Ibid. (The numerical constant has been corrected.)

illustrate the difference between the two metal-oxide interfaces, which were formed in quite different ways.

These preliminary results illustrate some of the phenomena which warrant further investigation. In particular, the temperature and time dependence of the hysteresis effect are of interest. Also the dependence on some of the processes of construction of the samples should be investigated.

IV. Conclusions

In addition to transients of the order of milliseconds which occur under long-pulse operation of oxide cathodes, additional emission transients with time constants of a few seconds are being observed. The emission decay, and recovery upon cessation of dc current drain, can be quantitatively measured by the use of a train of 3 μ sec pulses which lead to a display of the I-V characteristics of the diode as a family of curves.

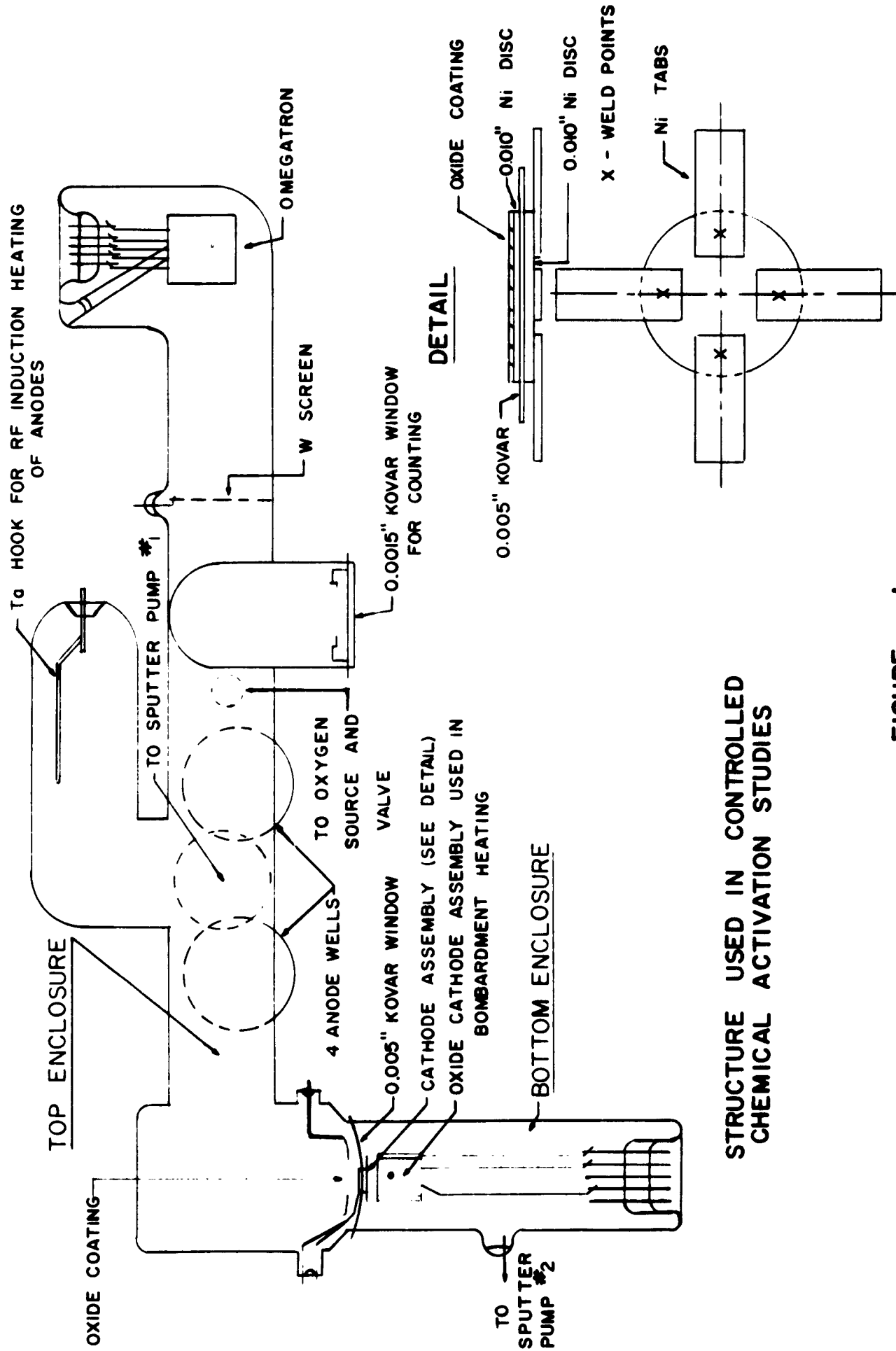
Preliminary results indicate a correlation between the photoelectric yield and the thermionic pulse emission from a BaO coating. An enhancement of the dc thermionic emission with incident photons in the 3.5 to 3.9 eV range has been observed with the cathode temperature at 230°C. Two thin film BaO coatings have been prepared and measurements inaugurated.

The emission of electrons into a vacuum from a "cold cathode" consisting of field emission of electrons from a metal into an insulating film with subsequent penetration through, and escape from, a thin metal overlayer, has not been observed. However, thin film diodes have been constructed and studied using Ta-Ta₂O₅-Al and Al-Al₂O₃-Al as the base, insulator, and overlayer respectively. Emission through the insulator has been observed in both cases. The I-V characteristics of the device indicate such phenomena as rectification and time-dependent hysteresis. Consequently, detailed studies of time constants and temperature-dependence of these characteristics are indicated before the exact nature of the emission mechanism can be determined.

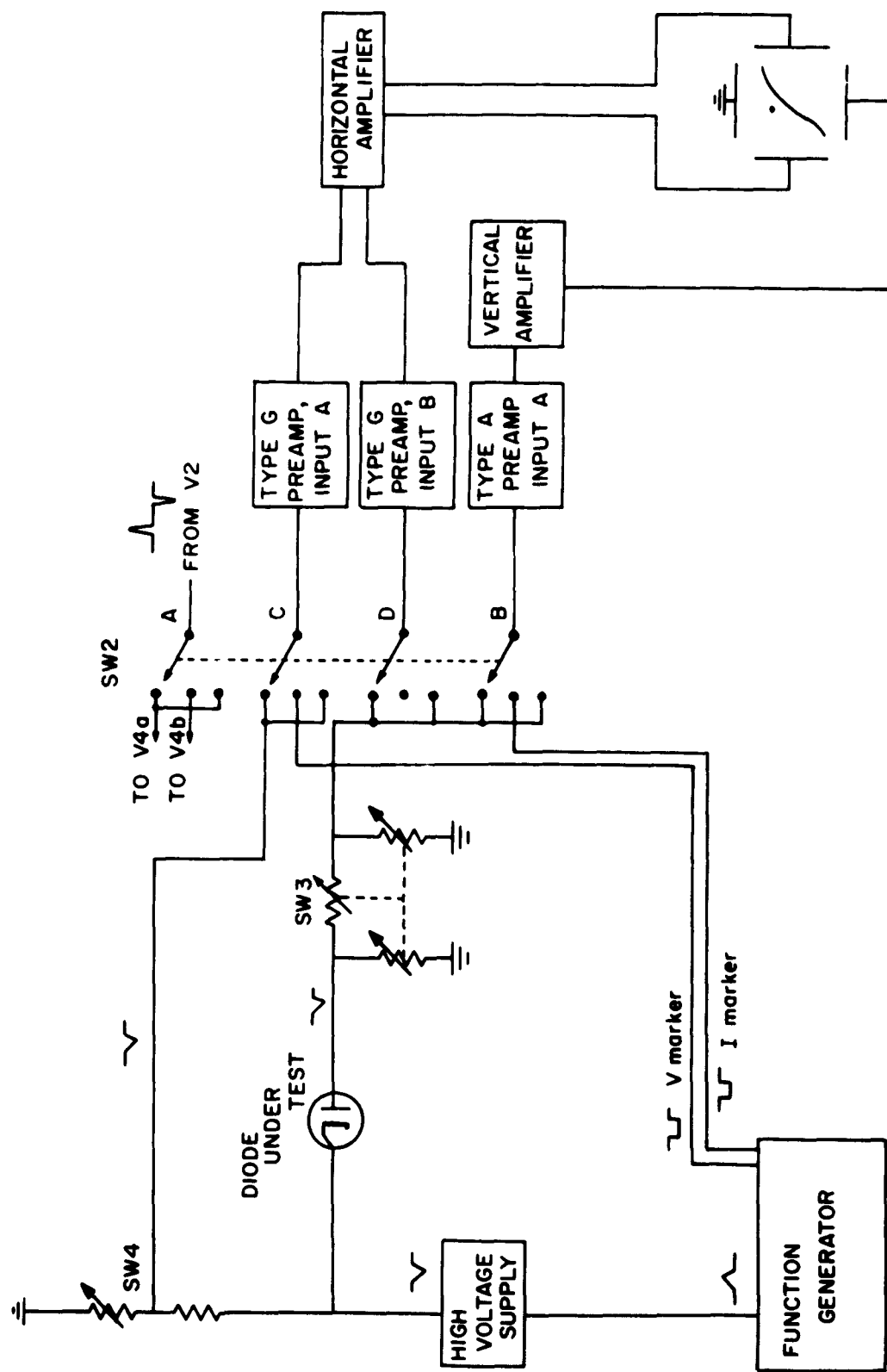
V. Personnel Employed on Contract

	<u>Percent</u>	<u>Man Months</u>
W. G. Shepherd, Professor	10	3.0
K. M. van Vliet, Associate Professor	5	3.0
D. E. Anderson, Associate Professor	25	3.0
D. A. Campbell, Research Fellow	60	3.0
O. L. Nelson, Research Fellow	100	3.0
E. D. Savoye, Research Fellow	100	3.0
R. H. Springer, Research Fellow	100	3.0
C. A. Stolte, Research Fellow	100	3.0
*R. J. Kirk, Research Assistant	50	1.0
Secretary	50	3.0
Engineer	11	3.0
Laboratory Technical Assistants	2,026.8 Man Hours	

*Terminated employment March 31, 1961.



