

Metallic Interfaces. II. Influence of the Exchange-Correlation and Lattice Potentials

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An electron-gas model of a metallic interface is constructed by joining two semi-infinite half-planes of unequal positive charge and adding electrons until a charge-neutral system is achieved. Our earlier treatment of this model is extended in several directions. The exchange-and-correlation effective one-electron potential, formerly taken in the "dipole approximation" to equal its bulk value in each material, is calculated using the local-density approximation. In the case where the low-density material has the smaller separation energy, the size of its depletion region and the height of the barrier potential are increased. In the case where the low-density material has the larger separation energy, the use of the local-density exchange-and-correlation potential scarcely alters the results obtained using the dipole approximation. A modified self-consistent free-electron model of a metal-intrinsic semiconductor junction adequately accounts for several features of the experimental data concerning the dependence of the barrier height on the components and method of fabrication of the junction. A primary effect of energy gaps associated with the periodic potential is the introduction of a long-range contribution to the junction potential in the semiconductor. An examination of (solvable) one-dimensional models suggests that if the semiconductor energy gaps are small relative to the metal bandwidth, then the modified free-electron model correctly describes the modification of the short-range ($\sim 1-5 \text{ \AA}$) dipole layers at the metal-semiconductor interface. In this case the modified free-electron model adequately determines the barrier height at the interface, although it never describes the details of the space-charge potential in the semiconductor.

I. INTRODUCTION

In a previous paper¹ (I), a self-consistent-field model of a bimetallic junction was constructed by joining two semi-infinite half-planes of unequal positive charge and adding electrons until a charge neutral system is achieved. We investigated the role of the surface dipole layer in equalizing the Fermi levels of the high- and low-density metals and in determining the barrier between them. A highly simplified model containing no adjustable parameters was used in which (i) the exchange and correlation energy in each metal was taken equal to its bulk value as calculated from the Wigner interpolation formula²; (ii) the periodic lattice potential was totally neglected (i.e., a jellium model was used which cannot be applied directly to describe metal-semiconductor contacts). In this paper, these restrictions are removed.

The new features of the present work are best described by reviewing the historical development of our understanding of metal-semiconductor junctions. In an early theory,³ Mott and Gurney postulated that the voltage drop necessary to equalize the Fermi energies of the two materials took place entirely in the semiconductor and was equal in magnitude to the contact potential between the materials. The barrier height φ_b therefore is given by

$$\varphi_b = \varphi_m - \chi_b + E_F, \quad (1.1)$$

in which E_F is the Fermi energy measured relative to the conduction band edge, φ_m is the metal's work function, and χ_b is the semiconductor's electron

affinity. Experimental determination of metal-semiconductor barrier heights⁴⁻¹² indicate that Eq. (1.1) is satisfied only for wide-band gap semiconductors. Two simple origins of the failure of (1.1) suggest themselves. First, as emphasized by Fan,¹³ the total contact potential voltage drop is divided between the dipole layers of the metal and the semiconductor. Equation (1.1) describes the case in which all of this voltage drop occurs across the semiconductor. Of more significance, however, is the modification of the surface dipole layer at the metal-semiconductor interface, relative to the dipole layers at the metal-vacuum and semiconductor-vacuum interfaces. Equation (1.1) involves the work function and electron affinity as obtained from measurements of metal-vacuum and semiconductor-vacuum interfaces, respectively. As Bardeen and Wigner¹⁴ have emphasized, these quantities consist of at least two contributions, that of the (bulk) separation energy and that of the Coulomb (dipole) surface potential. The

⁴ See, e.g., A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland Publishing Company, Amsterdam, 1965).

⁵ V. Heine, *Phys. Rev.* **138**, A1689 (1965).

⁶ C. R. Crowell, S. M. Sze, and W. G. Spitzer, *Appl. Phys. Letters* **4**, 91 (1964).

⁷ R. J. Archer and M. M. Atalla, *Ann. N. Y. Acad. Sci.* **101**, 697 (1963).

⁸ C. R. Crowell, W. G. Spitzer, L. E. Howarth, and E. E. La Bate, *Phys. Rev.* **127**, 2006 (1962).

⁹ C. A. Mead and W. G. Spitzer, *Phys. Rev.* **134**, A713 (1964); *Phys. Rev. Letters* **10**, 471 (1963).

¹⁰ W. G. Spitzer and C. A. Mead, *J. Appl. Phys.* **34**, 3061 (1963).

¹¹ D. V. Geppert, A. M. Cowley, and B. V. Dore, *J. Appl. Phys.* **37**, 2458 (1966); D. Kahng, *Bell System Tech. J.* **43**, 215 (1964); S. M. Sze, C. R. Crowell, and D. Kahng, *J. Appl. Phys.* **35**, 2534 (1964).

¹² F. G. Allen and A. B. Fowler, *J. Phys. Chem. Solids* **3**, 107 (1957); F. G. Allen and G. W. Gobeli, *J. Appl. Phys.* **35**, 597 (1964).

¹³ H. Y. Fan, *Phys. Rev.* **61**, 365 (1942); **62**, 388 (1942).

