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New Quantum and Electronic Theory of Metal-Semiconductor Contacts

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The Schottky, Davydov, Bardeen, and Heine theories of metal-semiconductor contacts are improved and developed by using a new general expression for the junction capacitance and by accounting for quantum-mechanical tunneling of free electrons from the metal into the semiconductor's forbidden energy gap. The Poisson equation for electric field and potential is first solved to obtain general expressions for the junction capacitance, the built-in voltage on the junction capacitance, and the barrier height. The electron wave function is then calculated using effective-mass and WKB approximations and the continuity of probability density and current at the metal-semiconductor interface. Finally, the density of states of electrons which tunnel from the metal into the semiconductor's forbidden energy gap is deduced from the electron wave function. In practice, these calculations are intradependent and cannot be completely separated. For metal-n-type semiconductor contacts, the most significant differences between this theory and previous theories are the *increases* of both the energy barrier height and the built-in voltage of the contact capacitance. For metal-p-type semiconductor contacts, tunneling of electrons from the metal to the semiconductor *reduces* the barrier height and width and built-in voltage of the contact capacitance. As a consequence, the hole-tunneling probability and reverse current are both increased. The results agree with published experimental measurements of capacitance, photoemission, and current.

I. INTRODUCTION

A well-known conclusion of the Schottky[1-6] and Davydov[7] theories of metal-semiconductor contacts is that electrons in the metal must overcome an energy barrier to enter an n-type semiconductor. The barrier height φ_{SD} is equal to the difference between the metal work function φ_M and the semiconductor electron affinity χ. It is equally well known that experimental measurements of capacitance, photoemission, and current[8-14] do not agree with this result. In particular, photoemission experiments on metal-n-type semiconductor junctions (M-n contacts) measure a barrier height which is larger than φ_{SD} except for high-work-function metals (Pt and Au). For metal-p-type semiconductor junctions (M-p contacts), photoemission measurements yield a barrier height smaller than the theoretical one of $E_G - \varphi_{SD}$, where E_G is the semiconductor energy gap. Junction-capacitance experiments yield barrier heights which are larger (in both cases) than the height measured by photoemission or current experiments.

The Tamm[15] and Shockley[16] theories of surface states and the Bardeen[17] interface model are also not sufficient to explain all of the preceding experiments. The Bardeen model may explain why the actual barrier height is larger than φ_{SD} when an interfacial layer exists between the metal and semiconductor. A model proposed by Heine[18] further develops the Bardeen model and ascribes the surface states to a tailing of the metallic-electron wave functions. The Heine model is the most accurate previous model, but it does not explain the experimental results because of its simplified and incomplete formulation of both the classical and quantum-mechanical nature of the problem.[19-21]

In this paper, a model is presented which completes the classical and quantum-mechanical formulation of the Heine model. Quantum-mechanical penetration of electrons from the metal into the semiconductor energy gap is considered and the Poisson equation is solved in an appropriate way. The model is able to simply and completely explain the experimental results.

In particular, the theory that is proposed here consists firstly in solving Poisson's equation for the electric field and potential in order to obtain new general relationships for the junction capacitance, the energy barrier height, and so on, which take into account the quantum space charge. The latter is then evaluated directly from the electron wave function ψ which is calculated by means of the effective-mass method and of the WKB approximation using the continuity of ψ and of the probability current as boundary conditions at the interface between the two substances.

The analytical results so deduced seem to agree well with the experimental values obtained by many authors, especially in the case of contacts built by evaporating the metal onto a vacuum-cleaved semiconductor sample. Such contacts are probably better approximations to the model discussed here and by Schottky, Davydov, and Heine. In particular, the theory applied in this paper (i) to contacts between n-type CdS and Au, Cu, Ag, and Pt, (ii) to contacts between n-type GaAs and Au, Cu, Sn, Al, and Ag, and (iii) to contacts between p-type GaAs and Au and Al leads to numerical values which match the experimental values obtained by Spitzer and Mead.[9]

II. JUNCTION CAPACITANCE AND ENERGY BARRIER

A. Metal–n-Type Semiconductor Contacts

When a metal [Fig. 1(a)] is brought into contact with an n-type semiconductor [Fig. 1(b)], a region of the latter to the right of the interface $x_1 = 0$ is depleted of its conduction-band electrons and at the same time its forbidden energy gap becomes occupied by electrons as a result of the quantum-mechanical tunneling from the conduction band of the metal. The electric space charge so created by the "quantum electrons" and the ionized donors may give rise to electric potential and electron energy diagrams of the type drawn in Figs. 1(c) and 1(d), respectively.

In this section the properties of such a space-charge region will be analyzed, solving the Poisson equation so as to evaluate the junction capacitance C and the energy barrier height φ_n [Fig. 1(d)].

Let W be the "width" of the semiconductor depletion layer and let $x_1 = w$ $(w < W)$ represent an arbitrary abscissa in the depletion layer where neither electrons of the semiconductor conduction band[22] nor electrons from the metal band penetrate to any appreciable extent [Figs. 1(c), 1(d), 2(c), and 2(d)]. Such a section exists (i) if w is much greater than the mean length λ of quantum penetration of the metal electrons into the semiconductor and (ii) if at the same time $e[v_c - v - v_i(w)] \gg kT$, where k is Boltzmann constant, T is the absolute temperature, e is the charge of the electron, v is the voltage applied externally to the contact [Figs. 1(b) and 2(b)], $v_i(w)$ is the electric potential at the abscissa w [Figs. 1(c) and 2(c)], $v_c = (E_S - E_M)/_c$ is the "contact" potential difference [Figs. 1(a) and 2(a)], and E_M and E_S are the Fermi levels of the metal and semiconductor, respectively [Figs. 1(a) and 2(a)]. Both the preceding conditions may be satisfied in general, since λ is of order of few Å,[18,19] whereas W may be of the order of 10^3 Å.

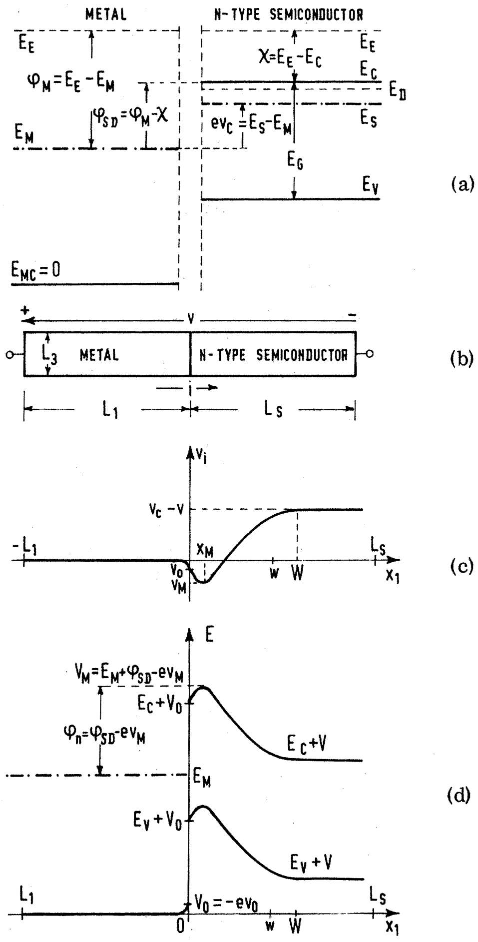


FIG. 1. (a) Energy-band diagrams for a metal and an n-type semiconductor before being brought into contact; (b) metal–n-type semiconductor contact (M–n contact); (c) electric potential diagram; (d) energy-band diagram for the two materials in contact.

Across the plane $x_i = w$ there is only a displacement current, so that the junction capacitance of the contact may be expressed as

$$C = A\epsilon_S \frac{dF(w)}{dv} , \tag{1}$$

where A is the contact-surface area [Figs. 1(b) and 2(b)], ϵ_S is the semiconductor dielectric constant, and $F(w)$ is the electric field at the abscissa w. The capacitance evaluation therefore reduces to the calculation of $F(w)$. To obtain the electric field the Poisson equation is integrated with respect to the electric potential v_i for $x_1 \geq w$ (one-dimensional case) on the assumption that the concentration N_D of the donor atoms be constant in this region of the semiconductor. One finds that

$$v_i(w) = -\epsilon_S F^2(w)/2eN_D + v_c - v_e - v , \tag{2}$$

where, for $E_G \gg E_C - E_S \gg kT$,

$$v_e = (kT/e)[a(1+\sigma) - \ln a] , \tag{3}$$

and in the latter expression

$$a \simeq (1 + e^{(E_S - E_D)/kT})^{-1} \tag{4}$$

is the fraction of the donor atoms which are ionized in the semiconductor bulk. The quantity σ appearing in (3) is given by

$$\sigma \simeq \frac{0.89297760}{(\pi kT)^{1/2}} \left[\frac{\hbar e}{2}\left(\frac{10 N_D kT}{m_e^* \epsilon_S}\right)^{1/2}\right]^{1/3} , \tag{5}$$

and is due[22] to the electron quantum-penetration from the conduction band into the forbidden energy gap of the semiconductor [Fig. 1(d)]. In the pre-

