THE SCHOTTKY EFFECT FOR COMPOSITE SEMI-CONDUCTOR ELECTRON EMITTERS

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The present paper is a theoretical treatment of the Schottky effect for modern composite emitters of thermal, photoelectric and secondary electrons, the emitters having a semi-conductor nature. It is shown that in such cases one encounters very important features that did not take place in the case of ordinary metallic emitters. Formula (11) is obtained for the change in the work function of thermionic emission that differs greatly from Schottky's usual formula for metals.

At present it can be regarded as a reliably established fact that almost all recent effective composite emitters of thermal, photoelectric and secondary electrons are semi-conductors of a specific volume and surface structure (1). In this connection such semi-conductor cathodes possess a number of specific features not inherent in ordinary metallic cathodes. Unfortunately, the latter fact is not always given sufficient consideration, as the systematic study of these very important semi-conductor properties of modern composite cathodes is still at its beginning only. The present paper deals with a very essential feature of such composite semi-conductor cathodes which is related to the so-called Schottky effect.

As well known, when an external electric field of strength E is applied, the electron work function for metallic cathodes decreases by the magnitude $\Delta\varphi=\sqrt{eE}$, which usually brings about a corresponding increase in thermionic emission of the cathode (the Schottky effect). Consider now what will be the result of the same electric field applied to the surface of a semi-conductor cathode.

Consider, for instance, a usual electronic semi-conductor with a donating admixture, the potential diagram of its surface being, as shown in Fig. 1 to the left (*I*). Here μ is the chemical potential level, a and b are the levels corresponding to the lower edges of the conduction and fordidden zones respectively of the semi-conductor, c is the level of the admixture. Upon application of the electric field the potential diagram alters as shown in Fig. 1 to the right (*II*). From Fig. 1 the application

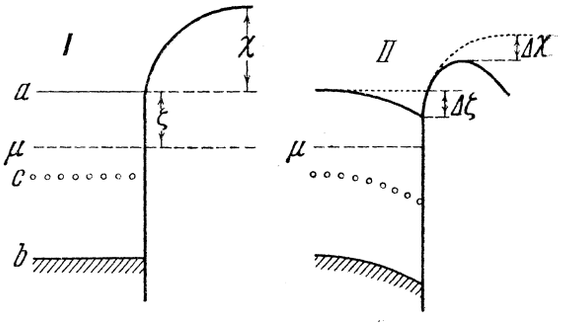

Fig. 1

of an external accelerating field is seen to bring about two effects: 1) a reduction in the outer work function χ by value $\Delta\chi$ and 2) a narrowing of the zone width ζ by value $\Delta\zeta$. In other words, the complete thermionic work function for a semi-conductor cathode $\varphi=\chi+\zeta$ from formula:

$$I=A_0T^2\exp\left(-\frac{e\varphi}{kT}\right), \qquad (1)$$

decreases under the action of external field E by the value

$$\Delta\varphi = \Delta\chi + \Delta\zeta. \qquad (2)$$

We now proceed to a more detailed discussion of the both terms of formula (2).

1. For semi-conductors and dielectrics the outher work function of an electron χ is like for metals reducible with a certain approximation to the work done against the electrostatic image forces. In this case ([2]), if a charge e is located, for instance, at distance r beyond the surface of a perfect insulator with a dielectric constant ε, its electrostatic image e' is located at the same distance on the other side of this surface "within" the substance, but in its absolute magnitude the image charge is $e' = -(\varepsilon-1/\varepsilon+1)\,e$, *i. e.* the image force attracting the charge is

$$F(r) = -\frac{ee'}{(2r)^2} = -\frac{\varepsilon-1}{\varepsilon+1}\frac{e^2}{4r^2}.$$

The expression derived for an insulator differs from the familiar one for a metal by the factor $\varepsilon-1/\varepsilon+1$. It is quite natural that in the intermediate case of an electronic semi-conductor the above formulae for e' and $F(r)$ become

$$e' = -\alpha e, \quad F(r) = -\alpha\frac{e^2}{4r^2},$$

where the factor α lies within the following, usually rather narrow, range

$$\frac{\varepsilon-1}{\varepsilon+1} \leqslant \alpha \leqslant 1. \qquad (3)$$

From condition $eE = F(r_0)$ there is deduced in the usual way the following expression for the decrease in the value of χ in electric field E

$$\Delta\chi = Er_0 + \frac{1}{e}\int_{r_0}^{\infty} F(r)\,dr = \sqrt{\alpha eE}. \qquad (4)$$

Expression (4) differs from that for a metal by factor $\sqrt{\alpha}$ only.