¹ A. J. Bennett and C. B. Duke, *Phys. Rev.* (to be published).

² E. P. Wigner, *Phys. Rev.* **46**, 1002 (1934).

³ See, e.g., N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1948).

former effect is due to the exchange and correlation potential of the system which in the case of a vacuum interface is responsible for the image force felt by a charged particle far outside the material. The dipole contribution depends on the nature of the interface, and its modification at the metal-semiconductor interface relative to the vacuum interface of the metal and semiconductor can cause the failure of Eq. (1.1).

Several kinds of experimental results suggest the importance of explicitly accounting for modifications in the surface dipole layers of atomic dimensions before using an equation of the form (1.1) to analyze data from which φ_b is to be determined. For example, analysis of data¹¹ used to determine an effective metallic work function φ_m in Eq. (1.1) indicates that for a given metal (e.g., Au) the value of φ_m increases as the band gap of the semiconductor increases (e.g., GaAs, GdSe, and GdS). In our model such a correlation is a consequence of the reduction of the (usually positive¹⁴) dipole contribution to the "effective" metallic work function as the band gap of the semiconductor (and hence the evanescent charge density in the semiconductor) decreases. Another, often quoted,⁵ aspect of the experimental data which suggests the necessity of considering corrections to the surface dipole layers relative to their vacuum counterparts, is the fact, illustrated in Fig. 1, that for a given semiconductor, the Fermi energy lies a distance

$$\xi = E_g - \Phi \quad (1.2)$$

above the top of the valence band, with ξ being essentially independent of the metal used in the contact. In fact, Heine⁵ recently has noted that ξ is constant to within about 0.2 eV independent of (a) the degree of doping^{6,7} which swings the bands in the bulk material by something of the order of 1 eV; (b) the metal that is used,⁸⁻¹¹ some differing from the semiconductor by several volts in the work function; (c) the crystallographic orientation of the surface^{11,12}; (d) whether there is a monolayer or so of oxygen or oxide between the metal and the semiconductor.^{7,11}

Bardeen¹⁵ explained the independence of the barrier potential from the above factors by postulating surface states in the interface. The junctions used in the early

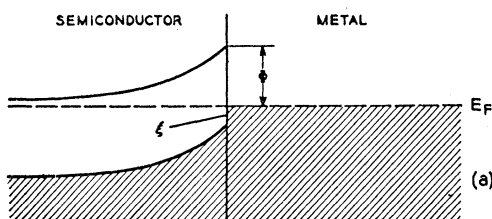


FIG. 1. Definition of Φ and ξ at a metal-semiconductor junction (from Ref. 5).

¹⁴ E. Wigner and J. Bardeen, *Phys. Rev.* **48**, 84 (1935); J. Bardeen, *ibid.* **49**, 653 (1936).

¹⁵ J. Bardeen, *Phys. Rev.* **71**, 717 (1947).

experiments were made by pressing the two materials together and the presence of imperfection-caused surface states was thus quite likely. Later technical developments permitted junction fabrication by cleaving the semiconductor in a metallic atmosphere. The barrier height still exhibited the characteristics listed above. Heine⁵ noted that conventional⁴ surface states were absent in such junctions, and that their analog was localized charge due to evanescent waves in the semiconductor energy gap and below the metal's conduction band. Heine studied these contributions to the charge density by using the nearly-free-electron model.

The present paper and I both indicate that short-range components of the potential barrier at the metal-semiconductor junction are due to the contributions (calculated in a self-consistent manner) of all the mobile electrons in both materials. The potential in the junction region is caused by and causes charge deviations in a self-consistent fashion. Therefore, we have completed Heine's shift in emphasis from surface to bulk properties of the junction components as the determining factors of the junction potential for intimate contacts. Our analysis demonstrates that a self-consistent dynamical treatment of Coulomb, exchange, and correlation energies of the mobile electrons suffices to describe the (equilibrium) one-electron potential near the contact. The introduction of surface states and other specifically surface properties is not required.

We recall that the analysis described in I exhibited two major limitations. The local changes near the interface in the exchange-correlation contributions to the dipole potential were neglected and no discussion was given of the effects of the periodic lattice potential. The numerical example considered in most detail in I, a free-electron gas of density 10^{22} cm⁻³ joined to a free-electron gas of density 10^{21} cm⁻³, is studied again, but with the exchange and correlation potential taken to be a function of the local electron density.¹⁶ There are no qualitative changes in the results of I. Among these results are the absence of *bona fide* surface states, the four-region nature of the net charge distribution near the junction, and the absence of any general relationship between the barrier height and the work functions of the two materials.

Even a free-electron model of a metal-semiconductor junction differs in a qualitative way from the numerical example considered in I. For electron gases of density less than or equal to 10^{22} cm⁻³, the magnitude of the electron separation energy is a monotonically increasing function of density. Hence, the surface dipole potential in the 10^{22} - 10^{21} cm⁻³ junction raises the potential in the high-density material with respect to that in the low-density material. The free-electron analog of most semiconductor metal junctions is one in which the

¹⁶ P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965); **145**, 561 (1966).

