

Thin Film Field Emission

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Aluminum, oxidized electrolytically, and subsequently treated with caesium and oxygen possesses new and interesting properties when subjected to electron bombardment in the presence of an adjacent collector electrode whose potential is held positive with respect to the aluminum. True secondary electron emission from the treated surface results in the establishment of a positive charge on the surface and a polarization of the oxide film. This positive charge acting through the thin oxide film produces a high gradient, resulting in the emission of electrons through the surface. The emission increases with collector voltage and beam currents, obeying power laws, but

exhibits saturation tendencies. The removal of the primary beam does not result in the immediate cessation of the field emission, but rather in a slow decay which is due to the fact that the surface charge takes an appreciable time to leak away. Similar time lags are noticed when the beam is first applied, particularly if the collector voltage has been reversed while the beam impinges on the surface. The surfaces are also light sensitive, in that light causes a decrease in the field emission and a speeding up of decay. Attempts were made to demonstrate this effect for other surfaces, but, with a few exceptions, the results were negative.

INTRODUCTION

THIS paper constitutes a more extended report of a letter published recently¹ under the title "Anomalous Secondary Electron Emission." Considerable criticism of this name for the phenomenon involved has arisen as not being descriptive of its apparent nature and, consequently, the above title suggested by Dr. J. A. Becker has been adopted.

In a search for a surface possessing a high secondary emission ratio, a considerable number of composite surfaces of various types were investigated. In the case of aluminum oxide treated with caesium and oxygen in a manner to be described below, it was found that a primary electron beam impinging upon the surface caused a current flow to a positive collector which, in certain cases, was several thousand times as great as the primary current. The phenomenon differed from that in the case of normal secondary emission in that the collector current was dependent upon the collector potential and primary current density. It exhibited very marked time lag characteristics and was also affected by light.

EXPERIMENTAL PROCEDURE

A. Tube and circuit

A diagram of the tube employed, together with the accompanying circuit is shown in Fig. 1.

* Now at RCA Manufacturing Company, Camden, New Jersey.

¹ Malter, Phys. Rev. **49**, 478 (1936).

The cathode was of the barium oxide-strontium oxide type. The electron gun parts were made of tantalum. The electrodes on the walls of the tube were platinum formed by the reduction of Hanovia platinizing solution. The regions around the "side contacts" were coated with silver formed by the reduction of Hanovia silver paste.

The platinum film consisted of two portions, the first serving as the so-called "second anode" of the electron gun. The second portion served to collect the electrons emitted from the target. If a single film is used as both second anode and collector, a change in collector voltage (V_c) causes a much greater change in beam spot size than if two separate films are employed as shown. This precaution was necessary in view of the dependence of the collector current upon beam spot size.

The caesium was produced by exploding compressed pellets of powdered caesium chromate and zirconium in a side tube.

Two pairs of deflecting coils (not shown in Fig. 1), mounted just beyond the first anode (at right angles to each other), served to position the beam on the target.

B. Formation of the oxide film

The aluminum oxide was formed by making the aluminum the anode in a bath wherein the cathode was a platinum foil. Various composition baths were tried. Satisfactory results were obtained with a saturated solution of borax and boric acid.

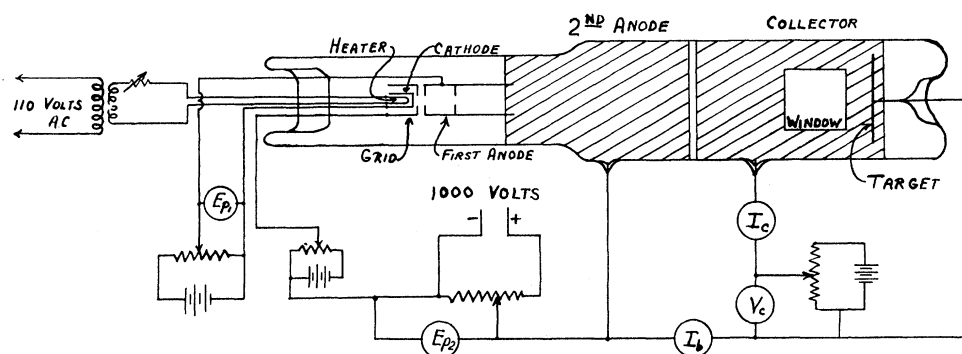


FIG. 1. Schematic diagram of apparatus.

It has been shown² that for times of formation in excess of a few minutes the thickness of the oxide film formed is practically independent of the time and the bath employed. The thickness is given by the relation

$$D = 17.0 V,$$

where D is the oxide thickness in Å and V is the applied potential in volts. However, the resistance of the film does depend upon these factors. No real study of the effect of the nature of the bath upon the film properties appears to have been made.

If at any time during the oxidation process, the applied voltage is gradually reduced, it is found that plots of the logarithm of the applied voltage against the logarithm of the current through the film yield curves of the form shown in Fig. 2. It is seen that below a certain voltage the curve is linear. Güntherschulze and Betz³ have shown that over this linear region the current is purely electronic, whereas above this point ions move through the oxide lattice and contribute to an increase in its thickness. The portion of the current lying below the extended linear portion of the curve is electronic, whereas that above is ionic.