In making use of formula (4), it should be kept in mind that the polarization of the free electronic gas in the semi-conductor occurring at the moment of the electron emission, proceeds slowly and hence $\alpha \approx \varepsilon-1/\varepsilon+1$. This relation will evidently hold only when the time τ taken by the emitted electron to traverse the main range of the electrostatic image force $l < 10^{-6}$ cm with a heat velocity, say, $u \approx 10^7$ cm/sec. will be much shorter than the relaxation time of the electronic gas in the semi-conductor $\tau_1 = \varepsilon\rho_1/4\pi$, *i. e.* $\tau \ll \tau_1$. For the majority of modern activated semi-conductor cathodes and in particular for barium-oxide coated thermocathodes, even when heated, this condition is found to hold.

And finally, in making use of the obtained results, one should bear in mind that for the considered cathodes, as well as in the case of the metallic ones there arises a difficulty connected with the irregular relief of the emitter surface. The true electric field at the emitter surface might be considerably higher than its mean macroscopic value E, and simultaneously the effective emitting surface of the cathode, which is less than the geometrical one, does not remain constant but increases in a certain manner with increasing E. Since this problem, in spite of its being put forward long ago, is not as yet solved even for metallic cathodes, we leave this problem open to discussion also for our case of semi-conductor cathode.

2. Because of the limited concentration of free electrons n in a semi-conductor, the external electric field E is not screened at the very surface as in metals, but partly penetrates into the semi-conductor, thus stimulating a reduction by $\Delta\zeta$ [formula (2)] in the width of the zone ζ near the surface, as shown in Fig. 1. As a result the free electron concentration near the surface of the semi-conductor increases as compared with the concentration within its body up to the value $n' > n$, where

$$\frac{n'}{n} = \exp\left(\frac{e\Delta\zeta}{kT}\right). \qquad (5)$$

In our cases of thermionic emission from semi-conductor cathodes the following condition always holds ([3]):

$$\lambda = \frac{eI\rho}{\sigma_1 kT} \ll 1,$$

where I is the emission current density, σ_1 — the specific conductivity of the semi-conductor, ρ — the Debye-Hückel screening radius:

$$\rho = \left(\frac{\varepsilon kT}{4\pi e^2 nP}\right)^{1/2}. \qquad (6)$$

On the other hand, there exists the following relation between the external electric field

in vacuum E and the internal field at the semi-conductor surface E':

$$E = \varepsilon E' \mp 4\pi\sigma, \tag{7}$$

where $\mp\sigma$ is the surface density of free charges (negative electrons and positive holes), situated on localized levels at the outer surface of our semi-conductor emitter.

In our case of $\lambda \ll 1$ the relation between the value $\Delta\zeta$ from (2) and (5) and the external accelerating field strenght E is representable as ([3])

$$\frac{e\varphi}{kT} E' = \frac{e\varphi}{\varepsilon kT}(E \pm 4\pi\sigma) =$$

$$= \sqrt{2}\left[\left(\frac{n'}{n}\right)^{1/2} - \left(\frac{n}{n'}\right)^{1/2}\right] = 2\sqrt{2}\,\mathrm{sh}\left(\frac{e\Delta\zeta}{2kT}\right) \tag{8}$$

or, otherwise,

$$\Delta\zeta = \frac{2kT}{e}\,\mathrm{arg\,sh}\left[\frac{1}{2\sqrt{2}}\frac{e\varphi}{\varepsilon kT}(E \pm 4\pi\sigma)\right]. \tag{9}$$

Thus we have deduced an explicit and convenient form of the relation $\Delta\zeta = f(E)$.

As in the previous case, we as yet leave open the question as to the possible part played by the relief of the emitter surface. We only note that, if the absolute magnitude of the relief irregularities is much less than the shielding radius ρ from (6), the influence of the relief upon the value of $\Delta\zeta$ can be disregarded, *i. e.* the actual field at the emitter surface can be considered as equal to the macroscopic field E.