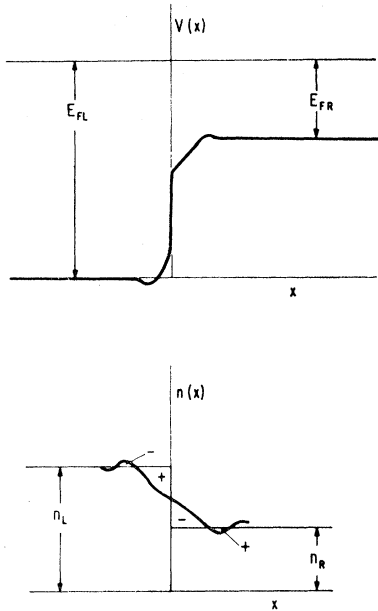


FIG. 2. The potential energy and charge density near the interface of a material of higher density (lower separation energy) with a material of lower density (higher separation energy).

higher-density material (the semiconductor) has a smaller separation energy than the lower-density material (the metal). (This situation corresponds¹ to homogeneous electron gases of density greater than 10^{22} cm^{-3} .) Therefore, the direction of the surface dipole potential needed to equalize the Fermi levels is in a direction opposite to that obtained for the 10^{21} – 10^{22} cm^{-3} junction. The general character of the potential in the junction region is shown in Fig. 2, together with a charge density of the type needed to account for the potential. The self-consistent calculation indicates that the four-region nature of the model charge density used in the previous calculation is no longer essential to a description of the interface potential. In particular, the charge in the two outer regions which was of prime importance in I is no longer required.

Before considering the effects of the crystal potential, we should emphasize that the above free-electron model with the addition of experimental values for the cohesive energy of the semiconductor is adequate to explain those features of the existing experimental data on the properties of metal-semiconductor junctions listed above. In the present model the equilibrium characteristics of the junction are determined by bulk properties of the materials rather than those connected with the surface, e.g., bulk separation energies rather than experimental work functions. Therefore its predictions are unaffected by the surface changes (c) and (d). Since the separation energies of typical metals which enter our calculation vary in general by less than 0.2 eV, the lack of dependence on the particular metal (b) is satisfied. Since the density of impurities added is

much less than the normal density, in our free-electron model, doping has little effect on the position of the Fermi level and separation energy. Therefore in this model the junction characteristics are essentially unaffected by dopants (a). Experimentally, however, the widths of the junction-potential barrier in the semiconductor are well known to be sensitive functions of the doping.⁴ Therefore, when commenting on the invariance of ξ to doping, we must examine the influence of band-structure effects on the junction potential.

As electrons are added to a semiconductor by doping, the band structure energies remain relatively rigid with respect to the vacuum energy. Because of the energy gap, a small number of donor electrons raises the Fermi energy substantially and thus lowers the semiconductor's one-electron separation energy. The dipole potential across the junction which is equal to the difference in the semiconductor's and metal's separation energies is increased and greater band bending occurs. This band bending leads to a region of uncompensated donors near the semiconductor surface which are customarily (Schottky model) taken to cause the additional voltage drop required by the lowering of the semiconductor's separation energy to occur in the semiconductor. ξ remains constant. While we do not further discuss extrinsic semiconductors in this paper, these remarks indicate that the experimental data concerning them are not inconsistent with our results for metal-intrinsic semiconductor junctions.

Although we expect a modified free-electron model to account for many aspects of the data, it is necessary to consider the effects of the periodic lattice. In order to treat those effects, we consider the various approximations required to obtain a tractable analog of the jellium model. The restrictions necessary are so severe that only qualitative results can be obtained. The weaknesses of the model preclude any numerical computations. A particular band structure in which the "semiconductor" has a gap in its energy spectrum for the crystal momentum in the junction direction and is free-electron-like parallel to the junction is introduced in order to illustrate certain general features of the metal-semiconductor contact.

The primary effect of the band structure is the introduction of energy gaps with associated evanescent contributions to the charge density of the semiconductor of range $\sim (2\mu E_g/\hbar^2)^{-1}$, where μ is the reduced mass of the two bands separated by a vertical energy gap E_g . This contribution to the charge density is often small because it is de-emphasized by phase-space weighting factors. In I, where free-electron band structures were assumed for both materials of the junction, the three-dimensional nature of the physical problem was reflected in the one-dimensional integral expression for the density by a factor $(E_F - E_x)$. Here E_x is the electron energy associated with motion perpendicular to the interface, and $(E_F - E_x)$ is an effective two-dimensional

density of states for motion parallel to the interface. This phase-space factor de-emphasizes the contributions of states near the Fermi energy which often are those most affected by the semiconductor band structure. Although the evanescent wave functions in the energy gap may make a long-range contribution to the charge density in the semiconductor, the barrier height at the interface is relatively insensitive to the presence of small band gaps in the semiconductor.

In the next section, we recall some of the formulas of I, investigate the effect of including a density-dependent exchange and correlation potential in the numerical example of I, and present a free-electron-model calculation of the characteristics of a metal-semiconductor interface. Section III contains an examination of the effects of the crystal lattice on the charge density near the junction, and a summary of our results.