The prepared aluminum foil was mounted on a nickel plate for support and its edges were painted with willemite in order to permit the position of the beam to be seen by the fluorescence excited. Equally spaced circles were

scratched lightly on the willemite in order that it be possible to determine the size of the spot. For intense beams (in excess of 3 to 4 microamperes) a faint blue fluorescence appeared on the oxide surface, permitting of a direct determination of the position and diameter of the electron beam.

The tube was pumped and baked at 475°C until the pressure dropped below 10^{-5} mm of Hg. After cooling, the parts of the electron gun were outgassed by means of high frequency and the oxide cathode activated so as to be thermionically emissive.⁴

Caesium was now introduced into the tube and

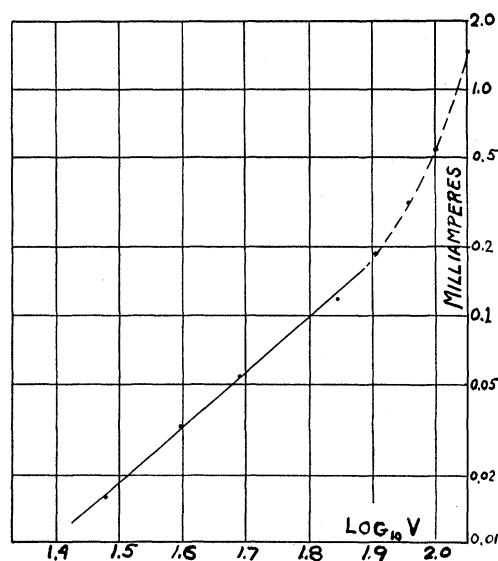


FIG. 2. Current voltage characteristic of aluminum oxide film after formation in saturated borax and boric acid bath for one hour.

² Güntherschulze and Betz, *Zeits. f. Elektrochemie* **37**, 8-9 (1931).

³ Güntherschulze and Betz, *Zeits. f. Physik* **92**, 367 (1934).

⁴ Dushman, *Rev. Mod. Phys.* **2**, 381 (1930).

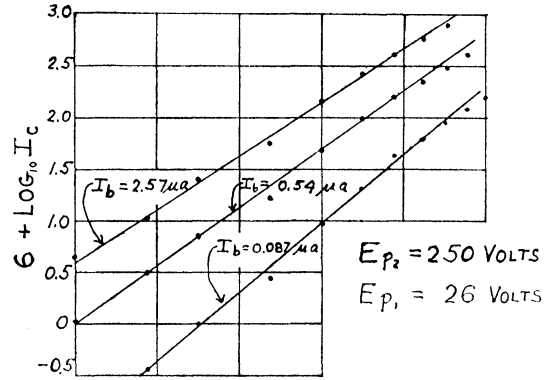
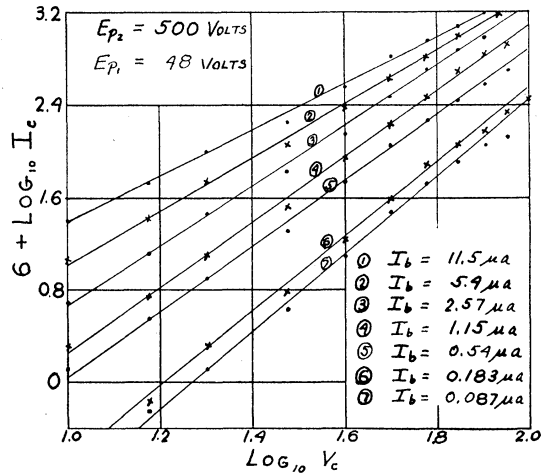


FIG. 3 (left) and FIG. 4 (right). Variation of collector current with collector potential for different values of beam current. Spot size held constant.

the tube then baked at 200°C for ten minutes. After cooling, oxygen was admitted into the tube to a pressure of 1 mm of Hg and pumped out after a few seconds. This treatment was sufficient to bring about the appearance of the thin film field emission, or enhance it in cases where it was present prior to any treatment.

It was found impossible to secure completely reproducible results. In an effort to determine the possible reason for this, all chemicals used were recrystallized and the water redistilled, and, in addition, the purest obtainable aluminum was secured from the Rheinische Blattmetall A.G.⁵ However, their material was no better in this respect than the available commercial "electrolytic condenser" aluminum.

EXPERIMENTAL RESULTS

Except where noted the measurements given were obtained from a tube having aluminum with an oxide thickness of 2000Å. While the exact results obtained differ from those in other foils with the same oxide thickness, the essential conclusions and laws are the same, the actual magnitudes only being affected.

A. Variation of collector voltage (V_c)

If the beam current (I_b), second anode voltage (Ep_2) and spot size are held constant, the

variation of the collector voltage (V_c) causes a rapid variation in the collector current (I_c).

The results for different values of I_b for the cases wherein ($Ep_2=500$ volts, $Ep_1=48$ volts) and ($Ep_2=250$ volts, $Ep_1=26$ volts) have been plotted in logarithmic coordinates in Figs. 3 and 4. These combinations of Ep_1 and Ep_2 yield the same spot size.

In general, it is seen that:

$$I_c = B(V_c)^m. \quad (1)$$

At this point, it should be made clear that the results apply to only one region of the target. The values of I_c obtained from different regions of this surface vary considerably. However, if one restricts oneself to a particular region and is careful not to alter the surface in the manner to be described below, the results are reproducible. In these measurements as well as in those that follow (except where noted) all the data were obtained at the spot on the surface which yielded largest collector currents.