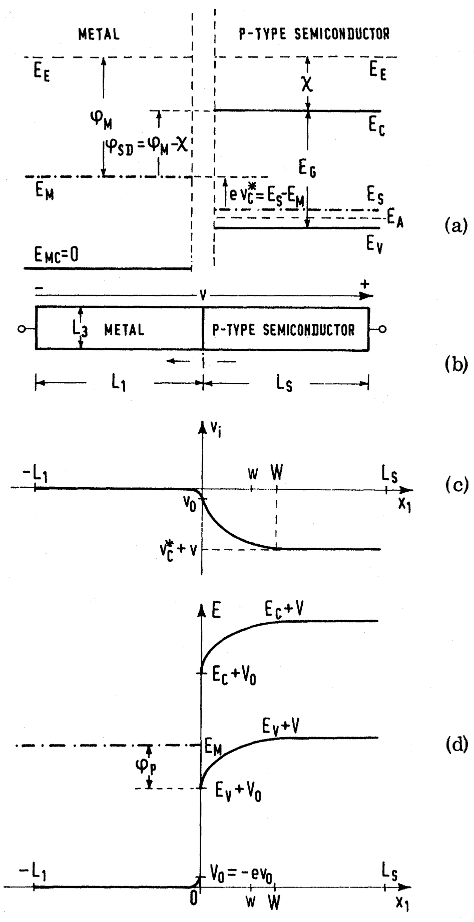


FIG. 2. Same as Fig. 1, for a metal—p-type semiconductor contact (M-p contact).

ceding relationships E_C is the electron energy at the bottom of the conduction band in the semiconductor [Figs. 1(a) and 2(a)], E_D (E_A) is the energy of the donor (acceptor) states in the n-type (p-type) semiconductor [Figs. 1(a) and 2(a)], $h = 2\pi\hbar$ is the Planck constant, m_e^* and m_h^* are the electron effective masses in the conduction and valence bands, respectively, of the semiconductor.

By integrating the Poisson equation twice with respect to x_1 in the interval 0, w so as to obtain v_i as a function of x_1 and taking as boundary conditions at $x_1 = w$ that the electric field $F = F(w)$ and the potential $v_i = v_i(w)$, one obtains for $x_1 = 0$, on eliminating $v_i(w)$ with the aid of (2), a second-degree equation in $F(w)$ which when solved gives

$$F(w) = \frac{eN_D w}{\epsilon_S} - \left(\frac{2eN_D}{\epsilon_S}(v_b - v)\right)^{1/2} , \tag{6}$$

where

$$v_b = v_c + v_q - v_e - v_0 , \tag{7}$$

$$v_q = -(1/\epsilon_S)\int_0^w x_1 q(x_1)dx_1 , \tag{8}$$

$$q(x_1) = q_T(x_1) - eN_D , \tag{9}$$

with $v_0 = v_i(0)$ the electric potential at the contact surface [Figs. 1(c) and 2(c)] and $q_T(x_1)$ the total density of the electric charge, due to any cause, in the semiconductor.

By substituting the expression for $F(w)$ given by (6) in Eq. (1) one obtains C in the general form

$$C = A\left(\frac{e\epsilon_S N_D}{2(v_b - v)}\right)^{1/2}\left(1 - \frac{dv_b}{dv}\right) , \tag{10}$$

which holds, not only for M-n contacts, but also for every type of junction and for any charge density $q_T(x_1)$ between 0 and w (in particular, q_T could be due to surface states at $x_1 = 0$ and to a nonconstant doping between 0 and w).

If v_0 and v_q do not depend on the voltage v applied externally to the contact, i.e., if a range of v exists in which $|dv_b/dv| \ll 1$, then in such an interval the capacitance is given by the relationship

$$C = A\left(\frac{e\epsilon_S N_D}{2(v_b - v)}\right)^{1/2} , \tag{11}$$

which differs from the Schottky expression[5,6] for the classical and quantum correction terms v_0 and v_q, respectively, of the built-in voltage v_b. Such terms, as shown in Sec. IV, have a great importance with respect to the others appearing in Eq. (7) and explain many experimental results.

From the previous analysis it also follows that the electric field $F_0 = F(0^+)$ corresponding to $x_1 = 0^+$ is given by the equation

$$F_0 = -\frac{1}{\epsilon_S}\int_0^w q(x_1)dx_1 - \left(\frac{2eN_D(v_b - v)}{\epsilon_S}\right)^{1/2} , \tag{12}$$

which, useful for itself, may also be used to determine the electric potential $v_0 = v_i(0)$ that appears in (7). In fact, by integrating the Poisson equation in the region $x_1 \leqslant 0$ with the boundary condition $\epsilon_M F(0^-) = \epsilon_S F(0^+)$, where ϵ_M is the dielectric constant of the metal, and by taking into account Eq. (49), which gives the metal electron density $m_{MC} = N_M(1 + 3ev_i/2E_M)$, N_M being given by (50), one obtains the Thomas-Fermi relationship[23,24]

$$v_0 = -\frac{\epsilon_S}{e}\left(\frac{2}{3}\frac{E_M}{\epsilon_M N_M}\right)^{1/2} F_0 , \tag{13}$$

which, together with Eqs. (7), (8), and (12), gives an equation for v_0.

When F_0 as expressed by (12) is positive, the electric potential $v_i(x_1)$ [Fig. 1(c)] has a minimum for $x_1 = x_M > 0$; by solving Poisson's equation and using Eq. (12), x_M may be shown to satisfy the condition

$$N_D x_M - \frac{1}{e}\int_{x_M}^w q(x_1)dx_1 - \left(\frac{2\epsilon_S N_D(v_b - v)}{e}\right)^{1/2} = 0 , \tag{14}$$

which holds for $x_M \ll w$. The value $v_M = v_i(x_M)$ may then be expressed as a function of x_M:

$$v_M = v_0 - v_q + \frac{1}{\epsilon_S}\left(\frac{eN_D x_M^2}{2} - \int_{x_M}^{w} x_1 q(x_1)\,dx_1\right) . \tag{15}$$

When $q(x_1)$ is given as a function of v_i, one can obtain v_M directly from the Poisson equation by means of the relationship

$$\tfrac{1}{2}\epsilon_S F_0^2 = \int_{v_0}^{v_M} q\,dv_i + eN_D(v_M - v_0) . \tag{16}$$

Finally, the correct value φ_n of the height of the energy barrier which the electrons must overcome to pass from the metal Fermi level into the semiconductor [see Fig. 1(d)], from the definition of v_c and from (7), is given by

$$\varphi_n = \varphi_{SD} - ev_M = [e(v_b + v_e) + E_C - E_S] - e(v_M + v_q - v_0) ; \tag{17}$$

$$\varphi_n = \varphi_{SD} - ev_0 = [e(v_b + v_e) + E_C - E_S] - ev_q \tag{18}$$

for $F_0 > 0$ and $F_0 < 0$, respectively. It follows that in the former case the contact could be rectifying, i.e., $\varphi_n > 0$, even when the energy barrier height $\varphi_{SD} = \varphi_M - \chi$ obtained from the Schottky–Davydov theory (SDT) is negative, namely, when the contact should be Ohmic according to that theory. The experimental results confirm this conclusion in many cases; for instance, this happens in the systems CdS-Au, CdS-Cu, and CdS-Ag[9,10] (Sec. IV).

In the Schottky theory the barrier height φ_{nc} obtained from the measures of the capacitance is given by

$$\varphi_{nc} = e(v_b + v_e) + E_C - E_S , \tag{19}$$

whereas the height φ_{nph} deduced from the experimental values of the photocurrent, if the barrier lowering due to the tunnel effect is neglected, coincides with φ_n. {The barrier-height correction due to the "image force" should be negligible and, in any case, is difficult to calculate because the barrier peak [Figs. 1(c) and 1(d)] is at an abscissa x_M where the number of mobile electrons, due to the quantum penetration, is much greater than the number of ionized atoms.} In the case of $q(x_1) < 0$ and $F_0 > 0$, which seems to be the most frequent in practice, from Eqs. (15), (17), and (19) it follows that

$$\varphi_{nc} = \varphi_{nph} + \frac{1}{\epsilon_S}\left(e\,\frac{N_D x_M^2}{2} - \int_{x_M}^{w} x_1 q(x_1)\,dx_1\right) , \tag{20}$$

so that $\varphi_{nc} > \varphi_{nph}$, in agreement with the experimental results.[9-13] From (18) and (19) it may be seen that the latter condition, $\varphi_{nc} > \varphi_{nph}$, also holds in the case that $F_0 < 0$, provided that $v_q < 0$.

Both (17) and (18), as a consequence of (19), lead to the relationship

$$v_q - v_0 = (\varphi_{nc} - \varphi_{SD})/e , \tag{21}$$

which can be used to verify the validity of the preceding analysis, especially when, for $F_0 > 0$, v_M is not known (see Sec. IV).

From (12), (16), and (17), on the assumption that $|q(x_1)|$ is independent of v and much greater than eN_D between 0 and x_M [see also Figs. 1(d) and 3(d)], it follows that the height φ_n of the barrier increases and its tunnel transparency decreases when v increases. Also, this theoretical result is verified experimentally by the forward-current measurements made by many authors[25-30] on several types of metal-semiconductor systems.

It is useful to note that the present analysis holds independently of the sign of φ_{SD} and v_c [Figs. 1(a) and 2(a)].