STRUCTURE USED IN CONTROLLED
CHEMICAL ACTIVATION STUDIES



PULSE EMISSION TRACER SIMPLIFIED BLOCK DIAGRAM

I-V CHARACTERISTICS FOR
DIFFERENT VALUES OF TIME
DURING DC CURRENT DRAIN

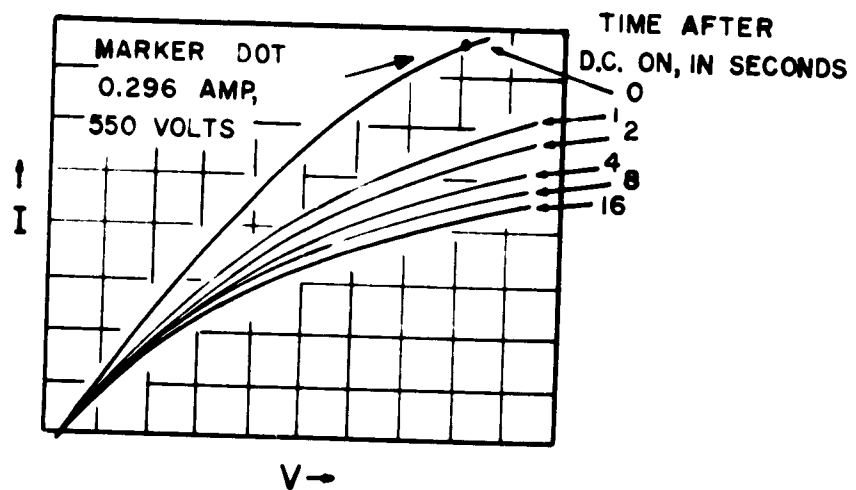


FIGURE 3

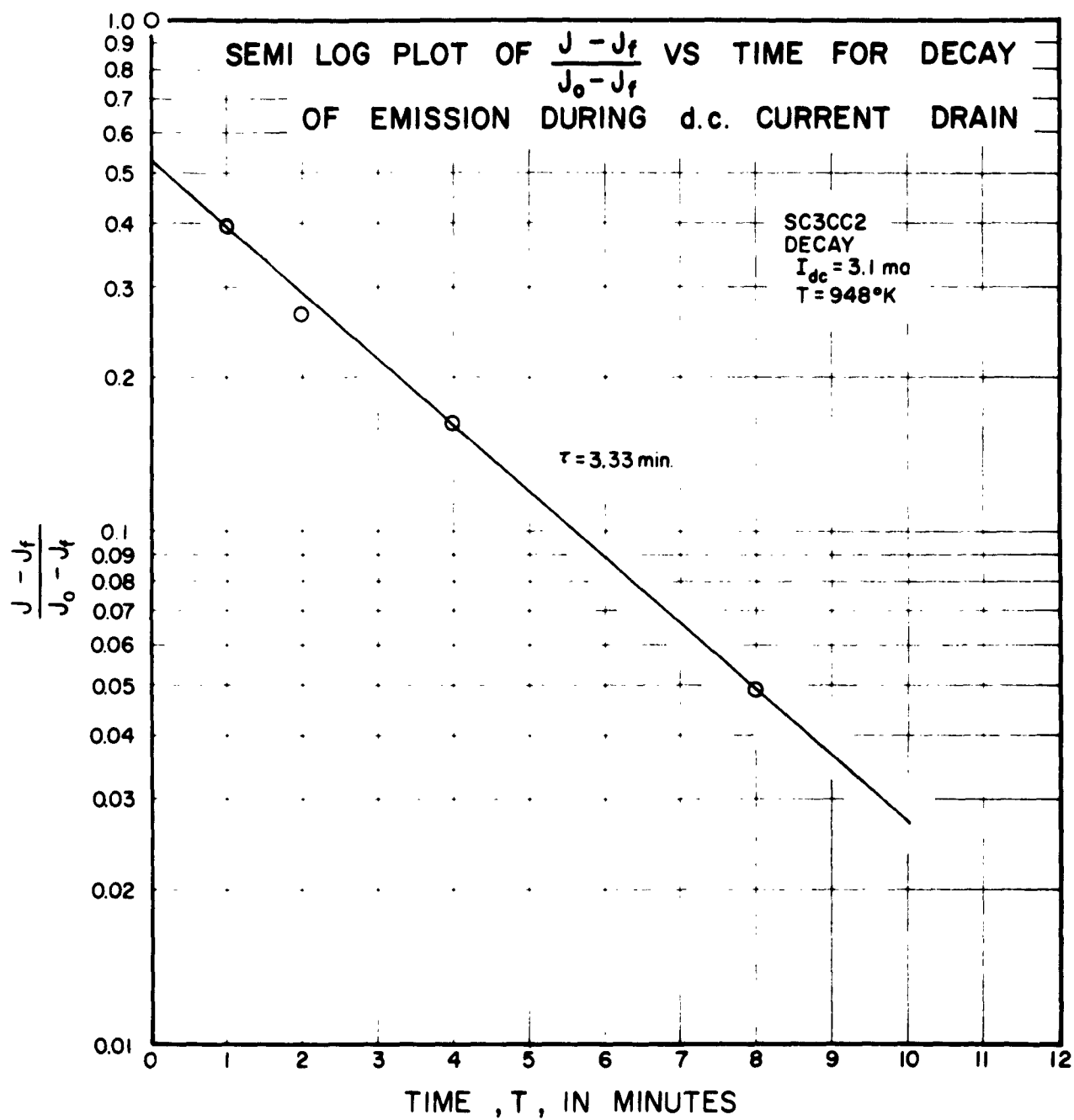
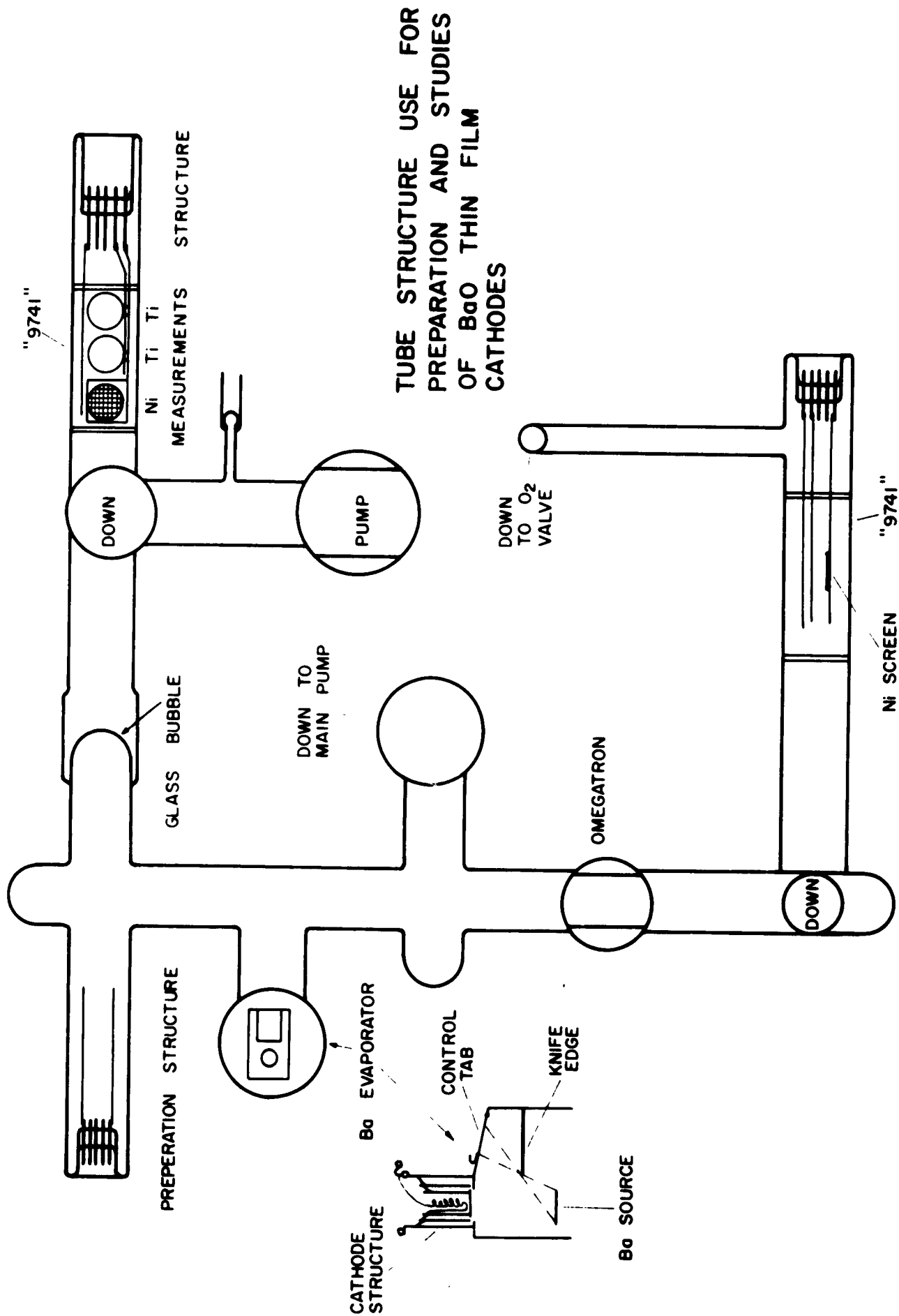