II. FREE-ELECTRON MODEL

A. Summary of Formulas

Let us first review the procedure used in I to obtain a self-consistent solution for the junction potential. The junction is constructed by joining two semi-infinite half-planes of unequal positive charge and adding electrons until a charge neutral system is obtained. The self-consistent procedure for determining the junction potential in the dipole approximation consists of the following sequence of operations:

(1) The bulk values of the exchange and correlation potential $V_{ec}(x)$ in each metal are added to an assumed dipole starting potential $V_d(x)$. $V_{ec}(x)$ is calculated using the Wigner interpolation formula and the bulk electron density in Eq. (2.13) to follow. The dipole starting potential is taken to be

$$V_d(x) = \frac{-rV_d e^{h_L x}}{1+r} \theta(-x) - V_d \left[1 - \frac{e^{-h_R x}}{1+r} \right] \theta(x), \quad (2.1a)$$

$$V_d = S_{nR} - S_{nL}, \quad (2.1b)$$

$$r = h_R/h_L, \quad (2.1c)$$

where h_R and h_L are the Thomas-Fermi decay lengths, and S_{nR} and S_{nL} are the bulk-separation energies in each material.

(2) The one-electron potential

$$V(x) = V_d(x) + V_{ec}(x)$$

is used in the Schrödinger equation in order to find the one-electron wave functions by solving the equations

$$[\epsilon_1(p_x) + V(x) - E_x] \Psi_{E_x}(x) = 0, \quad (2.2a)$$

$$\epsilon_1(p_x) = p_x^2/2m_1 = -(\hbar^2/2m_1) d^2/dx^2, \quad (2.2b)$$

$$V(x) = V_d(x) + V_{ec}(x), \quad (2.3)$$

$$\Psi(\mathbf{r}) = \exp(i\mathbf{k}_{11} \cdot \boldsymbol{\rho}) \Psi_{E_x}(x)/2\pi, \quad (2.4)$$

$$E = \hbar^2 k_{11}^2/2m_{11} + E_x. \quad (2.5)$$

(3) The electron density (obtained by filling all states of the system up to the Fermi energy at zero temperature) is calculated from

$$n(x) = n_c(x) + n_{ss}(x), \quad (2.6)$$

$$n_c(x) = \frac{(2s+1) m_{11}}{2\pi \hbar^2} \sum_i \int_0^\mu |\Psi_{E_x^{(i)}}(x)|^2 \times (\mu - E_x) dE_x, \quad (2.7)$$

$$E_x = \hbar^2 k_x^2/2m_1, \quad (2.8)$$

$$n_{ss}(x) = \frac{(2s+1) m_{11}}{2\pi \hbar^2} \sum_b (\mu + E_b) |\Psi_{E_b}(x)|^2, \quad (2.9)$$

where $n_c(x)$ and $n_{ss}(x)$ are the densities due to continuum states and surface states, respectively. Continuum normalization is used for the unbound wave functions.

(4) A model charge density $n_m(x)$ is fitted to the calculated charge density subject to the subsidiary requirements of obtaining both over-all charge neutrality and the proper voltage drop across the junction. The model charge density

$$\begin{aligned} n_m(x) &\equiv n_p(x) - n_e(x) \\ &= -n_{L2}, \quad -x_{L2} \leq x \leq -x_{L1} \\ &= n_{L1}(1+x/x_{L1}), \quad -x_{L1} \leq x \leq 0 \\ &= -n_{R1}(1-x/x_{R1}), \quad 0 \leq x \leq x_{R1} \\ &= n_{R2}, \quad x_{R1} \leq x \leq x_{R2} \\ &= 0, \quad \text{otherwise} \end{aligned} \quad (2.10)$$

contains eight parameters of which only six are independent because of the two subsidiary requirements. These six parameters are determined according to some well-defined "fitting" procedure, one of which is described in I.

(5) The dipole potential (given in I) obtained by inserting the model charge density into Poisson's equation [Eq. (2.1) of I] is employed in step (1) and the five steps are repeated until convergence is obtained.

The modifications of this procedure introduced in subsequent sections consist of more refined calculations of $V_{ec}(x)$ for use in step two. Although we estimate the effects of a periodic potential in Sec. III, complete self-consistent-field calculations are performed only for free-electron-like one-electron dispersion relations $\epsilon(p) = p^2/2m$ in Eq. (2.2).

B. Effect of the Density-Dependent Exchange and Correlation Potential

In I, a major approximation in the self-consistent calculation of the electron density in the vicinity of the barrier was the use of the bulk values of the electron density in calculating the exchange and correlation potential in each metal. We now consider the effects of the varying electron density on the exchange-correlation potential and hence on the self-consistent electron density and junction potential.

