Secondary Electron Emission

KENNETH G. McKAY

Bell Telephone Laboratories, Murray Hill, N. J.

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INTRODUCTION

This article is a review of the present state of knowledge of secondary electron emission by electrons from metals, insulators, and complex surfaces. The technical applications of secondary emission have been fully dealt with in some of the publications listed in the bibliography and consequently have not been considered in this text. Nor has secondary emission induced by ion bombardment been included, since, theoretically, it constitutes a different phenomenon and should be considered as a separate field. For the most part, the material presented arises from work which has been performed within the past ten years. However, some aspects of the subject have not been actively investigated recently and since secondary emission, as a complete subject, has been treated rather sporadically in English scientific literature, a summary is presented of much of the earlier work. The standard reference on the subject up to 1936 is a German review by Kollath.[72] A more recent publication in book form by Bruining[216] deals with the subject up to 1941.

For convenience, the bibliography has been split into two parts: the first part consists of text references to secondary emission publications prior to 1936 and other incidental text references; the second part forms a reasonably complete list of the secondary emission publications since 1936. In cases where essentially the same material has appeared in more than one article, only one reference has been given. For a complete bibliography prior to 1936, Kollath[72] and Bruining[216] should be consulted.

It would be desirable at this stage to give an accurate, concise definition of secondary emission but this is not easy. The most general definition is that secondary emission consists of the emission of electrons from a solid due to the impact on that solid of "primary" electrons. This applies reasonably well in the case of pure metal targets. However, it breaks down for some targets of insulators where several mechanisms are invoked which are quite different from that which is normally considered to be the mechanism of secondary emission. For example, the Malter effect is accepted as field emission which is merely initiated by electron bombardment. Until more is known about the details of field enhanced emission or bombardment enhanced thermionic emission, it cannot be said whether these should be classified as true secondary emission or not. For the purposes of this article, the general definition is assumed and the following symbols or abbreviations are used:

SE: Secondary electron emission.
δ: Yield, equal to the total number of emitted electrons divided by the total number of bombarding or primary electrons.
V_p: Energy of the primary electrons, which are assumed to be monochromatic, in electron volts.
V_s: Most probable energy of emission of secondary electrons in electron volts.

I wish to express my thanks to Dr. J. B. Johnson for many stimulating discussions in the course of the preparation of this review.

I. Pure Metals

1.1 Yield

The most widely investigated property of SE is the yield as a function of primary electron energy V_p. Unless stated otherwise, it is always assumed that the primary electrons impinge normal to the surface and that all the emitted secondaries are collected. The plot of δ vs. V_p is the yield curve and has the same general shape for all materials, i.e., for low V_p, δ is much less than unity; it increases with V_p and for pure metals reaches a maximum value not greater than $\delta = 2$ for V_p equal to a few hundred volts. δ then decreases slowly as V_p is further increased. Thus although the entire yield curve may sometimes be required or the yield at some specified value of V_p, the various yield curves are sufficiently similar so that it is often adequate to specify merely the maximum value of δ, (δ_m), and the value of V_p, ($V_{p\,max}$), for which this occurs.

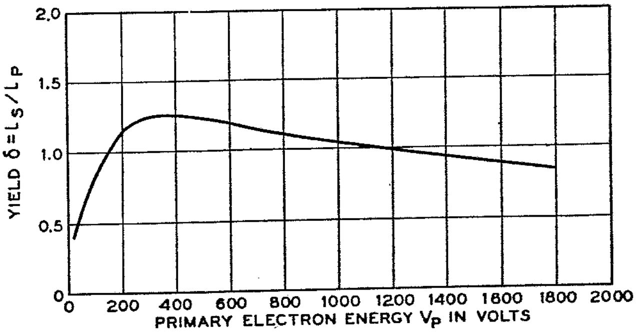

Fig. 1.—Yield curve for molybdenum.[72]

As the effects of surface contamination became apparent a great deal of effort was expended in producing cleaner surfaces which would yield more accurate values for δ. Warnecke stipulated that the metal should be given as extensive a heat treatment as possible until it reached an "end point" after which any further heat treatment made no change in the yield. Even this is open to criticism in the case of some metals such as aluminum where the oxide is much less volatile than the metal itself. Thus if the surface is once oxidized, it may not be possible to clean it off purely by heat treatment. Bruining and others have attempted to overcome this objection by using targets which have been

TABLE I. Maximum secondary emission yields of various clean metals and some semiconductors.

Element	δ_{max}	$V_{p(max)}$ volts	Principal references
Ag	1.5	800	87, 56, 72
Al	1.0	300	66
Au	1.46	800	56, 230, 72
Ba	0.83	400	66
Be	0.6	200	66, 230
C	1.0	300	86
Cd	1.1	400	230
Co	1.2	600	152, 108
Cs	0.72	400	66, 95
Cu	1.3	600	87, 56, 230, 72
Fe	1.3	350	72, 7
K	0.7	200	195, 134
Li	0.5	85	66
Mg	0.95	300	66, 95
Mo	1.25	375	56, 72
Nb	1.2	375	56, 72
Ni	1.3	550	152, 66, 56, 72
Pd	1.3	250	5
Pt	1.6	800	72
Rb	0.9	350	216
Th	1.1	800	66
Ti	0.9	280	86
W	1.4	600	56, 121, 72
Zr	1.1	350	86
B	1.2	150	250
Ge	1.2	400	250
Si	1.1	250	250
Ag_2O	1.1	...	120
Cu_2O	1.2	...	120
MoO_2	1.1	...	120
MoS_2	1.1	...	120
SnO_2	1.1	600	258
WS_2	1.0	...	120

evaporated on in vacuum. Even where relatively clean surfaces have been obtained, the yield will still be affected by the degree of roughness of the surface and by the crystal structure. Thus it is not surprising that even the best results on a metal such as tungsten, which can be outgassed more thoroughly than most metals, exhibit considerable variation from author to author. For these reasons, the compilation of values of δ_{max} in Table I represents only what is believed to be the best available results. In most instances, for a well outgassed, smooth polycrystalline target, the values of δ_{max} are probably consistent to better than 10%. However, since many yield curves have a very broad maximum, the values of $V_{p(max)}$ may exhibit much wider variations. The principal references from which these data have been compiled are listed in the table and these should be consulted for the complete yield curves. In general, if the values quoted are substantially the same as that given by Kollath,[72] only that and more recent references are given. The most striking change since Kollath's compilation is the low values of δ_{max} for the low work function metals such as the alkalies. Due to outgassing problems, it is very probable that much of the early work was actually done on alkali oxides, which may give values of δ_{max} several times that of the pure metal. Data on certain semiconductors have also been included. The only justification for this is that the yields of these substances are much like those of metals. Nothing has been published concerning their other SE properties and these may not necessarily be similar to metallic behavior.

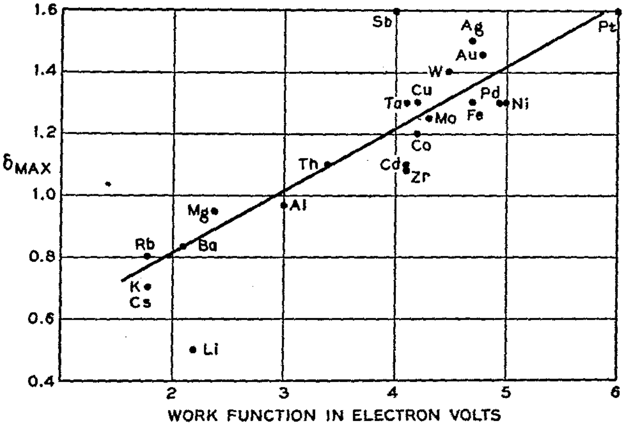

FIG. 2.—Relation between δ_{max} and work function of different targets.

A correlation between work function and yield is illustrated in Fig. 2 where the values of δ_{max} from Table I have been plotted against work function. These values of work function have been obtained from Becker[28] and most are for polycrystalline surfaces. Here again we do not know the surface conditions, particularly the predominant crystal orientation. This and other factors render unreliable some of these work function values so that too much importance should not be attached to this plot. However, this does illustrate a possible classification of pure metals, i.e., those with high work functions have high SE yields and those with low work functions have low SE yields. The ~~inference should~~ not ~~be drawn that by increasing the work function of a metal the SE~~ yield will be ~~increased since~~, as ~~will be discussed~~ later, this is believed to be untrue. Rather, it is believed that the work function itself plays a relatively minor role in determining the SE yield but that it is linked with other properties of the metal which play a dominant role in determining the yield. Almost as good a correlation can be obtained by plotting $\delta_{\max}$ against the density of the target.

Attempts have been made to correlate $\delta_{\max}$ with position in the periodic table, atomic constants, etc., but these have usually produced trends rather than correlations.

1.2 Shape of the δ vs. V_p Curve

A rough explanation for the maximum in the δ vs. V_p relation can be given by defining d_p = maximum depth of production of secondaries and d_s = maximum depth from which secondaries can escape. Then for $V_p < V_{p(\max)}$, $d_p < d_s$ and $\dfrac{\partial \delta}{\partial V_p} > 0$. Similarly for $V_p > V_{p(\max)}$, $d_p > d_s$ and $\dfrac{\partial \delta}{\partial V_p} < 0$. Khlebnikov[95] pointed out that according to this formulation, changes in the surface potential which affect δ but which do not affect d_p or d_s should have no effect on the value of $V_{p(\max)}$. Thus it should be possible to distinguish between volume effects and solely surface effects by measurements of $V_{p(\max)}$. However, since the maximum is usually rather flat, this is not a particularly sensitive criterion.

Extending this concept, Geyer[225] has plotted $\log \left(\dfrac{\partial \delta}{\partial V_p}\right)$ against V_p in the range 50 volts $< V_p < V_{p(\max)}$, using his own experimental data and also data from Bruining and de Boer, and Copeland. He obtained linear relations in all such plots and by extrapolating to $V_p = 0$ obtained values of the zero voltage intercept $\vartheta_0 = \log \left(\dfrac{\partial \delta}{\partial V_p}\right)_{V_p = 0}$. He found that for a given target material, ϑ_0 was independent of surface contamination, work function, angle of incidence, and depth of penetration. Moreover, metals with the same value of the principal quantum number "n" of the outermost electron shell gave the same value of ϑ_0. However, the same metals in compounds yielded much different values of ϑ_0. From this Geyer concluded that ϑ_0 is a function of the mechanism of the generation of secondaries.

Such plots depend upon careful determinations of the slope of the yield curve. Small errors in the latter may result in large errors in the slope. The author has attempted to fit data other than those given by Geyer to such plots with considerable lack of success. In particular, various published curves on tungsten by Ahearn,[20] Warnecke,[56] Coomes,[121] and McKay[221] give widely differing results, and even the values for tungsten by Sixtus[15] which are quoted by Geyer do not agree with his classification. Moreover, it is not possible in general to fit Wooldridge's[151] theoretical curves to such a linear plot. However, in spite of these contradictions, careful analyses of this type may yield information about the mechanism of secondary electron generation.

Considering the section of the yield curve where V_p is greater than $V_{p(\max)}$, Chaudri and Khan[191] have plotted log δ against V_p and obtained a linear relation for nickel. They show that if all the energy of the primary electrons is used up in the production of secondaries and if the absorption of secondaries in the metal is exponential, a relation of the

$$\delta = \delta_{\max} e^{\alpha(V - V_{p(\max)})} \tag{1}$$

form is obtained agreeing with their experimental results for $600 < V_p < 4000$ volts. To obtain this formula they assume that practically all the secondaries are produced at some point at which the primary energy has dropped down to a certain value. This is certainly an oversimplification of the process. Moreover, as V_p increases, the importance of reflected primaries also increases and this aspect was neglected. It is difficult to check this against other data in the literature since usually the yield has decreased very little from the maximum at the highest values of V_p used. However, Trump and Van de Graff[259] have measured some SE coefficients in the range 30 kv $< V_p <$ 340 kv in which they have separated the yield due to high energy secondaries or reflected primaries from the total yield. If the log $\delta/\delta_{\max}$ is plotted against V_p for the yield due to low energy secondaries from their data, a linear relation does not exist. The values of $\delta_{\max}$ were taken from Table I but small variations of these values still do not produce a linear relation. Thus apparently Chaudri and Khan's formula does not hold for very large values of V_p and certainly does not when reflected primaries are included.

Copeland[26] and Warnecke[84] have plotted the slope of the yield curve at a certain point where V_p is greater than $V_{p(\max)}$ against the atomic number of the target and have obtained a general decrease with increasing atomic number. This could best be approximated by a linear relation but the agreement was not very good. It will be seen that such a procedure is equivalent to an approximate determination of α in Chaudri's formula when the yield curve falls off very slowly.

1.3 Soft X-Ray Critical Potentials

A great deal of early work in SE was devoted to a careful analysis of the "fine structure" of the yield curve in which numerous small humps and inflexion points between zero and about 40 volts were revealed. These were correlated with the energy required to produce various soft x-rays which, according to a theory by Richardson,[18] in turn produced secondary electrons. However, later experiments showed that most of this fine structure disappeared following a really thorough degassing of the target and it is now believed to have arisen from the excitation or ionization of adsorbed gas atoms on the surface. Possibly some was due to elastically reflected primaries. Nevertheless, Warnecke[57] has observed that even after a very thorough outgassing, a few inflexion points still remain for tungsten, tantalum, and nickel. An attempted correlation between these points and possible soft x-ray energies exhibits discrepancies which would appear to be greater than the experimental error. It is possible that they might be related to the target band structure.

1.4 Effect of Work Function on the SE Yield

One method of determining the effect of the work function on the SE yield, without varying any other parameter which might affect the yield, is to deposit a thin layer of a different element on the target such that the resulting change in work function can be measured independently. De Boer and Bruining[118] have calculated that an adsorbed layer, which is equal to or less than a monomolecular layer thick, should contribute a negligible amount to the SE yield due to secondaries arising within the adsorbed layer itself, provided V_p is greater than about 50 volts. This method has been used by Sixtus[15] using thorium on tungsten, Treloar[83] with barium on tungsten and thorium on tungsten, de Boer and Bruining[118] with barium on tungsten, Coomes[121] with thorium on tungsten, and McKay[221] with sodium on tungsten. In these experiments, the work function was measured either thermionically, photoelectrically, or by contact potential. All the results, except those of Coomes, have shown a systematic increase in SE yield as the work function is lowered, passing through a maximum coincidentally with the attainment of the optimum adsorbed layer thickness for minimum work function. Both Sixtus and Treloar obtained relations of the form $\log \delta = A - b\varphi$ where φ is the surface work function and A and b are constants for a given metal and V_p. This equation, of course, holds only for adsorbed layers which are thinner than those for minimum work function. Treating the problem classically, Treloar has shown theoretical justification for such a relation and Wooldridge's[151] quantum-mechanical treatment not only predicts it but is in good numerical agreement with Treloar's experimental results. Coomes' results with thorium-coated tungsten are remarkable in that no systematic variation of yield with work function was observed although he did obtain an increase in yield with lowered work function with an oxygenated thorium coated tungsten target. The latter condition is too complex to be treated here while the former results are very difficult to explain unless the target surfaces were not what Coomes believed them to be. In this connection it is noted that Coomes' δ vs. V_p curves for clean tungsten were not completely reproducible following deposition and subsequent evaporation of a thorium layer. Afanasjeva and Timofeev[62] also obtained an increase in SE yield which passed through a maximum as potassium was evaporated on gold, silver, or platinum. However, as no corresponding maximum was observed in the photoelectric yield, this work is open to question.