FIGURE 4



TUBE STRUCTURE USE FOR
PREPARATION AND STUDIES
OF BaO THIN FILM
CATHODES

FIGURE 5

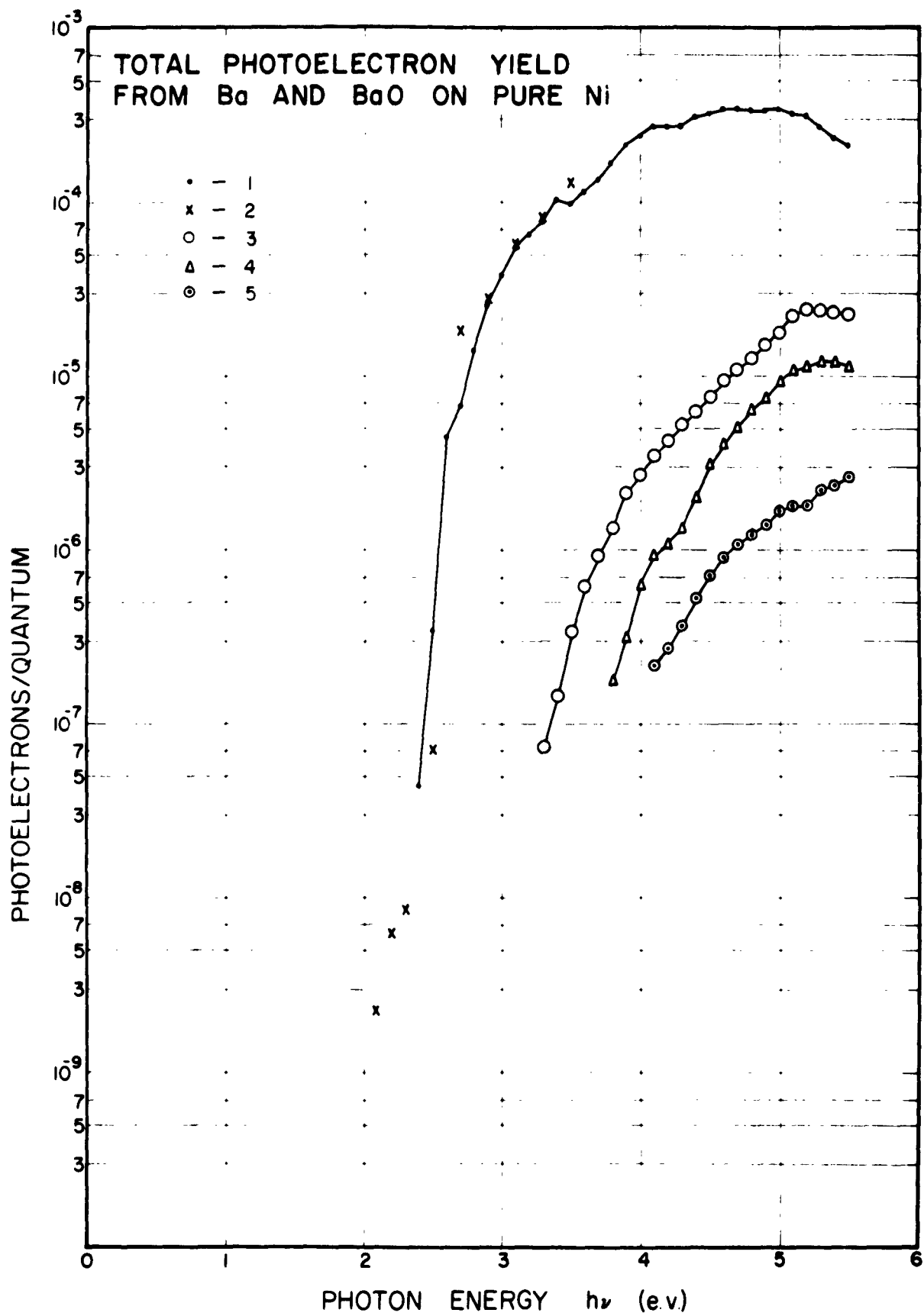


FIGURE 6

