Origin of secondary-electron-emission yield-curve parameters*

Gerald F. Dionne

Massachusetts Institute of Technology, Lincoln Laboratory, Lexington, Massachusetts 02173 (Received 11 March 1975)

From an analysis of the one-dimensional constant-loss theory of secondary electron emission, maximum yield (δ_m) , primary electron energy at maximum yield (E_{om}) , and both crossover energies E^1_{oc} and E^{11}_{oc} are shown to depend on the surface and bulk properties of the emitting material through simple relations. In particular, the results strongly suggest that the first crossover energy can be very dependent on surface properties, whereas the energy at maximum yield is entirely controlled by bulk properties. Refinement of the low-energy part of the reduced yield curve by means of the results of the more realistic three-dimensional theory leads to the development of the expression $E^1_{oc} = 0.51 E_{om} \delta_m^{-1.32}$. Comparison between theory and experiment for several secondary-emitting materials is presented to demonstrate the accuracy of this useful relation. Finally, the implications of these results for different classes of materials are discussed in terms of basic physical properties, such as density, electrical conductivity, work function, and band gap.

PACS numbers: 79.20.H

I. INTRODUCTION

Electron emission from solid surfaces, including photoelectric, thermionic, secondary, and field emission, invariably depend on the surface work function. However, because secondary emission involves the creation of "hot" electrons at depths below what would be considered surface layers, secondary emission is also affected significantly by the bulk properties of the solid. This means that a material with a low work function may be a superior thermionic or photoelectric emitter, but may still have unimpressive secondary-emission characteristics. The converse is also true, as in the case of high-work-function (> 5 eV) platinum, where its thermionic emission is low in comparison with most other metals, but its secondary-emission yield is the highest (~1.8) of all metals.

In the phenomenological theories of secondary emission developed by Salow¹ and Bruining,² the roles played by surface and bulk properties of the emitter are embodied in the semiempirical material constants which define quantities such as escape probability and primary-electron-energy absorption. In a recent article,³ the present author has compared one- and three-dimensional forms of the power law and constant-loss versions of elementary secondary-emission theories and has shown that the one-dimensional model is an excellent approximation for calculating reduced yield curves. Therefore, this model should also be a reasonable basis for individual yield curves, provided that care is taken to define the material constants with reference to the one-dimensional model.

The purpose of this article is to demonstrate how the material constants relate to the important yield-curve parameters and to compare the results with the measured values of common secondary-emitting materials. The following theoretical development is based on the constant-loss version of the theory for two reasons:
(i) the inclusion of primary electron scattering makes it a more realistic approximation than the simple power law and (ii) the mathematical expression for the secondary-emission yield lends itself readily to the type of analysis involved.

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II. THEORY

The constant-loss modification to the one-dimensional power-law theory of secondary electron emission produces the following equation for the yield³:

$$\delta = (B/\zeta)(An/\alpha)^{1/n}(\alpha d)^{(1/n-1)}(1 - \epsilon^{-\alpha d}), \tag{1}$$

where B is the escape probability, ζ is the secondary-electron excitation energy, α is the secondary-electron absorption constant or inverse mean free path. A is the primary electron absorption constant, d is the maximum penetration depth, and n is the power-law exponent.

From the power law absorption of energy, the penetration depth is related to the primary electron energy $E_{\rm 0}$ by

$$d = E_0^n / An. (2)$$

From Eq. (1),

$$\frac{\partial \delta}{\partial (\alpha d)} = \frac{B}{\xi} \left(\frac{An}{\alpha} \right)^{1/n} \left[(\alpha d)^{1/n-2} \left(\frac{1}{n} - 1 \right) \left(1 - \epsilon^{-\alpha d} \right) + (\alpha d)^{1/n-1} \epsilon^{-\alpha d} \right]. \tag{3}$$

A. Primary energy at maximum yield, E_{om}

To determine the primary energy at maximum yield, E_{0m} , defined in Fig. 1, Eq. (3) must be reduced to an expression for αd_m by setting $\partial \delta/\partial (\alpha d) = 0$ for peak yield. As a result, it may be easily shown that

$$\alpha d_m = (1 - 1/n)(\epsilon^{\alpha d_m} - 1). \tag{4}$$

In this analysis, the value of n will be taken as 1.35 because it provides the most reasonable fit to the data over the energy range of interest.³ For this value of n, αd_m in Eq. (4) is 2.28 and, from Eq. (2), the energy at peak yield becomes

$$E_{0m} = 2.3(A/\alpha)^{0.74}.$$
 (5)