B. Variation of beam current

A series of readings were taken, everything being held constant except I_b . The results for $Ep_2=500$ volts, $Ep_1=48$ volts, and different values of V_c are plotted in Fig. 5. All of these curves are "repeats." It is found that if I_b is increased in steps, and corresponding values of I_c obtained, a curve is obtained which does not

⁵ Rheinische Blattmetall A. G. Grevenbroich (Niederrhein).

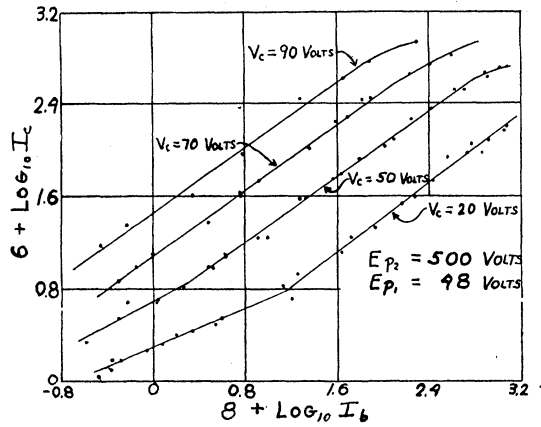


FIG. 5. Variation of collector current with beam current for different values of collector voltage. Spot size held constant.

repeat itself at low values of I_b . However, after the first run, all succeeding curves do repeat themselves. These stabilized I_b , I_c points, which are plotted in Fig. 5, and the curves obtained, are the "repeats" referred to above.

To illustrate the nature of this deviation for the initial run at low values of I_b , three successive runs are plotted in Fig. 6. The circles are the first run, the crosses and triangles the second and third, respectively. It is seen that after the first run, the succeeding runs lie along the same line. The nature of the polarization and time lag effects which give rise to the deviations in the first run will receive more detailed consideration below.

Returning to a consideration of Fig. 5, it is seen that except for low values of V_c and I_b , the

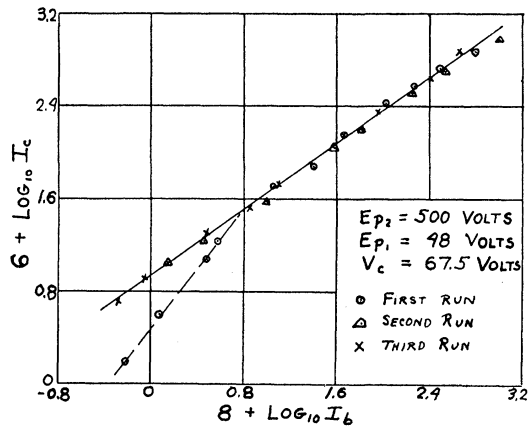


FIG. 6. Demonstration of variation between first and succeeding runs wherein beam current is varied.

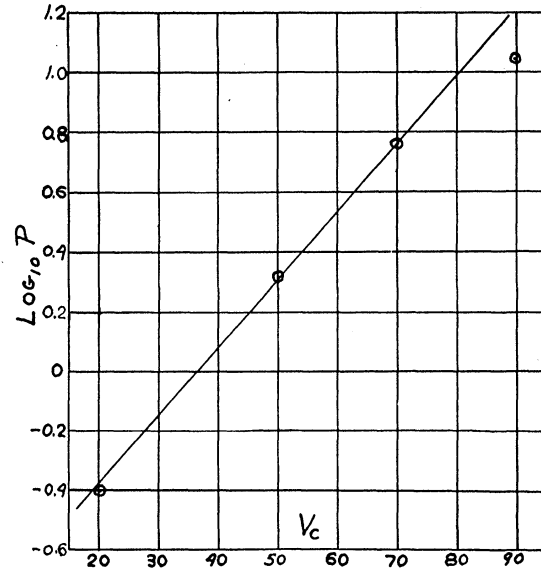


FIG. 7. Plot of intercepts of collector current—beam current characteristics as a function of collector voltage.

curves are all straight lines of the same slope. These results can be represented by:

$$I_c = P I_b^{0.71} \quad (2)$$

$\log_{10} P$ as a function of V_c is plotted in Fig. 7. If $V_c < 70$ volts,

$$P = 0.145 \times 10^{0.023 V_c} \quad (3)$$

By substituting (3) in (2), there results:

$$I_c = 0.145 \times 10^{0.23 V_c} (I_b)^{0.71} \quad (4)$$

This relation holds for all values of I_b and I_c except for those beyond the linear regions of the curves of Figs. 5 and 6.

C. Variation of spot size

In order to see whether Eqs. (1) and (4) could be expressed in terms of current density, a series of runs were taken at different spot sizes, the spot sizes being determined by deflecting the spot onto the willemite. Because of a slight misalignment of the first anode, the spot was oval instead of circular. This made the determination of the spot size quite inaccurate, but it was felt that an approximation of the current density law could certainly be obtained.