B. Metal-*p*-Type Semiconductor Contacts

The v_i distribution of Fig. 1(c) and, in particular, the existence of the minimum $v_M = v_M(x_M)$ depend on the sign and value of $q(x_1)$, which in turn, as will be seen in the following sections, depend on E_M, φ_M, m_e^*, m_h^*, E_G, and E_S, that is, of course, on the nature of the two substances in contact and, in particular, through E_S, on the type and density of the semiconductor impurities. In other words, as is well known, on changing the

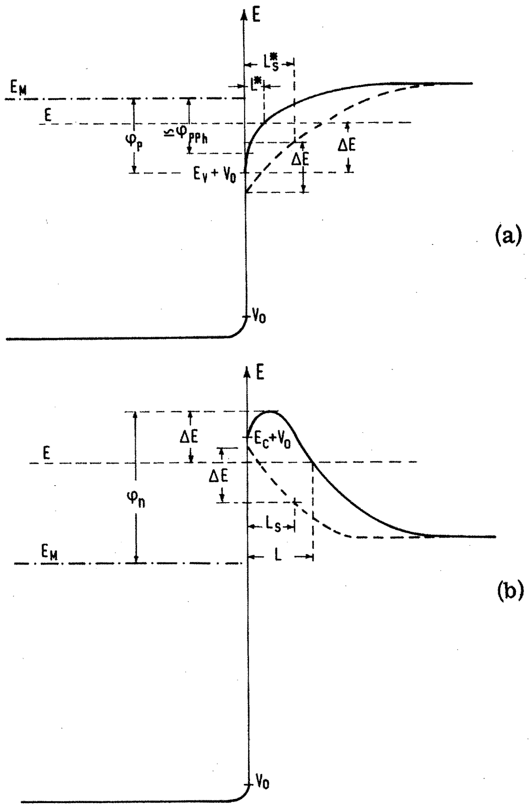


FIG. 3. Energy barrier for the charge carriers (a) in *M*-*p* contact and (b) in *M*-*n* contact.

doping the Fermi level E_S may vary with continuity from $E_S > E_0$ to $E_S < E_V$, where E_V is the electron energy at the top of the valence band in the semiconductor [Figs. 1(a) and 2(a)]. As a consequence the v_i distribution can change, through intermediate conditions, from the shape of Fig. 1(c) to that of Fig. 2(c), which will be discussed here.

The quantities of the metal–p-type semiconductor system of Fig. 2, which shall be labeled with an asterisk, may be deduced in an analogous fashion to that presented in Sec. II A. The quantities σ^*, a^*, and v_e^* are again given by (5), (4), and (3), respectively, after the substitutions $|m_h^*| \to m_e^*$ and $N_A \to N_D$ in (5) and in (3), and $E_A - E_S \to E_S - E_D$ in (4), $N_A =$ const being the acceptor atom density for $x_1 \geqslant w$. The capacitance built-in voltage becomes

$$v_b^* = -v_c^* - v_q^* + v_0^* - v_e^* \ , \tag{22}$$

where v_q^* is again given by (8) after replacing N_D with $-N_A$ in (9). With the substitution $N_A \to N_D$ and $v_b^* \to v_b$, Eqs. (10)–(12) hold also for C^* and F_0^* [the sign of the square root in Eq. (12) must also be changed]. Finally, Eq. (13) gives v_0^* after replacing F_0 with F_0^*.

From (22) and from the previous analysis it follows that, in the most frequent case of $q(x_1) < 0$, the built-in voltage v_b^* on capacitance is lower than that obtained in the Schottky theory.

From the definition of v_c^* [see Fig. 2(a)] and from (22), the height φ_p of the energy barrier [see Fig. 2(d)] which the holes must overcome to go from the metal Fermi level E_M into the semiconductor becomes

$$\varphi_p = E_G - \varphi_{\mathrm{SD}} + ev_0^* = [e(v_b^* + v_e^*) + E_S - E_V] + ev_q^* ; \tag{23}$$

that is, φ_p is lower than the barrier height $E_G - \varphi_{\mathrm{SD}}$ obtained in SDT [$v_0^* < 0$ for $q(x_1) < 0$].

In the Schottky theory the barrier height φ_{pc} obtained from the capacitance measurements is given by

$$\varphi_{pc} = e(v_b^* + v_e^*) + E_S - E_V \ , \tag{24}$$

while the value φ_{pph} obtained from the photocurrent measurements should be equal to φ_p, so that, from (23) and (24), φ_{pc} should be lower than φ_{pph}. This does not really happen experimentally, because $\varphi_{pph} < \varphi_p$, for reasons which shall be seen later on.

From (23) and (24) one obtains the equation

$$v_q^* - v_0^* = [(E_G - \varphi_{\mathrm{SD}}) - \varphi_{pc}]/e \tag{25}$$

as the analog of (21).

The sum of the barrier heights of an M-n contact and of an M-p contact, both built with the same metal and the same semiconductor, from (17), (18), and (23), is given by

$$\varphi_n + \varphi_p = E_G + e(v_0^* - v_M) \ ,$$

$$\varphi_n + \varphi_p = E_G + e(v_0^* - v_0) \ , \tag{26}$$

respectively, for $F_0 > 0$ and $F_0 < 0$ in the M-n contact. Therefore the new value of $\varphi_n + \varphi_p$ is different from the value E_G obtained in SDT. When $E_G - (\varphi_{\mathrm{SD}} + V_0)$ [see Figs. 1(d) and 2(d)] is a large fraction of E_G, the concentration of the metal electrons which penetrate in a quantum way into the semiconductor becomes much greater than the impurity density and is practically independent of the semiconductor Fermi level E_S, so that $F_0 \simeq F_0^* > 0$, $v_0 \simeq v_0^*$, $v_q \simeq v_q^*$, and, in consequence, from (26) and from Fig. 1(c), $\varphi_n + \varphi_p > E_G$. It is also useful to note that the sum $\varphi_{nc} + \varphi_{pc}$, which, from Eqs. (17), (18), (19), (23), and (24), is given by

$$\varphi_{nc} + \varphi_{pc} = E_G + e(v_q - v_q^*) + e(v_0^* - v_0) \ , \tag{27}$$

reduces in this case to E_G. This happens, for instance, for the Al-GaAs systems.[9]

Since, in general, F_0^* is much greater than the corresponding SDT value, the width L^* [Fig. 3(a)] of the M-p junction energy barrier relative to a given ΔE is lower, often much lower, than the corresponding Schottky–Davydov value L_S^* and, for the same reason, is much lower than the width L of the barrier of the M-n contact [Fig. 3(b)], so that the electrons with energy $E > V_0 + E_V$ may cross the barrier in virtue of the tunnel effect. {That happens with greater difficulty in the case of electrons with energy $E < V_0 + E_C$ in the M-n contact in which the barrier-tunnel transparency is reduced just by the increased L value [Fig. 3(b)].} The consequences of this fact confirmed by the experimental results[9,10] are that the barrier-height values φ_{pph} obtained from the photocurrent measurements are not well defined and lower than φ_p [Fig. 3(d)], the reverse current in the M-p contacts is much higher than in the M-n ones, and the forward current, for $ev \gg kT$, does not obey[25–31] the Richardson–Dushman law $i = i_0 e^{ev/\alpha kT}$, with $\alpha \geqslant 1$.

III. WAVE FUNCTION AND DENSITY OF ELECTRONS WHICH PENETRATE IN A QUANTUM WAY INTO SEMICONDUCTOR

A. Electron Wave Function

In order to develop the calculations proposed in the previous general electrical analysis it is necessary to know the extra charge $q(x_1) = q_T(x_1) - eN_D$ [or $q(x_1) = q_T(x_1) + eN_A$] which may be due to any cause whatever.

Heine[18] and the other authors[19–21] do not deduce the preceding general electrical properties of the metal-semiconductor contacts. At the same time, from considerations on the tails of the metal wave functions they assume $q(x_1) = -en_0 e^{-x_1/\lambda}$ and give only a semiquantitative way to evaluate n_0 and λ. In particular, Heine, in deriving $q(x_1)$, treats the valence and conduction states of the semiconductor and the conduction electrons of the metal as free-electron gases, assumes the electron potential energy as constant in the semiconductor and in the metal, and refers his calculation to the case of one-dimensional band structures.

In this section the contribution to $q(x_1)$ due to the electrons which enter the semiconductor forbidden energy gap in a quantum way from the metal will be calculated, instead, taking into account the various details and implications associated with the electron wave function. The latter is calculated by means of the effective-mass method and of the WKB approximation imposing the continuity of the probability density and current at the interface $x_1 = 0$.

In what follows the following additional symbols will be adopted: j is the index of the Cartesian axes ($j = 1, 2, 3$), m is a suffix which indicates the substance type ($m = M$ in the metal, $m = S$ in the semiconductor), b is another suffix that indicates the band ($b = C$ in the conduction band, $b = V$ in the valence band), k_{mj} are the Cartesian components of the reduced wave number $\vec{k}_m$, $E_k = E_{kmb}$ $(\vec{k}_m)$ is the electron energy when no potential is applied to the crystal, E_{0mb} is the value of E_{kmb} at the extremum of the band $\{E_{0MC} = E_{MC} = 0,\ E_{0SC} = E_C,\ E_{0SV} = E_V$ [Figs. 1(a) and 2(a)]$\}$, $V = -ev_i(x_1)$ and E are the potential and total electron energy, respectively [Figs. 1(d) and 2(d)], and $\psi_{mb}(x_1, x_2, x_3)$ is the electron wave function.