B. Maximum yield, δ_m

By substituting $\alpha d_m = 2.28$ into Eq. (1), the maximum yield may be expressed as

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$$\delta_m = 0.9(2.28)^{1/n-1} (B/\zeta) (An/\alpha)^{1/n}. \tag{6}$$

For n=1,35, Eq. (6) reduces to

$$\delta_m = 0.9(B/\zeta)(A/\alpha)^{0.74}$$
 (7)

C. Crossover energies, E_{∞}^{I} and E_{∞}^{II}

By definition, the primary electron crossover energies are the points at which $\delta=1$. As shown in Fig. 1, there are two energies at which this occurs and the relation used to determine them is derived from Eq. (1),

$$(B/\zeta)(An/\alpha)^{1/n}(\alpha d)^{1/n-1}(1-\epsilon^{-\alpha d})=1.$$
 (8)

To determine the crossover energies, it is convenient to make the assumptions that $\alpha d_c^I \ll 1$ for $E_{0_c}^I$ and $\alpha d_c^{II} \gg 1$ for $E_{0_c}^{II}$. In general, these inequalities exist for $\delta_m > 2.5$ in the case of $E_{0_c}^I$ and $\delta_m > 1.2$ for $E_{0_c}^{II}$, as shown in the Appendix. For the low-crossover-energy case, $\epsilon^{-\alpha d_c^I} \simeq 1 - \alpha d_c^I$, and Eq. (8) reduces to

$$(B/\zeta)(An/\alpha)^{1/n}(\alpha d_{\alpha}^{I})^{1/n} \approx 1.$$
(9)

By replacing d_c^I with E_{0c}^I from Eq. (2), Eq. (9) may be reexpressed as

$$d_c^{\rm I} = (E_{0c}^{\rm I})^n / An \simeq (\zeta/B)^n (1/An) \tag{10}$$

or

$$E_{0c}^{\mathrm{I}} \simeq \zeta/B \quad \text{(for } \delta_{m} > 2.5).$$
 (11)

For the higher crossover energy, $\alpha d_c^{II} \gg 1$ and $\epsilon^{-\alpha d_c^{II}} \sim 0$. Equation (8) reduces to

$$(B/\zeta)(An/\alpha)^{1/n}(\alpha d_{\alpha}^{II})^{1/n-1} \simeq 1.$$
 (12)

Upon substituting Eq. (2) into Eq. (12), it may be shown that

$$E_{0c}^{11} \simeq [n(B/\zeta)(A/\alpha)]^{1/(n-1)},$$
 (13)

For n = 1, 35,

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$$E_{0c}^{\text{II}} \simeq 2.36[(B/\zeta)(A/\alpha)]^{2.86}$$
 (14)

From the above results, it is possible to relate the maximum yield to the primary energy at maximum yield

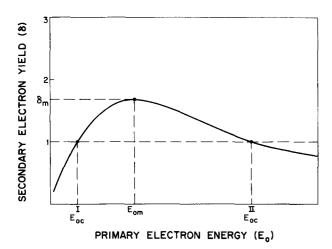


FIG. 1. Definition of secondary-electron yield-curve parameters.

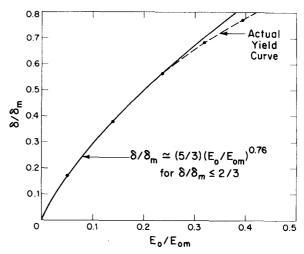


FIG. 2. Comparison between approximation to reduced-yield curve given by Eq. (17) and the actual reduced-yield curve calculated from three-dimensional constant-loss theory (Ref. 3). The points represent calculated values of δ/δ_m .

and the first crossover energy by substituting Eqs. (5) and (11) into Eq. (7) to obtain

$$\delta_m = 0.39 E_{0m} / E_{0c}^{I}. \tag{15}$$

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$$E_{0c}^{1} = 0.39 E_{0m} / \delta_{m}. \tag{16}$$