It is difficult to picture any mechanism of secondary emission in which lowering of the surface work function does not increase the yield somewhat. However, what is most important is the relatively minor role that the work function plays. McKay showed that an adsorbed layer of sodium which effectively reduced the work function of tungsten by a factor of 2 increased the SE yield by only 60%, which is in rough agreement with Treloar's results of $-(\partial/\partial\varphi)(\log_e \delta_{\max}) \sim 0.12ev^{-1}$. However, this should be compared with the case of thermionic emission where such a reduction in work function would increase the thermionic emission current by a factor of about 10^6. This contrasting behavior is attributed roughly to the relatively high average emission velocity of secondary electrons to be discussed later. One consequence of this is that it appears unlikely that very high SE yields can be attained merely by a lowering of the surface work function, i.e., if Treloar's results be assumed to be valid for any value of work function, then the $\delta_{\max}$ from tungsten on reduction of the work function to zero would still be less than three.

1.5 Effect of Crystal Structure on the SE Yield

Work by Becker,[28] Nichols,[37] and others has established that the work function of a surface depends upon the orientation of the exposed crystal face. Thus, from §1.4 we should expect some variation in SE yield from this source. To estimate the magnitude of the effect, let us assume Treloar's result for variation of yield with work function for tungsten in conjunction with Nichols' data showing that the work function of tungsten varies from 4.35 volts for the (111) crystal direction to at least 4.65 for the (110) direction. This would give a change in δ_{max} of about 3%. However, Wooldridge's theory[151] implies that the crystal orientation may produce variations in yield other than those caused by change in work functions.

Early work by Rao[17] showed a decrease in δ_{max} from 1.3 to 0.76 in going from polycrystalline nickel to the (100) face of a single crystal of nickel. However, it is doubtful if the vacuum techniques employed were sufficient to insure that the surfaces were free of adsorbed gas.

Bekow[188] has published a preliminary note indicating that for a copper single crystal, δ is different for each crystal face and is a maximum for the (100) face. Knoll and Theile[128] have demonstrated the effect strikingly by forming an electron-optical picture of the surface of a silicon-steel target using the secondary electrons themselves. The resultant picture shows intensity variations which resemble the expected polycrystalline structure, the interpretation being that each crystal face exhibits a characteristic yield.

One method of determining the effect of crystal structure is to vary the temperature of the target and to observe changes in the SE yield as the target passes through a structure transformation point. Treloar[108] could observe no change in yield within an accuracy of a few per cent in passing through the Curie point of nickel at 358°C., the hexagonal to face-centered transformation of cobalt at 410°C., or the Curie point at 770°C. and body-centered to face-centered transformation of iron at 910°C. Wooldridge[183,184] improved the relative accuracy of such measurements to about 0.1% by adjusting V_p so that the SE yield was always unity. He observed no change in passing through the Curie point of nickel at 358°C. or of iron at 770°C. He did observe erratic changes of about 1% in the iron transformation at 910°C. but concluded that he was dealing with large crystal faces and that variations from one face to another rendered the results unreliable. He also obtained a reproducible change in SE yield of 0.4% at the hexagonal to face-centered transformation of cobalt at 410°C. Simultaneous measurements of work function by contact potential measurements showed that the change in work function was in the wrong direction to account for this change in yield.

Kollath[96,98] obtained increases in δ when evaporated beryllium targets were heated above 700°C. He attributed this to a structural change although he had no data on any known crystal transformations for beryllium at this temperature. However, the changes in δ were so large that it is doubtful if they could have been due solely to changes in crystal structure.

Suhrmann and Kundt[144,145,229] compared the SE yield of targets of copper, silver, or gold condensed at 83°K. with that obtained at room temperature. At low temperatures, the targets were assumed to be disordered and at room temperature to be ordered. They obtained yields in the ordered cases of up to 30% greater than when disordered. Due to the importance of Van der Waals' adsorption of gas at low temperatures, it would appear very likely that adsorbed gas layers might play a prominent part in this type of experiment. Wooldridge and Hartman[185] proposed that order in an alloy produces long period regularity in the lattice fields resulting in a splitting of some of the bands and making possible transitions between levels which could not exhibit interaction processes in the disordered alloy. However, measurements on a Cu_3Au target, in which disorder begins at 250°C. and is completed at 391°C., exhibited no change in SE yield greater than the experimental accuracy of 1%.

Morozov[206] has measured a change in SE yield of up to 10% in lead, antimony, and bismuth in going from the solid to the liquid state. The direction of the change depended on the bombarding velocity and also on the target. His explanation of these results is based on conductivity changes rather than crystal structure.

The effect of crystal structure on the directional scattering of reflected primary electrons will be considered in a later section.

This experimental evidence shows clearly that the crystal structure plays a role in determining the SE yield, although detailed data on the correlation between yield and structure are entirely lacking. It should be noted that even a substance which is polycrystalline does not necessarily expose all crystallite faces on the surface with equal probability. Previous cold working or heat treatments may produce preferred orientations of the surface faces. For example, tungsten wire, following heat treatment, usually develops crystals with the (110) direction parallel to the wire axis. It is possible that even before heat treatment the crystallites still maintain a preferred orientation.

1.6 Effect of Temperature on SE Yield

Changes in temperature of the target may alter the density of adsorbed gas if present; they may alter the crystal structure or the surface roughness. Any of these may influence the SE yield. However, when these complications are not present, many experimenters[108,121,133,221] have demonstrated no observable change in SE yield of metals with temperature. In particular Morozov[205] and Wooldridge[183,184] have shown that for cobalt, iron, molybdenum, and nickel the SE temperature coefficient must be less than the temperature coefficient of linear expansion. Such a result is in accord with a later modification of Wooldridge's theory of SE.[184]

Reichelt[169] reported an increase in the proportion of high velocity secondaries at 1500°C. with a tungsten target, resulting in an increase in the mean energy of the secondary electrons of about a volt from that at room temperature. Kollath[197] has reported measurements which contradict this and suggested that Reichelt's results might be due to an experimental error.

1.7 Effect of Angle of Incidence of Primary Electrons on SE Yield

Although most SE yield measurements have been made with normal incidence of the primary beam, a number of investigators have examined the variation of yield with incident angle. The general effect of oblique incidence may be seen by reference to Fig. 3 where for normal incidence, the average range of a primary electron is d_p. In the case of oblique incidence, secondaries produced at the end of the range d_p will be only a distance $d_p \cos\theta$ from the surface, where θ is the angle of incidence, and thus have less chance of being absorbed before reaching the surface. From this we might predict that the effect will be greater for $V_p > V_{p\,\max}$ where the yield is predominantly limited by adsorption of secondaries. We might expect that for low primary velocities where the penetration is small very little variation in yield with incident angle would be observed, and this has been verified experimentally by Bruining.[41] He has also shown that a rough etched surface shows practically no variation of yield with incident angle. Such a result is to be expected since the actual incident angle is very poorly defined in this case.

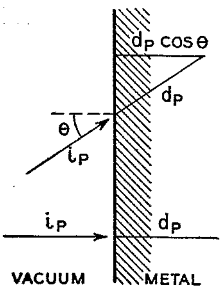

FIG. 3.—Effect of variation of angle of incidence on the path length of the secondaries.

Müller[78] investigated a series of metals with $1000 < V_p < 4000$ volts and concluded that over the range $0° \leq \theta \leq 80°$, the yield varied as $(\cos\theta)^{-1}$ with deviations from this ascribed to spreading of the primary beam. However, the assumptions he used to derive a theoretical expression of this form are such that they greatly oversimplify the problem. He also showed that the relative change in yield with incident angle varied in an inverse way with the target density.

Bruining[41,88] assumed that the secondaries are absorbed exponentially with distance and derived a relation of the form

$$\delta_\theta = \delta_0 e^{\alpha x_m (1-\cos\theta)} \tag{2}$$

where δ_θ is the yield at incidence angle $= \theta$
δ_0 is the yield at zero incidence
x_m is the mean depth of liberation of secondaries
α is the coefficient of absorption of secondaries.

This expression was verified experimentally for lithium, barium, and nickel by showing that for a given target and V_p, αx_m was a constant independent of θ within 20%. From his data it is also possible to extrapolate and obtain a value of $\delta_{90°}$, i.e., the yield to be expected when the primary beam strikes the target just at grazing angle. It might be expected that a curve of $\delta_{90°}$ versus V_p would not show a maximum since there is essentially no absorption of secondaries. Actually there is a broad maximum at a mugh higher value of V_p than for normal incidence and this is attributed to the scattering of primary electrons into the target thus still producing some absorption of secondaries.

Lukjanov[99] has derived an expression for δ_θ of essentially the same form as Bruining's and has shown that it fits Müller's experimental curves. Lukjanov shows that x_m should vary inversely as the density which is in accord with the experimental fact that the greatest relative change in yield occurs with the metals of least density.

1.8 Effect of Primary Current on SE Yield

Since the SE yield is normally quoted merely as a function of V_p, it is implied that it is independent of primary current. For metals, this has been confirmed by many observers under widely differing conditions of primary current density.

1.9 Effect of Mechanical Condition of Surface on SE Yield

There is considerable experimental evidence to show that a rough or porous surface results in a lowering of the SE yield. This is qualitatively explained by postulating that a rough surface can be likened to a series of holes or wells. A secondary electron, produced at the bottom of such a well, may be trapped by the sides of the well and hence will not be emitted from the surface. Such a surface can be produced artificially by covering the target with carbon soot either smoked on or from a colloidal suspension. Optically "black" surfaces can also be prepared by evaporating various metals onto the surface through a rare gas atmosphere so that metallic agglomerates are formed before striking the target surface. Fig. 4 by Bruining[86] shows the reduction in yield with carbonized nickel. He concludes that the greatest reduction in yield occurs when the carbon granules are about 30 A. in diameter forming a fine labyrinth.[65] If other metals are used to form the surface, they should have a high sintering temperature. Otherwise, upon heating the target, the agglomerates will sinter together forming a compact high yield surface. Jonker[92] suggests a series of ribs mechanically formed on the target to reduce the SE yield still further.

1.10 Effect of Adsorbed Gas on SE Yield

In §1.4 we saw that the work function of a surface could be altered by an adsorbed metallic layer on the surface. The same, of course applies to adsorbed gas layers.[29] An adsorbed layer may also yield an appreciable number of secondaries in itself if it is sufficiently thick. However, a monatomic layer probably has a yield of the order of 0.02 for V_p around 200 volts[118] and thus the variation in yield caused by a monatomic layer is probably due almost entirely to the work function variation.

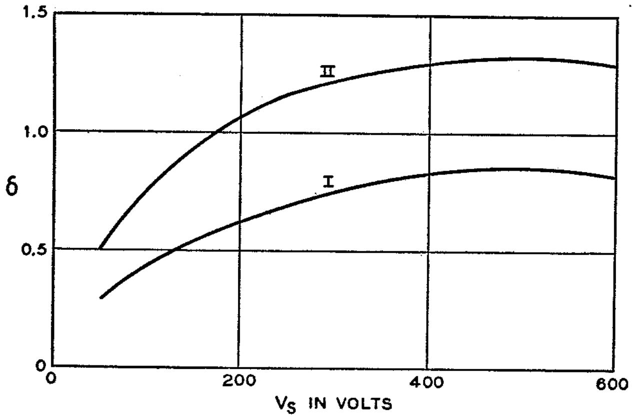

FIG. 4.—Variation of yield with surface roughness:[86] I, soot; II smooth carbon.

Most papers on SE give some data on the variation of the yield as a function of the heat treatment so the actual amount of information available is quite considerable. Of course, the heat treatment may cause changes other than the removal of adsorbed impurity layers, e.g., it may alter the crystal structure.[98] Moreover, when gas layers are being removed, they are usually of unknown thickness and composition. Thus we can only generalize that usually the removal of adsorbed gas through heat treatment causes the yield to drop possibly by as much as 50% or more and most frequently the final yield curve is lower than any other obtained during heat treatment. The removal of adsorbed gas also removes many kinks in the yield curve as described in §1.3. A good example of this general type of behavior is presented in detail by Ahearn[20] in work on the SE of tungsten. Actually the presence of oxygen on the surface may either raise or lower the yield since the physical adsorption of a monatomic layer of oxygen on most metallic surfaces causes an increase in the work function due to the formation of an electrical double layer. Such a reduction in yield has been observed.[221] However, if the oxygen forms a thick layer of oxide before or during heat treatment, the yield will be greatly altered and probably increased. Since, in some cases, the vapor pressure of the oxide is very much less than that of the metal, the oxide surface layer, once formed, can never be removed by mere heat treatment. This is probably the explanation of Warnecke's high values for the yield from aluminum.

There is but little information available about the effects of other gases. Khlebnikov[95] has increased the yield of tantalum by exposing it to hydrogen or helium. It is possible here that the hydrogen was adsorbed as ions. On the other hand, Suhrmann and Kundt[144] observed that exposure to hydrogen had no noticeable effect on the yield from copper, silver, or gold. This is in accord with the fact that physical adsorption of a monolayer of hydrogen atoms should not make any appreciable change in the work function. The behavior of complex surfaces prepared by deliberate oxidation is too extensive to be treated in this section.

1.11 Properties of Secondary Electrons

In the preceding paragraphs, the various factors which may influence the total SE yield from metals have been discussed. In the following, we shall consider some properties of the secondary electrons and related matters.

1.12 Angular Distribution of Secondary Electrons

No recent work is available on the angular distribution of secondary electrons but the results of earlier workers in the field[4,5,14] agree that if the relatively small contribution due to reflected primaries is neglected, the number of secondaries emitted per unit solid angle is greatest in the direction normal to the emitting surface and decreases with increasing angle of emergence φ as $\cos \varphi$. This is independent of the angle of incidence of the primary beam although as discussed previously the absolute value of the yield is not. A result of this type is to be expected since presumably the secondaries which are emitted at large emergence angles must, on the average, traverse a greater path length in the target than those emitted normally, and thus have a greater probability of being absorbed. It should be noted that at very high or very low values of V_p, the proportion of reflected primaries becomes appreciable and their effect is to alter the cosine distribution law as discussed later.