If the valence and conduction bands have nondegenerate edges at the central point of the Brillouin reduced zone, and if the constant energy surfaces near the central point are ellipsoids, having their axes coincident with the Cartesian ones, one can express E_{km} using the truncated McLaurin series expansion

$$E_{kmb} = E_{0mb} + \frac{\hbar^2}{2} \sum_{j=1}^{3} \frac{k_{mj}^2}{m_{mbj}^*} , \tag{28}$$

where

$$\frac{1}{m_{mbj}^*} = \frac{1}{\hbar^2} \left. \frac{\partial^2 E_{kmb}}{\partial k_{mj}^2} \right|_{k_{mj}=0} , \tag{29}$$

m_{mbj}^* being the principal component of the effective-mass tensor of the electron. When the quantities

$$\rho_{mj} = m_{mCj}^* / m_{mVj}^* \tag{30}$$

have the same value ρ_m for $j = 1, 2, 3$, then introducing the relation (see Fig. 4)

$$E_{Bm} = E_{0mC} - \frac{E_{0mC} - E_{0mV}}{1 - \rho_m} ,$$

it may be seen that Eq. (28) holds for $m = C$ (namely, in the conduction band) when $E_{km} > E_{Bm}$, while it holds for $m = V$ (i.e., in valence band) when $E_{km} < E_{Bm}$.[32] Finally, the truncated McLaurin series expansion (28) holds for $|k_{mj}| < k_{mbj}^*$, where $k_{m\,bj}^*$ are appropriate real positive values of the Cartesian components of $\vec{k}$ (Fig. 4). It is important to note, with the help of Fig. 4 sketched qualitatively for the semiconductor, that for given values of k_{S3}, of $k_{S2} > k_{Sb2}^*$, and of E_{kS} (for instance, E'_{kS}) the corresponding value $|k'_{S1}|$ of k_{S1} is so high that the associated values of the wave function become negligible (see Appendix A) when compared with those depending on k''_{S1} relative to the same state except $k_{S2} < k_{Sb2}^*$. Therefore the electron quantum penetration into the forbidden energy gap of the semiconductor is due essentially to the states with transverse wave numbers which satisfy the relationship

$$k_{Sj} < k_{Sbj}^* ,\ j = 2,\ 3 . \tag{31}$$

When (28) holds and the electron potential energy $V(x_1)$ varies slowly over an atomic distance, the electron "wave function" $\psi_{mb}(x_1, x_2, x_3)$ may be obtained, in the ambit of the effective-mass theory, by means of the pseudo-Hamiltonian (Schrödinger-like equation[33])

$$- \beta_{mb}^* \frac{\hbar^2}{2} \sum_{j=1}^{3} \frac{\partial}{\partial x_j} \left(\frac{1}{\beta_{mb}^* m_{mbj}^*} \frac{\partial(\beta_{mb}\psi_{mb})}{\partial x_j} \right) + (V + E_{0mb})\beta_{mb}\psi_{mb} = E\beta_{mb}\psi_{mb} , \tag{32}$$

in which it is required that $\beta_{mb}\psi_{mb}$ and the function contained inside the large parentheses be continuous; i.e., in particular, the following relations must be satisfied:

$$\beta_{Mb}\psi_{Mb}\big|_{x_1=0} = \beta_{Sb}\psi_{Sb}\big|_{x_1=0} , \tag{33}$$

$$\frac{1}{\beta_{Mb}^* m_{Mb1}^*} \left. \frac{\partial(\beta_{Mb}\psi_{Mb})}{\partial x_1} \right|_{x_1=0} = \frac{1}{\beta_{Sb}^* m_{Sb1}^*} \left. \frac{\partial(\beta_{SB}\psi_{Sb})}{\partial x_1} \right|_{x_1=0} , \tag{34}$$

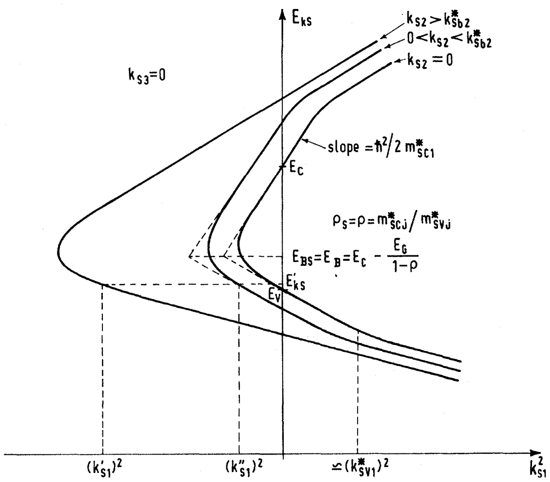


FIG. 4. Electron energy diagrams in the semiconductor as function of k_{S1}^2 for some value of k_{S2} and k_{S3}.

where the constants β_{mb} are appropriate average values of the Bloch functions introduced so as to ensure the matching of the true wave functions.

Assuming that every well-behaved solution of (32) may be expanded as a linear combination of the special solutions $\psi_{mb}=\prod_j X_{mbj}(x_j)$,[34] on separating the variables in (32) and assuming $\psi_{mb}\equiv 0$ outside the region occupied by the two materials in contact [Figs. 1(b) and 2(b)] one obtains[22]

$$X_{mbj} = B_{mbj}\sin k_{mj}x_j\,,\quad j=2,\ 3 \tag{35}$$

where, in virtue of (33),

$$k_{Mj}=k_{Sj}=k_j=(\pi/L_j)n_j\,,\quad n_j=1,\ 2,\ 3,\ \ldots,\quad j=2,\ 3 \tag{36}$$

and L_1, L_2, and L_3 are the metal dimensions [Figs. 1(b) and 2(b)]. The function $X_{mb1}(x_1)$ is the solution of the equation

$$-\hbar^2\frac{\partial^2 X_{mb1}}{\partial x_1^2}+\Lambda_{mb}X_{mb1}=0, \tag{37}$$

where

$$\Lambda_{mb}=2m^*_{mb1}[V(x_1)-H_{mb}]\,, \tag{38}$$

and from the separation of variables in (32),

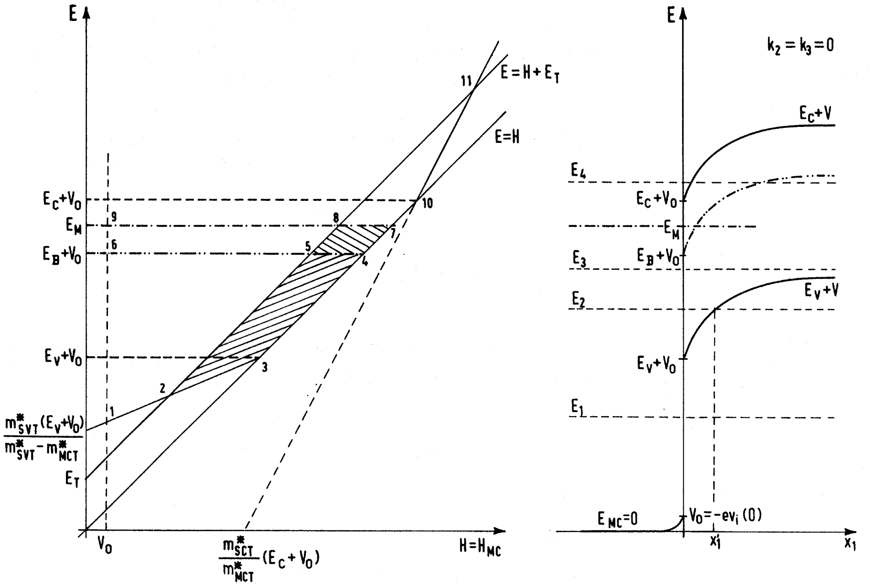
$$H_{mb}+\frac{\hbar^2}{2}\left(\frac{k_{m2}^2}{m^*_{mb2}}+\frac{k_{m3}^2}{m^*_{mb3}}\right)=E-E_{0mb}\,. \tag{39}$$

For a given value of the parameters E, k_2, and k_3 and of the variable x_1 the component X_{mb1} of the wave function, which must be deduced from (37), concerns a particular band of one of the two materials in the forbidden or allowed part [Fig. 5(b)] according to the sign of $E-V(x)-E_{Bm}$, x_1, and Λ_{mb}, respectively. Such various parts of X_{mb1} which correspond to different intervals of the x_1 axis must match one another at the extremities of these intervals according to what was previously said about ψ_{mb}. In order to evaluate the density of the metal free electrons one must calculate X_{MC1} in the metal conduction band, that is, for $-L_1\leqslant x_1\leqslant 0$, $\Lambda_{MC}\leqslant 0$, and $E\geqslant 0$ (Fig. 5). Instead, to evaluate the contribution to the extra charge $q(x_1)$ due to the electron quantum penetration into the forbidden energy gap, one must determine X_{Sb1} for

$$\Lambda_{Sb}>0, \tag{40}$$

that is, for instance, between 0 and x_1' in the case $E=E_2$ and $k_2=k_3=0$ of Fig. 5(b). In fact, the electrons in such states are in excess of those which assure the semiconductor electrical neutrality by occupying the allowed states of the valence band ($\Lambda_{SV}<0$). The function X_{Sb1} corresponding to (40) consists of the sum of two parts, X^+_{Sb1} and X^-_{Sb1}, which, respectively, decrease and increase in modulus when x_1 increases from 0 to x_1', since $\Lambda_{Sb}(x_1')=0$. One may simplify the calculations by evaluating separately X^+_{Sb1}, corresponding to the electrons which enter the semiconductor forbidden energy gap from the metal, and X^-_{Sb1}, relative to the electrons that penetrate into the same energy range from the valence band of the semiconductor itself, on the assumption that $|X^+_{Sb1}(0)|\gg|X^-_{Sb1}(0)|$ and $|X^+_{Sb1}(x_1')|\ll|X^-_{Sb1}(x_1')|$. In fact, in this case the boundary conditions at $x_1=0$ and $x_1=x_1'$ concern only X^+_{Sb1} and X^-_{Sb1}, respectively. The function X^-_{Sb1} is not calculated here; nor is X_{Sb1} calculated for $x_1\geqslant x_1'$.