In Fig. 8, the values of I_c/A and I_b/A for various values of I_b are plotted on logarithmic scale, where A is the spot size. When consider-

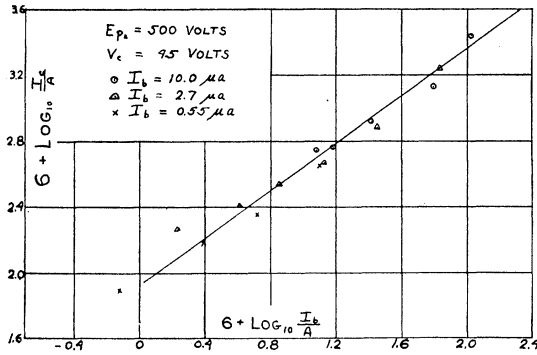


FIG. 8. Variation of collector current divided by spot size with beam current density.

ation is taken of the large error in the determination of A , it seems that the best representation of the results is a straight line drawn among the widely scattered points. We have thus:

$$\log 10^6 I_c/A = 1.92 + 0.73 \log 10^6 I_b/A. \quad (5)$$

The fact that the slope is practically the same as that for Eq. (4) indicates that the linear relationship expressed in Eq. (5) is a reasonable representation.

The agreement between Eqs. (4) and (5) is very good and consequently Eq. (4) may be generalized into the form:

$$A(I_c/A) = 0.145(10)^{0.023V_c} A^{0.71} (I_b/A)^{0.71} \quad (6)$$

and since Eq. (4) was derived at $E_{p2} = 500$ volts, $E_{p1} = 48$ volts, for which values $A = 0.72 \text{ cm}^2$; we

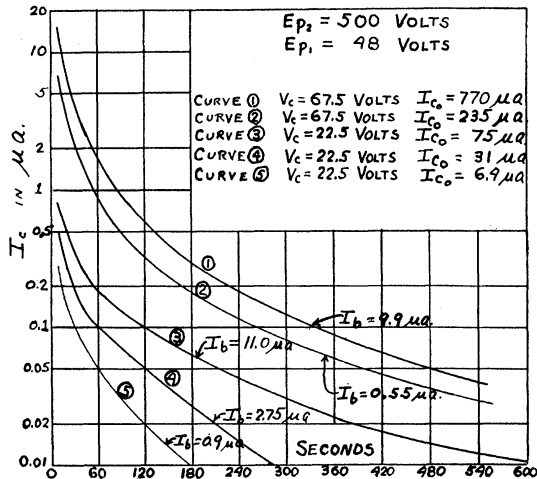


FIG. 9. Typical decay characteristic after removal of primary beam.

can insert this value of A in Eq. (6) and obtain:

$$J_c = 0.160(10)^{0.023V_c} J_B^{0.71}, \quad (7)$$

where $J_B = I_B/A$ and $J_c = I_c/A$.

Eq. (7) is the law representing the collector current as a function of beam current, spot size, and collector voltage for the oxide thickness employed and over the surface region investigated. In general, the law is of the form:

$$J_c = \alpha \epsilon^{\beta V_c} J_B^{\gamma}, \quad (8)$$

where α , β , and γ are functions of the oxide thickness and formation conditions. This law does not apply if V_c and I_c are above or below certain values. Possible reasons for this will be discussed below.

D. Decay characteristics

If I_b is suddenly reduced to zero by increasing the negative voltage on the grid of the electron gun, it is found that I_c does not immediately vanish but decreases rapidly at first, and then more slowly, and finally approaches a zero value asymptotically.

Samples of the decay characteristics for the same surface for which the preceding gain studies were made are shown in Fig. 9. Decay characteristics are extremely erratic in that small motions of the spot position cause large

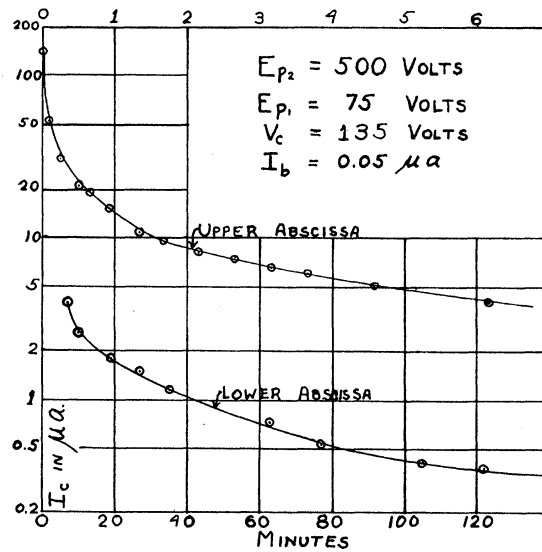


FIG. 10. Example of very slow decay.

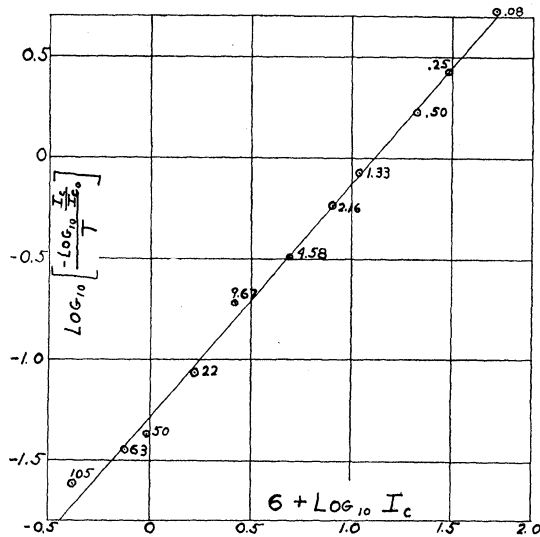


FIG. 11. Illustration of linear relation obeyed by persistent emission.

changes in the rate of decay. However, in general it is true that the greater the gain, the slower the absolute decay but the more rapid the relative decay. To show the extreme variability of the decay characteristics another curve is shown in Fig. 10. This is the decay characteristic for an entirely different surface, formed at the same voltage as the one previously described. The gains from this surface were slightly higher than from the one studied. Unfortunately, before further measurements could be made, this surface was destroyed by overheating with high frequency. The decay time for this surface was of an entirely different order of magnitude, being measured in minutes rather than seconds. Current to the collector could be detected after 24 hours.