1.13 Shot Effect

The SE yield normally defines the average number of secondaries produced per impinging primary. This is, of course, merely a statistical mean since the total number of secondaries produced by any one primary may vary widely. The study of the resulting fluctuations can result in an estimate of the maximum time of liberation of secondaries but apart from that is now not of much importance to the theory of SE. However, the technical applications, particularly of the results of fluctuation studies by SE multipliers, are of great significance.

A number of workers such as Hayner,[31] Kurrelmeyer and Hayner,[76] Ziegler,[59,60] Shockley and Pierce,[107] and others have studied this statistical problem and their results are essentially in agreement. It would not be appropriate to derive their results here but it should be noted that analyses of the experimental results suggest that the distribution function governing the probability of emission of a given number of secondary electrons per incident primary electron, should be more general than that obtained by the use of a Poisson distribution, i.e., the relative mean square deviation of δ may not be equal to the reciprocal of δ. Shockley and Pierce have shown that for an electron multiplier with n stages each of average gain m, the mean square noise current in a frequency band Δf in the output circuit is given by

$$I_s^2\Delta f = M^2 I_p^2 \Delta f + d^2 \frac{M(M-1)}{m(m-1)} \cdot 2e\bar{I}_p\Delta f \tag{3}$$

where $I_p^2\Delta f$ = mean square noise in the primary current in a frequency band Δf
$\bar{I}_p$ = average component of primary current
d^2 = mean square deviation of m
$M = m^n$ = average overall gain
e = electronic charge.

This result applies for frequencies so low that the period is large compared with the time of collection on the final anode of all the electrons descended from the same primary electron at the input, i.e., the burst duration. Sard[254] has extended the frequency range of the analysis and has shown that for the R.C.A. type 931 photomultiplier tube, the noise spectrum should be essentially uniform from zero frequency to about 100 Mc and should fall rapidly to a very low value for higher frequencies.

1.14 Time of Liberation of Secondaries

In general it has been assumed that the time between the arrival of a primary electron and the emission of a secondary is essentially zero.

By means of shot effect measurements, Hayner[31] concluded that the emission time must be less than 10^{-6} seconds and is possibly less than 10^{-8} seconds. Wang[247] has replaced the reflector in a reflex klystron by a SE surface and has obtained satisfactory operation at 4000 Mc. From this he concluded that the emission time lag must be less than 2×10^{-10} seconds or, if greater, the time lag dispersion must be less than 2×10^{-10} seconds. Greenblatt and Miller[256] made similar observations in a 3000 Mc secondary electron multiplier from which they concluded that at least some of the secondary electrons were emitted in less than 5×10^{-11} seconds. Although these measurements are all somewhat indirect, it is probable that the actual time lag in emission is less than about 10^{-12} seconds and is thus negligible in most experimental work involving SE from metals.

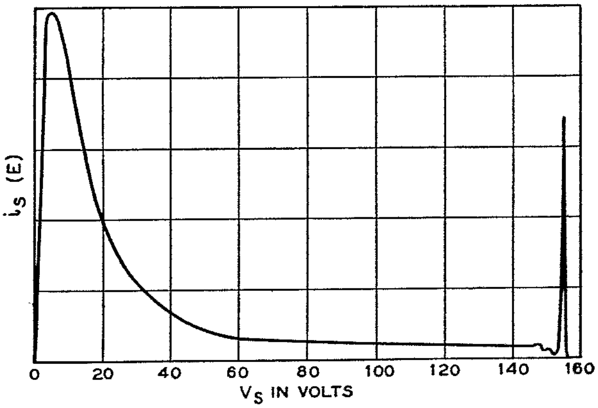

FIG. 5.—Secondary electron velocity distribution from gold.[50]

1.15 Velocity Distribution of Secondary Electrons

It is evident that the velocity distribution of the emitted secondary electrons is of the greatest importance, both in applications of secondary emission and in the theoretical interpretation of the process. It is strange that very little work has been reported concerning this phase recently and consequently we must rely mainly on earlier experimental work, some of which is difficult to interpret.

The general form of the velocity distribution curve resulting from medium values of $V_p(20 < V_p < 1000$ volts) has been nicely demonstrated by Rudberg,[50] one of whose curves is reproduced in Fig. 5. He used a transverse magnetic analyzer with angles of incidence and emergence both equal to 45°. The curve is interpreted as follows: the large majority of the electrons are emitted with energies of a few volts. These are regarded as true secondaries. Merged in this group and extending somewhat uniformly out to energies almost equal to V_p is a relatively small number of inelastically reflected primaries. Finally there is a sharp peak, at energy equal to V_p, of elastically reflected primaries. Apart from experiments expressly designed to investigate reflected primaries, practically all the work on secondary emission deals essentially with the "true" secondaries, i.e., low velocity secondaries. It will later be shown that complete neglect of the reflected primaries is not always possible without introducing considerable error.

1.16 Velocity Distribution of "True" Secondary Electrons

Although many measurements have been made of this aspect of secondary emission, most of them are subject to the same criticisms that have been made of the yield measurements: inadequate outgassing, absence of data on the condition of the target surface or on the crystal structure. It is very difficult to estimate the extent to which the data are affected by these parameters since but few measurements have been made of the velocity distribution as a function of anything but V_p.

The distribution curve is similar, although it does not correspond exactly, to a Maxwellian distribution. The most probable emission energy will be denoted by $V_{s\,\max}$. This is always somewhat smaller than the average emission energy. According to Becker,[3] Brinsmade,[9] and others, for any given target $V_{s\,\max}$ is independent of V_p for 20 volts $< V_p <$ 1000 volts in agreement with a theory by Kadyschevitsch[242] in which it is also shown that $V_{s\,\max}$ should decrease as the surface work function is decreased. Such behavior has been verified by Bronstein[224] who measured the energy distribution as a function of layer thickness of silver on a nickel base.

As discussed in §1.6 there is unconfirmed evidence that the mean energy of secondaries from tungsten can be increased about 1 volt by heating the target to 1500°C.

Kushnir and Frumin[199] have reported that for molybdenum and silver $V_{s\,\max}$ increases as the angle of emergence increases. There is also evidence[33,50] that the velocity distribution is affected by adsorbed gas on the target. Thus the situation is analogous to that for the yield curve: the velocity distribution is determined by a large number of parameters not all of which are known for any given experiment. Even in cases where all the most important parameters have been determined, it is not possible to compare directly the results of different experimenters since the experimental conditions differ and there is not enough known about the effect of the various parameters to enable one to extrapolate from one set of conditions to another.

Table II shows a summary of the most recent data on the energy distribution of slow secondary electrons. The methods used, as described in §1.24 are as follows: RE, retarding electric field; TM, transverse magnetic field; LM, longitudinal magnetic field. The incompleteness of the available data is evident. This is due in most part to the experimental problem of making such measurements with reasonable accuracy. Experimentally and theoretically, the problem of the energy distribution is much more difficult than that of the yield curve. Apart from Kadyschevitsch's[242] work, the problem has not been treated theoretically. Attempts to correlate $V_{s\,\max}$ with the atomic number of the target have not proved successful. Haworth[30,46] has detected some slight subsidiary peaks in the energy distribution curves for molybdenum and columbium but these results have not been confirmed by other experimenters, e.g., Kollath's[163] recent work on molybdenum.

TABLE II. Summary of available data on most probable secondary electron energy.

Target	Method	Inc. angle	Emer. angle	V_p volts	$V_{s\,\max}$ volts	Author	Reference	Year
Ag	TM	45°	45°	155	5.4	Rudberg	50	1936
Ag	RE	70°	0°	10–100	2–3	Langewalter	33	1935
Al	TM	45°	45°	36–176	5–6	Brinsmade	9	1927
Au	TM	45°	45°	155	5.4	Rudberg	50	1936
Be	LM	0°	~ 30°		3	Kollath	163	1940
Cb	TM	45°	45°	147	4.5	Haworth	46	1936
Cu	TM	45°	45°	155	3.3	Rudberg	50	1936
Fe	RE	30°	0°	24–2075	2	Becker	3	1925
Mo	TM	45°	45°	150	3	Haworth	30	1935
Mo	TM	45°	45°	7.5–100	4	Soller	19	1930
Mo after heat treatment	TM	45°	45°	7.5–100	10–20	Soller	19	1930
Mo	LM	0°	~ 30°		2.9	Kollath	163	1940
Pd	RE	70°	0°	10–100	2	Langewalter	33	1935
Pt	RE	70°	0°	10–100	2–3	Langewalter	33	1935
Ta	LM	0°	~ 30°		2	Kollath	163	1940

1.17 Velocity Distribution of Reflected Primary Electrons

Owing in part to the relatively small number of reflected primaries for medium values of V_p, i.e., 20 volts $< V_p <$ 1000 volts, in comparison with what here has been defined as "true" secondaries, the general behavior of reflected primaries has not received much attention. Here it is necessary to specify clearly the range of V_p with which one has to deal.

a. V_p less than about 10 volts. For very low values of V_p it has been clearly demonstrated, notably by Gimpel and Richardson[226] (for $V_p = 1$ volt), that all the secondaries are emitted with the same energy as the primaries, i.e., we are dealing with elastically reflected primaries. In such experiments, therefore, the secondary emission coefficient is replaced by a "reflection coefficient." For such low values of V_p, the effects of contact potential, inhomogeneity in the primary velocities, and adsorbed gas play such an important role as to make the experiments very difficult to perform. Gimpel and Richardson[226] showed that for a copper target, the reflection coefficient is equal to 0.24 which remains constant within 20% for 0.35 volts $\leq V_p \leq$ 10 volts. It is probable that their results were to some extent affected by adsorbed gas on the surface. Bruining[39] has also measured the reflection coefficient at low velocities and showed that for silver $\delta_{\text{reflec.}} = 0.1$ at $V_p = 25$ volts rising to 0.2 at $V_p = 3$ volts. Over the same range of V_p, barium has a $\delta_{\text{reflec.}} = 0.05$ rising to 0.1 for $V_p = 3$ volts. Over this voltage range, Bruining had to separate out the reflected primaries from the true secondaries or inelastically reflected primaries by plots of the energy distribution. The value of V_p at which the emission contains only reflected primaries is not sharply defined. Data on this are so meager that one can only say that the ratio of elastically reflected primaries to the total emission decreases from 100% for very low V_p to a very small fraction around $V_{p\ \text{max}}$.

Modern theoretical treatments[35] of the reflection of slow electrons by an image force type of surface barrier indicate that as $V_p \rightarrow 0$ the reflection coefficient should approach a limiting value of something less than 10% for most metals.

b. V_p greater than 10 volts. The type of energy distribution curve obtained in this voltage range was shown in Fig. 5. Rudberg[50] investigated the fine structure for energies approaching the primary energy, for targets of copper, gold, and silver and for composite targets of calcium on silver, calcium oxide on silver, and barium oxide on silver. He found several discrete peaks differing from V_p by a few volts. Although their magnitude varied with V_p, their position relative to V_p did not, indicating that they represent discrete energy losses due to inelastic collisions of the primary electrons. These peaks were found to be characteristic of the target material and, indeed, by evaporating barium or calcium on the target, he found that the resulting changes in the loss peak structure were sufficient to identify surface layers of only a few atom diameters in thickness. Rudberg and Slater[51] developed a quantum mechanical theory dealing with this phenomenon which will be discussed later.

Farnsworth[21,45,110] has made extensive investigations of the scattering of the elastically reflected primaries using polycrystalline or single crystal targets along the lines of the classic experiments of Davisson and Germer.[10] He has shown that for $V_p = 200$ volts, at least 90% of the elastically reflected primaries arise from the first two atomic layers. Such electrons do not obey the cosine law discussed in §1.12 but are emitted preferentially in accordance with the Bragg law. However, such studies form a rather specialized field. Although they enable us to obtain considerable information about some aspects of the interaction of electrons with matter, they are not of general interest in secondary emission since for all but very small values of V_p, these electrons usually form an extremely small fraction of the total emission. There are some special cases in which the elastically reflected primaries cannot be ignored. Davisson and Germer's[10] experiments on electron reflection showed that when a single crystal is bombarded by primaries of the right velocity and angle of incidence to satisfy the conditions for Bragg reflection, as many as 40% or more of the incident primaries may be elastically reflected. Since these primaries are reflected in beams whose directions are determined by the crystal structure, they may produce appreciable deviations from the cosine law of angular distribution of secondaries.

Although usually the elastically reflected primaries form a negligible part of the total emission, the sum of these and the inelastically scattered primaries certainly may not. Unfortunately there is very little information available on this phase. Although it is impossible to separate slow inelastically reflected primaries from the mass of true secondaries, it is perhaps useful to pick an arbitrary value of energy and, merely for the sake of classification, define as scattered primaries, those electrons which are emitted with energies greater than this value. From Rudberg's curves it is reasonable to pick 50 ev as the arbitrary distinguishing energy. Such a classification could only apply for values of V_p considerably larger than this limit. Let us assume that it holds for all V_p greater than 100 volts. Although this definition is without physical basis, nevertheless it is a very useful concept practically. For example, early work by Farnsworth[5] showed that for copper with $V_p = 102$ volts, 25% of the emitted electrons had energies greater than 50 ev. A crude integration of Rudberg's published curves shows that with $V_p = 155$ volts, the corresponding percentage of scattered primaries of over 50 volts energy is: gold 21%, silver 31%, copper 35%. Although these figures are not very exact, they are such as to indicate that the high speed scattered primaries are by no means negligible. Most SE yields are obtained with an electron gun bombarding a target which is more or less surrounded by a collector. The primary current is often measured by putting the collector at a negative potential of about 50 volts with respect to the target and measuring the target current. Obviously, this may give an erroneous value for the primary current. If these high speed electrons strike the collector, they may in turn produce secondaries which will be collected on the target thus possibly reducing the actual error but not the uncertainty. It is true that the beam current can be determined by measuring the total current leaving the cathode if it can be guaranteed that practically none of the electrons leaving the cathode strike anything other than the target. However, this is frequently not the case. Thus it must be emphasized that a detailed knowledge of the behavior of high velocity scattered primaries must be obtained before very accurate SE measurements can be assured.