After the above remarks, X^+_{Sb1} relative to (40) and the corresponding X_{MC1} may be evaluated by



(a) (b)

FIG. 5. (a) Existence region, in the plane HE, of the metal electrons which enter the energy gap of the semiconductor in a quantum way; (b) energy-band diagram for *M-p* contact.

means of the WKB approximation, which holds for[35]

$$|m^*_{mb1}|\,\hbar e\,|F|/|\Lambda_{mb}|^{3/2} \ll 1, \tag{41}$$

and gives[34]

$$X_{MC1} = B_{MC1}(-\Lambda_{MC})^{-1/4}\cos\left[\hbar^{-1}\int_0^{x_1}(-\Lambda_{MC})^{1/2}dx_1 + \theta\right], \tag{42}$$

$$X^+_{Sb1} = B_{Sb1}(\Lambda_{Sb})^{-1/4}\exp\left[-\hbar^{-1}\int_0^{x_1}(\Lambda_{Sb})^{1/2}dx_1\right]. \tag{43}$$

Moreover, from the Wilson–Sommerfeld quantization rule,[34] in the case that (40) holds, k_{M1} is given by

$$k_{M1} = \frac{(2m^*_{MC1}H_{MC})^{1/2}}{\hbar} = k_1 = \frac{\pi}{L_1}\,n_1, \qquad n_1 = 1, 2, 3, \cdots . \tag{44}$$

The constant $B_M = B_{MC1}B_{MC2}B_{MC3}$ may be obtained from the existence condition of the electron in the metal,[22] which turns out to be

$$B_M^2 = 8\hbar k_1/L_1L_2L_3 . \tag{45}$$

Instead, from (33) and (34) the quantities $B_{Sb} = B_{Sb1}B_{Sb2}B_{Sb3}$ and θ are given for β_{Sb} real by the equations

$$B_{Sb} = B_M\,\frac{\beta_{MC}}{\beta_{Sb}}\left(-\frac{\Delta_{Sb}(0)}{\Lambda_{MC}(0)}\right)^{1/4}\cos\theta , \tag{46}$$

$$\tan\theta = \frac{\beta_{MC}m^*_{MC1}}{\beta_{Sb}\,m^*_{Sb1}}\left(-\frac{\Lambda_{Sb}(0)}{\Lambda_{MC}(0)}\right)^{1/2} \times\left[1 + \frac{\hbar e F_0 m^*_{Sb1}}{[\Lambda_{Sb}(0)]^{3/2}}\left(\frac{1}{2} - \frac{\epsilon_S\beta_{Sb}\Lambda_{Sb}(0)}{2\epsilon_M\beta_{MC}\Lambda_{MC}(0)}\right)\right], \tag{47}$$

$$\Lambda_{mb}(0) = 2m^*_{mb1}(V_0 - H_{mb}) ,$$

which together with the other relationships allow one to determine completely the wave functions ψ_{MC}, ψ^+_{SV}, and ψ^+_{SC}.

B. Electron Density

The density dn_{mb} of the electrons in the interval k_j, $k_j + dk_j$ ($j = 1, 2, 3$) belonging to the band b of the material m is given by

$$dn_{mb} = 2f\,|\psi_{mb}|^2\,\frac{L_1L_2L_3}{\pi^3}\,dk_1dk_2dk_3, \tag{48}$$

where $f = \{1 + \exp[(E - E_M)/kT]\}^{-1}$ is the Fermi–Dirac factor, and where all the quantities, because of Eqs. (36), (39), and (44), may be expressed as functions of both k_j and x_j. The wave number of the electron k_j corresponds to the metal conduction band where $V(x_1) = 0$; in deriving (48) the relations (36) and (44), the Pauli exclusion principle, and the electron spin have been taken into account.

By integrating (48) in the ranges $0 \leqslant k_2 < \infty$, $0 \leqslant k_3 < \infty$, and $(2m^*_{MC1}V)^{1/2}/\hbar \leqslant k_1 < \infty$, by taking account of (35), (38), (42), (44), and (45) and by replacing the squared sines with their mean value $\frac{1}{2}$,[22,35] one obtains the density n_{MC} of the electrons belonging to the metal conduction band in the form[22,36]

$$n_{MC} = N_M\left[\left(1 + \frac{ev_i}{E_M}\right)^{3/2} + \frac{\pi}{8}\left(\frac{kT}{E_M}\right)^2\left(1 + \frac{ev_i}{E_M}\right)^{-1/2}\right] \simeq N_M\left(1 + \frac{3}{2}\,\frac{ev_i}{E_M}\right), \tag{49}$$

where

$$N_M = \frac{16(\sqrt{2})\hbar(m^*_{MC1}m^*_{MC2}m^*_{MC3})^{1/2}E_M^{3/2}}{3h^3} . \tag{50}$$

Also, the density dn_{Sb} of the electrons which penetrate into the semiconductor forbidden energy gap from the metal may be expressed as a function of k_j. Nevertheless, in order to simplify the calculation of Sec. IV it is useful, under the condition that $m^*_{mb2} = m^*_{mb3} = m^*_{mbT}$, to make the variable substitutions $\Phi = \arcsin[k_3/(k_3^2 + k_2^2)^{1/2}]$ for $0 \leqslant \Phi \leqslant \frac{1}{2}\pi$, $H = H_{MC} = \hbar^2 k_1^2/m^*_{MC1}$, and $E = \frac{1}{2}\hbar^2[k_1^2/m^*_{MC1} + (k_2^2 + k_3^2)/m^*_{MCT}]$, with $E \geqslant H$, which follow from (44) and, respectively, from (39) for $m = M$ and $b = C$. Moreover, one must observe that in (47) the sum contained in the large parentheses is in practice near to 1, so that, if (41) is verified for $x_1 = 0$, the second member of (47) reduces itself to the factor outside the large square brackets. Finally, by again replacing the squared sines with their mean value $\frac{1}{2}$ and by assuming $\beta_{MC} \simeq \beta_{Sb} \simeq 1$ from (35), (36), (38), (39), (43), and (45)–(48) one obtains

$$dn_{Sb} = \frac{16(\sqrt{2})fm^*_{MCT}(m^*_{MC1})^{1/2}}{h^3}\left(\frac{(H - V_0)[V_0 + E_{0Sb} - E + (m^*_{MCT}/m^*_{SbT})(E - H)]}{V + E_{0Sb} - E + (m^*_{MCT}/m^*_{SbT})(E - H)}\right)^{1/2} \times\frac{\exp(-(2/\hbar)\int_0^{x_1}\{2m^*_{Sb1}[V + E_{0Sb} - E + (m^*_{MCT}/m^*_{SbT})(E - H)]\}^{1/2}dx_1)}{H - V_0 + (m^*_{MC1}/m^*_{Sb1})[V_0 + E_{0Sb} - E + (m^*_{MCT}/m^*_{SbT})(E - H)]}\,dE\,dH\,d\Phi , \tag{51}$$

which, because of the limitations (31) on the "transverse" wave numbers k_{S2} and k_{S3}, and of (36) and (39), is valid when

$$H \leqslant E \leqslant H + E_{Tb} , \tag{52}$$

where $E_{Tb} = \hbar^2(k^{*2}_{Sb2} + k^{*2}_{Sb3})/2m^*_{MCT}$. Moreover, for the validity of (51), from (40), the following condition must hold:

$$m^*_{Sb1}[V + E_{0Sb} - E + (m^*_{MCT}/m^*_{SbT})(E - H)] > 0 . \tag{53}$$

In Fig. 5(a) the closed line 2, 3, 10, 11, 2 fixes the boundaries of the zone of the plane H, E in which, for $x_1 = 0$ and $E_{TV} = E_{TC} = E_T$, the relations (52) and (53) are verified, and in which (51) holds. The boundary between the valence and conduction bands in Fig. 5(a) is at $E = E_B + V_0$.

A more general expression of dn_{Sb} is reported in Appendix A.