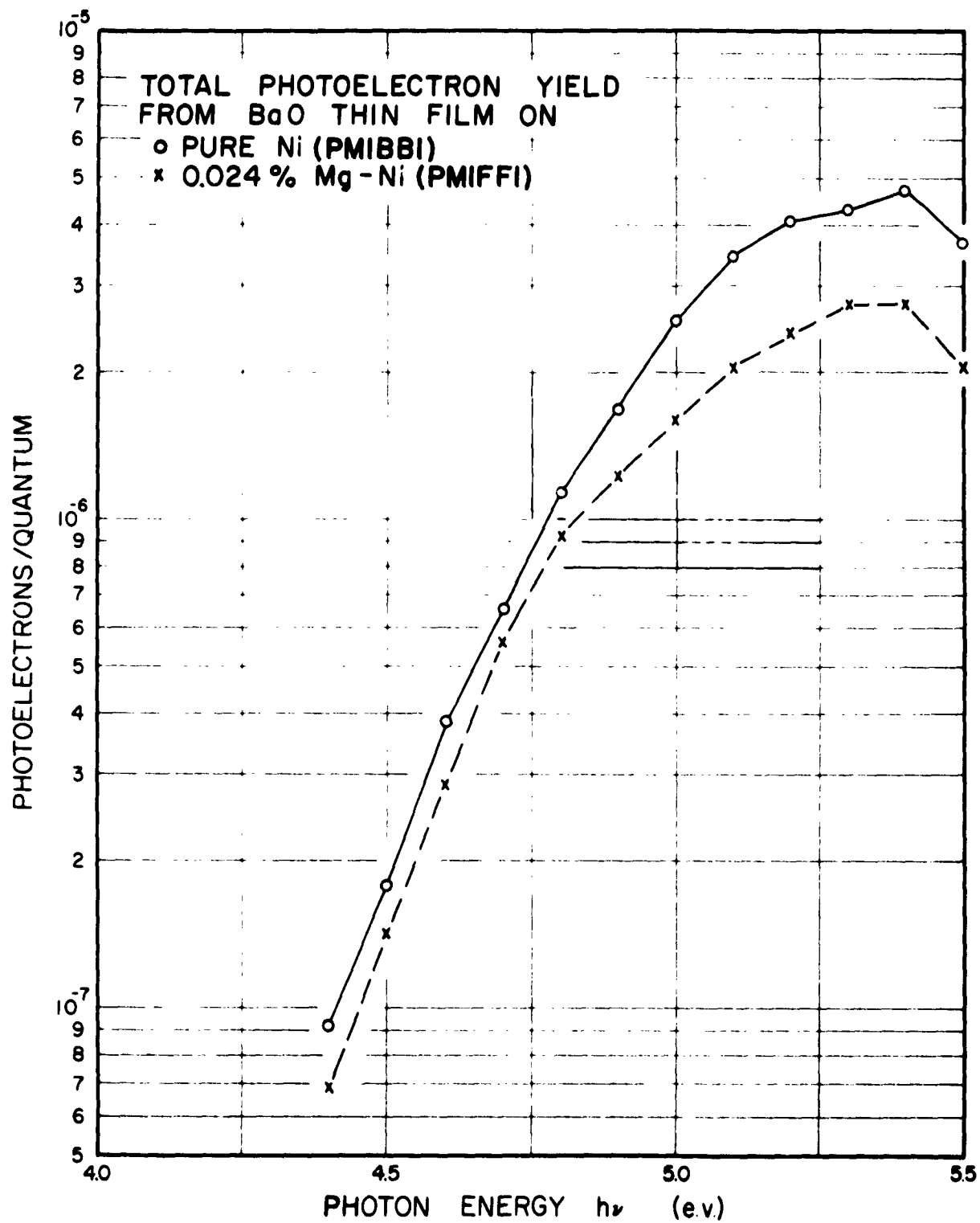


FIGURE 7

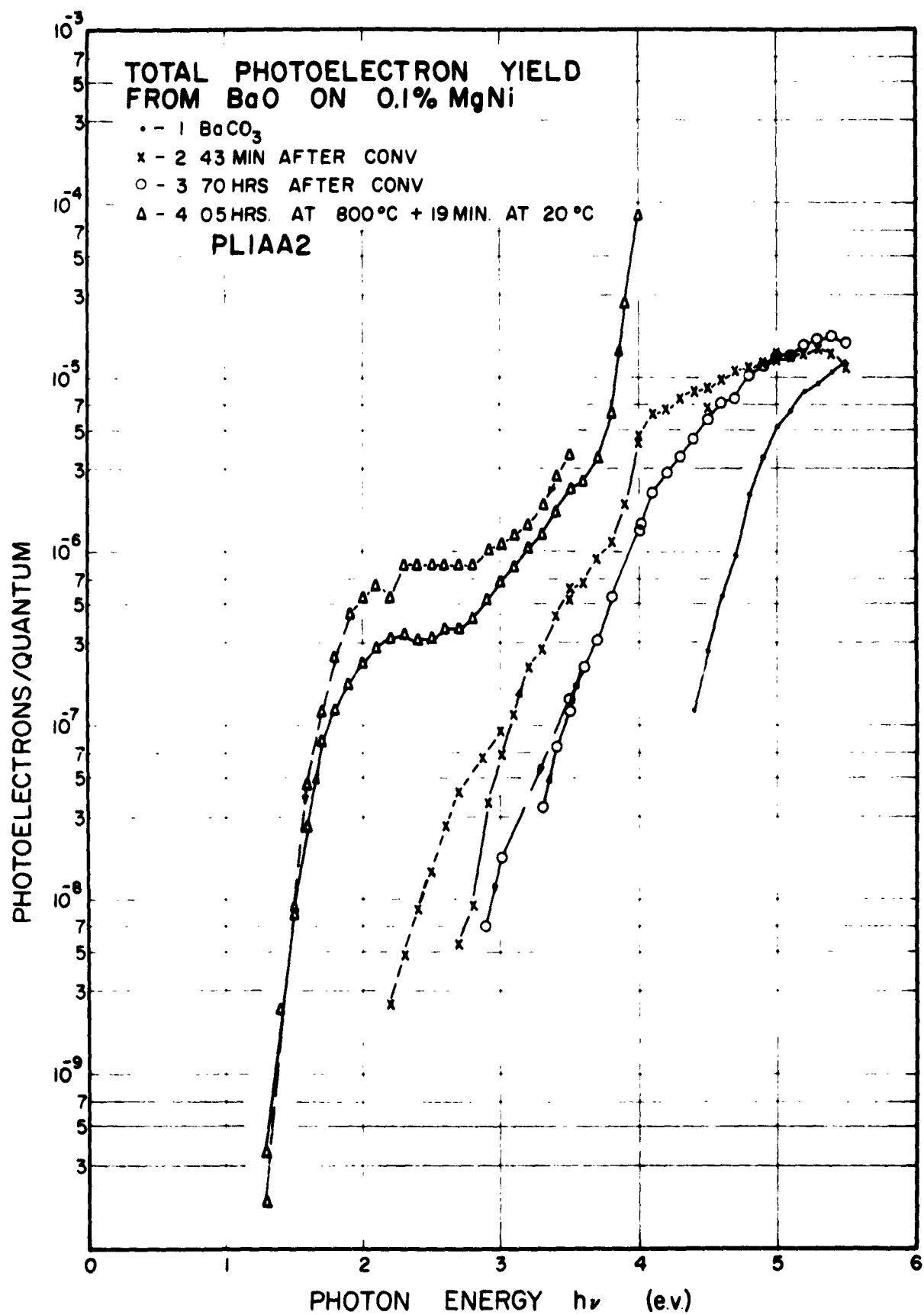


FIGURE 8

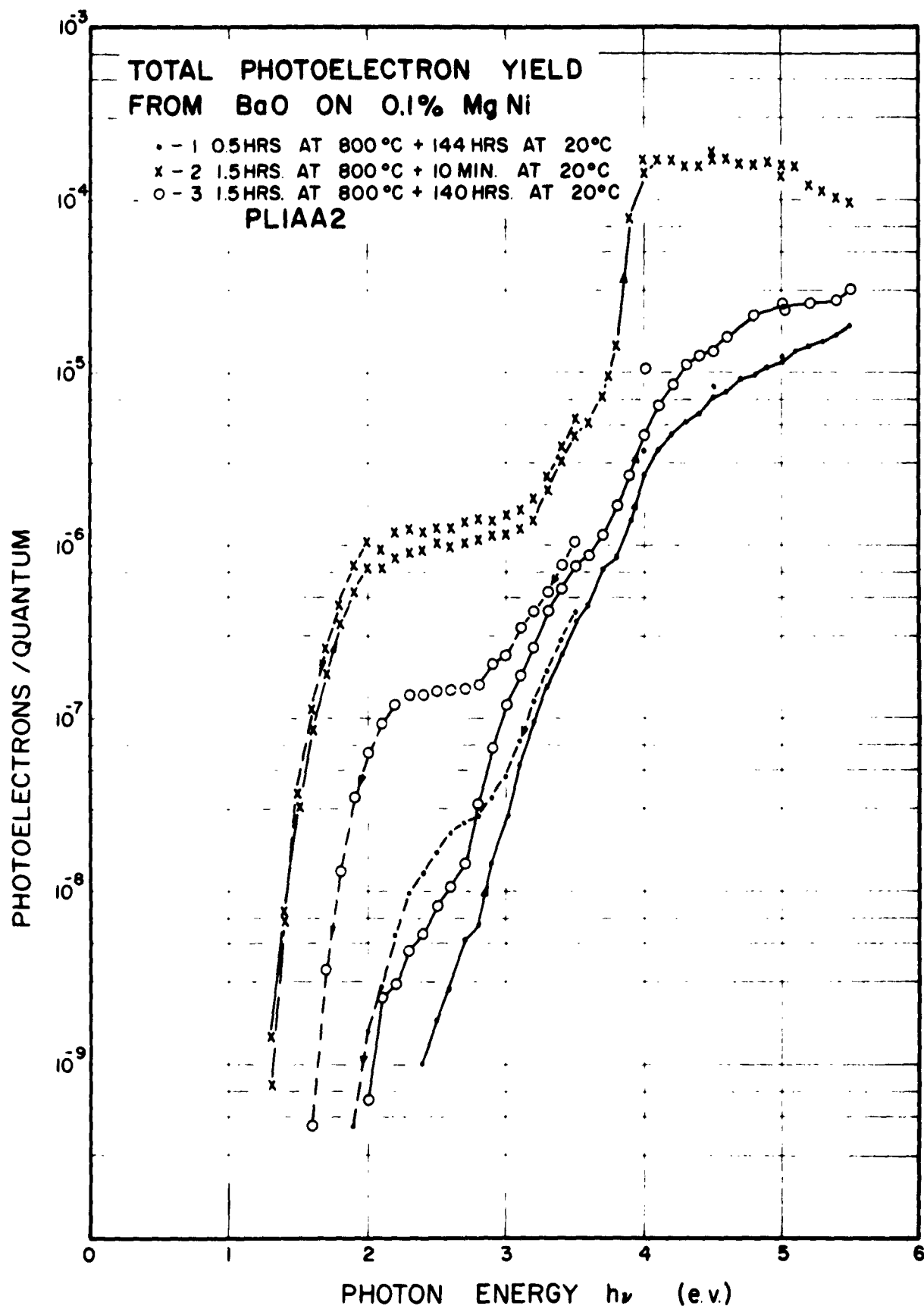