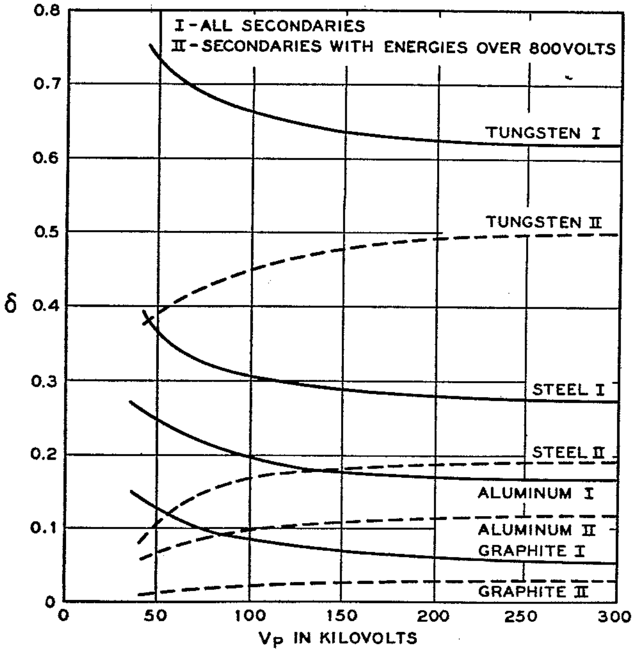

FIG. 6.—Variation of yield for high V_p.[259]

For higher values of V_p, the proportion of high velocity electrons increases. Stehberger[12] gives the following values for a gold target:

V_p Volts	Electrons Emitted with Energies Greater Than 50 Ev (in %)
1000	20
2000	28
7600	42
11000	48

Recent work by Trump and Van de Graff[259] is shown in Fig. 6. As they observed practically no electrons with energies between 20 ev and 800 ev, the dotted curves represent essentially what we have defined as high speed scattered primaries. In this work V_p is very large compared with 800 volts so the relative lack of electrons in this range is to be expected if the high speed electrons have a more or less equal probability of being obtained at any voltage between 50 volts and V_p. In Fig. 7 is shown a replot of Fig. 6 giving the percentage of scattered primaries as a function of V_p.

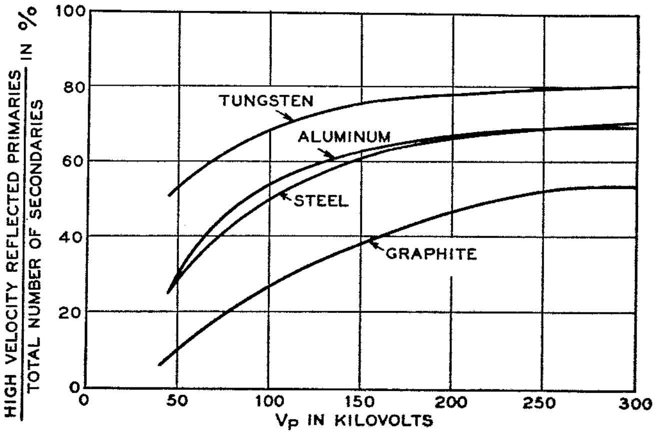

FIG. 7.—Replot of Fig. 6 showing percentage of reflected primaries as a function of V_p.

1.18 *Range of Primary and Secondary Electrons*

From the discussion in §1.2 on the shape of the yield curve, it is evident that two extremely important factors are: (1) the rate of loss of energy of the primary electrons and (2) the rate of absorption of the secondary electrons. The entire problem of the rate of energy loss of electrons in passing through matter is too extensive and complex to be dealt with adequately here. Rather, we shall discuss only those aspects which are pertinent to secondary emission. Bethe[16] has given an excellent wave mechanical treatment of the rate of energy loss of electrons with energies greater than several thousand electron volts, and this theory is in good agreement with experimental results. However, Bethe's equations are not valid for lower electron energies and thus cannot be integrated to give the total range, i.e., the total distance that is traversed before the electron becomes indistinguishable from an electron with thermal velocity. Moreover, the most direct experimental approach, which consists of measuring the electron transmission of thin foils, becomes very difficult for low velocity electrons. The foils must be extremely thin and there is considerable danger that most of the transmission is due to thin spots or actual holes through the foil. Another potential source of error has been pointed out by Katz[70] and Was and Tol,[38] who have shown that changes in the crystal structure of such thin films can be brought about by electron bombardment which alters the transmission. Thus it cannot always be assumed that the behavior of electrons in a thin foil is the same as in the bulk material.

It is generally assumed that the electron density I decreases exponentially with distance x, i.e., $I = I_0e^{-\alpha x}$ where α is the absorption coefficient. Becker[13] has investigated the transmission of nickel foils in the low velocity region giving a value of $\alpha = 1.5 \times 10^6$ cm.$^{-1}$ which is nearly independent of primary velocity up to 1000 volts.

From classical theory, Whiddington[1] has shown that the rate of energy loss is given by

$$[eV(x)]^2 = (eV_p)^2 - ax \tag{4}$$

where $eV(x)$ is the electron energy at distance x from the surface
eV_p is the electron energy at the surface
a is a constant.

Terrill[2] has shown that for many metals $a/\rho = 0.40 \times 10^{12}$ volt^2 cm.$^{-1}$ within an accuracy of about ±10% where ρ is the density. As will be shown later, Bruining[216] and others have constructed classical theories of secondary emission using these two formulas. Bruining has shown that

$$eV_{p\,\max} = 0.92\sqrt{a/\alpha} \tag{5}$$

If known values of $V_{p\,\max}$ and Terrill's values of a are used, values for α can be calculated. By this means, Bruining obtained values for α ranging from 4×10^6 cm.$^{-1}$ for cesium to 2×10^7 cm.$^{-1}$ for molybdenum. The value for nickel was 1.2×10^7 cm.$^{-1}$ which is considerably in excess of Becker's experimentally determined value. This probably reflects mainly the extent of the error involved in assuming eq. (4) for the rate of energy loss of the primary electrons.

With a value for α and also data on the variation of yield with incident angle, it is possible to arrive at a figure for the mean depth of origin of the secondary electrons. As shown in §1.7 Bruining[41] obtained a value for αx_m by this method. Using Becker's value for α for nickel, he obtained for the mean depth of origin in nickel, $x_m = 30$ A. or 14 atomic layers, for $V_p = 500$ volts.

Another method of determining x_m is to cover the target with successively thicker layers of another metal with a considerably different value of δ. For very thin films δ will be characteristic of the target metal; for thick films it will be characteristic of the layer material. The intermediate region is of such a layer thickness as would correspond to x_m. Kadyschevitsch[243] has pointed out that when the SE is also a function of the work function, such a procedure may yield misleading results. Essentially the argument is that the work function of a thin layer is characteristic of neither the target material nor of the layer material in bulk. This argument would appear to be valid mainly for low velocity primaries where x_m is only a few atomic layers. Using the layer technique Copeland[155] obtained the maximum depth of origin of secondary electrons from platinum on aluminum, as shown in Fig. 8. It will be seen that the maximum depth of origin increases linearly with V_p for small V_p.

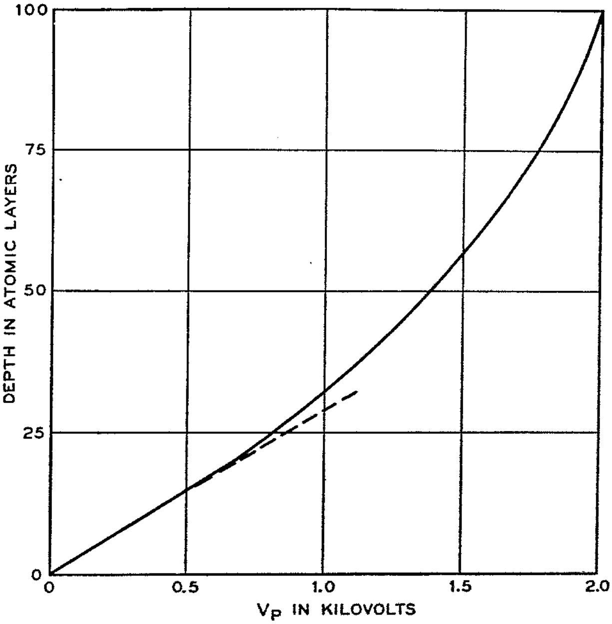

FIG. 8.—Maximum depth of origin of secondaries in platinum.[155]

Hastings,[158] studying silver on platinum, concluded that secondaries with less than 20 ev energy originate within 15 atomic layers of the surface while those of less than 50 ev energy originate within the first 30 atomic layers. He also concluded that most of the high velocity scattered primaries arise within the first atomic layer. This last conclusion is in agreement with work by Farnsworth[45] and Rudberg.[50]

Truell[223] studied layers of magnesium on carbon with primary energies from 2000 to 8000 volts. He concluded that the depth of origin of secondary electrons in the energy range from 10 volts to 200 volts varies from 2×10^{-7} cm. to 4×10^{-5} cm.

1.19 Theory of Secondary Electron Emission from Metals

A number of attempts have been made to construct a purely classical empirical theory of secondary emission.[63,171] Here we shall follow Bruining's exposition.[216] Let us assume that the primaries lose energy according to the Whiddington law (see §1.18), i.e., $[eV(x)]^2 = [eV_p]^2 - ax$. We assume that the rate of energy loss of primaries is proportional to the number of secondaries produced per unit path length and also that the secondaries are absorbed exponentially with an absorption coefficient α. Then the number of secondaries available in vacuum which arise from a layer of thickness dx at a distance x from the surface is:

$$di_s = -Ki_p e^{-\alpha x} \cdot \frac{d[eV(x)]}{dx}\, dx \tag{6}$$

where K is the constant of proportionality. Using the Whiddington law

$$di_s = \tfrac{1}{2} Kai_p e^{-\alpha x}(e^2V_p^2 - ax)^{-\frac{1}{2}} dx \tag{7}$$

The maximum penetration of the primaries is given by putting $eV(x) = 0$ in eq. 4. Hence $x_{\max} = \frac{e^2V_p^2}{a}$. Thus

$$i_s = \frac{1}{2} Kai_p \int_0^{x_{\max}} [e^2V_p^2 - ax]^{-\frac{1}{2}} e^{-\alpha x} dx \tag{8}$$

$$= Ki_p \sqrt{\frac{a}{\alpha}}\, e^{-r^2} \int_0^r e^{y^2} dy \tag{9}$$

where $r = eV_p \sqrt{\frac{a}{\alpha}}$. The substitution here is $x = \frac{e^2V_p^2 - (a/\alpha)y^2}{a}$. To obtain $V_{p\,\max}$ we differentiate eq. 9 with respect to eV_p and equate to zero.

$$\frac{di_s}{d(eV_p)} = Ki_p \left(1 - 2re^{-r^2} \int_0^r e^{y^2} dy\right) = 0 \tag{10}$$

which is solved for $r = eV_p \sqrt{\alpha/a} = 0.92$ or

$$eV_{p\,\max} = 0.92 \sqrt{a/\alpha} \tag{5}$$

Using known values of a and α for nickel, Bruining obtained $V_{p\,\max} = 1420$ volts as against the experimental value of 550 volts.

For $V_p \gg V_{p\,\max}$ the integral in eq. 9 can be expanded by partial integration and all terms but the first neglected yielding an error of only

2% for $r = 5$. This gives

$$i_s = Ki_p \frac{a}{2\alpha \cdot eV_p} \qquad (11)$$

For $V_p \ll V_{p\,\max}$, eq. 9 reduces to

$$i_s = Ki_p eV_p \qquad (12)$$

which is independent of a and α, i.e., there is negligible penetration of the target. It must be emphasized that these expressions do not include reflected primaries, which for the two limiting cases, become quite important.

Such a theory as this demonstrates the three main processes involved in secondary emission: loss of energy by the primaries, transfer of energy to secondary electrons, and absorption of secondaries before emission. However, nothing is said about the detailed mechanism involved in any of these processes. Inasmuch as this involves the interaction of electrons with densely packed matter, little progress was made theoretically until the advent of quantum mechanics. Since then several theories have been developed. However, a detailed exposition of these would be far too lengthy to be warranted in this review; only the principal features of each can be mentioned.

1.20 Rudberg and Slater's Theory

Rudberg and Slater[51] developed a quantum mechanical theory to account for the reflected primaries which have suffered discrete energy losses as discussed in §1.17. Using the wave functions for an infinite crystal, they considered the probability of excitation of a bound electron to a higher energy level. The inelastically reflected primary electron would demonstrate this energy loss. Detailed calculations for copper showed good agreement with experiment for small energy losses. The departures from experiment for higher losses were attributed to the fact that the free-electronlike wave functions used were not a proper approximation to the actual functions in the region of the surface.

1.21 Wooldridge's Theory

Following the work of Born, Bethe, and others, Fröhlich[22] developed a theory of secondary emission based on wave mechanics. The theory predicts about the right order of magnitude for the secondary emission and also the approximate course of the δ vs. V_p curve. Later Wooldridge[151,184] pointed out some errors in Fröhlich's treatment and formulated a more complete and quantitative theory.

Wooldridge uses Bloch eigenfunctions for the simple crystal lattice and then treats the effect of the primary electron as a perturbation problem. He shows that the principal source of energy loss by primary electrons with energy not very much greater than $V_{p\ \max}$ is caused by the production of secondary electrons which arise from loosely bound valence electrons. He shows that the contribution by inner shell electrons is very small. This differs from Bethe's theory of rate of energy loss by electrons in which he considers primaries of much higher velocity. The boundary between the two theories lies in the region of 1000 ev primary energy. Wooldridge shows that the primaries lose energy in discrete units which, in the case of silver, amount to about 25 ev. Thus primary electrons of energy lower than this value (inside the metal) should not produce appreciable SE.

Having developed an expression for the rate of loss of energy of the primaries and for the production of secondaries, he considers how many of these secondaries can escape assuming exponential absorption. Due to uncertainty concerning the lattice fields and the absorption coefficient, the final expression for the yield involves an undetermined parameter in addition to the energy constants of the metal. This parameter is determined by matching the value of $\delta_{\max}$ to that determined experimentally. By this procedure he obtains good agreement with experimentally determined yield curves for high density metals. However, the agreement is not nearly as good for low density materials. He suggests that this may be due to neglect of energy loss by the primaries due to free electron or Rutherford scattering which becomes increasingly important as the atomic volume increases. Wooldridge also estimates that the change in yield with work function should agree with experimental results by Treloar and others. (See §1.4.)

1.22 Kadyschevitsch's Theory

Kadyschevitsch[160,196,242] has developed a theory of secondary emission on somewhat different lines from Wooldridge. It is essentially based on classical dynamics and quantum mechanics is used to determine the limits of validity of such approximations and to set up the electron band picture. He justifies the use of classical mechanics by postulating a sufficiently high relative velocity between the primary and the incipient secondary electrons. This restricts the theory to the range of $V_p \gtrsim 200$ volts. He considers only the reaction between a primary electron and a perfectly free electron in the Fermi gas. He concludes that the number of bound electrons which can be emitted as secondaries is negligibly small. This is in disagreement with Wooldridge's conclusions. Since lattice interaction in the collision process is neglected, a normally directed primary cannot produce any secondaries in the metal with velocity components pointed toward the surface. Therefore he then considers the dispersion and absorption of secondaries in detail and develops expressions for the dispersion following multiple elastic collisions. His final expression for the yield contains the electrical constants of the metal (work function, etc.) and also the mean free paths for elastic and inelastic collisions of primary and secondary electrons. Since the mean free paths were not subject to direct measurement, these quantities were estimated indirectly. He concludes that when the ratio of the effective mean free paths of the primary to the secondary electrons is equal to 0.56, the yield is a maximum for normal primary incidence. For silver and nickel he obtains good agreement with experimental data for δ/V_p restricting V_p to the range 200–1400 volts, although the details of calculation are not given.