It has been found that if $\log [-\log (I_c/I_{c0})/T]$ is plotted against $\log I_c$, a straight line is obtained. (T is the decay time). The case corresponding to Fig. 10 is shown in Fig. 11. The small numbers adjacent to the points represent the corresponding decay time in minutes. This linearity indicates that the neutralization of the surface charge is due primarily to the field emission itself.

If at any time during the decay the lead to the collector is opened momentarily, it is found on closing the circuit that I_c has dropped to practically zero. If V_c is reduced at any time during the decay, the rate of decrease of I_c is not affected

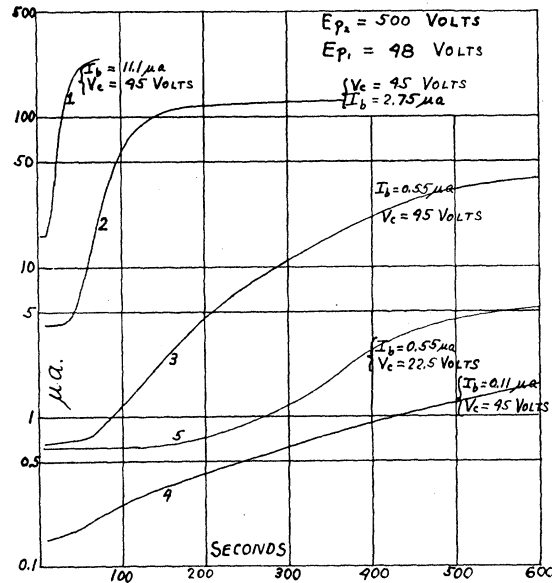


FIG. 12. Building-up curves obtained after reversal of collector potential with beam impinging on target.

unless V_c is reduced below some definite value, this value being lower the longer the decay period that has elapsed.

A more detailed consideration of the significance of decay characteristics will be given after the theory of the effect.

E. "Building-up" characteristics

If, at any time, I_b is first cut off by an increase in the grid bias, and then after I_c has dropped to a negligible value, I_b is suddenly restored to its original value, I_c returns to its final value very rapidly. If, instead of biasing off I_b , V_c is reduced to zero and then restored to its original value, I_c also returns to its original value very rapidly.

If, however, instead of reducing V_c to zero with I_b unchanged, V_c is actually reversed in direction so that the collector is negative with respect to the target, upon restoring V_c to its original positive value, the building-up takes on new and interesting forms. Some of these results are shown in Fig. 12 for cases wherein $V_c = 22.5$ volts and 45 volts. It is seen that the lower the values of I_b and V_c , the slower the building up. A curious feature is the fact that I_c remains constant for a considerable time before beginning its rise, particularly for low values of I_b and V_c .

If, instead of reversing V_c , a negative voltage

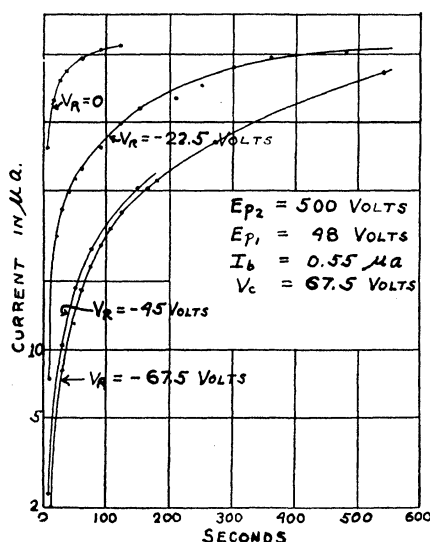


FIG. 13. Building-up curves when collector potentials are reversed to different negative values and subsequently restored to same positive value.

(V_R) different from V_c is applied to the collector and then the collector voltage is restored to its original V_c value, the building-up curves are altered. In Fig. 13 are plotted the building-up characteristics for $V_R = 0$, -22.5 , -45 and -67.5 volts, for the case where $V_c = 67.5$ volts. As V_R is made smaller in absolute value, the building-up becomes more rapid. An interpretation of the various building-up curves will be given below.

F. Scintillations and alteration of characteristics

If V_c and I_b are increased beyond certain points, scintillations are observed on the aluminum oxide surface, their number and frequency increasing as V_c and I_b are raised. These scintillations alter the surface characteristics and, consequently, in the preceding experimental work, care was taken to keep them at a minimum. Their complete elimination is impossible except for very low values of V_c . Scintillations are undoubtedly due to momentary ruptures of the oxide film.