FIGURE 9

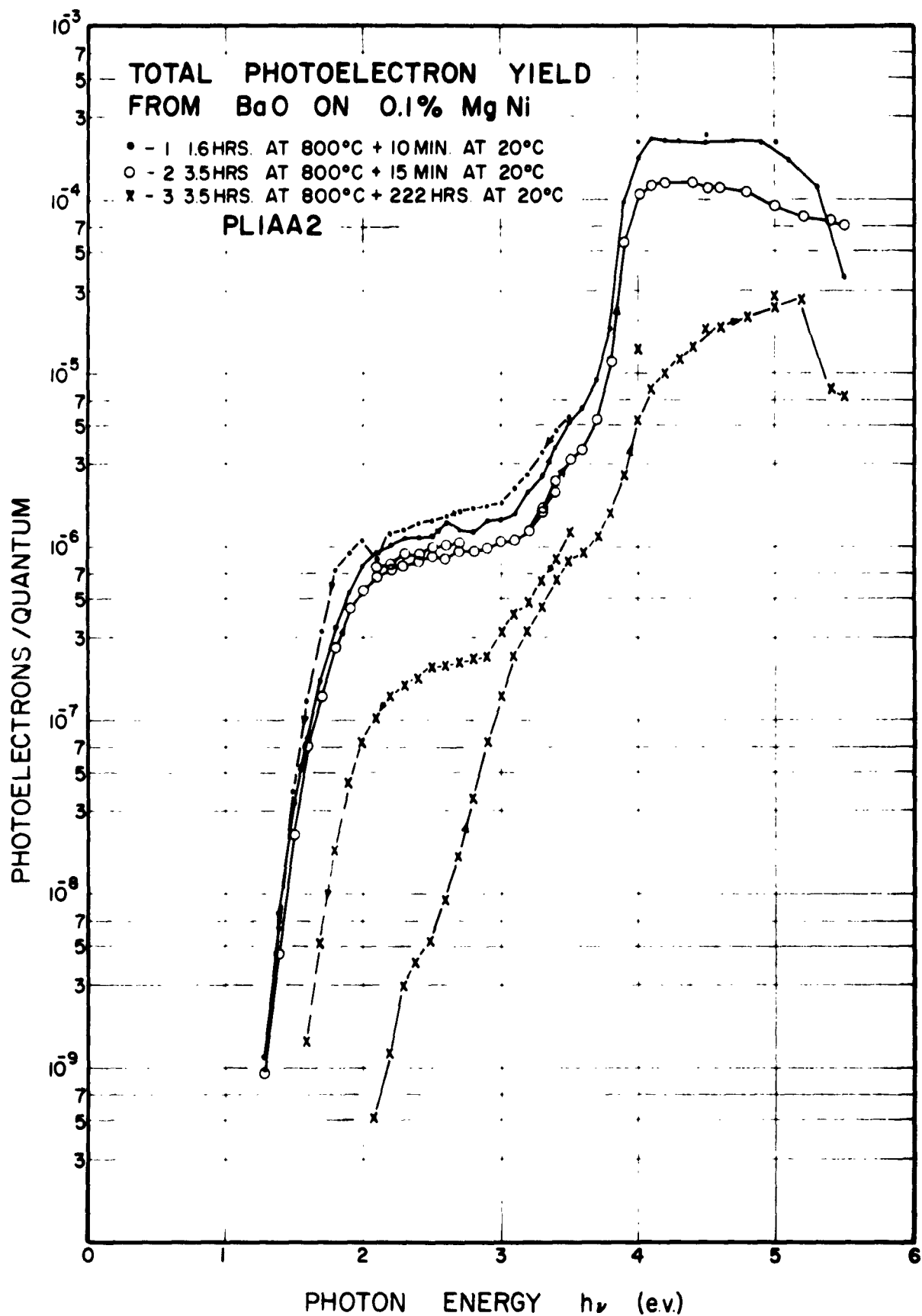


FIGURE 10

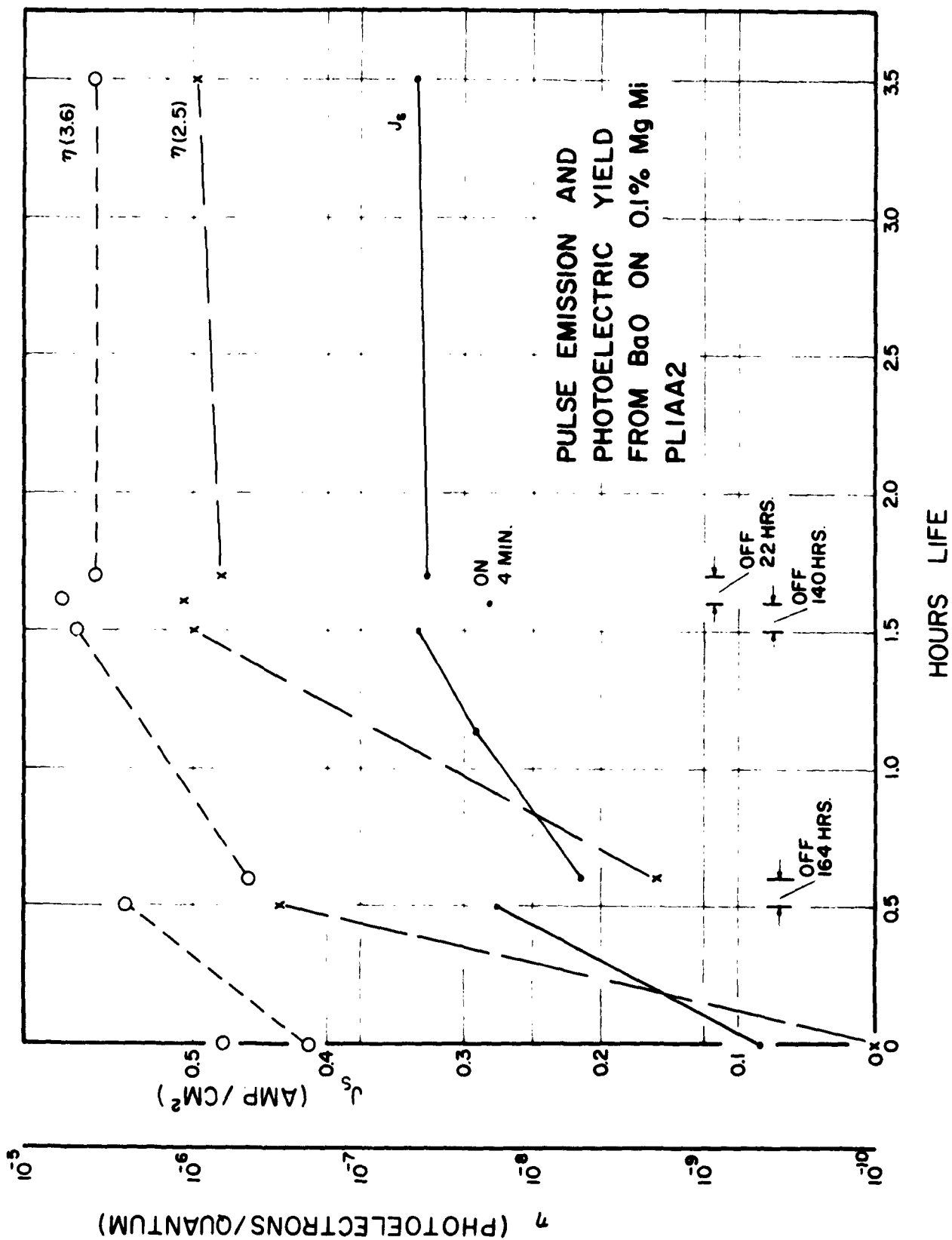
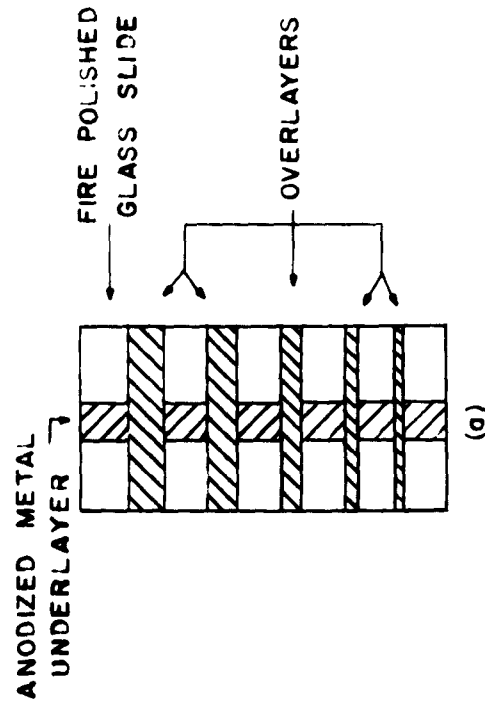