Although Eq. (16) represents a convenient approximation, it is of only qualitative value because of the assumptions inherent in the one-dimensional model. To develop a relation that would permit the calculation of more accurate low crossover energies from measurements of $E_{\rm om}$ and $\delta_{\rm m}$, it is necessary to make use of the results of the three-dimensional constant-loss theory, where secondary electron scattering is taken into account. In Fig. 2, the low-energy portion of the reduced yield curve for n=1.35 is plotted together with the results of calculations based on the empirical relation

$$\delta/\delta_m \simeq \frac{5}{3} (E_0/E_{0m})^{0.76}. \tag{17}$$

For $\delta/\delta_m \leq \frac{2}{3}$, the agreement is excellent. Therefore, it may be concluded that Eq. (17) is useful in predicting E_{0c}^{I} for $\delta_m > 1.5$. The low crossover energy may be found from Eq. (17) by letting $\delta = 1$, with the result that

$$E_{0c}^{I} = 0.51 E_{0m} \delta_{m}^{-1.32}. \tag{18}$$

In Fig. 3, Eq. (18) is plotted for $1.5 \le \delta_m \le 10$ over a range of E_{0m} that would include most secondary emitting materials of practical importance.

III. COMPARISON WITH EXPERIMENT

In Table I, the low-energy crossover points calculated from Eq. (18) are compared with corresponding values measured by the present author for a number of common secondary emitting materials. The experimental technique employed was a straightforward application of the retarding potential method, with a grounded collector and a primary electron beam energy of 1050 eV. The yield curve was determined by varying the potential on the target between -50 and -1050 V. With

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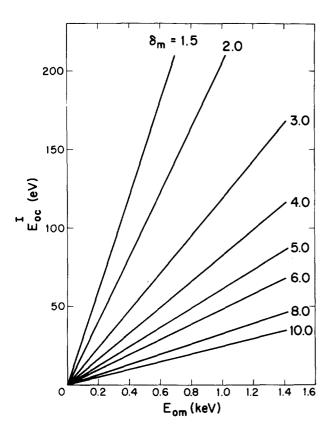


FIG. 3. Calculated results of $E_{\rm oc}^{I}$ as a function of $E_{\rm om}$ for several values of $\delta_{\rm m}$.

this simple circuit, δ is the ratio of the target current (determined from a meter placed between the target and ground) to the sum of the target current and the fixed primary electron beam current (predetermined from a Faraday cup measurement).

In general, the theoretical values in Table I are slightly higher than the measured ones. Since the agreement is reasonably good in each case, the method for predicting E_{0c}^I may be judged as effective and particularly useful in situations where direct measurement of this parameter is not convenient.

In Fig. 4, the yield curves of a Si sample are presented to illustrate the distinction between surface and bulk effects on the yield-curve parameters. The initial curve represents the yield of SiO₂, since an oxide layer is always present on Si after exposure to air (see Fig. 5). During electron bombardment by a cylindrical mirror analyzer integral gun, the surface condition was altered either by removal or addition of contaminant (e.g., cracking of CO₂ to leave a carbon residue, as suggested by the Auger spectrum in Fig. 5).

TABLE I. Comparison of calculated with experimental values of first crossover energy $E_{\rm oc}^{\rm I}$.

Material	E ^I _{oc} (experimental) (eV)	$E_{ m oc}^{I}$ (calculated) (eV)	
Pt	150	164	
Al_2O_3	60	65	
MgO-Au (cermet)	24	24	
SiO ₂	44	52	

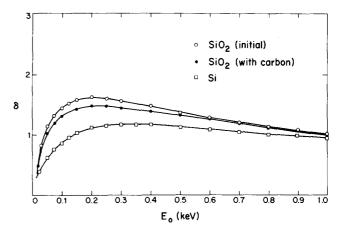


FIG. 4. Secondary-electron yield of a ${\rm SiO}_2$ sample before and after electron bombardment and argon-sputter etching.

The yield curve indicates a reduction in $E_{0c}^{\rm I}$ and δ_m , but no change in E_{0m} . The final curve represents the sample after argon-sputter etching, where most of the oxide has been removed, leaving a relatively clean Si surface (see Fig. 6). In this case, the secondary yield curve shows further reduction in $E_{0c}^{\rm I}$ and δ_m , accompanied by an increase in E_{0m} to fit more closely the yield curve of Si.²

These qualitative observations are in accord with the results of the foregoing theory. In Eq. (5), E_{0m} is a function of A/α , with no dependence on B or ζ . Therefore, E_{0m} should not change when only the surface condition is altered, since neither A nor α describe surface phenomena. On the contrary, when the sample is altered beyond merely the surface layers, as in the above case of sputter-etch removal of an oxide, both surface and bulk effects influence the yield curve, and changes in all the parameters should be anticipated.