The theory is also applied to compute the variation of δ with incident angle of the primaries, the distribution of the secondary electrons in energy and direction, and the forward yield of secondaries from a thin target, all of which are in reasonable agreement with experiment.

Unfortunately, this theory contains a number of parameters which can be determined only by indirect methods. It is most difficult to estimate the extent of the possible errors involved. Consequently, data are lacking to enable one to predict the yield curve for other metals.

1.23 Conclusions about Existing Theories

At the present time, the available theories of secondary electron emission can explain the process in general terms but lack the detailed data necessary to give a complete quantitative description. As yet, little attention has been given to the effect of the surface except to postulate a surface barrier. Yet experimentally it has been demonstrated that the condition of the surface plays a considerable role in determining the yield and thus it would appear that any complete theory must consider the surface of the metal in detail.

1.24 Methods of Measurement of SE for Metallic Targets

Apart from the original discovery of secondary emission, probably the most important development has been the realization of the extensive degassing treatment and careful high vacuum techniques which are essential to give reproducible and reliable results. The importance of this was emphasized by Warnecke and by many subsequent experimenters. The subject of high vacuum technique is too extensive to be treated here and reference should be made to some of the recent papers where careful descriptions of the experimental techniques have been made.

Nearly all yield measurements on metals have been made by one of two methods, the triode method or the electron gun method, which are as follows:

In its simplest form, the triode method involves an ordinary triode tube in which the grid is positive in potential with respect to the plate, which is in turn positive with respect to the cathode. The plate forms the secondary emitter, the secondary electrons being collected by the grid. Let the current leaving the cathode be i_k of which the grid intercepts a fraction s. Then the primary current striking the plate is $i_k(1 - s)$ and the secondary current leaving the plate which is collected by the grid is $\delta i_k(1 - s)$ where δ is the secondary yield of the plate at V_p = plate to cathode potential. Thus the current in the plate circuit is

$$i_p = -(\delta - 1)(1 - s)i_k \tag{13}$$

and the current in the grid circuit is

$$i_g = \delta i_k(1 - s) + si_k \tag{14}$$

Solving for δ we get

$$\delta = 1 - \frac{i_p}{(1 - s)(i_g + i_p)} \tag{15}$$

together with the obvious relation

$$i_k = i_g + i_p \tag{16}$$

Examination of eq. 15 shows that the fraction s intercepted by the grid must be determined independently and all the variations of the triode method hinge on this determination. These will be mentioned briefly; they are discussed in much greater detail by Treloar.[109] Several depend on the fact that for a given geometry, s is a function only of the ratio V_p/V_g where space charge is neglected.

The most direct approach is to calculate s from the geometry.[8] This requires a specially designed tube and even then is none too satisfactory. Hyatt[11] measured s by using positive ions instead of electrons with $|V_p|$ less than 100 volts where the number of secondaries produced is very small. However, he found s essentially independent of V_p/V_g which is not normally true. Lange[6] used low velocity electrons ($V_p < 10$ volts) and assumed that the secondary emission was negligible. Since we expect $\delta \sim 0.2$ due to reflected primaries, this is of doubtful validity. Moreover, when using very low voltages, the problem is further complicated by the potential drop across the filament, the initial velocity distribution of the primaries, and the effect of contact potentials and space charge. Lange also used another method consisting of a magnetic field parallel to the tube axis to suppress the relatively slow moving secondary electrons. It was shown that this is valid only for $V_p/V_g \sim 1$ and thus is of limited application. Myers[79] made use of the difference in energy of the primary and secondary electrons and measured the temperature rise of the anode. Correlating this with the secondary electron velocity distribution, he obtained a measure of s which was independent of space charge. However, the experimental techniques required are very difficult and the method is valid only for $V_p > 200$ volts. De Lussanet de la Sablonière[25] developed a graphical analysis of the tube characteristics which by successive approximations gives the desired result. However, severe restrictions are placed on the voltage range which can thus be used. Treloar[109] constructed a second tube, identical with the triode on which measurements were to be made, except for a suppressor grid between the grid and plate. He obtained s from the second tube in which the secondary electrons were suppressed.

A variation of the triode method was developed by Treloar[55] in which the yield from a target in filament form can be measured. The filament was mounted near the cathode inside the grid of a cylindrical triode. By a graphical analysis of the tube characteristics, he obtained values of the yield from the filament target which checked quite well with yields obtained by other methods on flat targets. For large V_p, δ so determined will be too large since not all the primaries strike normal to the surface.

The majority of the yield measurements are now done by the electron gun method. Here a well defined narrow electron beam is formed and passes through a hole in the collector so as to strike the target. The secondaries so produced are taken up by the collector which surrounds the target. By careful collimation it can be arranged that practically no primaries strike the collector. As discussed in §1.17, some difficulty may be experienced due to primaries reflected with or without energy loss from the target. This method allows a nonuniform target to be explored by deflecting the primary beam. In general, the results are more easily interpreted than in the triode method. It requires a more complicated tube, and in particular, careful electron gun design, to give a well collimated, monochromatic primary beam with a constant focus spot over a wide range of primary voltage.

For measurements of the effect on the yield of various parameters other than V_p, an especially accurate technique is available. In an electron gun tube the target current is measured and V_p adjusted until the target current is zero; i.e., $\delta = 1$. The parameter, such as temperature, is then changed and V_p adjusted to give zero target current again. The actual change in δ must be obtained from an independent determination of the slope of the yield curve around $\delta = 1$. This has the advantage common to all null methods that very high amplification can be used in the measurement circuit itself.

Three methods have been used for measurements of the energy distribution of the secondaries; retarding electric field, transverse magnetic field, or longitudinal magnetic field which are abbreviated respectively to RE, TM, LM. In the RE method, the collector in an electron gun tube is run negative with respect to the target and the secondary current is plotted as a function of the collector to target potential. The first differential of this curve is the desired energy distribution. It should be emphasized that the collector should be spherical in shape, with the target of relatively small size, at the center. Otherwise a true energy distribution will not be obtained; e.g., if target and collector are parallel planes, only the normal component of velocity is measured.

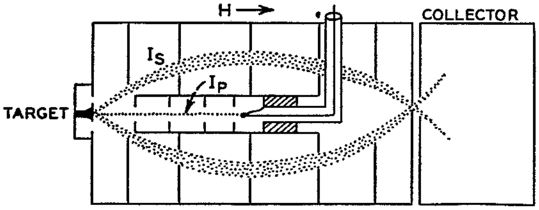

FIG. 9.—Measurement of secondary electron velocity distribution with a longitudinal magnetic field.[163]

In the TM method, electrons coming off the target in some given direction are fed into a magnetic analyzer consisting of a semicircular apertured tube in a uniform transverse magnetic field. The current to a Faraday Cage collector at the output end of the analyzer is obtained as a function of the magnetic field and this determines the energy distribution directly. In general this is more accurate than the RE method as it does not depend on a differentiation of the results. However, the TM method measures only those electrons which are emitted in one specified direction while the RE method includes all the emitted secondaries. For a complete description of the TM method, refer to Rudberg.[50]

Recently Kollath[163] employed another method originally used by Klemperer for β-rays. Termed the LM method, a magnetic field is parallel to the primary beam. Apertures are set up so that all secondaries emitted within a certain cone enter the linear analyzer. The axial focusing properties of the magnetic field are used to select secondaries of a given velocity which are measured in a Faraday Cage. As in the TM method, the relation of the Faraday Cage current to the magnetic field gives the energy distribution directly. The LM method allows many more secondaries to be used in the measurement than in the TM method.

Hence a smaller primary current may be used giving a greater protection against space charge effects. However, it does assume that the energy distribution is the same in all directions making a given angle with the normal to the target surface. As far as is known this assumption is correct for polycrystalline targets although it might not be valid for some coarsely crystalline targets.

All energy distribution measurements require the elimination of stray fields and of space charge effects and corrections for contact potential. Thus the experimental techniques are much more difficult than those involved in simple yield measurements.

II. INSULATORS

2.1 Secondary Emission from Insulators

Insulators are normally defined as those substances which have resistivities in excess of about 10^6 ohms-cm. at room temperature. Any insulator, which can be raised to a sufficiently high temperature without changing form, can be classed as a semiconductor. If the yield depends markedly on the conductivity, this presents a certain ambiguity which is, however, no worse than some others which occur in this phase of SE. The number of variables involved in the SE from insulators is much greater than for metals and so are the experimental difficulties. Consequently, apparent contradictions in results and their interpretations by various authors are not uncommon. Since much of the available information cannot be simply classified, this section cannot contain descriptions of all recent work but rather presents those results which, it is hoped, will be of most general interest.

2.2 Sticking Potentials and Yield

Most insulators have a δ/V_p curve similar in shape, although not necessarily in magnitude, to that for metals in which, for a certain range of V_p, the yield is greater than unity. There will thus be two bombarding voltages for which the yield is unity. These will be designated at V_p^{I} and V_p^{II} corresponding to positive and negative slopes respectively of the δ/V_p curve. These points assume greater importance with insulators than they do with metals because if an insulator is bombarded by a continuous flow of electrons, these points serve to separate three different types of operation. If V_p is less than V_p^{I}, the surface charges negatively until it approaches the cathode potential when no more primary electrons can strike it. If V_p is greater than V_p^{I} but less than V_p^{II}, the surface will charge positively up to a potential nearly equal to that of the collector such that the space charge reduces the effective yield to unity. If

TABLE III. SE yield of various insulators.

Insulators	δ_{max}	V_p max volts	V_p^{I} volts	V_p^{II} k volts	References
Glasses					
Pyrex	2.3	400	....	2.4	244
Pyrex	2.3	340	< 40	2.3	170
Nonex	....	....	....	3–5	136, 103
Soda	2.1	300	....	0.90	159
Cover	1.9	330	< 60	1.7	170
Ground	3.1	420	....	3.8	170
Quartz	2.1	400	30	2.3	170
Quartz	2.9	440	< 50	2.3	170
Phosphors					
Willemite	....	....	....	3–7	80
Willemite	....	....	....	5–10	136
Willemite	....	....	....	20	103
Zinc sulfides	....	....	....	6–9	136
Calcium tungstate	....	....	....	3–5	136
Alkali Halides					
LiF	5.6	....	....	....	120
NaF	5.7	....	....	....	120
NaCl	6.8	....	....	....	120
NaCl	....	....	20	1.4	125
NaCl	6	600	....	....	147
KCl	7.5	....	....	....	120
RbCl	5.8	....	....	....	120
CsCl	6.5	....	....	....	120
NaBr	6.2	....	....	....	120
NaI	5.5	....	....	....	120
KI	5.5	....	....	....	120
Alkaline Earth Compounds					
CaF_2	3.2	....	....	....	120
BaF_2	4.5	....	....	....	120
BeO	3.4	2000	....	....	218
MgO	2.4	1500	....	....	218
MgO	4.0	400	....	....	87
CaO	2.2	500	....	....	218
SrO	2.6	500	....	....	218
BaO	2.3	1600	....	....	218
BaO	4.8	400	....	....	87
Oxide cathode (BaO, SrO)	8	1500	60	3.5	252
Oxide cathode (BaO, SrO)	5–12	1400	40	....	257
Miscellaneous					
Al_2O_3	1.5	400	....	1.7	159
Al_2O_3	4.8	1300	....	....	218
Al_2O_3	2.5	350	....	....	87
Al_2O_3	....	....	20	1.2	125
Mica	2.4	300	....	1.7	159
Mica	2.4	380	30	3.3	170
Mica	....	....	....	3.5	172
Mica	....	....	20	1.0	125

V_p is greater than V_p^{II}, the surface will charge negatively until the yield is unity; i.e., the surface potential becomes equal to V_p^{II}. In many actual insulators, V_p^{II} is to some extent a function of the collector voltage; i.e., as the collector voltage is increased in excess of V_p^{II}, the latter also increases slowly. Nelson[103] concluded that in the absence of a strong field at the surface, negative charges on various parts of the surface exert a "grid" effect which prevents other secondaries from escaping. This will be discussed more fully in §2.3.

Since the unity yield voltages or sticking potentials form the limits for different types of behavior which are important in practice, it is desirable when specifying the yield of insulators to include values for V_p^{I} and V_p^{II}. Table III gives a summary of most of the available information on the maximum yield and the sticking potentials of insulators. These are all supposedly thick targets and as such the results should not include any thin film phenomena, although it is not always easy to ensure this latter condition. These results are also for room temperature or, at least, a temperature such that the yield is not expected to be appreciably different from that at room temperature. Where the "heat conduction" method is used (see §2.9 on measurement methods) this may not be a valid conclusion.

2.3 Saturation of SE Yield

In metals, it is only necessary to apply a collecting field at the surface of the target sufficient to overcome space charge effects in order to collect all the emitted secondaries. A possible exception to this is the case of a very rough target surface. In some insulators, however, it is frequently found[103,244,119] that a considerable field strength is required to obtain saturation of the secondary electron current. Nelson[103] suggested that owing to inhomogeneities in the distribution of potential on the surface, some areas are effectively shielded by others which thus produce a "grid" effect, and that to penetrate to these shielded regions a higher field is required. Such an effect is also created by the finite conductivity of the target if this has not been taken into account by the method of measurement, as discussed in §2.4. Bruining[119] has suggested an alternative mechanism for certain cases based on his observations that a certain time is required for the secondary current to build up to its full value. He proposed that small surface particles become highly charged under the influence of the field and thus secondaries are drawn through the particles with sufficient velocity to create tertiary electrons. This is essentially one hypothesis of "field enhanced emission" which will be discussed more fully in §2.7. Where a definite saturation is finally obtained, it appears probable that the former explanation holds although it is conceivable that both effects could take place simultaneously. If field enhanced emission is involved it is possible that at very high field strengths it would change to thin film field emission (Malter effect).

2.4 Effect of Temperature and Conductivity on SE Yield

Unlike the situation with metals, the yield from insulators may change considerably with temperature if processes are involved which depend on the conductivity. However, if these are not present, if chemical changes are not involved, and if the methods of measurement are not sensitive to changes in conductivity, there is evidence that the yield from at least some insulators is temperature independent. Mueller[244] found that the unsaturated or "apparent" yield from pyrex glass was temperature dependent but that the true yield was independent of temperature over the range studied of 100 to 385°C. Vudynski's[147] work on NaCl and KCl although rather indefinite, indicates no appreciable change in yield on heating to 250°C.