FIGURE 11

SCHEMATIC OF SAMPLE USED FOR TUNNEL CURRENT MEASUREMENTS



SCHEMATIC OF MEASUREMENT TECHNIQUE FOR TUNNEL CURRENT DEVICES

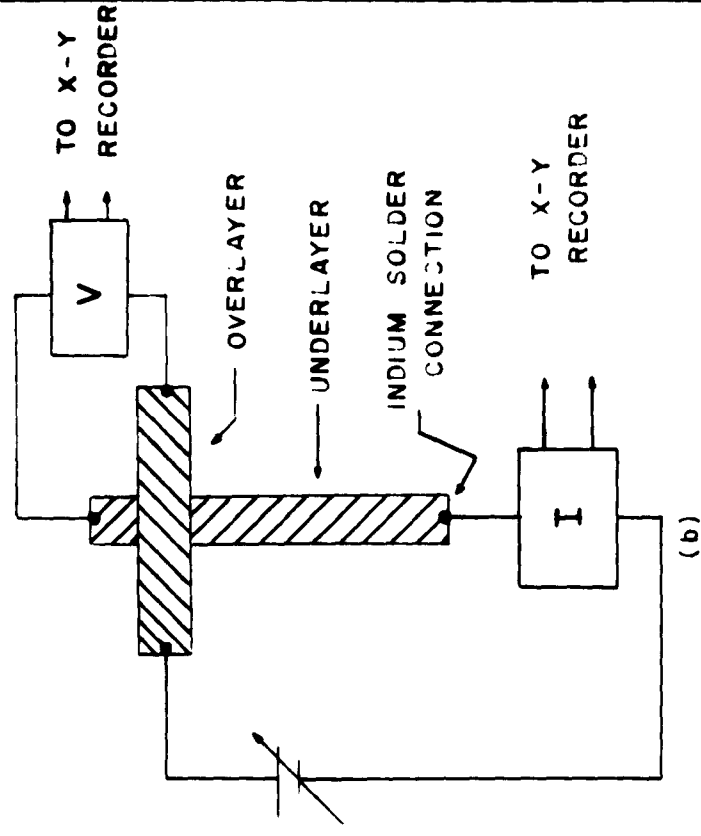


FIGURE 12

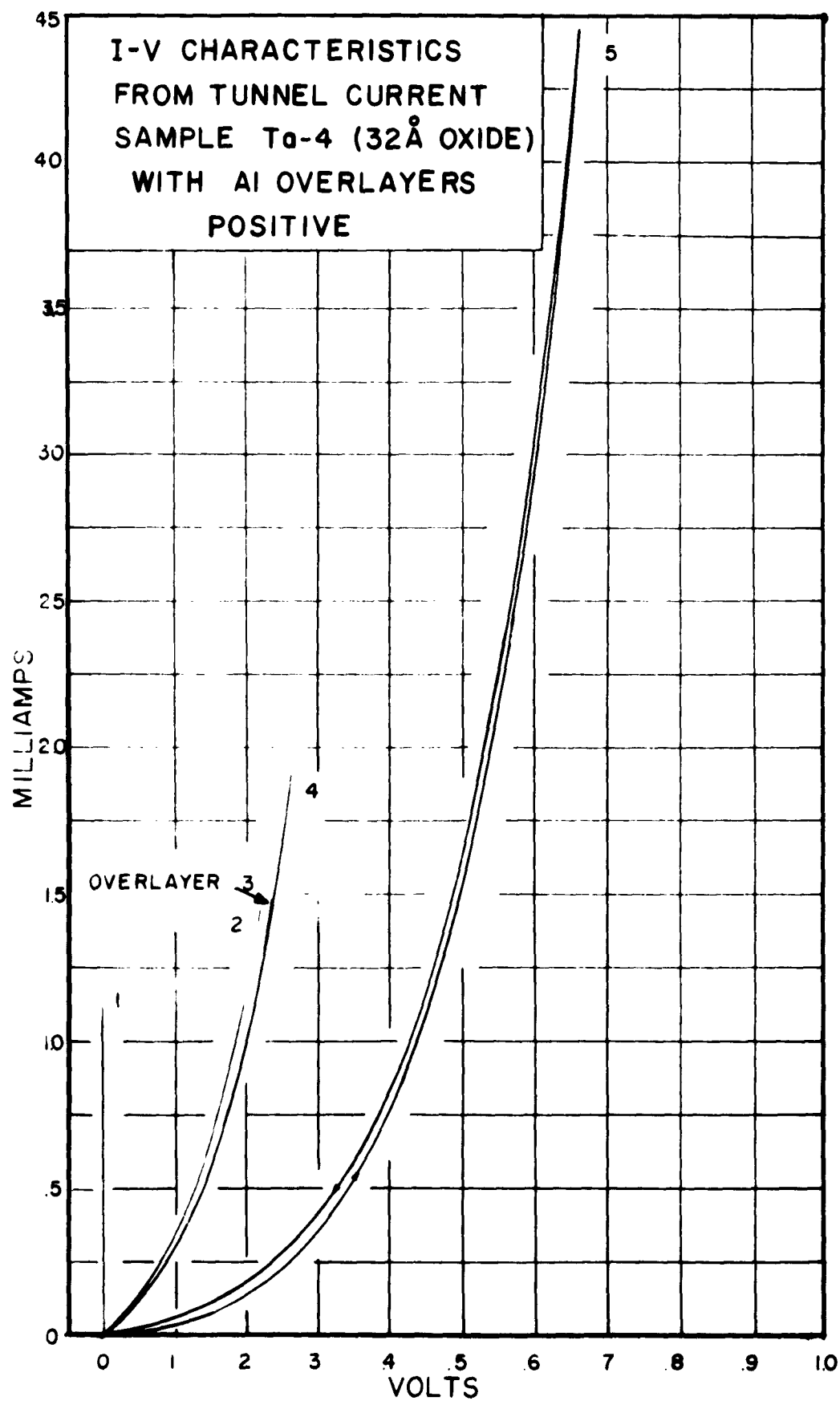


FIGURE 13

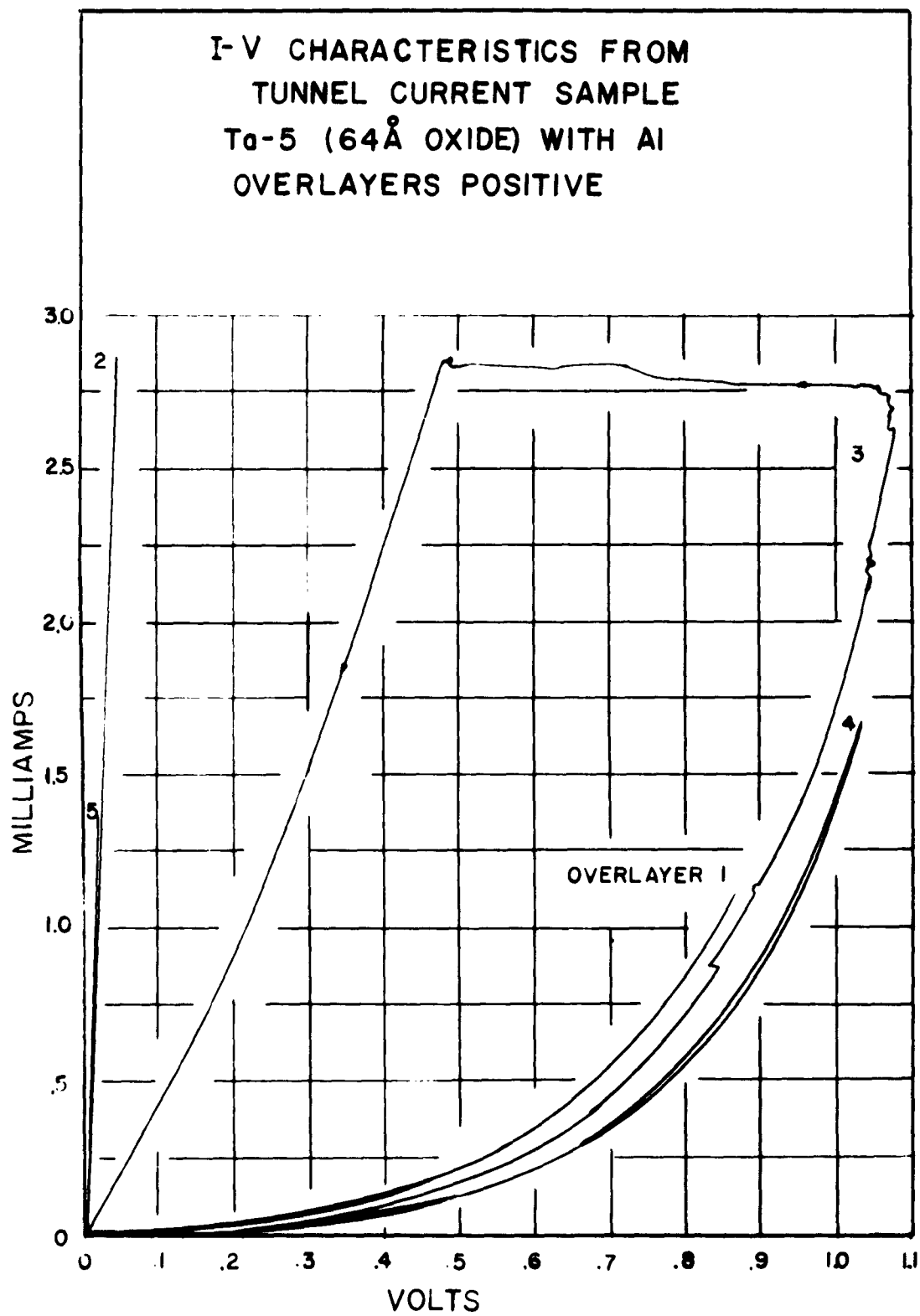