Continued scintillation causes a slow decrease in the gain characteristics, but a very rapid alteration in the decay characteristics. Continuous and rapid scintillations finally cause the complete disappearance of the thin film emission. A surface formed at 12 volts was run with

$V_c = 90$ volts. Under these conditions, the surface was covered with a uniformly dense distribution of pin-points of scintillation. After one-half hour these scintillations had completely disappeared, but so had the thin film emission.

G. Light effects

It was noted that the shining of light upon the surface always causes a marked decrease in I_c . In addition, light causes a marked increase in the rate of decay after I_b is cut off. The effects upon gain and decay were most marked for tubes with the longest decay. In certain cases a decrease in I_c of 200 microamperes was observed when a flashlight was shone upon the surface. The same light impinging upon a caesiated silver oxide surface resulted in a current yield of only 10 microamperes. Thus when used in this way the device is many times more "photosensitive" than the best surface heretofore known.

DISCUSSION OF EXPERIMENTAL RESULTS AND PROPOSED DESCRIPTION OF THE PHENOMENON

In the case of normal secondary electron emission, the primary electron reacts with the conduction electrons of the substance being bombarded in the presence of the force fields of the atoms or ions constituting the latter, resulting, in certain cases, in the transfer of sufficient backward momentum to conduction electrons to permit of their escape through the surface. The theory for the case of the uniform metallic lattice has been treated by Fröhlich.⁶

Thin film field emission appears to be due to an entirely different mechanism. The phenomenon appears to be closely related to one described by Güntherschulze⁷ wherein extremely fine particles of aluminum oxide (among other substances) sprinkled on a semiconductor which serves as the cathode in a gas discharge, emit a copious stream of electrons with velocities corresponding to the cathode-anode difference of potential. In this case, according to Güntherschulze, positive ions lodge on the sides of the oxide particles away from the semiconductor and build up a positive charge thereon. If the gradient across any of the

⁶ Fröhlich, Ann. d. Physik 13, 229 (1932).

⁷ Güntherschulze, Zeits. f. Physik 86, 778 (1933).

particles becomes sufficiently great, electrons will be extracted from the underlying semiconductor. The effect disappears after several hours, apparently due to the mechanical rupture of the oxide particles by the high fields and high current densities present, with a consequent destruction of their insulating structure.

In the case of the thin film field emission the primary electrons impinging upon the treated aluminum oxide surface cause the release of true (i.e., normal) secondary electrons therefrom, these being attracted to the collector electrode. If the secondary emission ratio is greater than unity, more electrons will leave the surface than impinge upon it. Because of the high resistance of the oxide film, a positive charge is built up on the surface, this charge ultimately causing the extraction of electrons from the aluminum and aluminum oxide because of the intense gradients established. Thus in this case the emitted true secondary electrons take the place of the arriving positive ions in Güntherschulze's experiment.

Concomitant with the building up of the surface charge, the oxide becomes polarized, the polarization as well as the surface charge persisting after the removal of the primary beam. Evidence for the persistent polarization of aluminum oxide has been found by Güntherschulze and Betz.⁸ In addition, space charges are established within the oxide, the sign of the charge depending upon the sign of the collector.

This picture enables the various manifestations of the phenomenon to be explained in a very convincing manner. These will be considered in turn.

1.

The reason for the special treatment required with caesium and oxygen is made clear. This treatment serves to form a thin, nonconducting film on the surface of the aluminum oxide whose true secondary emission ratio is considerably greater than unity, resulting in the rapid building up of the positive charge on the surface when bombarded with primary electrons. It is believed that the layer of caesium oxide is monomolecular. This belief is founded upon the following evidence:

(1) The amount of caesium beyond a certain minimum amount does not appear to affect the magnitude of the phenomenon.

(2) No change can be detected in the appearance of the oxide surface. In the case of silver oxide, on the other hand, the reduction of the oxide to appreciable depths by means of caesium is shown by the decided change in appearance.

(3) The heat of formation of aluminum oxide is so high that it cannot be reduced by metallic caesium. It is quite likely, however, that the heat of adsorption of caesium on aluminum oxide exceeds the heat of formation of the oxide.

The mere formation of the caesium layer on the surface, while it enhances the true secondary emission, does not by itself result in the appearance of the anomalous effect. This is due to the fact that the pure caesium film on the surfaces is conducting and thus prevents the positive charge from being established.

2.

The relation between collector current, beam current and collector voltage is expressed by Eqs. (1) and (4). It is of interest to note that Eq. (1) is of the same form as the relation between voltage and current for the composition material "Thyrte."⁹ For this material the current is given by:

$$I = BV^m, \quad (9)$$

where B and m are constants which depend upon the proportions and nature of the constituents. Thyrte is composed of particles of carborundum coated with silica imbedded in a highly resistive matrix. Güntherschulze has ascribed the non-ohmic characteristic to the establishment of high gradients across the particles with a resultant "cold emission" through the particles. This view is borne out by the fact that the "cold emission" through the oxide films in this experiment, i.e., the thin film field emission, obeys a law of the same type.

The identity in form of the Thyrte law, Eq. (9), and the thin film field emission law, Eq. (1), indicates that in the case of this effect, the potential of the front surface of the aluminum oxide surface with respect to the underlying aluminum (denoted by (V_s)) is proportional to V_c , i.e.,

$$V_s \propto V_c.$$

⁸ Güntherschulze and Betz, *Zeits. f. Physik* **73**, 580 (1932).