The Hartree-Fock equation contains a term due to the correlation in electron position caused by the Pauli principle which keeps electrons of parallel spin apart. Slater¹⁷ rewrote that term in the form

$$-\sum_{k=1}^n \left[\frac{U_i^*(\mathbf{x}_1) U_k^*(\mathbf{x}_2) U_k(\mathbf{x}_1) U_i(\mathbf{x}_2) (e^2/4\pi\epsilon_0 r_{12})}{U_i^*(\mathbf{x}_1) U_i(\mathbf{x}_1)} d^3x_2 \right] \times U_i(\mathbf{x}_1). \quad (2.11)$$

It is apparent from (2.11) that there is a different effective exchange potential for each eigenfunction U_i of the system, i.e., the potential is both momentum- and energy-dependent. After arguing that the potential in fact depends rather weakly on those quantities, Slater substituted a weighted average of the potential over all occupied electron states of the system. A further approximation (the "statistical" one) consisted of using the average potential as function of local electron density as calculated from the eigenstates of a free-electron system. The exchange potential in that approximation is given by

$$V_{ec}(\mathbf{r}) = -3 \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{3}{8\pi} n_e(\mathbf{r}) \right)^{1/3}, \quad (2.12)$$

where $n_e(\mathbf{r})$ is the local density of electrons. The validity of the statistical approximation has been examined by various authors. Juretschke¹⁸ considered an electron gas bounded by an infinitely high barrier. He found that the statistical approximation agreed reasonably well with the averaged potential calculation using the proper wave functions, in regions of high density but rather poorly in regions of low-electron density near the barrier. Other authors¹⁹ have investigated the non-negligible effect of correlation corrections (the correlation between electrons of antiparallel spin) on Slater's work.

More recently, Hohenberg and Kohn,¹⁶ and Kohn and Sham,¹⁶ have developed a generalized treatment of the inhomogeneous electron gas in terms of the properties of a uniform electron gas. A term in the potential, analogous to the Slater potential, was found which systematically includes not only exchange but also correlation effects. Their lowest-order expression for the exchange and correlation potential is

$$V_{ec} = \partial[n\epsilon_{ec}(n)]/\partial n, \quad (2.13)$$

where $\epsilon_{ec}(n)$ is the exchange and correlation energy per electron of a uniform electron gas of density n . Besides including correlation effects not present in Slater's work, their expression contains an exchange term which for the case of a free-electron gas differs by a factor of $\frac{2}{3}$ from that of Slater. This approximation is asserted to

give the exact result for systems of slowly varying density or very high density, i.e., when

$$r_s/r_0 \ll 1 \quad \text{or} \quad r_s/a_B \ll 1, \quad (2.14)$$

respectively. Here r_0 is a typical length over which changes in the density occur. Unfortunately, neither of these conditions is satisfied in the junction region. Higher-order corrections expressed in terms of gradients of the electron density may become important.

Since the coefficients of the various higher-order terms depend critically¹⁶ on refinements in the theory of the polarizability of the homogeneous electron gas, we have performed the self-consistent calculation using only the lowest-order expression. The exchange and correlation potential as given by the Wigner interpolation scheme is evaluated as a function of local electron density. We follow in detail the procedures used in I for the performance of step (4), in which the calculated electron density is represented by a model charge density by means of which total charge neutrality and the proper voltage drop across the junction is insured at each stage of the calculation. In order to achieve a "sensible" self-consistent procedure, this same model charge density is used in calculating the density-dependent exchange and correlation potential.

The particular numerical example used in I, an electron gas of density 10^{22} cm^{-3} next to an electron gas of density 10^{21} cm^{-3} , is again considered. The zeroth-

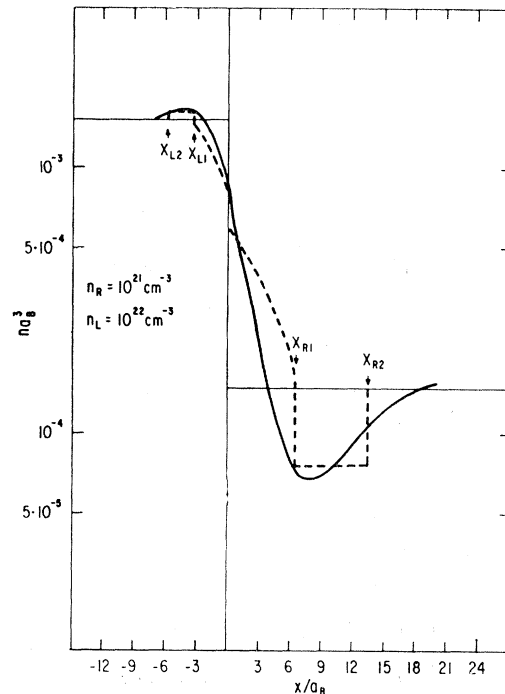


FIG. 3. The actual electron density and model electron density in the neighborhood of a bimetallic junction (10^{22} cm^{-3} - 10^{21} cm^{-3}) as calculated in the first iteration using a density-dependent exchange and correlation potential calculated from the model charge density of Fig. 5 of I.

¹⁷ J. C. Slater, Phys. Rev. **81**, 385 (1951).

¹⁸ H. J. Juretschke, Phys. Rev. **92**, 1140 (1953).

¹⁹ T. L. Loucks and P. H. Cutler, J. Phys. Chem. Solids **25**, 105 (1964); J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters **9**, 215 (1962).