C. Calculation of v_q and F_0

In order to determine from (51) the electron densities $n_{Sb}(x_1)$ on which the various quantities of Sec. II depend, one should know the electron potential energy $V = -ev_t(x_1)$ that, in turn, depends on $n_{Sb}(x_1)$. One may partly avoid the difficulties of such a self-consistent calculation by making some suitable approximations. For instance, by making the assumption that $V(x_1) \simeq V_0$ in (51), one can calculate directly the quantum correction v_q of the capacitance built-in voltage and the electric field F_0 on the interface $x_1 = 0$ between the two materials. Infact, since $q_T(x_1) = -e[n_{SV}(x_1) + n_{SC}(x_1) - N_D(x_1)]$, on the assumption that $N_D(x_1) = \text{const} = N_D$ it follows from (9) that

$$q(x_1) = -e[n_{SV}(x_1) + n_{SC}(x_1)] . \tag{54}$$

In virtue of the previous hypothesis $V(x_1) \simeq V_0$, and from (8), (12), (51), and (54), by assuming $f = 1$ for $E < E_M$ and $f = 0$ for $E > E_M$, namely, by neglecting the contribution due to the low fraction of the electrons with energy greater than the Fermi level E_M, and by integrating with respect to Φ (between 0 and $\frac{1}{2}\pi$), x_1 (between 0 and ∞), E and H {on the zone 2, 3, 7, 8, 2 of the plane H, E [Fig. 5(a)]}, one obtains the relationships

$$v_q = \frac{em^*_{MCT}}{2(\sqrt{2})\pi\epsilon_S h}\left(\frac{E_M - V_0}{m^*_{MC1}}\right)^{1/2}(\gamma_C + \gamma_V) , \tag{55}$$

$$F_0 = \frac{2em^*_{MCT}}{\epsilon_S h^2}(E_M - V_0)(\delta_C + \delta_V) - \left(2\,\frac{eN_D(v_b - v)}{\epsilon_S}\right)^{1/2} , \tag{56}$$

whose dimensionless quantities δ_b and γ_b are calculated and reported in Appendix B.

Another approximation may consist of using the Heine equation $q(x_1) = -en_0e^{-x_1/\lambda}$, where, in our case, $n_0 = n_{SV}(0) + n_{SC}(0)$ and the mean value of λ can be calculated, by means of an appropriate assumption, from (51).

IV. NUMERICAL AND EXPERIMENTAL RESULTS

A. Preliminaries

The numerical results deduced, by means of a computer, from the preceding theory are compared in this section with the experimental values obtained by Spitzer and Mead[9] on a series of metal-semiconductor contacts built by evaporating, in the vacuum, different metals onto "vacuum-cleaved" samples of n-type CdS and n- and p-type GaAs. More exactly, the value of the transverse energy E_T which leads to values of v_0 and v_q that satisfy (21) [or (25)], where the second member is deduced from the experimental data, is computed; that is, E_T is calculated in such a way as to fit the theoretical results with the experimental ones. The validity of the theory appears to be confirmed by the fact that E_T assumes practically the same value for different contacts built by means of the same semiconductor (this is true especially for cadmium sulfide) and that such an E_T value agrees with the one deducible from the literature.

The calculation comprises the following steps. The Fermi level E_M of the metal is computed by means of (50), in which one makes $m^*_{MCj} = m_0$ (= free-electron mass) ($j = 1, 2, 3$), and $N_M = \nu N_{at}$, N_{at} being the metal-atom density and ν the electron number per atom belonging to the conduction band. From the calculus it follows that the values of v_q, v_0, F_0, and E_T do not depend appreciably on ν; this is in agreement with the fact that the integration zone 2, 3, 7, 8, 2 and the quantities γ_C, γ_V, δ_C, and δ_V depend essentially on the position of the metal Fermi level with respect to the semiconductor energy bands and not on the E_M value. In Table I the data obtained from the literature and from the calculation for the metals used here are summarized. The values 1, 2, and 2 of ν for Al, Pt, and Sn, respectively, are those which give the best results for E_T. For the metals $\epsilon_M = \epsilon_0 =$ (vacuum dielectric constant).

In Table II are reported the data, required by the calculation, for CdS and for GaAs (one assumes $m^*_{SCj} = m^*_e$ and $m^*_{SVj} = m^*_h$ for $j = 1, 2, 3$) relative to the room temperature $T = 300$ °K to which all the experimental and theoretical results are here referred. In Table II, v_e and v^*_e deduced from (3)–(5) for $N_A = N_D = 4 \times 10^{17}$ cm^{-3} in the approximation $a = 1$, namely, on the assumption that at room temperature all the impurities be ionized, are also indicated.

In the preceding theory the Schottky–Davydov energy barrier height $\varphi_{SD} = \varphi_M - \chi$ must be calculated by means of the "inner" values of the metal

TABLE I. Summary of data for some metals at room temperature $T = 300$ °K.

Metal	ν	N_M ($\times 10^{28}$ m^{-3})	E_M (eV)	φ_M (eV)
Au	1^{a}	5.90^{a}	5.5^{a}	4.70^{b}
Ag	1^{a}	5.76^{a}	5.5^{a}	4.31^{b}
Cu	1^{a}	8.50^{a}	7^{a}	4.52^{b}
Al	1	6.03	5.58	4.20^{b}
Pt	2	13.2	9.43	5.32^{b}
Sn	2	7.4	6.41	4.21^{c}

[a] See Ref. 37. [b] See Ref. 38. [c] See Ref. 39.

TABLE II. Summary of data for CdS and GaAs at $T = 300\,°\mathrm{K}$.

Semiconductor	χ (eV)	E_G (eV)	m_e^*/m_0	$-m_h^*/m_0$	ϵ_S/ϵ_0	v_e (mV)	v_e^* (mV)
CdS	4.8[a]	2.42[b]	0.5[c]	0.7[d]	11.6[e]	37	36
GaAs	4.07[f]	1.435[g]	0.072[h]	0.68[h]	11.1[i]	41	36

[a] Reference 40.
[b] Reference 42.
[c] Reference 9.
[d] Reference 44.
[e] Reference 46.
[f] Reference 41.
[g] Reference 43.
[h] Reference 45.
[i] Reference 47.

work function φ_M and of the semiconductor electron affinity χ, i.e., by means of their volume contribution without the surface dipoles on the free surfaces. It is this which represents the difference in the binding of an electron in the two materials at contact. However, in the following calculations the measured values of φ_M and of χ reported in Tables I and II will be used, since the contributions to them due to the surface dipoles partly compensate each other in the difference $\varphi_M - \chi$, and since they are small[18,48] and in any case unknown.

It should be observed that φ_{SD} could perhaps be evaluated directly by means of a variational procedure of the type applied, for instance, by Bonch-Bruyevich[49] to the contact of two heavily doped semiconductors. For this purpose one could use, for example, the wave functions and the electric potential deduced in the preceding analysis, taking as a variational parameter the energy barrier height φ_{SD} itself. Any attempt to make such a calculation is beyond the scope of the present analysis.

B. Cadmium Sulfide

In columns 2, 3, and 5 of Table III are reported the experimental values of v_b, $E_C - E_S$, and $\varphi_{nph} = \varphi_n$, respectively, obtained by Spitzer and Mead[9] on contacts built by evaporating, in the vacuum, different metals onto "vacuum-cleaved" samples of n-type CdS. In column 4 is reported the value of φ_{nc} deduced by means of (19). The density N_D of the donors, required to calculate F_0 by means of (56), is deduced from the relationship $N_D = 2(2\pi m_e^* kT)^{3/2} e^{(E_S - E_C)/kT}/h^3$ on the assumption that N_D be equal to the free-electron concentration. After all this the calculation is made by giving tentative values to E_T and v_0 from which initial values of δ_C, δ_V (see Appendix B), and of F_0, for $v = 0$ [see (56)], are obtained. Then, by means of (13), a new value of v_0 is deduced which is used in the following step. The calculation is repeated until the difference between the new and the old values of v_0 is lower, in modulus, than 3 mV. The v_0 value so obtained is employed to determine γ_C, γ_V (see Appendix B), and, by means of (55), v_q. If v_0 and v_q do not satisfy Eq. (21), whose second member is obtained using the experimental values of Tables I–III, the calculation is repeated for another value of E_T, and so on until (21) is fitted. The values thus obtained for v_q, v_0, E_T, and F_0 are reported in columns 7, 8, 9, and 10, respectively, of Table III.

The theory seems confirmed by the fact that the transverse energy E_T assumes practically the same value in all the cases examined and the common value so obtained $E_T = 0.50 \pm 0.04$ eV is in agreement with that which can be deduced from the literature.[50] In fact, if one assumes roughly as an E_T value the value for which the function $E_k(k)$ has a flex, then for CdS E_T lies between 0.4 and 0.6 eV.[50]

The electric field F_0 at the interface between the two substances, reported in column 10 of Table III, is positive and much greater in modulus than that (negative) deduced from the Schottky theory, which, for instance, corresponding to the values of the third row of Table III, is equal to -6.5×10^6 V/m. Nevertheless, F_0 satisfies the condition (41) required for validity of the WKB method. In fact, from (41) and (38), for $|V_0 - H_{mb}| \simeq 0.5$ eV, it must be $F_0 \ll 3\times10^9$ V/m.

In column 6 the Schottky–Davydov barrier height $\varphi_{\mathrm{SD}} = \varphi_M - \chi$ is indicated. Its negative value implies that the contacts, on the basis of the SDT, should be Ohmic, which does not happen. The present theory, instead, explains completely the rectifying properties and the other characteristics of the contacts.