⁹ McEachron, U. S. Patent #1,822,742.

3.

The time lags which are a feature of this effect are immediately explained by this picture. If the beam is turned on or increased, it takes an appreciable length of time for the region being bombarded to come to equilibrium under the opposing actions of the charging due to the true secondary emission and discharging due to leakage through the film, as well as for the polarization of the oxide and internal space charge to assume equilibrium values.

The time lag of the space charge is apparently very much greater than that of the surface charge. This belief is borne out by the experiments in which V_c was reversed with the beam on. On restoring V_c to its original direction, the surface charge undoubtedly reassumes its original positive value in a time no greater than the building up required when V_c is not reversed, but merely reduced to zero. Yet, the reversal of V_c greatly increases the building-up time. This increase can be due only to the fact that the field effective in extracting the electrons is weakened by the presence of negative space charge produced while the collector potential was reversed.

The persistence of the surface charge when the beam is cut off is demonstrated by the slow decay of I_c . Only a small portion of the field emission serves to neutralize the surface charge. This is also borne out by the virtual disappearance of collector current after a momentary opening of the collector circuit.

4.

The scintillations which appear for intense beams and high collector voltages are due to a violent breakdown of the oxide film. It was thought at first that this rupture would occur only if the surface target potential exceeded the formation voltage of the film. However, it was soon found that scintillations occurred when the collector voltage was less than the formation voltage. It was then believed that scintillations should not occur if the target surface potential were less than the critical potential V_b in the formation curve. (See Fig. 3.) It would appear that if the surface potential exceeded V_b there would be a tendency for ions to move through the film. However, since there is no electrolytic bath to supply the loss of ions at the outer

surface, a rupture would occur. However, it was found that scintillations occurred when the collector voltage was considerably less than V_b . Apparently the breakdown is due to there being weak spots in the oxide film. When the sample is in the bath, any tendency to breakdown is overcome by the oxidizing action of the bath. This cannot, of course, occur in the vacuum tube. It is probable that invisible breakdowns occur down to very small values of V_c . Recently, Zauscher¹⁰ has established a relation between film thickness and breakdown voltage for a film in air. For small thicknesses ($<4000\text{\AA}$), the relationship is given by:

$$\text{Breakdown Voltage} = 8 \times 10^5 d,$$

where d , the film thickness, is measured in cm.

Thus for the 2000 $\text{\AA}$ film studied above, the breakdown voltage is 16 volts, whereas V_b is 78 volts and the formation voltage 116 volts.

The deviations from the laws as expressed in Eqs. (1) and (4) at high values of V_c may be due to V_s exceeding some definite value which may be the critical value of Zauscher's relation.

The fact that the deviation from linearity at the upper ends of Fig. 8 occur for approximately the same value of I_c and appear to be independent of V_c indicates that V_s is a function of I_c/A only.

5.

The sensitiveness of the treated surface to light appears to be explainable only by the ad hoc hypothesis that the aluminum oxide is photoconductive. Light falling upon the oxide causes a decrease in its effective resistance. When the electron beam and light are simultaneously impinging upon the surface, the surface equilibrium potential will take on a smaller value than with the light absent. The light also causes an increase in decay rates by permitting the surface charge to leak away more rapidly through the lessened effective resistance of the oxide film.

THIN FILM FIELD EMISSION FROM OTHER SURFACES

Güntherschulze and Fricke¹¹ obtained field emission from a number of substances in a gas

¹⁰ Zauscher, *Ann. d. Physik* **23**, 597 (1935).

¹¹ Güntherschulze and Fricke, *Zeits. f. Physik* **86**, 821 (1933).

discharge where the positive surface charge was produced by positive ions. A set-up similar to theirs was employed in which finely powdered material was rubbed onto an aquadag surface. The tube was treated with caesium and oxygen in the same manner as for aluminum oxide surfaces. The materials were then bombarded by an electron beam with an adjacent collector highly positive with respect to the aquadag. Field emission would be demonstrated by the presence of scintillations. The following materials were tried in this way: Ta_2O_5 , MgO , CaCO_3 , Al_2O_3 , Zn_2SiO_4 , willemite, BeCO_3 , SiO_2 , ZrO_2 , and ThO_2 , all of these materials having yielded positive results in the experiments of Güntherschulze and Fricke. Scintillations were observed in the cases of Al_2O_3 , SiO_2 , MgO , and willemite. The nonoccurrence of scintillations for the other materials does not indicate that field emission did not occur, but simply that the gradients established were not sufficient to cause breakdown. The coverage of the materials used was too small to enable the demonstration of any field effects as regards the collector current.

In addition, a number of other oxides were tried in tubes, but the results were generally negative. However, E. R. Piore, of the Electronic Research Laboratory of the RCA Manufacturing Company, obtained a pronounced field effect from Be oxidized in a glow discharge, then caesiated, and finally heated to dull redness inside the tube by means of high frequency induction. He has also observed the phenomenon with hot activated barium and strontium oxide cathodes.