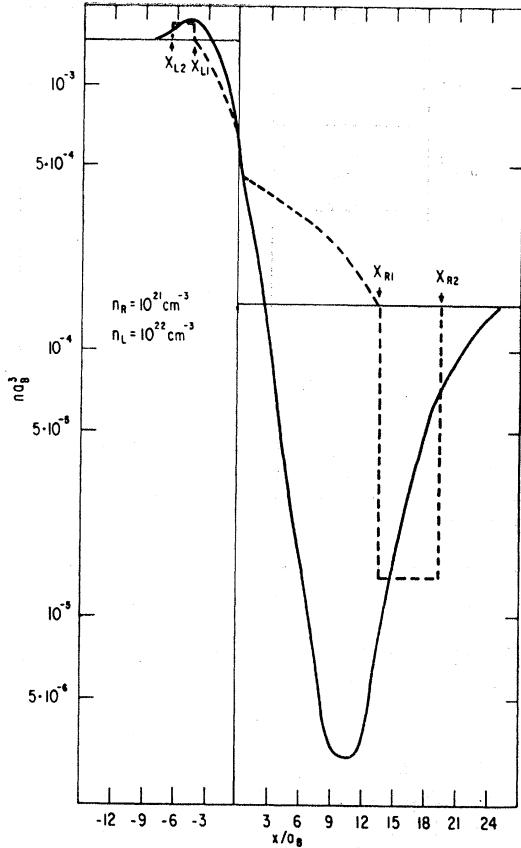


FIG. 4. The actual electron density and model electron density in the neighborhood of a bimetallic junction (10^{22} cm^{-3} – 10^{21} cm^{-3}) as calculated in the third iteration using a density-dependent exchange and correlation potential calculated from the model charge density of the second iteration.

order charge density used in the first iteration is taken from Fig. 5 of I. The results for the density in the first and third steps of the iteration are shown in Figs. 3 and 4. The potential $V(x)$ used in those calculations is shown in Fig. 5. Only rough self-consistency is achieved in which the model charge density and the calculated charge density remains somewhat the same in the last two steps of the iteration. Furthermore, the model charge density is not a good representation of the calculated density. It is appropriate to recall that the results of the self-consistent-field calculation depend on the details of step (4) of the self-consistency procedure in which the six independent parameters of the model charge density are determined from the numerically evaluated density resulting from Eqs. (2.6), (2.7), and (2.9). A thorough analysis at this step of the calculation requires use of a chi-squared (χ^2) determination of local minima in a six-dimensional parameter space. The simple procedure outlined in I is one of several which we tried in order to circumvent the use of the more lengthy χ^2 analysis. Therefore the agreement between the model and numerical charge densities probably could be improved considerably by the introduction of a

more refined determination of the parameters in $n_m(x)$. However, as each numerical calculation of the electron density requires three hours of (GE 235) computer time, the performance of a more complete χ^2 analysis is not practical using our present machine programs and computer.

The results shown in Figs. 3, 4, and 5 must be compared with Figs. 7, 8, and 10 of I, respectively, where the exchange and correlation potential was taken equal to its bulk value in each material. The general effect of the spatial dependence of the exchange-correlation potential is an increase in the size of the depletion region in the low-density material. The height of the potential barrier between the two materials is also increased. The four-region nature of the electron density in the junction region, emphasized in I, is, however, maintained as is the failure of any simple relation between the barrier height and the work function of the two materials.

In order to consider the effect of our use of the model charge density to calculate V_{ec} rather than the actual density, we exhibit Fig. 6, which shows the charge density calculated from V_{ec} using the model density and actual density of Fig. 8 of I, respectively. The calculated densities are rather similar. We expect that the errors

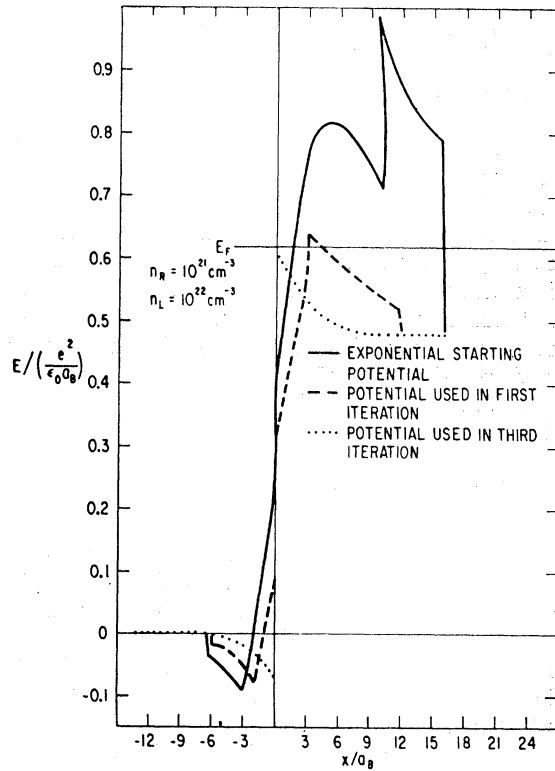


FIG. 5. The starting potential and potentials used to calculate the electron density in the first and third iterations (Figs. 3 and 4). In order to achieve a systematic self-consistent scheme, the density-dependent exchange and correlation potential was calculated from the same model charge density used in calculating the Coulomb dipole potential.