In column 11 are reported the values of $-v_M = (\varphi_{nph} - \varphi_{\mathrm{SD}})/e$. One observes the high values of v_q, $-v_0$, and of $-v_M$.

C. n-Type Gallium Arsenide

Table IV, obtained in the same way as Table III, summarizes the experimental and theoretical results for the contacts built, with the same technique, with n-type GaAs ($N_D = 4\times10^{17}\ \mathrm{cm}^{-3}$).

The preceding conclusions also hold in this case; only E_T has a greater range of values. Its mean value $E_T = 0.56 \pm 0.09$ eV also agrees with the theoretical one comprised between 0.4 and 0.6 eV (see p. 522 of Ref. 50).

The preceding computational method, which leads to $v_q - v_0 > 0$, cannot be applied to the contact Pt-(n) GaAs because, in this case, since $\varphi_{nc} - \varphi_{\mathrm{SD}} < 0$ ($v_b = 0.98$ V,[9] $\varphi_{nph} = 0.88$ eV[9] for $E_C - E_S = 0$), Eq. (21) cannot be satisfied.

The failure of the theory in this case could depend on having neglected the quantum penetration of the valence-band electrons into the forbidden energy gap of the semiconductor which determines, as one may deduce from the theory of Franz[51] and Keldysh,[52] an electron concentration $n_V(x_1) \propto |F(x_1)|^{1/3}$. In fact, in the case that $F_0 < 0$, which may be true for metal having a high work function

TABLE III. Summary of experimental and theoretical results for metal—*n*-type cadmium sulfide contacts.

1 Metal	2 v_b[a] (V)	3 $E_C - E_S$[a] (eV)	4 φ_{nc} (eV)	5 $\varphi_{nph} = \varphi_n$[a] (eV)	6 $\varphi_{SD} = \varphi_M - \chi$ (eV)	7 v_q (V)	8 $-v_0$ (V)	9 E_T (eV)	10 F_0 ($\times 10^8$ V/m)	11 $-v_M$ (V)
Au	0.66	0.09	0.787	0.75	−0.10	0.630	0.237	0.48	3.48	0.85
	0.79	0.08	0.907	0.80	−0.10	0.733	0.271	0.55	3.98	0.90
	0.75	0.10	0.887	0.78	−0.10	0.717	0.272	0.54	3.98	0.88
	0.65	0.12	0.807	0.78	−0.10	0.657	0.255	0.50	3.74	0.88
	0.60	0.16	0.797	0.75	−0.10	0.649	0.256	0.49	3.76	0.85
Cu	0.32	0.05	0.407	0.36	−0.28	0.503	0.190	0.49	2.96	0.64
Ag	0.45	0.16	0.647	0.54	−0.49	0.811	0.326	0.49	4.77	1.03
	0.40	0.16	0.597	0.55	−0.49	0.767	0.310	0.48	4.53	1.04
Pt	0.70	0.16	0.897	0.84	0.52	0.284	0.096	0.49	1.62	0.32
	0.68	0.16	0.877	0.88	0.52	0.256	0.090	0.46	1.51	0.36

[a] Reference 9.

[see (12)], such an electron quantum penetration cannot occur in the region $x_1 \geq 0$ near the interface, because the semiconductor valence band from which the electrons would have to be supplied does not exist for $x_1 \leq 0$. It is such a lack of $n_V(x_1)$ for $F \neq 0$ which may be considered as a positive charge if one assumes, at least to a first approximation, that the band bending does not induce an electric space charge. It is this positive charge which may make $v_q < 0$ and $v_0 > 0$ [see (8), (9), (12), and (13)] and may allow one to fit (21) also in this case of $\varphi_{nc} - \varphi_{SD} < 0$.

D. *p*-Type Gallium Arsenide

Table V summarized the results for some metal–*p*-type gallium arsenide contact. In this case Eq. (25) is used. The mean value of E_T is practically equal to the one obtained for the *n*-type GaAs (except for the contact with Au).

The theoretical values of φ_p, indicated in column 11, are much greater than the experimental values φ_{pph} of the energy barrier height obtained from the photocurrent measurements. This is due to the fact that the tunnel transparency[35]

$$D \simeq \exp[-2(2|m_h^*|)^{1/2}(\Delta E)^{3/2}/3\hbar e F_0]$$

[see Fig. 3(a)] for the values of F_0 reported in column 10 of Table V is high. For instance, for the data of the third row, D has the value 7×10^{-2}, 1.7×10^{-2}, 3.85×10^{-3}, and 5.6×10^{-4}, respectively, in correspondence with the values 0.3, 0.4, 0.5, and 0.6 eV of ΔE. The high value of D explains also the large leakage current, the difficulty of obtaining reliable photodata, and the nonlinearity of the photoresponse curve obtained by Spitzer and Mead.

It follows from the comparison of Tables IV and V that for the contacts Al-GaAs, for which $\chi + E_G - \varphi_M = 1.305$ eV is a large fraction of $E_G = 1.43$ eV, F_0 and F_0^*, v_0 and v_0^*, v_0 and v_q^* have about the same value, so that, in particular, [as may be seen from (27)], $\varphi_{nc} + \varphi_{pc} \simeq E_G$, as has been found by Spitzer and Mead.

V. CONCLUSIONS

The proposed electronic and quantum theory of the metal-semiconductor contacts is very general, leads to self-consistent calculations fitting the experimental results, gives exhaustive answers to the problems unsolved by the Schottky, Davydov, Bardeen, and Heine theories, and attains new significant results. The most important of these is the proof that the metal free electrons enter the forbidden energy gap of the semiconductor in a quantum way and create a space charge and an en-

TABLE IV. Summary of experimental and theoretical results for metal—*n*-type gallium arsenide contacts.

1 Metal	2 v_b[a] (V)	3 $(E_C - E_S)$[a] (eV)	4 φ_{nc} (eV)	5 $\varphi_{nph} = \varphi_n$[a] (eV)	6 $\varphi_{SD} = \varphi_M - \chi$ (eV)	7 v_q (V)	8 $-v_0$ (V)	9 E_T (V)	10 F_0 ($\times 10^8$ V/m)	11 $-v_M$ (V)
Au	0.98	0	1.021	0.90	0.63	0.351	0.040	0.45	0.59	0.27
Cu	0.83	0	0.871	0.78	0.45	0.377	0.047	0.51	0.74	0.33
Sn	0.68	0	0.721	0.67	0.14	0.503	0.077	0.55	1.18	0.53
	0.74	0	0.781	0.63	0.14	0.551	0.089	0.61	1.37	0.49
Al	0.81	0	0.851	0.80	0.13	0.615	0.105	0.61	1.56	0.67
Ag	0.94	0	0.981	0.88	0.24	0.629	0.110	0.65	1.63	0.64

[a] Reference 9.

TABLE V. Summary of experimental and theoretical results for metal–p-type gallium arsenide contacts.

1 Metal	2 v_b[a] (V)	3 $E_S - E_V$[a] (V)	4 φ_{pc} (eV)	5 φ_{pph}[a] (eV)	6 $\varphi^*_{SD} = E_G - \varphi_{SD}$ (eV)	7 v^*_q (V)	8 $-v^*_0$ (V)	9 E_T (eV)	10 F^*_0 ($\times 10^8$ V/m)	11 $\varphi_p = \varphi_{pc} + ev^*_q$ (eV)
Au	0.34	0.13	0.506	0.46	0.80	0.253	0.046	0.32	0.69	0.759
Al	0.44	0.13	0.606	0.45	1.30	0.573	0.121	0.60	1.80	1.179
	0.47	0.13	0.636	0.44	1.30	0.547	0.114	0.59	1.70	1.183
	0.52	0.13	0.686	0.54	1.30	0.513	0.105	0.51	1.57	1.199
	0.50	0.13	0.666	0.52	1.30	0.530	0.110	0.55	1.63	1.195

[a] Reference 9.

ergy barrier in the depletion layer of the semiconductor which, alone, may make the contact rectifying also when the metal work function is lower than the semiconductor electron affinity. This happens, for instance, for several metal cadmium sulfide systems.

Furthermore, the quantum space charge affects the contact junction capacitance by changing appreciably its built-in voltage; it produced a strong electric field F_0 at the interface between the two substances directed (save for high-work-function metals) towards the semiconductor, which, in particular, by rendering the energy barrier of the metal–p-type semiconductor contacts highly transparent, makes their forward and reverse currents "great"; in the M-n contacts the quantum charge, instead, makes the height and the transparency of the energy barrier dependent on the voltage externally applied to the diode.[19] In both cases the high value of F_0 produces a non-negligible contact potential difference v_0 in the metal.

The quantum space charge also makes the photobarrier lower than that deduced from the capacitance measurements and causes the sum of the barrier heights of two contacts built with the same metal and the same semiconductor, but of different type, n and p, of the latter, to differ from the semiconductor energy gap E_G.

Such new conclusions have been obtained by means of the new general expressions of the junction capacitance and of the barrier height deduced in the electric part of the theory. This holds for a nonuniform electric charge; that is, it not only allows one to account for the electrons penetrated in a quantum way into the semiconductor, but may also be applied when the doping is not constant in the semiconductor and/or there is a field-induced space charge and when on the interface between the two materials there are electric charges due to any cause, e.g., to surface states.