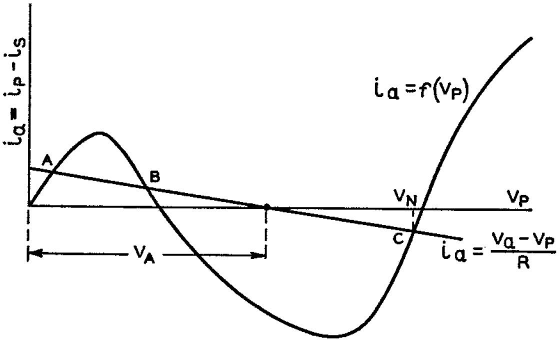

FIG. 10.—Effect of target conductivity on surface potential.

It is evident that both the "grid" effect and field enhanced emission discussed in §2.3 should disappear as the temperature, and with it the conductivity, is increased. However, in the former case the yield should increase with temperature and in the latter case it should decrease. If these were the only temperature dependent processes involved, they could thus be distinguished. Another important effect of the conductivity variation occurs if conventional methods of yield measurement are employed which neglect the effect of the finite conductivity of the target. This is illustrated in Fig. 10 where, following Bruining, we have drawn the dynatron characteristic of the target surface; i.e., the current through the target which equals the difference between the primary and secondary currents, plotted against the energy of the primary electrons V_p as they strike the target. The exact shape of the dynatron characteristic as $V_p \rightarrow 0$ will be determined by the reflection coefficient and by space charge effects in the primary beam. In any case $i_a = 0$ for $V_p < 0$ so that the exact shape at the origin will not affect the following argument. If the target has a finite resistance R, we can also represent the current through it by Ohm's law; i.e., $i_a = \frac{V_a - V_p}{R}$ where V_a is the potential between the cathode and the electrode on the target. Such a line may cut the dynatron characteristic at three points represented by A, B, and C of which B is unstable. If the collector voltage is sufficiently high, there are then two points of stable equilibrium; one for which $\delta \sim 1$ and the other where $\delta \sim 0$. The initial potential of the surface determines at which point the surface will remain. Of course, the target surface cannot exceed the potential of the collector. If the collector potential is less than V_N and i_a is negative, i_s/i_p will be greatly dependent on the collector potential since the target surface potential will tend to follow the collector. In a true insulator where $R = \infty$ it is obvious that special methods of measurement such as discussed in §2.9 must be used. However, this is not always obvious with targets of finite resistivity where standard methods are frequently used. In these cases the effects of target resistivity should be carefully analyzed.

The oxide coated cathode. Owing to its importance technically, the variation of yield with temperature of the oxide coated cathode has been studied in considerable detail. Such a target consists of a thin layer (about .001-inch thick) of a mixture of barium oxide and strontium oxide. At room temperature it is a fair insulator with a resistivity of about 10^8 ohm-cm. This decreases to about 10^3 ohm-cm. at 800°C., the normal operating point as a thermionic emitter. However, the resistivity is a function of the degree of activation and this may introduce some degree of uncertainty as to the validity of close comparison between the results of different workers.

Morgulis and Nagorsky[101] used a standard electron gun measuring technique and relied on the use of small currents to eliminate effects due to the layer resistance. Their highest value of V_p was 1200 volts which was insufficient to reach $\delta_{\text{max.}}$ At $V_p = 1000$ volts they obtained $\delta = 3$ which is much lower than that obtained by Pomerantz or Johnson at that voltage for a well activated target. As the temperature of the target was increased they found that the yield increased exponentially, attaining a value of $\delta = 12$ for $V_p = 1000$ volts at 850°K. where the thermionic emission was considerably larger than the secondary emission. They fitted their curves to the expression

$$\Delta\delta = Ae^{-Q/(2kT)} \tag{17}$$

where $\Delta\delta$ = increase in yield over that at room temperature
$Q = 0.70$ electron volts and is independent of V_p.
They also measured the energy distribution of the normal component of velocity of the secondaries and concluded that the most probable energy, which equalled 4 volts at room temperature, decreased to 2.3 volts at 600°K. Finally, they concluded that further work must be done to ensure that the results had not been affected by the target resistance.

Pomerantz,[252,253] using a DC triode method, obtained values for $\delta_{\max}$ ranging from 3.2 to 6.8 at room temperature for $V_p \doteqdot 1500$ volts and indicated that targets of low activation have substantially lower yields than those with normal activation. He observed an exponential increase in the yield as the target temperature was increased and fitted the results to the same expression as that used by Morgulis and Nagorsky. His values for Q ranged from 0.8 to 1.5 ev. Although thermionic emission was too copious at 850°C. to enable SE measurements to be made, he assumed that the exponential increase in δ observed at lower temperatures would be valid at 850°C. and thus obtained extrapolated values of δ at that temperature ranging from 84 to 136. Such DC measurements do not permit the determination of short time yield variations. To overcome this objection, Pomerantz conducted some pulsed measurements as described in §2.9. Operating in the millisecond range, he could not observe any variations in yield with time which might indicate Malter effect. Using microsecond pulses, he observed nothing abnormal until the target reached such a temperature that it was emitting an appreciable thermionic current. Then he observed the same behavior as that ascribed by Johnson to "Bombardment Enhanced Thermionic Emission" which is described later. Pomerantz obtained similar behavior on bombarding a tantalum target that had been heated by a separate filament so as to emit thermionically. From this he concluded that the effect observed by Johnson "depends critically upon certain experimental factors including the geometrical disposition of components of the experimental tube and is a property to be associated with space charge rather than with the target itself." Pomerantz obtained good agreement of yields measured by the DC method with those observed with the pulsed method and stated that significant increases in δ occurred before the onset of detectable thermionic emission from the target.

Pomerantz also made some retarding potential measurements which, from his tube geometry, must be interpreted not as true energy distributions of the secondaries but rather as some function thereof. He observed a decrease in the peak value of this function as the temperature increased, which he interpreted as being in agreement qualitatively with the results reported by Morgulis and Nagorsky.

We have considered Pomerantz's results in some detail because they contain some substantial points of disagreement with those of Johnson, supposedly on the same type of target. All of Johnson's reported work[235,248,249,257] has been done with a pulsed technique using pulses of a few microseconds duration. At room temperature, he obtains values of $\delta_{\max}$ for $V_p \doteqdot 1400$ volts ranging from 5 to 12, depending on the condition of the target. Defining the yield as that obtained from the peak value of SE current during the pulse, he obtains a variation in yield with temperature as shown in Fig. 11. The waveforms shown are those of the current through the target corresponding to the different temperature ranges. At low temperatures, the current charges up the target surface, causing it to approach the collector potential and thus reducing the effective yield, near the end of the pulse. This effect was not observed by Pomerantz, which suggests that his targets had considerably higher conductivity. As the temperature increases, the yield decreases, levelling off around 500°C. In this temperature region, the conductivity has increased sufficiently to eliminate charging up of the surface. When

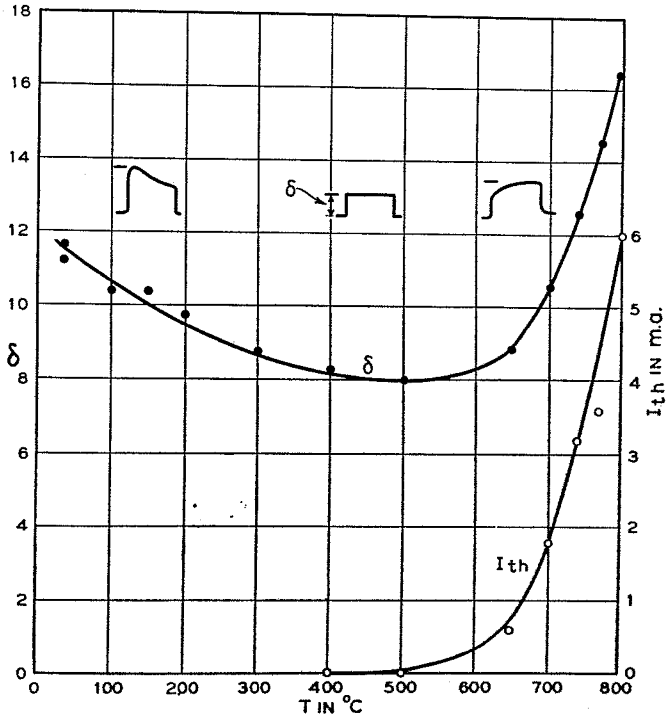

FIG. 11.—Variation of yield of oxide coated cathode with temperature.[257]

thermionic emission sets in, the yield increases sharply but the pulse shape shows that this increase is due to electrons which are not emitted simultaneously with the arrival of the primaries but increase in number with time more or less as $1 - e^{-t/\tau}$ and continue to be emitted after the primary beam is turned off, finally dying away after a few microseconds. If $\Delta\delta$ is defined as the difference between the yield at high temperatures and that at 500°C., Johnson can fit his results to the same equation used by Morgulis and Nagorsky. He interprets the observed yield at high temperatures as being due to a true secondary yield with a δ probably equal to that obtained at 500°C., and, superimposed on this, a temporary enhancement of the thermionic emission caused by a change in the thermionic emission constants as a result of the electron bombardment.

Johnson has shown that the enhanced part of the yield appears to vary linearly with primary beam current (as does the true SE yield), that it is practically independent of bombarding voltage above $V_p = 200$ volts which is radically different from the behavior of the true yield, and that the enhanced yield is roughly proportional to the steady thermionic current. He has obtained these results with a number of targets, with different tubes of differing construction geometrically, and over a range of primary currents. It is difficult to imagine any space charge mechanism, such as was suggested by Pomerantz, which could account for such behavior under these widely differing circumstances, and it appears probable that Johnson's interpretation is essentially correct. If we do not accept it, we are faced with the formidable problem of formulating some other mechanism which can account for the very high yields observed at high temperatures. At present, there is no theoretical justification for such yields from a target with high conductivity. However, when we accept Johnson's interpretation, we have the difficulty of accounting for the increase in yield with temperature at lower temperatures observed by Morgulis and Nagorsky and by Pomerantz, as contrasted with the decrease observed by Johnson. We can only surmise that the target materials were not the same. It is tempting to suppose that Johnson's high yields at room temperature were caused by field enhanced emission which would decrease as the conductivity increased. This will be discussed further in §2.7.

To sum up, it is evident that the effects of temperature on the yield of insulators may be quite complicated and it is probable that only through the use of pulsed techniques can the various processes involved be evaluated properly.

2.5 Velocity Distribution of Secondary Electrons from Insulators

Geyer[217] has measured the velocity distributions of slow or "true" secondaries (see §1.15) for layers of various thickness of NaCl and MgF_2

on a base of nickel by a DC retarding field method. For films sufficiently thin to give adequate conduction, he found that the most probable energy of the secondaries $V_{s\ \mathrm{max}}$ was equal to 1 volt or less.

Vudinsky[149] has also investigated the velocity distribution of sodium chloride by a similar method. He showed that the distribution is the same for a single crystal as for a powdered layer and that $V_{s\ \mathrm{max}}$ is essentially independent of the bombarding voltage V_p although the average energy of the secondaries does increase slightly as V_p increases from 300 to 1500 volts. He obtained values of $V_{s\ \mathrm{max}}$ which were just below 1 volt although no correction was made for "contact" potential. To obtain adequate conductivity, Vudinsky heated up his targets. However, both he and Geyer observed a substantial increase in the yield as the potential of the collecting sphere was made positive with respect to the target; i.e., lack of saturation. Vudinsky observed that although a change in primary current altered the shape of the distribution curve it did not affect the position of $V_{s\ \mathrm{max}}$. Thus, although it is probable that both experiments were affected by the lack of conductivity, yet the values of $V_{s\ \mathrm{max}}$ may be reasonably reliable.

Johnson[257] has shown that the mean velocity of emission of secondaries from an oxide cathode is much less than that from nickel. We may conclude that at least for those few insulators which have been studied, the mean energy and the most probable energy of emission of secondaries from insulators are considerably less than from metals. This is in agreement with conclusions reached by Kadyschevitsch[242] based on an extension of his theory of SE from metals and dielectrics.

Very little is known about reflected primaries from insulators. Bruining[89] has shown that in the range of $3 \text{ volts} < V_p < 25 \text{ volts}$, the yield or reflection coefficient from barium oxide is several times that from barium. Krenzien[220] has obtained similar results on thin layers of alkali halides. He also concluded that the reflection was completely elastic until V_p exceeded a value which corresponded to the long wavelength limit of ultraviolet absorption of the crystal. Rudberg[50] observed loss peaks of BaO and CaO which differed from those of barium and calcium but no data are available concerning the yield of reflected primaries, including all those which have been inelastically reflected for medium or large values of V_p.

2.6 Miscellaneous Properties of SE from Insulators

Practically no information is available on the range of slow electrons in insulators. On indirect evidence, Geyer[217] concluded that electrons with less than 1000 ev energy could travel more than 300 molecular diameters in NaCl. Bethe[189] and others have suggested that the mean free paths of secondaries in insulators should be much greater than in metals since there are relatively few conduction electrons to which they can lose energy. Thus to be absorbed they must recombine with a positive hole or be trapped by an impurity or imperfection. The fact that the maximum yield from insulators usually occurs at a higher V_p than for metals suggests that this may be correct if the depth of penetration of the primaries is roughly the same in both cases.

In some cases the apparent yield from insulators is not independent of primary current. Where surface charging effects take place, the time rate of change of surface potential will be a function of the primary current. Moreover, Bruining[80] has shown that the yield from alkali halides, in particular sodium chloride, decays to lower values with time of bombardment. Presumably this is due to the creation of color centers by the primary bombardment. Eventually metallic agglomerates are formed which effectively change the target composition. The rate at which they are formed is again a function of primary current. Vudinsky[212] has reported an increase in yield of KCl and NaCl with increased primary current. It is probable that this was due to the additional conductivity introduced by the color centers which increased the apparent yield as distinguished from the true yield. He has also "stabilized" the yield from these insulators by exposure to vapors of alkali metals, thus creating more color centers.

It was once thought that the variation of yield with angle of incidence for insulators was quite different from that for metals, involving certain critical angles where abrupt changes in yield occurred. This has since been attributed to surface charging phenomena. Recently Salow[171] and Scherer,[172] using quite different methods, have shown that for mica, glass, and ZnS the variation of yield with angle of incidence agrees well with Müller's data on metals.