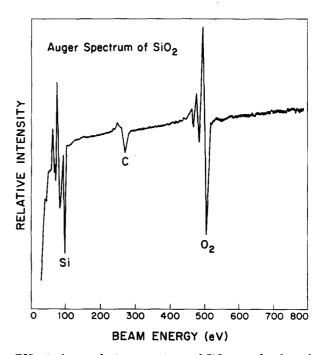


FIG. 5. Auger electron spectrum of SiO_2 sample after electron bombardment.

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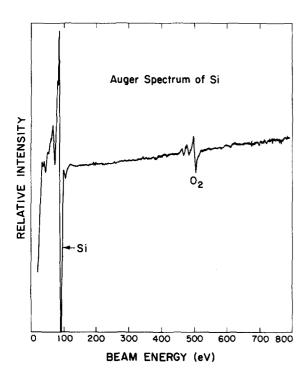


FIG. 6. Auger electron spectrum of SiO₂ sample after argon-sputter etching with only a small amount of oxide remaining.

IV. DISCUSSION

The results of the theoretical analysis provide simple, but approximate, relations between the secondary-emission yield-curve parameters and variables which describe some of the electronic and chemical properties of the material. Unfortunately, the meanings of A, α , ζ , and B will vary somewhat among metals, semiconductors, and insulators. In an attempt to gain further insight into the physics of the phenomena involved, it is appropriate to examine more carefully the definitions of these quantities for the different classes of materials.

It will be recalled that A is the primary-electronenergy absorption constant. In other words, it represents the electron "stopping power" of the solid and should be directly proportional to the physical density ρ^4 . Therefore, heavy elements (e.g., Au, Pt, and Pb)

TABLE II. Correlation between density and yield-curve parameters for several good conductors.

Materials	ρ (g/cm ³)	φ (= ζ) a (eV)	E _{om} b (eV)	δ_m^{b}
Pt	21.4	5.32	800	1.8
Au	19.3	4.3	750	1.46
Ag	10.5	4.3	800	1.50
Li	0.53	2.38	85	0.5
Mg	1.85	3,64	300	0.95
ΑÏ	2.70	4.25	300	1.0

^aV.S. Fomenko, *Handbook of Thermionic Properties* (Plenum, New York, 1966).

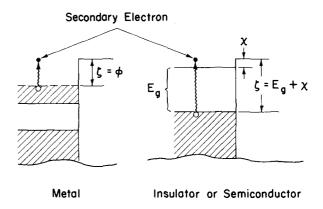


FIG. 7. Definition of semiempirical material constant ξ for metals and insulators (or semiconductors). For metals, ξ is the minimum energy required for emission of an electron from the conduction band; for insulators, it is the minimum energy required for emission of an electron from the valence band.

should have large A values, while lighter elements (e.g., Li, Na, and Mg) should have small ones. By definition, α is an inverse mean free path and should be dependent on the electron density, mobility, and lifetime, which could be all lumped into the electrical conductivity σ . Thus, metals should have large α values and insulators, small ones. Since A/α appears in the expressions for δ_m , E_{0m} , and E_{0g}^{II} , it is instructive to examine the implications of this ratio. Since α should be reasonably uniform among many metals, A will most likely control this ratio and the dependence of A on higher densities should carry over to A/α for these materials.

Based on Eqs. (5), (7), and (14), this conclusion suggests that heavy metals should have larger values of δ_m and E_{0m} than lighter metals. To illustrate this effect, comparison of several good conductors is presented in Table II. It should be noted that the work functions vary somewhat, but generally by less than a factor of 2. For insulators or semiconductors, the α 's will be smaller than for metals (depending on σ) and the A's will vary somewhat according to the particular chemical composition. The smaller α values undoubtedly contribute to the higher δ_m and E_{0m} values of insulators.

For both metals and insulators, the definitions of A and α apply equally well. This is also true for B, the escape probability for electrons at the top of the potential barrier, which may be represented by (1-r), where r is a quantum-mechanical reflection coefficient that varies among different materials, and may also depend on the physical condition of the surface. However, since a secondary electron must acquire a minimum initial energy ξ , sufficient to raise it to the top of the potential barrier, then the definition of ξ will differ somewhat between metals and insulators.