The quantum-mechanics part bases itself on the assumption that the bands theory holds for a finite crystal up to the lattice boundary and that the metal free electrons with a transverse energy greater than an appropriate value E_T do not penetrate to any appreciable extent into the semiconductor. It has been developed by means of the effective-mass theory and of the WKB method in the case of nondegenerate and nonwarped bands having edges at the central point of the Brillouin reduced zone. The theory may be extended to the case of degenerate bands having extrema outside the central point of the reduced zone and/or to the case in which the contact surface between the two substances is not perpendicular to a symmetry axis of each crystal. Instead, a general calculation of the electron density by means of a direct solution of the Schödinger equation, which, moreover, takes into account the electron interactions with each other, appears to be an extremely difficult problem.

An important quantum part which remains to be discussed and developed concerns the existence, or not, of a field-induced space charge in the semiconductor boundary regions.

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APPENDIX A

One may give (51) a more general and compact form by using the variables k_j ($j = 1, 2, 3$) and noting that the various quantities of (51) itself derive from the equation

$$E = V(x_1) + E_{kmb}\left[k'_{m1}(x_1),\, k_{m2},\, k_{m3}\right], \tag{A1}$$

solved with respect to $k'_{m1}(x_1)$ by using the McLaurin series expansion (28). If one solves (A1) directly with respect to $k'_{m1}(x_j)$ for given values of x_1, $k_{m2} = k_2$, $k_{m3} = k_3$, and k_1 ($E = \frac{1}{2}\hbar^2 \sum_{j=1}^{3} k_j^2 / m_{MCj}$), one obtains

$$dn_S = \frac{4fk_1 \exp\left[2i\int_0^{x_1} k'_{S1}(x_1)\,dx_1\right] dk_1\,dk_2\,dk_3}{\pi^3 k'_{S1}(x_1)\left[k'_{M1}(0)/k'_{S1}(0) - (m^*_{MC1}/m^*_{Sb1})^2 k'_{S1}(0)/k'_{M1}(0)\right]}\ , \tag{A2}$$

where $m^*_{Sb1} = m^*_{SC1}$ and $m^*_{Sb1} = m^*_{SV1}$ for $E < V(0) + E_B$ and $E > V(0) + E_B$, respectively.

From (A2) it results that, if, for given values of k_2, k_3, E, and x_1, $|k'_{S1}(x_1)|$ is "too great" (Fig. 4), the corresponding value of dn_S is "strongly attenuated," so that its contribution may be neglected. It is on the basis of such considerations that the limitations (31) are assumed.

APPENDIX B

From (8), (51), (54), and (55), by assuming $f = 1$ and $f = 0$ for $E < E_M$ and $E > E_M$, respectively, by putting $V(x) = V_0$, and by integrating with respect to Φ (between 0 and $\frac{1}{2}\pi$) and x_1 (between 0 and ∞), one obtains

$$\gamma_V = \frac{1}{(E_M - V_0)^{1/2}} \iint_Z \frac{(H - V_0)^{1/2}\left[E_V + V_0 + H/u_{VT} - (1 + 1/u_{VT})E\right]^{-1}}{E_V + (1 + u_{V1})V_0 + (1/u_{VT} - u_{V1})H - (1 + 1/u_{VT})E}\, dE\, dH\ , \tag{B1}$$

where

$$u_{bT} = |m^*_{SbT}|/m^*_{MCT}\ , \quad u_{b1} = |m^*_{Sb1}|/m^*_{MC1}\ ; \tag{B2}$$

the integration zone Z of the plane H, E is the one bounded by the line 2, 3, 4, 5, 2 of Fig. 5(a). The calculation of the integral (B1) can be simplified if, by noting that in practice $u_{V1} < 1$ and $1/u_{VT} \gg u_{V1}$, the quantity $u_{V1}(V_0 - H)$ is added to the sum contained between the square brackets of (B1) itself.

If γ'_V denotes the value obtained from (B1) by making the integration on the zone 1, 2, 5, 6, 1 of the plane H, E [Fig. 5(a)], it follows that

$$\gamma_V = \gamma'_V\big|_{E_T=0} - \gamma'_V\big|_{E_T}\ , \tag{B3}$$

where, for $u_{bT} = u_{b1} = u_b$,

$$\gamma'_V = \frac{u_V}{(1 + u_V)(E_M - V_0)^{1/2}} \left[\frac{2}{1 + u_V} \left(\frac{R}{1 - u_V} + \frac{2\sqrt{P}}{u_V}\right) + \frac{u_V\sqrt{N}}{(1 - u_V^2)^{3/2}} \ln \frac{\sqrt{N} - (1 - u_V^2)^{1/2}R}{\sqrt{N} + (1 - u_V^2)^{1/2}R} \right.$$
$$\left. + \frac{\sqrt{P}}{(1 + u_V)^{3/2}} \ln \frac{\left[(1 + u_V)^{1/2}R - \sqrt{P}\right]\left[(1 + u_V)^{1/2} + 1\right]}{\left[(1 + u_V)^{1/2}R + \sqrt{P}\right]\left[(1 + u_V)^{1/2} - 1\right]}\right]\ , \tag{B4}$$

with

$$R = (E_B - E_T)^{1/2}\ , \quad P = E_V - (1 - 1/u_V)E_T\ , \quad N = (1 + u_V)E_B - u_V E_V\ , \quad M = \{u_V[(1 + u_V)E_B - E_V] + E_T(1 - u_V^2)\}^{1/2}\ .$$

In an analogous way one has

$$\delta_V = \delta'_V\big|_{E_T=0} - \delta'_V\big|_{E_T}\ , \tag{B5}$$

$$\delta'_V = \frac{2u_V^{3/2}}{(1 + u_V)(E_M - V_0)} \left[\frac{RM}{(\sqrt{u_V})(1 - u_V^2)} + \frac{(\sqrt{u_V})N}{(1 - u_V^2)^{3/2}} \left(\arctan \frac{M}{(N - M^2)^{1/2}} - \frac{\pi}{2}\right) \right.$$
$$\left. + \frac{P}{(\sqrt{u_V})(1 + u_V)} + \frac{P}{(1 + u_V)^{3/2}} \ln \frac{M + R(u_V + u_V^2)^{1/2}}{(\sqrt{P})\left[u_V + (u_V + u_V^2)^{1/2}\right]}\right]\ , \tag{B6}$$

$$\gamma_C = \gamma'_C\big|_{E_T=0} - \gamma'_C\big|_{E_T}\ , \tag{B7}$$

$$\delta_C = \delta'_C\big|_{E_T=0} - \delta'_C\big|_{E_T}\ , \tag{B8}$$

$$\gamma'_C = \frac{u_C}{(1 - u_C)(E_M - V_0)^{1/2}} \left[\frac{2}{1 - u_C^2}(R_B - R_F) + \frac{u_C}{(1 - u_C^2)^{3/2}} \left(\sqrt{N_F} \ln \frac{\sqrt{N_F} - R_F(1 - u_C^2)^{1/2}}{\sqrt{N_F} + R_F(1 - u_C^2)^{1/2}} \right.\right.$$
$$\left.\left. - (\sqrt{N_B}) \ln \frac{\sqrt{N_B} - R_B(1 - u_C^2)^{1/2}}{\sqrt{N_B} + R_B(1 - u_C^2)^{1/2}}\right) - \frac{S_R}{1 - u_C} \ln \frac{(R_F - S_R)(R_B + S_R)}{(R_F + S_R)(R_B - S_R)}\right]\ , \tag{B9}$$

$$\delta'_C = \frac{2u_C^{3/2}}{(1 - u_C)(E_M - V_0)} \left\{\frac{1}{(\sqrt{u_C})(1 - u_C^2)}(R_B M_B - R_F M_F) + \frac{\sqrt{u_C}}{(1 - u_C^2)^{3/2}} \left[N_F\left(\arctan \frac{M_F}{(N_F - M_F^2)^{1/2}} - \frac{\pi}{2}\right) \right.\right.$$
$$\left.\left. - N_B\left(\arctan \frac{M_B}{(N_B - M_B^2)^{1/2}} - \frac{\pi}{2}\right)\right] - \frac{L}{u_C(1 - u_C)^{3/2}} \left(\arctan \frac{M_F}{(L - M_F^2)^{1/2}} - \arctan \frac{M_B}{(L - M_B^2)^{1/2}}\right)\right\}\ , \tag{B10}$$

$$U_F=E_M-V_0\ ,\quad R_F=(U_F-E_T)^{1/2}\ ,\quad R_B=(E_B-E_T)^{1/2}\ ,\quad N_F=(1-u_C)U_F+u_CE_C\ ,\quad N_B=(1-u_C)E_B+u_CE_C\ ,$$

$$M_F=\{u_C[(u_C-1)U_F+E_C]+E_T(1-u_C^2)\}^{1/2}\ ,\quad M_B=\{u_C[(u_C-1)E_B+E_C]+E_T(1-u_C^2)\}^{1/2}\ ,$$

$$L=E_T(1-u_C)+u_CE_C\ ,\quad S_R=[L/u_C(1-u_C)]^{1/2}\ .$$

The preceding relationships hold for $E_B+V_0\le E_M\le E_C+V_0$. If $E_V+V_0<E_M<E_B+V_0$, it follows that $\delta_C=0$ and $\gamma_C=0$, whereas δ'_V and γ'_V must be calculated by replacing E_B with $U_F=E_M-V_0$.

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