2.7 Double Layer Formation and Field Enhanced Emission

The hypothesis of field enhanced emission has been proposed to explain the results obtained in a number of experiments with insulators and insulating films. Essentially, it is assumed that a field is created by positive surface charges or by other means which extends into the body of the insulator and thereby increases the yield either by creating an "avalanche" of electrons or by lowering the surface barrier in the vicinity of the surface charge. The effect is likened to an "inertialess" Malter effect (see §2.4); i.e., the secondary current does not exhibit the time lags characteristic of Malter effect. The hypothesis of field enhanced emission has been used to explain the very high yields obtained from some insulators, lack of saturation of secondary current with collecting field and certain discontinuities in the yield of insulators around unity yield points. Inasmuch as alternate hypotheses can be advanced to explain at least some of these effects, it is a somewhat controversial subject and all the evidence for or against it cannot be presented here. Instead, some representative experiments and arguments will be discussed. The experimental evidence is considered in greater detail in a recent article by Trey.[231]

Hintenberger[125] bombarded targets of mica, Al_2O_3 and NaCl using a DC technique and measured the surface potential as a function of time. For V_p slightly greater than V_p^1 so that $\delta > 1$, he observed that at first the surface charged up close to the collector potential. It then fell off slightly and finally fell abruptly to the cathode potential. For higher values of V_p, the surface remained near the collector potential throughout. He proposed that while the surface charged positively since $\delta > 1$, the primary electrons themselves formed a negative space charge underneath the surface. Thus a field was formed tending to expel electrons from the target, thereby enhancing the yield. Continued bombardment resulted in a movement of the internal space charge towards the surface since further primaries would not penetrate as deeply due to space charge repulsion. Finally when the space charge reached the surface, it would fall to cathode potential. It should be noted that this type of behavior could also be explained by a "patch" field theory in which part of the surface initially had a $\delta > 1$ and part with $\delta < 1$. As the low potential area charged towards cathode potential it would bombard the high potential area with slow electrons for which $\delta < 1$ and eventually the entire surface might fall to the cathode potential. This is probably not a very good hypothesis but at least it is a possible one which does not involve field enhanced emission.

Nelson[104,167] observed a sudden increase in yield with a film of MgO on nichrome as V_p increased through V_p^I where $\delta = 1$. He attributed this to field enhanced emission and showed that it coincided with an abrupt increase in the surface potential. Yasnopol'ski[186] has attributed this action to the layer resistance itself (see §2.4) although Nelson believed that the relation between the net flow of current through the film and the voltage across the film was nonohmic. Copeland[122] has also observed a sudden break as V_p increased through V_p^{II} for gassy sodium films which he attributes to double layer formation. Unfortunately he did not investigate the variation of surface potential simultaneously.

The importance of the hypothesis of field enhanced emission becomes evident when an explanation is sought for the high yields found in many insulators. Bruining and de Boer,[120] Maurer,[202] and Morgulis[164,165] believe that such high yields occur in insulators in which the first empty conduction band lies near or above the potential of the surface barrier (see §2.8) and that there is no special emission from so-called active centers, or enhancement of the yield due to fields formed in the insulator.* On the other hand, Timofeev,[175–181] Pyatnitski,[175] Frimer,[156] and others believe that, in all such cases, positive ions imbedded near the surface help to draw the electrons out in a modified form of Malter effect. Even though the lifetime of such ions before recombination may be very short, they may still help many electrons to escape. Timofeev and his coworkers have carried out a long series of experiments with complex surfaces, the results of which they have explained by this hypothesis. However, they have not used pulse techniques and their results are complicated by the effects of target conductivity so that alternative explanations of their results are applicable. In any case their ideas, right or wrong, have enabled them to prepare high yield surfaces of considerable stability which will be discussed in §3.3.

One of the main difficulties with these various hypotheses of field enhanced emission is that there is not enough information available to put them on a quantitative basis. The validity of Timofeev's assumption that a positive surface charge augments the yield by lowering the work function, cannot be evaluated until more is known about the effect of work function on the yield from insulators. Although the work function plays a relatively minor role in determining the yield from metals, this may not be the case with insulators, especially those in which the bottom of the conduction band lies very close to the top of the surface barrier.

Another unknown factor is the magnitude of the field strength required across all or part of the target to produce an appreciable increase in yield. If this field serves merely to produce a drift velocity of secondaries toward the surface, it may not have to be very large since the secondaries may have a long life time in the conduction band. If, however, the field strength must be sufficient to produce tertiary electrons, as assumed by Bruining, it must be close to that required to induce dielectric breakdown, namely, $\sim 10^6$ volts/cm. In any of the proposed mechanisms of field formation, a finite time is required to set up the field and this suggests a possible approach to the problem. Let us examine the variation with time of the field strength E set up across a target by the production of a net positive charge on the bombarded surface with $\delta > 1$. If the primary electron penetration is negligible compared with the target thickness, then the field strength at any given

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* It should be noted that Bruining does admit the possibility of the existence of field enhanced emission in those cases where the secondaries exhibit a pronounced lack of saturation with collector voltage. He suggests that the secondaries may acquire sufficient energy from the field inside the insulator to produce tertiary electrons.[119]

instant of time "t" seconds after primary bombardment begins, is given by

$$E = (\delta - 1)\rho j_p(1 - e^{\frac{-1.13\times 10^{13}t}{\rho K}}) \text{ volts/cm.} \tag{18}$$

where ρ = specific resistivity in ohm-cm.
j_p = primary current density in amp./cm.^{2}
K = dielectric constant.

This field strength will continue to increase with time until the surface potential approaches that of the collector and space charge effects set in, or until the leakage current density through the target equals $(\delta - 1)j_p$ if space charge is negligible. Thus E cannot exceed either V_c/d or $(\delta - 1)j_p\rho$ where V_c is the potential of the collector relative to the target electrode and d is the target thickness. If the leakage current is neglected, eq. 18 reduces to

$$E = \frac{(\delta - 1)}{K} j_p t \cdot 1.13 \times 10^{13} \text{ volts/cm.} \tag{19}$$

If, instead of assuming that the field is effective throughout the target thickness, we accept Hintenberger's hypothesis that the field is formed between the positive surface and the trapped primary electrons, we would modify eq. 19 by replacing $(\delta - 1)$ by simply δ.

The possibility was mentioned earlier that the high yields which Johnson observed for oxide cathodes at room temperature might be caused by field enhanced emission. In a typical measurement he has observed that the SE pulse reaches its maximum value in less than 10^{-7} seconds. The other required values are $\delta = 11$, $j_p = 1.5 \times 10^{-4}$ amp./cm.^{2}, $K = 3.5$. Putting these in eq. 19, we find that the field strength across the thickness of the target at maximum yield is 480 volts/cm. If we assume that trapped primaries augment the field, we could increase this to 530 volts/cm. These would appear to be rather low field strengths compared to those required in photoconductivity work. It is unlikely that such low fields could affect the yield appreciably unless the bottom of the conduction band lies very close to, or above, the surface barrier since the secondaries will rapidly lose energy until they reach the bottom of the conduction band. The field will then produce merely a drift velocity in the direction of the surface and if the surface barrier cannot be traversed by electrons with thermal energies, they cannot contribute to the SE yield.

2.8 Theories of Secondary Emission from Insulators

Apart from the hypothesis of field enhanced emission which has already been discussed, several theories, mainly qualitative, have been proposed. Bruining and de Boer[120] assume that if the first conduction band available to the secondary electron is near or above the potential of the surface barrier, the secondary has an excellent chance to escape into vacuum, particularly since it probably has a very long mean free path. However, in a semiconductor possessing allowed energy levels which are well below the surface potential, a secondary electron may go to the lower level in which case it cannot escape. It may also go to a higher level, but then it has the possibility of dropping down to the lower unfilled levels thus reducing the probability of escape. They give the alkali halides as examples of the first group ($\delta \sim 5$), and compounds such as Cu_2O, MoS_2, ($\delta \sim 1$) as representative of the second. The latter usually show light absorption at longer wavelengths than the "red" limit of the external photoelectric effect. Bruining and de Boer also showed that for NaCl the actual emission was ten times the rate of formation of color centers by the primary beam. From this they concluded that the emission does not originate from active centers but from the lattice electrons themselves.

Maurer[202] has fitted these ideas into a more quantitative form but since his final equation for the yield involves a number of quantities, such as diffusion coefficients, which are at present unknown, it is difficult to make use of it except qualitatively and, in that sense, he is in agreement with Bruining and de Boer.

Kadyschevitsch[196] has extended his theory of SE from metals to include dielectrics and semiconductors. The treatment is extremely similar except for different parameters. In particular, he assumes that the secondaries must receive a large impulse from the primaries and hence the interaction can be considered as between two free electrons. The final conclusions are again essentially qualitative, since they depend on unknown parameters, and are in general agreement with Maurer.

As is the case for metals, little attention has been paid to the precise role of the surface in any of the theories of SE from insulators. The possible effects of surface states[36] has not yet been treated. There is no evidence that the surface is less important in insulators than in metals and it is indeed possible that here the surface effects are of great importance.

2.9 Methods of Measurement of SE for Insulating Targets

Measurements of the yield from insulators require either that the potential of the bombarded surface be fixed or else that it be measured simultaneously with the SE measurement. The means of accomplishing one or the other will be subdivided into static or quasi-static methods and dynamic methods.

Static Methods

Low current method. Most of the earlier work was done using low values of DC current in either the triode or electron gun method. Although the bombarded surface charges up (or down, depending on whether δ is greater or less than unity), the surface potential changes slowly and the yield can be plotted as a function of time. By extrapolation the actual yield can be deduced from this apparent yield. The inherent limitation to extremely small currents can be relieved if the surface potential can be controlled by some other means such as those that follow.

Heat conduction method. Upon heating an insulator, it becomes either an intrinsic or impurity semiconductor providing thermal decomposition does not occur. Metallic contact can be made to the outside target surface; i.e., the surface opposite to that which is bombarded. If the input resistance of the measuring circuit is much higher than the resistance through the semiconductor, the voltage drop through the target will be negligible. Nelson[103] and others[123,136] have used this method in the study of SE from luminescent screens inside cathode ray tubes. If a high sensitivity electrometer is used for the measurement, the glass envelope need not be heated excessively. The method was also used by Mueller[244] in a study of pyrex glass.

Thin film method. Geyer[217] and others have used very thin insulating films on a metallic base such that electrons could be drawn through the film and thus control the surface potential. However, it is doubtful if the properties of such thin films are representative of those of the bulk material.

Excitation by infrared. In studies on sodium chloride, Geyer[217] produced color centers by the electron bombardment. He then irradiated the target by infrared light, ejecting electrons from the color centers into the conduction band. These electrons then acted to neutralize the surface charge. However, the results are difficult to interpret since the density of color centers as a function of primary electron path length must be known.

In any conduction method it is evident that the concentration of electrons in the conduction band should remain low or else the yield may not be characteristic of that of the original insulator.

Direct measurement of surface potential. There is some doubt if an electrostatic measurement of the surface potential of an insulator is always valid because of the possibility of the formation of a charge layer under the surface.[125] However, the evidence for such behavior is not as yet conclusive. The following methods of surface potential measurement have been used.

Electron beam voltmeter. Scherer[172] and Piore and Morton[168] bombarded the target with an electron beam directed normally to it. A second electron beam was shot at right angles to this beam, parallel to the target surface and a few millimeters above it. The second beam was deflected by the surface potential of the target, the deflection being observed on a fluorescent screen. A deflection calibration was obtained by replacing the insulator by a metallic target and plotting the deflection as a function of target potential.

Grid method. Nelson[167] mounted an auxiliary filament and a collector close to the target surface and used the target surface potential as a "grid" to control the electron flow from the filament to the collector.

Velocity distribution method. Nelson[103] also mounted a Faraday Cage collector in such a way as to intercept secondaries from the insulator but presumably such that voltage variations of the cage would not affect the target surface potential. Plotting the cage current as a function of cage voltage, he obtained a sharp "break" where the cage voltage equalled that of the target.

Direct measurement method. Nottingham[80] embedded some fernico wire probes in the insulator near the bombarded surface and thus measured the surface potential.

Dynamic Methods

One of the reasons for the relatively small amount of work which has been done on SE from insulators is the difficulty or uncertainty of the static methods just described. It appears probable that the application of high frequency or pulse techniques, which are classified here as dynamic methods, will do much to develop this important field.

Direct pulsing method. Although the most recent historically, this is essentially the most basic of the dynamic methods. It was first used by Johnson[235,257] and later by Pomerantz[252] in the study of oxide coated cathodes. Fig. 12 shows Johnson's circuit schematically. The primary electron source is maintained at $-V_p$ but the beam is normally cut off by the negative grid bias. The back of the target is connected through a small resistor to ground and the voltage developed across it is amplified by a wide band video amplifier and displayed on an oscilloscope. Due to the small but finite conductivity of the target, the target surface is normally at ground potential. The pulser then delivers a short ($\sim$ 1μsec.) flat topped pulse to the grid which turns on the primary beam for this interval. This is synchronized with a fast horizontal sweep on the oscilloscope. The impedance of the target layer itself thus produces a current through the load resistor equal to $i_s - i_p$ which appears as a pulse on the oscilloscope. If the primary current and the target conductivity are such as to cause appreciable surface charging during the duration of the pulse, this will be observed as a reduction in pulse height towards the end of the pulse. By varying the recurrence frequency of the pulses i.e., the duty cycle, a sufficient time can be allowed between pulses to enable the target surface again to reach ground potential. The primary current can be measured by observing the pulse with the collector negative as shown or by observing the current pulse leaving the cathode if the beam is well focused on the target. The latter method eliminates the effect of high-speed secondaries as discussed in §1.17. The measurement of δ can be made quite accurately by the use of well designed attenuators in conjunction with the amplifier.

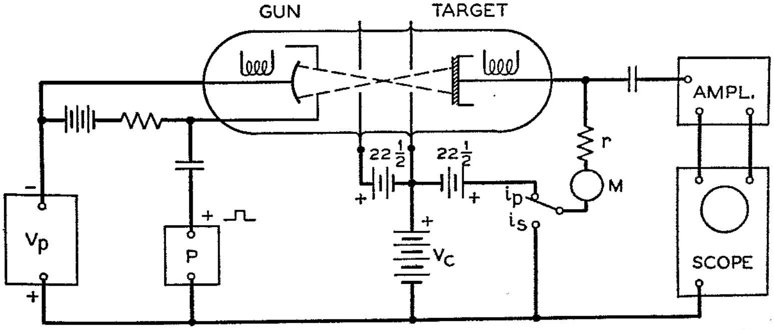

FIG. 12.—Schematic for SE yield determination by direct pulsing method.