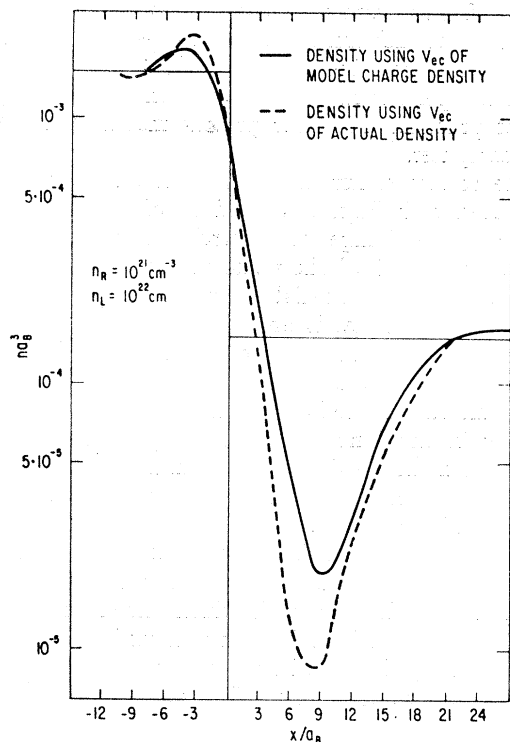


FIG. 6. A comparison of the electron density in the neighborhood of a bimetallic junction (10^{22} cm^{-3} – 10^{21} cm^{-3}) as calculated using exchange and correlation potentials derived from the model density and actual density of Fig. 8 of I.

introduced by ignoring density-gradient terms in the Hohenberg-Kohn-Sham theory are of the same order of magnitude as our choice of the model potential. Due to its discontinuities in the density, the model density is, of course, unsuitable for higher-order calculations.

Juretschke¹⁸ has shown that the statistical approximation tends to overestimate the effects of the varying density on the exchange and correlation potential. Therefore, the use of higher-order corrections is expected to decrease the size of the calculated depletion region.

C. Free-Electron Model of a Metal-Semiconductor Interface

We now consider the free-electron prototype of the metal-semiconductor junction in which the higher-density material (the semiconductor) has a smaller separation energy than the lower density material (the metal). The experimentally observed band bending indicates that this situation exists in most metal-semiconductor contacts. The dipole potential needed to equalize the Fermi levels in this case is in a direction (rising from the higher to the lower density material) opposite to that in the previous calculation.

The numerical example used to simulate the metal-semiconductor interface is the case of an electron gas of density $5 \times 10^{22} \text{ cm}^{-3}$ next to one of density 10^{22} cm^{-3} .

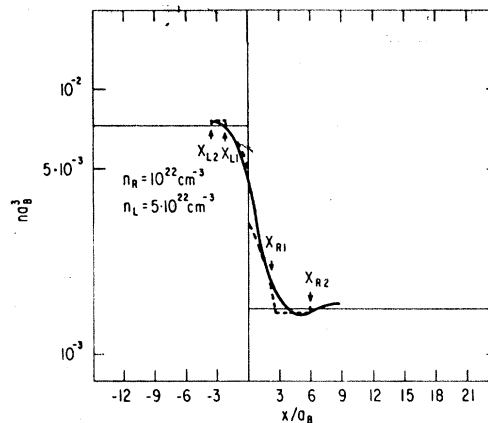


FIG. 7. The actual electron density and model electron density in the neighborhood of a bimetallic junction ($5 \times 10^{22} \text{ cm}^{-3}$ – 10^{22} cm^{-3}) as calculated from the starting potential used in the iteration procedure.

The separation energy as calculated from the Wigner interpolation formula is smaller for the high-density material than for the low-density material. The self-consistent procedure described above is followed again. Two calculations are performed, the first using the bulk values of V_{ec} in each material and the second using the density-dependent potential. The first step in each of these iterations consists of calculating the density using the bulk V_{ec} and a starting dipole potential of the form of Eq. (2.1). The resulting charge density (Fig. 7) is then fitted with a model charge density. The first iteration is performed with and without a density-dependent V_{ec} . The results of the two calculations are shown in Figs. 8 and 9; the total potentials used in Fig. 10. We see that reasonable self-consistency is obtained with one iteration in both cases. The effects of the density-dependent exchange and correlation potential appear to be small. The four-region model of the charge density in the junction

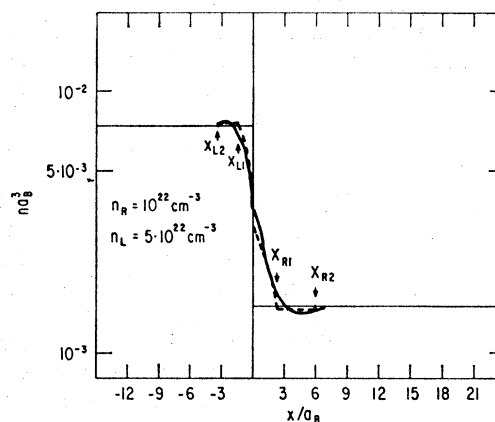


FIG. 8. The actual electron density and model electron density in the neighborhood of a bimetallic junction ($5 \times 10^{22} \text{ cm}^{-3}$ – 10^{22} cm^{-3}) as calculated in the first iteration using the bulk values of exchange and correlation potential.

region is unnecessarily complicated. The two outer regions are much smaller than the two inner regions and can probably be ignored. There is only a very small dip in the potential in the high-density material and as a result no surface states are bound in the junction region.