As depicted in Fig. 7, ζ represents the work function ϕ in the case of a metal, but the sum of the electron affinity χ and the band gap E_g for an insulator or semiconductor. For most metals, $\phi \sim 4-5$ eV, although the alkali metals have values of < 3 eV, and for insulators $\chi \sim 1$ eV, with E_g varying as high as 10 eV

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^bH. Bruining, Physics and Applications of Secondary Electron Emission (McGraw-Hill, New York, 1954).

for MgO or BeO and 1 eV for Si. Thus, ζ/B is directly proportional to band gaps of insulators and work functions of metals, with B largely an unknown unless estimated experimentally by thermionic emission. It should be pointed out that E_{ε} greatly influences the conductivity through an exponential function and may exert greater control of secondary emission by influencing α than by determining the value of ζ . This could be the reason why insulators with large band gaps have high yields—a small α value created by a large E_{ε} will more than offset a larger ζ in Eq. (7).

V. CONCLUSIONS

In conclusion, it may be stated that the yield-curve parameters are related to the basic properties of the material through semiempirical constants of the elementary secondary-emission theory. The maximum yield is dependent directly on the physical density and inversely on the conductivity and work function (in the case of an insulator or semiconductor, the sum of band gap and electron affinity). For these reasons heavy metals are superior emitters to light metals, and insulators with low conductivities resulting from large band gaps (e.g., MgO and BeO) feature very large yields.

The low crossover energy $E_{0_{\rm c}}^I$ will be directly proportional to band gap plus electron affinity for insulators where $\delta_m \ge 2.5$; since metals have maximum yields below this limit, the approximation in Eq. (11) would not apply. The primary energy at maximum yield E_{0m} is dependent directly on density and inversely on conductivity, with the result that heavy materials and insulators have peaks at higher primary energies.

From inspection of Eq. (14), the arguments applied to δ_m would carry over to E_{0c}^{II} , since both parameters depend on $(B/\zeta)(A/\alpha)$. It should be almost self-evident that high-yield materials will have large second crossover energies.

With regard to the question of surface contamination, it should be emphasized that only B and ζ are affected. However, it is not clear how B will vary with different adsorbates and the influence of reflection coefficients must remain a subject of speculation. In the case of ζ , it is well known that metal work functions are affected by adsorption of various substances and that the electron affinities of insulators and semiconductors may very greatly with monolayers of adsorbate; in some

cases (e.g., alkali-metal oxides) the value of χ is believed to become negative. Under these conditions, extremely high yields have been observed.⁵

Other contaminants have proven to reduce yields. Carbon layers have traditionally been accepted as detrimental to secondary emission. In the context of the model analyzed in this work, it is not clear to what extent ξ is affected by this contaminant, if at all, or whether it is the value of B that is reduced through an increase in the electron reflection coefficient.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to D.H. Temme for his interest and encouragement, and to J.F. Fitzgerald for assistance in the experimental aspects of the work.

APPENDIX

In the derivation of crossover energies E^I_{0c} and E^{II}_{0c} , Eqs. (11) and (14) were obtained by assuming that $\alpha d_c \ll 1$ in the first case and $\alpha d_c \gg 1$ in the second. The ranges of validity for these assumptions may be established by rewriting Eq. (8) for n=1.35:

1.25
$$(B/\zeta)(A/\alpha)^{0.74}(\alpha d_{\alpha})^{-0.26}(1-\epsilon^{-\alpha d_{\alpha}})=1$$
. (A1)

Upon substituting Eq. (7) and then rewriting Eq. (A1),

$$\alpha d_c = [1.39\delta_m (1 - \epsilon^{-\alpha d_c})]^{3.85}. \tag{A2}$$

This relation may be solved directly by iteration and the results are given in Table II for the higher solution αd_c^{II} , with the result that $\delta_m > 1.2$ produces a value of $\alpha d_c > 7.2$. This suggests that $\delta_m > 1.2$ is a reasonable limit for the approximation to E_{0c}^{II} expressed by Eq. (14).

If Eq. (A2) is rearranged to become

$$\alpha d_c = -\ln[1 - (\alpha d_c)^{0.26} / 1.39 \delta_m], \tag{A3}$$

the same procedure may be followed to determine the limits of δ_m for E^I_{0c} , as shown in Table II. In this case, $\delta_m > 2.5$ makes Eq. (11) a reasonable approximation.

*Work sponsored by the Department of the Army.

¹H. Salow, Z. Tech. Phys. 21, 8 (1940).

²H. Bruining, *Physics and Applications of Secondary Electron Emission* (McGraw-Hill, New York, 1954).

³G.F. Dionne, J. Appl. Phys. 44, 5361 (1973).

⁴O.C. Wells, Scanning Electron Microscopy (McGraw-Hill, New York, 1974).

⁵R. Martinelli, Appl. Phys. Lett. 17, 313 (1970).