In the case $E = 0$ and $\sigma > 0$ formula (9) becomes

$$(\Delta\zeta)_0 = \frac{2kT}{e}\,\mathrm{arg\,sh}\left(\frac{1}{2\sqrt{2}}\frac{e}{kT}\frac{4\pi\sigma\rho}{\varepsilon}\right). \tag{10}$$

This formula shows the decrease of the quantity ζ and, therefore, that of thermoelectronic work function $\varphi = (\zeta + \chi)$ (Fig. 1), which is associated with the presence of free positive charges of arbitrary origin on the outer surface of the semi-conductor cathode, on its local surface levels. These ions build up here a double layer with $(\Delta\zeta)_0 \approx 4\pi\sigma\rho/\varepsilon$ [for small $(\Delta\zeta)_0$], *i. e.* this double layer looks as if it were constructed of dipoles with a very large arm of the order of magnitude ρ/ε. In the ordinary case the film of polarized electropositive atoms sets up on the cathode surface a double layer the field of which practically does not penetrate into the interior of the semi-conductor; as a result the capacity of this double layer, $4\pi\sigma' a = \Delta\chi$, affects only the decrease of the quantity χ from Fig. 1 and hence also of the work function φ; this double layer looks as if it were built up of dipoles with an arm equal to an atomic value of a, *i. e.* to a value much below ρ/ε.

The changes in the surface film, that are associated with the uncertainty of state, polarized atom—ion, are here of no importance, because the frequency of these transitions is of the order of 10^{14} sec.$^{-1}$, which highly exceeds the above mentioned relaxation frequency for the electronic gas in the semi-conductor, τ_1^{-1}.

Summarizing the foregoing considerations, we arrive at the conclusion that if an external electric field E is applied, the thermionic work function $\varphi = \chi + \zeta$ of the semi-conductor from (1) and (2) decreases according to formulae (4) and (9), by the value

$$\Delta\varphi = \Delta\chi + \Delta\zeta = (\sigma eE)^{1/2} +$$

$$+ \frac{2kT}{e}\,\mathrm{arg\,sh}\left[\frac{1}{2\sqrt{2}}\frac{e\rho}{\varepsilon kT}(E \pm 4\pi\sigma)\right], \tag{11}$$

which is essentially other than Schottky's formula $\Delta\varphi = (eE)^{1/2}$ for metallic cathodes. This, in turn, must result, for instance, in an increased thermionic emission I of the semi-conductor, say, of the barium-oxide-coated cathode, in conformity with the following expression resulting from (1)

$$I = I_0 \exp\left(\frac{e\Delta\varphi}{kT}\right). \tag{12}$$

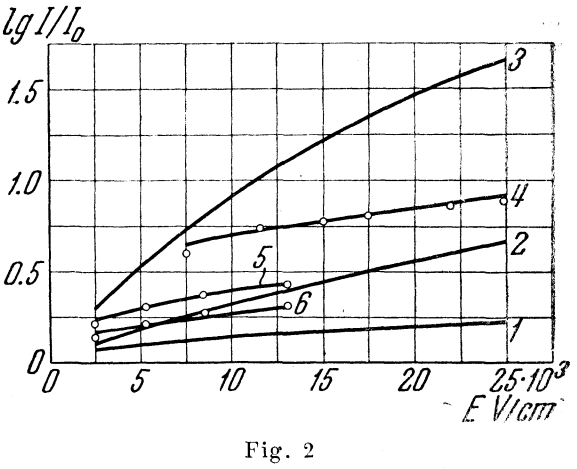

Fig. 2

To illustrate the results obtained, in Fig. 2 are given the curves for the relation $\lg(I/I_0) = f(E)$ as derived from (11) and (12) for the values: $\varepsilon = 5$, *i. e.* $\alpha = 0.66$, $\sigma = 0$, $T = 1100°\mathrm{K}$

and three various values of the shielding radius : $\rho = 0$ (curve *1*), $\rho = 2.5 \cdot 10^{-5}$ cm (curve *2*), $\rho = 12.5 \cdot 10^{-5}$ (rve *3*). From the graphs in Fig. 2 it is seen that with the usual reasonable values of radius ρ the correction to the quantity $\Delta\zeta$ disregarded heretofore may be of a very great, and sometimes even of a decisive significance. As a result the Schottky effect for semi-conductor cathodes will be of a nature entirely unlike that for metallic cathodes.