Dynamic two gun method. Salow[170] used essentially the same method that Johnson did except that he used long pulses and the very high recurrence frequency of 50 kc. In this case, the surface could not recover to its rest potential before the occurrence of the next pulse so Salow flooded the target with an intense DC electron beam from a second gun at such a potential that $V_p(\text{dc}) < V_p^{\text{I}}$ and thus the target surface remained essentially at the potential of the cathode of the DC emitter. A somewhat similar method has been used by Nemilov.[207]

Heimann and Geyer's method. Heimann and Geyer[159] maintained a steady beam current and pulsed the potential of the primary emitting cathode. To set the target potential initially, they located the upper crossover point V_p^{II}. With $V_p = V_p^{\text{II}}$ as the initial state, they suddenly reduced V_p to a smaller value by pulsing the cathode. The response was displayed in the same way as previously described and they could thus plot out the yield curve between the two crossover points. A limitation of this method is that it can only be used where $\delta > 1$ and it also requires a more powerful pulser than that needed for grid modulation. As they used it, it also required that the point V_p^{II} be located.*

III. COMPOSITE SURFACES

3.1 *Composite Surfaces and Thin Film Phenomena*

This section has been separated from that on insulators because it is not at all clear that the SE properties of thin insulating or semiconducting films on a metallic base are the same as they would be for the bulk material, even if pulsed methods were used which prevented surface charging effects. Moreover, the surfaces to be discussed are usually so complex that no attempt has as yet been made to explain their action except qualitatively. Consequently, both the results and their interpretations differ considerably and the overall picture can be presented only in very general terms. Unfortunately, these are the surfaces which are, at present, of the most commercial value since they may have high yields and also sufficient conductivity to eliminate charging effects. With few exceptions, all of the results to be quoted have been obtained by DC methods and in some cases surface charging probably has played a role.

3.2 *Yield from Photocathodes of the Form [Ag]-Cs_2O, Ag-Cs*

A typical photocathode is formed by oxidizing a silver backing plate so as to give a layer of silver oxide several hundred molecules thick. If cesium is then admitted, it is completely absorbed by the silver oxide. The system is then heated (to 250°C.) and a reaction takes place between the silver oxide and the cesium giving cesium oxide and free silver. Some excess cesium is absorbed on the surface of the layer and a sensitive photoelectric surface results.[29] It was used by Farnsworth[27] as a SE target in a SE multiplier and has since been the subject of many investigations. In general, $\delta_{\max}$ ranges from about 5 to 10 at values of V_p between 500 and 1000 volts. Weiss[58] has shown that the yield is relatively independent of the thickness of the Cs_2O layer although for a certain thickness it does reach a maximum about 20% higher than normal. He has also studied the effects of different base metals and showed that the highest yield, about 11, was obtained for silver and the lowest yield, 2.3, for gold with ten other metals in between. Penning and Kruithof[24] showed that the photoelectric sensitivity could vary considerably but the SE yield would remain essentially constant. Zworykin, Morton, and Malter[61] have shown that the amount of free cesium

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* A similar "manual" pulsing procedure has been used to measure the SE of iconoscope targets. See Janes and Hickock, *Proc. Inst. Radio Engs.*, **27**, 539 (1939).

present for the highest SE yield is less than that needed for maximum photosensitivity. These results have been confirmed by Timofeev and Pyatnitski[53] who obtained the highest yield for an oxide layer of about 200 molecular diameters on a silver base. They observed the SE and photoelectric yield simultaneously as the target was heated and the adsorbed cesium atoms were evaporated off. The maximum SE yield was obtained at a point where the free cesium concentration was much lower than that for optimum photosensitivity. Moreover, the SE yield was much less dependent on the free cesium concentration than was the photosensitivity. They obtained similar results with cathodes formed with rubidium or potassium in place of cesium.[82] From this they concluded that while the photoelectrons arise from the surface, the secondary electrons arise from so-called emission centers consisting of pieces of alkali metal distributed throughout the oxide, and the escape from the target of the secondaries is aided by field enhanced emission.[177]

Dobroljubski[42–44,67] observed that the SE yield correlated with the integral photosensitivity in the ultraviolet but not in the visible or infrared. He concluded that the secondaries arise either from the oxide layer or the base material. Treloar[109] obtained yields similar to Zworykin's using a base material of either silver or copper. He also prepared a target which did not contain free silver in the cesium oxide and obtained practically the same yields as previously. From this he concluded that the secondaries do not arise from metallic emission centers in the oxide as claimed by Timofeev and Pyatnitski. Borzyak[117] also arrived at the same conclusion as did Treloar. It should be mentioned that Treloar found that he could increase the yield from such targets by about 20% by "aging" them. This consisted of drawing a 1-milliampere space current from the target for several hours.

Kwarzchawa[48] observed a decrease in SE yield from a surface whose photoelectric yield had decayed and concluded that the secondaries must arise from the adsorbed cesium layer. As previously discussed, it is most unlikely that a monomolecular adsorbed layer could give rise to an appreciable SE yield. However, it is quite possible that the photoelectric exhaustion caused a change in conductivity and could thus affect the yield.

Khlebnikov and Korshunova[94] demonstrated that it was necessary to have free silver or free cesium atoms in the oxide layer to obtain a high yield and concluded that the secondaries arise principally from these active centers. However, they admitted that the role played by these free particles might be merely to increase the layer conductivity.

From all this mass of data, much of it conflicting, we can arrive at the important conclusions that the photoelectric sensitivity to visible light has nothing to do with the SE yield properties and that the secondaries arise from within the oxide layer. Bruining believes that the free metallic particles merely serve to improve the layer conductivity while Timofeev thinks they are electron sources and the emission is aided by a positive space charge. Experiments, which may show conclusively which point of view is more nearly correct, have not yet been performed.

3.3 Yield from Other Oxidized Targets

Certain alloys have been shown to give a very high SE yield following oxidation which is frequently hastened by subjecting the target to a high frequency discharge in an oxygen atmosphere. Zworykin, Ruedy, and Pike[215] have obtained yields as high as $\delta = 10$ with a silver magnesium alloy so treated. Such yields were somewhat unstable with time. However, a yield of $\delta = 7$ could be obtained which remained very stable after 200 hours aging. Yields of $\delta = 16$ have been obtained with this alloy by Friedheim and Weiss.[192] Malter[200] has made velocity distribution measurements on magnesium-silver alloy and reported values for the most probable velocity $V_{s\,\max}$ ranging from 5.5 volts for $V_p = 100$ volts to 4.0 volts for $V_p = 200$ volts. Such a dependence on primary voltage is most unusual. He employed a simplified magnetic analyzer and it is possible that the observed variation of $V_{s\,\max}$ might be caused by the method of measurement.

Gille[193] and Mathes[201] reported high yields for alloys of beryllium with nickel, cobalt, iron, copper, tungsten, and molybdenum, with the best results for beryllium-nickel. If the oxidation process is continued too long, instability and Malter effect result. Randenbusch[209] has observed that poisoning of such surfaces occurs if an oxide cathode is activated in the presence of the target. However, this poisoning can be removed by subsequent heat treatment.

Timofeev and Aranovich[176] describe surfaces of oxidized magnesium and oxidized barium. Optimum yields were obtained for layers about forty molecules in thickness. Such targets can stand much higher heat treatments than the photocathode type. With $\delta_m \sim 5$ at room temperature, it increases to $\delta_m \sim 7$ at 800°C. If heated much above this, it drops to $\delta_m \sim 3$ and remains there henceforth. These targets were prepared by evaporating the magnesium or barium onto the base metal in vacuum followed by subsequent oxidation. Aranovich[233] has also described surfaces of microdispersed MgO on nickel prepared by evaporating magnesium through an atmosphere of dry oxygen. He states that yields of $\delta_m \sim 80$ could be obtained which although showing time lag effects, responded sufficiently quickly to follow a 40 kc modulation of the primary beam. Yields as high as $\delta \sim 10{,}000$ were obtained but definitely exhibited Malter effect. Bruining and de Boer[119] had used this type of surface previously and reported yields of $\delta_m \sim 18$. Schnitger[173] believes that free magnesium is necessary in the oxide to obtain maximum yields. He has shown that MgO films are relatively insensitive to exposure to oxygen at room temperature although they are rapidly destroyed by water vapor.

Nearly all these high yield surfaces with yields greater than about 10 show a lack of saturation with collector voltage and a certain amount of instability which, if the oxidation is continued, may break over into Malter effect. The evidence suggests that the yields may be the result of field enhanced emission.

3.4 Malter Effect (Thin Film Field Emission)

In 1936 Malter[49] reported some remarkable results obtained with a cathode of composition [Al]-Al_2O_3-Cs_2O. These were formed by oxidizing an aluminum plate to give a film of Al_2O_3 about 2000 A. thick. He coated this with cesium, heated it, and oxidized it. With bombarding voltages of a few hundred volts he obtained emission currents from the target which were as much as one thousand times the primary current. He found that the emission current varied as a power of the collector voltage V_c and as a power of the primary current I_p, within certain limits of V_c and I_p. The emission current did not reach its full value until some time after the bombardment began. On shutting off the primary current, the emission current decayed rapidly at first, and then slowly approached the zero value asymptotically. This decay time could be very long; one surface exhibited a detectable emission 24 hours after cessation of the primary bombardment. He showed that the decay was greatly accelerated when the surface was irradiated by visible light. It was also found impossible to obtain completely reproducible results. At high values of V_c and I_p, scintillations were observed on the surface which altered the target characteristics; intense scintillations caused the phenomenon to disappear.

Malter interpreted these results as being caused by an action analogous to the "spray discharge" reported by Güntherschulze[23,24] in which he obtained a gas discharge without a negative dark space or cathode fall. Malter suggested that the surface has a yield greater than unity and that due to the high resistivity of the oxide layer, a positive charge is built up, upon bombardment, which eventually sets up sufficiently intense gradients to cause field emission from the aluminum and aluminum oxide. In addition, the oxide becomes polarized and both the polarization and the surface charge persist after the removal of the primary beam until neutralized by leakage and by a portion of the field emission. The relation between emission current and collector voltage is shown to be of a form similar to the current voltage characteristics for Thyrite. Güntherschulze has ascribed the nonohmic characteristics of Thyrite to field emission across oxide films which separate the particles of carborundum of which it is composed. The scintillations were presumably caused by actual breakdown at weak spots in the film. Malter also obtained scintillations from SiO, MgO and willemite and concluded that these should show thin film field emission. He obtained negative results with Ta_2O_5, CaO, Ag_2O, CuO, NiO_2, WO_2, and ZrO and concluded that, in the heat treatment, they were reduced by the cesium which greatly reduced their resistivity.

This phenomenon has subsequently attracted many investigators, partly because of its intrinsic interest and partly because it suggests a method of obtaining high yield surfaces of commercial value if it could be stabilized. Most of this work has confirmed Malter's observations and his interpretations, but has not yielded significantly improved surfaces from the point of view of stabilization and reproducibility.

Koller and Johnson,[73] and also Mahl,[77,100] have studied the effect by using the emitted electrons to form an electron-optical picture on a fluorescent screen. They showed that the surface does not emit uniformly but that the electrons come from distinct spots like pin points. New spots could be formed by making the emitted electrons return to the target by application of a magnetic field. They interpreted the scintillations as due to sudden bursts or eruptions of electrons which would tend to discharge the surface near the emission spot. Thus the surface potential changed continually and under the proper conditions it varied cyclicly. They showed that the "Malter" electrons are emitted with a wide range of velocities, and that some had an energy corresponding to the potential across the layer of 10–40 volts as measured by Mahl. Mahl interprets this to mean that there is field emission from the aluminum but that some electrons suffer energy losses in traversing the oxide. He could obtain the effect for bombarding voltages between 15 and 1000 volts. By momentarily cutting off the collector voltage and observing the partial neutralization of the surface charge, he obtained a value for the capacity between the surface and the aluminum base which agreed with the value calculated on the basis of the layer thickness.

Piore[81] has obtained Malter effect from surfaces prepared by evaporating barium borate or quartz on a metal plate and heat treating with cesium and oxygen. He obtained the same dependence of emission current on bombarding current and collector voltage as did Malter, although the particular constants involved changed from surface to surface. Bojinesco[115] used just Al_2O_3 on aluminum and obtained Malter effect with electron bombardment and also with bombardment by negative ions H^-, N^-, O^-, and O_2^-.

Using cathodes of the type described by Malter, Mühlenpfordt[102] has shown that on letting in argon or helium, at pressures of 10^{-5} mm. mercury or more, the thin film field emission discharge changed to a spray discharge just as described by Güntherschulze. He obtained two types of discharge: a low current discharge without cathodic scintillation and a high current discharge with scintillations. On pumping out the gas, he again obtained a Malter emission, the transition being a continuous one. He assumes that the surface charge is maintained by positive ions during the discharge and suggests that even under "high vacuum" conditions the contribution of such ions from the residual gas is not negligible but may play an essential role. In another experiment, Mühlenpfordt admitted oxygen at a pressure of 10^{-5} mm. mercury and then quickly pumped it out while the Malter current was decaying following cessation of primary bombardment. When the oxygen was admitted, the current dropped abruptly by three orders of magnitude and did not recover when the oxygen was pumped out. He had also observed that a freshly prepared surface must be activated by electron bombardment for some time before Malter effect occurred. On the basis of these observations, he suggested that a metallic cesium layer is essential to the process. However, when it is first evaporated onto the Al_2O_3, it comes into contact with the aluminum base through small holes in the oxide layer, thus effectively shorting it out. The subsequent oxidation of the cesium is designed to break up these short circuits and, finally, free cesium is produced only at the surface by the electron bombardment.

Zernov[240,241] believes that the role of the Cs_2O is to fill up the holes and irregularities in the Al_2O_3 layer rather than to provide free cesium eventually on the surface. He had also produced Malter effect with MgO films without the use of additional Cs_2O. He obtained a rapid decrease in emitted current, following cessation of bombardment, and then a stabilization of the current presumably due to the effect of residual gas. This latter effect was obtained with surfaces of [Al]-Al_2O_3-Cs_2O and MgO.

A point that has been brought out only by Mühlenpfordt is that all these characteristics are strongly dependent on the target temperature. The emission drops sharply with increasing temperature and simultaneously the decay rate of the decaying Malter current increases. This is explained by the positive temperature coefficient of conductivity of the Al_2O_3. At higher temperatures the increased leakage current prevents the surface from charging up as much and causes it to decay more rapidly after the excitation is cut off.

Paetow[139] has conducted some experiments which may have considerable bearing on this subject. He sprinkled an insulating powder with grain size less than 1 micron on a metallic cathode and with a gas pressure between 10^{-3} and 10^{-7} mm. mercury started a gas discharge with a few thousand volts on the anode. He reported that almost any gas would do and that many types of powder could be used, e.g., quartz, glass, MgO, Al_2O_3. On initiation of the gas discharge, the powder flew around explosively but left an active layer of fine powder on the cathode which stuck tightly to the metal. He then obtained two forms of the discharge: a steady low voltage form and an unsteady high voltage discharge accompanied by cathodic scintillation, i.e., spray discharge, and he likens these to the two forms of Malter current. The low voltage discharge could be maintained at pressures of less than 10^{-6} mm. mercury and between 10^{-2} and 10^{-6} mm. mercury the current is essentially independent of applied voltage. The maximum current density so obtained was 100 ma/cm.^{2}; above this it changed over to the high voltage form. Owing to sputtering the target life was a few weeks. The low voltage discharge exhibited time lags in its I/V characteristic although much less than in Malter effect. Paetow suggests that field omission may take place around the edges of the grains rather than through the grains themselves. Investigations of this type may lead to a more complete understanding of the mechanism involved in the Malter effect.

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