The reason for the appearance of the phenomenon only in the case of a few out of a host of oxides tried can be accounted for on the basis of the possible chemical interactions between caesium and oxides. If an oxide is capable of reduction by the caesium, then the introduction of caesium into the tube will cause the destruction of the resistive properties of the oxide film. This will, of course, prevent the appearance of the field effect. In Table I, column one shows the oxide studied, column two its method of preparation, column three the heat of formation of the oxide *per unit atom* of oxygen, and column four

TABLE I. *Field emission from various oxides.*

1	2	3	4
OXIDE	MODE OF PREPARATION	HEAT OF FORMATION PER UNIT OXYGEN ATOM (Cal.)	RESULTS FOR ANOMALOUS EFFECT
Al_2O_3	Electrolytically in borax plus boric acid bath	126,700	Positive
BeO	Glow discharge in oxygen	?	"
CaO	"	151,900	Negative
CbO	Electrolytically in H_2SO_4	?	"
Ag_2O	Glow discharge in oxygen	7,000	"
CuO	"	37,000	"
NiO	and heating in air Glow discharge in oxygen and heating in air	57,900	"
Ta_2O_5	Electrolytically in H_2SO_4	60,300	"
WO_2	"	65,700	"
ZrO	"	86,800	"

the results achieved in an attempt to obtain field emission.

Since the heat of formation of Cs_2O is 82,700 calories, only the oxides of Al, Ca, Mg, Si, and Zr in the above list should show the field effect. The result is believed to be negative in the case of Ca because of the low resistance of the oxide.

An attempt to evaporate SiO_2 from a carbon cup subjected to intense electron bombardment, as described by O'Brien,¹² failed because of the reduction of the SiO_2 by the carbon, with the consequent profuse evolution of CO resulting in a gas discharge. No further attempt was made to evaporate quartz. However, the previously described experiment with the quartz powder indicates that it should yield field emission.

The Zr yielded a negative result, although from the figures cited a positive result should have appeared. However, in heating the tube to 200°C to promote the distribution of the caesium, apparently the heat of formation of the zirconium oxide dropped below that of the caesium oxide. This is evidenced by the decided change in color of the zirconium oxide during caesiation.

This change in the appearance of the oxide upon caesiation occurred whenever field emission failed to occur. The aluminum oxide, on the other hand, shows no change in appearance under the same conditions. This is evidence in favor of the belief that the caesium on the aluminum oxide is in the form of a monatomic layer.

¹² O'Brien, Rev. Sci. Inst. 5, 125 (1934).

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Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals

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It is well known that if the interaction between electrons in a metal is neglected, the energy spectrum has a zonal structure. The problem of these "Brillouin zones" is treated here from the point of view of group theory. In this theory, a representation of the symmetry group of the underlying problem is associated with every energy value. The symmetry, in the present case, is the space group, and the main difference as compared with ordinary problems is that while in the latter the representations form a discrete manifold and can be characterized by integers (as e.g., the azimuthal quantum number), the representations of a space group form a continuous manifold, and must be characterized by continuously varying

parameters. It can be shown that in the neighborhood of an energy value with a certain representation, there will be energy values with all the representations the parameters of which are close to the parameters of the original representation. This leads to the well-known result that the energy is a continuous function of the reduced wave vector (the components of which are parameters of the above-mentioned kind), but allows in addition to this a systematic treatment of the "sticking" together of Brillouin zones. The treatment is carried out for the simple cubic and the body-centered and face-centered cubic lattices, showing the different possible types of zones.

I.

INVESTIGATIONS of the electronic structure of crystal lattices in particular in metals, made on the basis of Bloch's theory, led to the conception of the so-called Brillouin zones.¹ In

spite of these investigations, which cover a large part of the field, it seems desirable to develop the theory from a unique point of view. It appears that taking into account special symmetry properties of different lattices brings out interesting features of the constitution of the B-Z which are not evident from the existing general theory. These features can be dealt with

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¹The existence of these zones was first noticed by M. J. O. Strutt, *Ann. d. Physik* **85**, 129 (1928); **86**, 319 (1929); and then, independently, by F. Bloch, *Zeits. f. Physik* **52**, 555 (1928); cf. also P. M. Morse, *Phys. Rev.* **35**, 1310 (1930). From another point of view, they were discussed by R. Peierls, *Ann. d. Physik* **4**, 121 (1930). Their connection with x-ray reflection was first pointed out by L. Brillouin (cf. e.g., *Die Quantenstatistik* (Berlin, 1931)). Important physical applications were given by H. Jones, *Proc. Roy. Soc. A* **144**, 225 (1934); **147**, 396 (1934); H. Jones, N. F. Mott and H. W. B. Skinner, *Phys. Rev.* **45**, 379 (1934); J. C. Slater, *Phys. Rev.* **45**, 794 (1934); *Rev. Mod. Phys.* **6**, 209 (1934); F. Hund and B. Mrowka, *Ber. Sachs. Akad. D. Wiss.* **87**, 185, 325 (1935). Compare

also F. Hund, *Zeits. f. tech. Physik* **16**, 331, 494 (1935); *Zeits. f. Physik* **99**, 119 (1936). Hund's work deals with those properties of the Brillouin zones which are common to all zones of the same lattice (as matter of fact he does not discriminate between different types of zones at all). We consider here the different types of zone separately. The differences between the different types are of the same kind as e.g. the difference between even and odd terms in atomic spectra. It is surprising that there are at all common properties of all zones but Hund has shown that this is the case for the more complicated crystal structures.