It is difficult to compare the theoretical results deduced here in the form of formula (11) with the very scarce experimental data on the Schottky effect, *e. g.* for oxide-coated thermocathodes (4), since such comparison requires the knowledge of a number of parameters, namely, ρ, ε, α and σ entering this formula. Nevertheless, we have presented in Fig. 2 by means of three groups of circles, the data of the following experimental investigations: a) the circles on curve *4* are the data from Fig. 2 of H e i n z e's paper (4) assuming $E \approx 30$ V; b) the circles on curve *5* are S p r o u l l's data (4) from his Fig. 10 for the initial current i_0 corresponding to the instant $t = 0$, and c) the circles on curve *6* are S p r o u l l's data (4) from his Fig. 10 for the equilibrium current i_1. Then, by means of formula (11) the theoretical curves *4*, *5* and *6* in Fig. 2 were plotted for the values $\varepsilon = 5$ and the appropriate temperatures; the vaules of ρ and $\sigma = eN$ were chosen in such a way as to find out whether theoretical curves *4*, *5* and *6* can be made to agree with the experimental data indicated above (4). It was found, that such an agreement was possible only with the values of ρ and $4\pi\sigma$ listed in the following table:

No. of curve	$10^5 \cdot \rho$ (cm)	$10^{-4} \cdot 4\pi\sigma$ (V/cm)	$10^{-15} \cdot n$ (cm^{-3})	$10^{-10} \cdot N_p$ (cm^{-2})	$(\Delta\zeta)_0$ (eV)
4	1.8	+4.3	0.9	2.4	0.100
5	1.6	+1.4	1.0	0.8	0.031
6	1.0	+1.0	2.6	0.6	0.014

Examination of curves *4*, *5* and *6* in Fig. 2 and of the above table allows to draw the following conclusions.

1. Theoretical curves *4*, *5* and *6* derived here in all three cases do really agree very well in their general course with the experimental data of Heinze and Sproull, thereby affording to the present theory a high degree of certainty.

2. The values, derived here for the shielding radius ρ (column 2 of the table), are quite reasonable and result on the basis of (6) (if assumption $P = 1$ is made) in the values for the free electron concentration n listed in column 4 of the table. On the other hand, the experimental data obtained in measuring the transverse resistance of the oxide layer of the cathodes of operating electron valves, have resulted in values of the order of several hundred ohms per 1 mm^2; whence assuming the semi-conductor to be homogeneous, there is obtained the value $n \approx 10^{15}$ cm^{-3}, which in order of magnitude is in fair agreement with values listed in our table.

3. The values of σ derived here (column 3) are of a positive sign and for the surface concentration of free positive charges on the local surface levels N_p lead to the values presented in column 5 of the table. In column 6 are given the values of $(\Delta\zeta)_0$ as obtained from formula (10) with $E = 0$. The relative influence of these free positive charges, yielding dipoles with a large arm of the order of ρ/ε, on the reduction in values of ζ, and, therefore, on the work function $\varphi = (\chi + \zeta)$ (Fig. 1), is seen to be a very small one. The chief rôle in reducing greatly the work function of these effective oxide-coated thermocathodes belongs evidently to the comparatively dense film of adsorbed and polarized atoms of the electropositive barium which, as mentioned above, sets up a double layer with an arm of the atomic order, this film affecting only the value of χ (see Fig. 1).

4. Comparison of the data presented in the table for curves *5* and *6* enables to draw certain preliminary conclusions as to the changes occurring in an oxide-coated thermocathode resulting from thermionic emission. One gets the impression that this influence looks as though the emission results in an activation of the electrolytic processes in the cathode. As a result of these processes a certain amount of barium is released in the interior, this lead-

ing to an increase in n, and a certain amount of oxygen is released on the surface, this leading to a dercease in N_p and $(\Delta\zeta)_0$.

Thus comparison of our theory with experimental data enables to draw a number of additional conclusions of great physical interest.

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