FIGURE 14

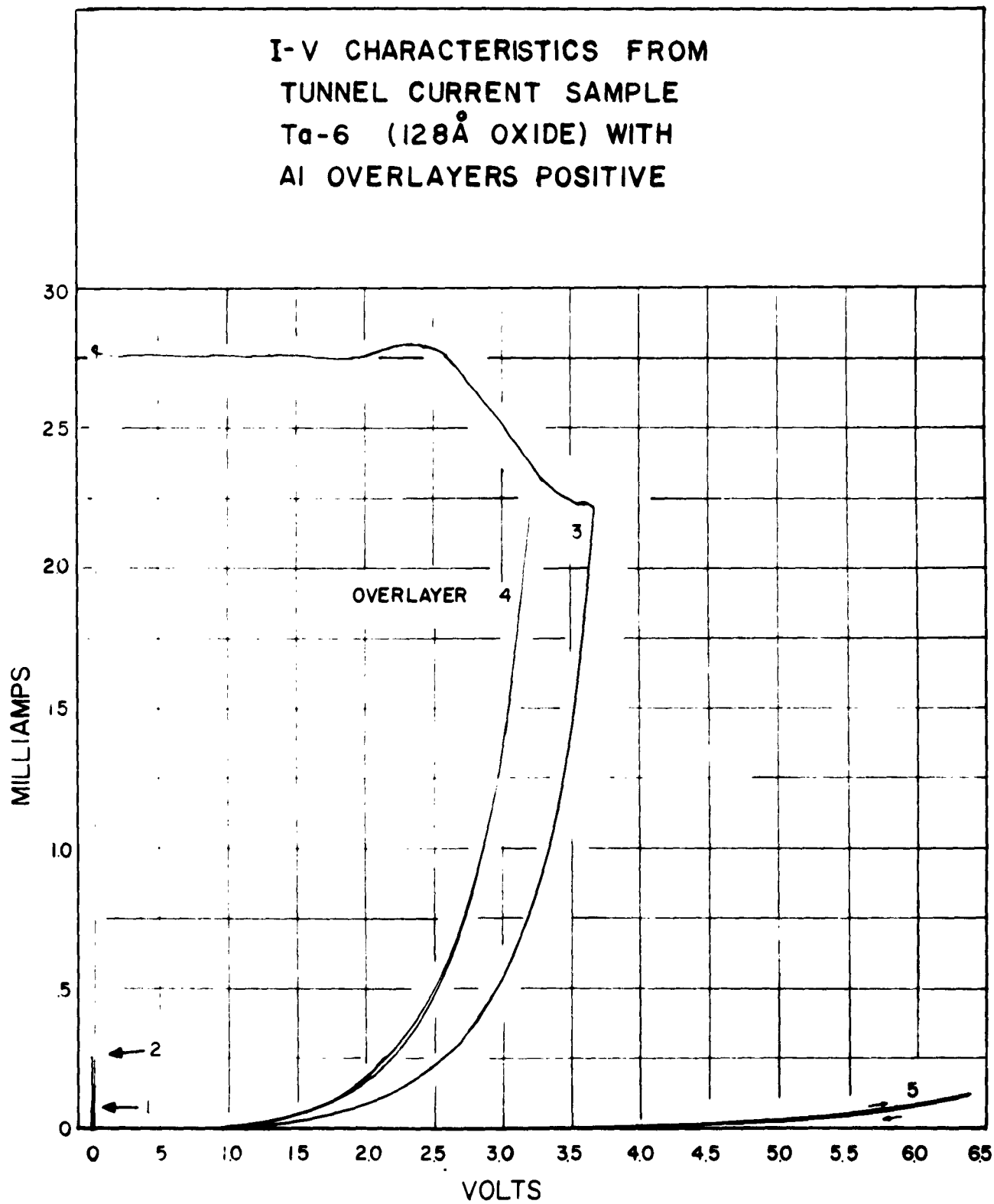


FIGURE 15

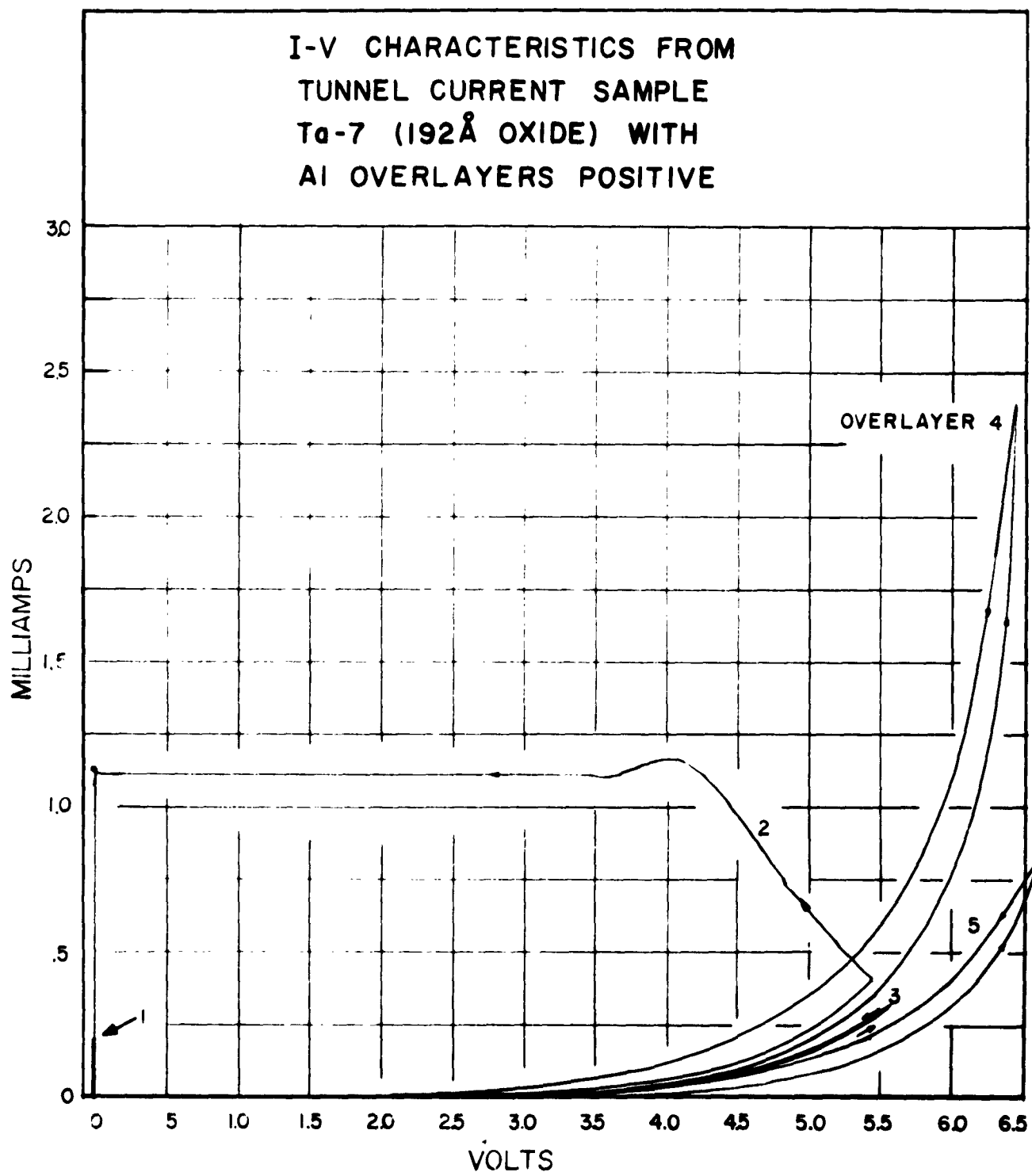


FIGURE 16

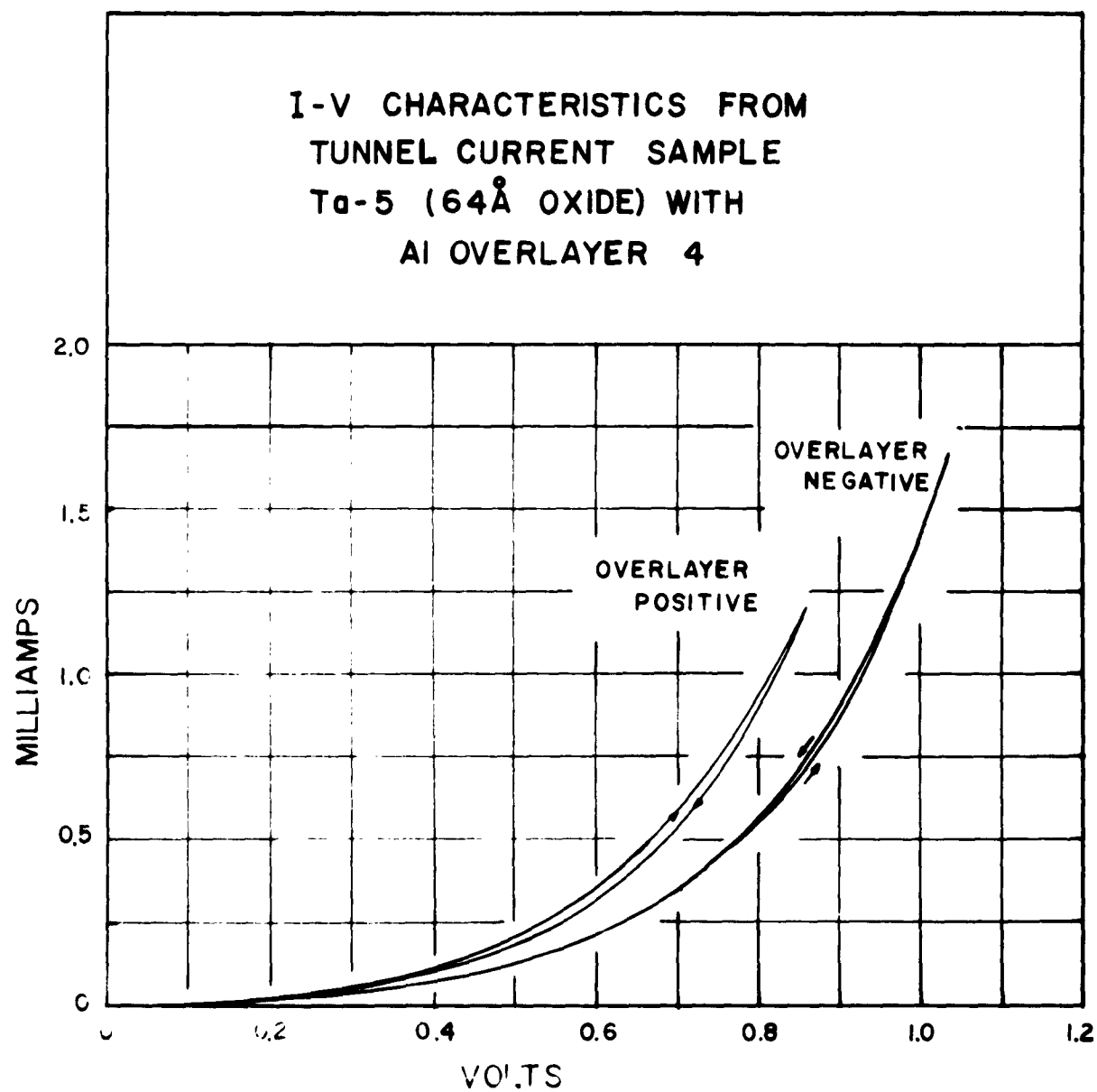


FIGURE 17

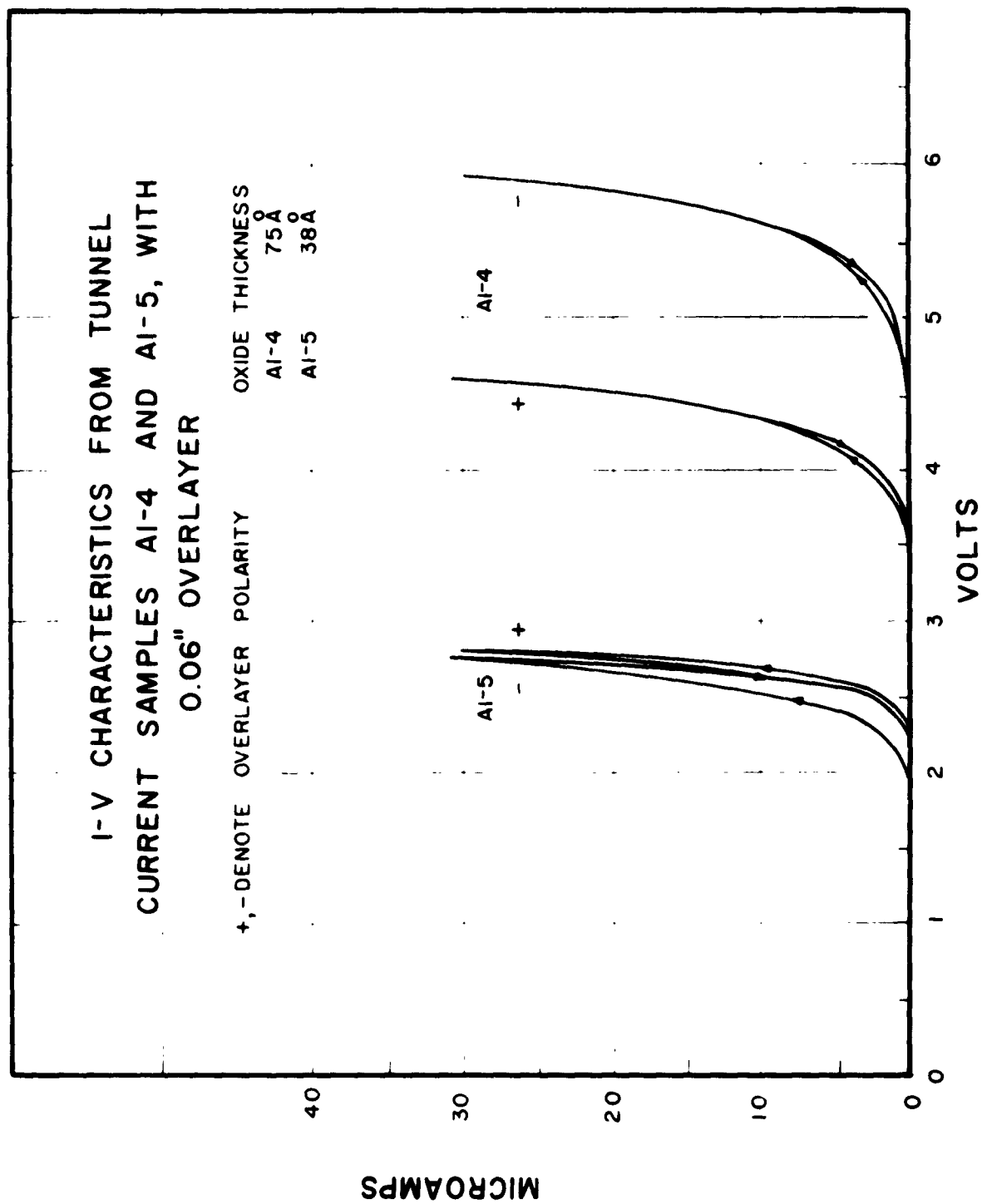


FIGURE 18

LOG I/V^2 VERSUS $1/V$
 FROM TUNNEL CURRENT SAMPLE
 Al-4 (75Å OXIDE) USING
 006" OVERLAYER

• VOLTAGE INCREASING
 X VOLTAGE DECREASING

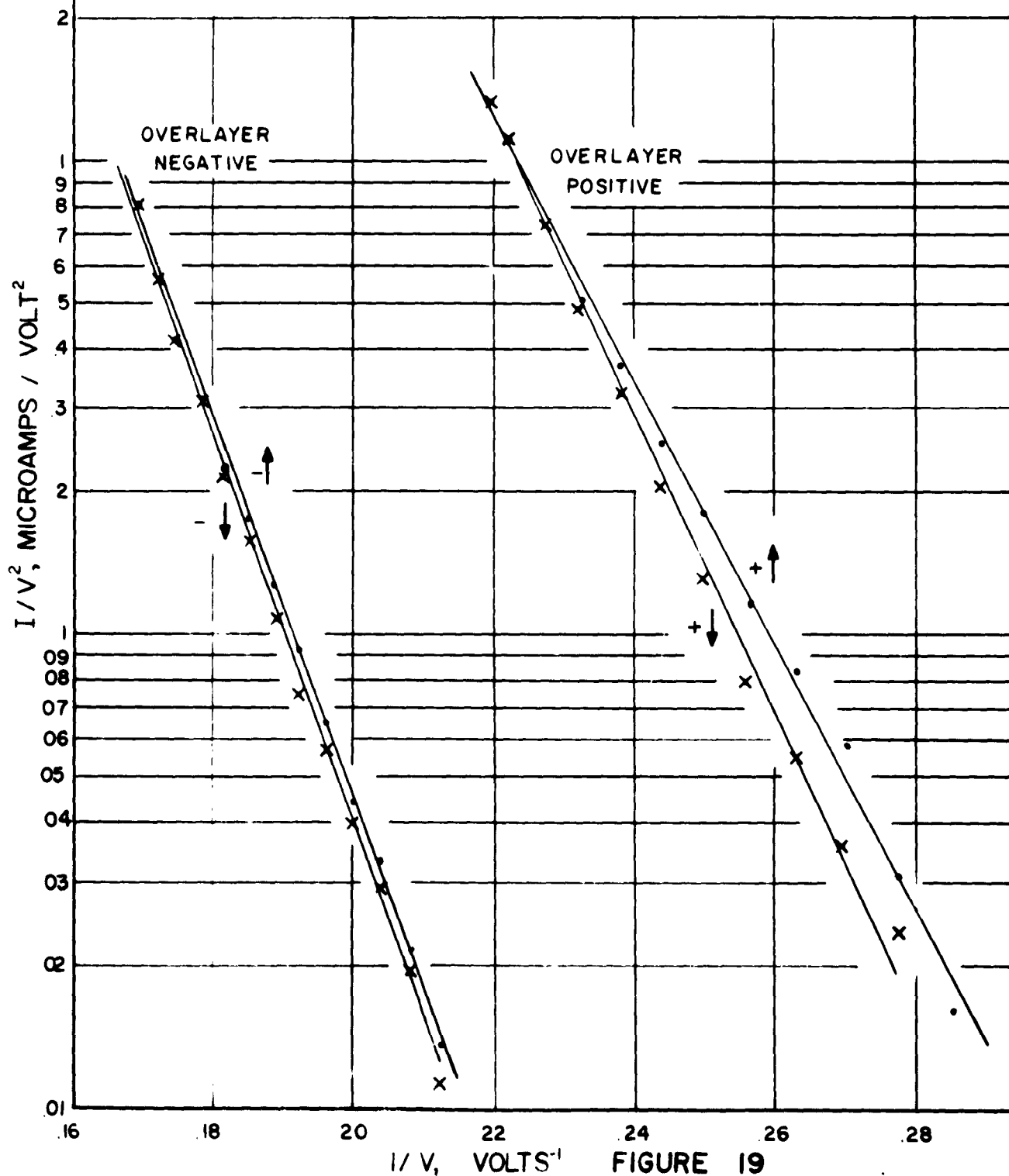


FIGURE 19

LOG I/V^2 VERSUS $1/V$
 FROM TUNNEL CURRENT SAMPLE
 Al-5 (38Å OXIDE) USING
 0.06" OVERLAYER