The free-electron model of a metal-semiconductor interface suffers from two obvious inadequacies: The separation energies in the semiconductor are not adequately approximated by the free-electron model and the periodic potential in the semiconductor severely modifies the one-electron eigenvalue spectrum $\epsilon_1(\mathbf{p})$ in Eq. (2.2a). Both of these inadequacies are associated with the accumulation of electronic charge along lines connecting the atoms in the semiconductor²⁰; a phenomenon which is often discussed in terms of chemical bonding. Nearly-free-electron models can describe this charge accumulation only by introducing a large number of terms in the lattice pseudopotential.²¹ It is evident that a jellium model never adequately describes such a charge density. The change in the separation energy due to the charge accumulation can be simulated in a jellium model by use of a phenomenological $\epsilon_{ec}(n)$ relation in Eq. (2.13). We show in Sec. III that the free-electron charge density is insensitive to the insertion of small energy gaps in $\epsilon(\mathbf{p})$ near the Fermi energy. However, such energy gaps result from a weak pseudopotential which does not suffice to create the known charge accumulation in the bulk semiconductor. Therefore, we conclude that a jellium model cannot provide a quantitative description of a metal-semiconductor contact. Its adequacy for a description of the qualitative features of these contacts rests upon the (hypothetical) insensitivity of the details of the junction potential to the directional properties of the charge density in the bulk semiconductor.

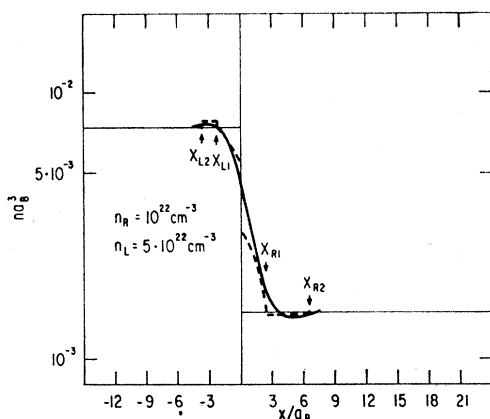


FIG. 9. The actual electron density and model electron density in the neighborhood of a bimetallic junction ($5 \times 10^{22} \text{ cm}^{-3}$ – 10^{22} cm^{-3}) as calculated in the first iteration using the exchange and correlation potential calculated from the model density of Fig. 7

²⁰ See, e.g., L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

²¹ W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

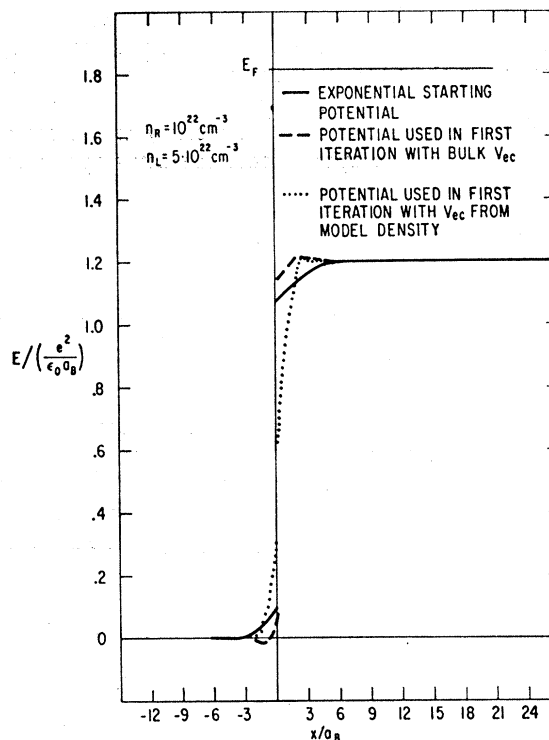


FIG. 10. The starting potential and the potentials used to calculate the electron density in Figs. 7–9. In order to achieve a systematic self-consistent scheme, the same model potential used to calculate the dipole potential was used to calculate the density-dependent exchange and correlation potential.

III. EFFECTS OF THE CRYSTAL LATTICE

A. Total Potential in the Junction Region: Application of the Effective Mass Approximation

In order to consider the influence of the lattice potential on the above calculations, we first investigate those approximations required to obtain a tractable model of a semiconductor analogous to the jellium model used in I and above for metals. The total potential seen by the mobile electrons in the semiconductor near the junction is a complicated functional of the one-electron eigenfunctions of the system. In a bulk system, the cancellation effects discussed by a variety of authors²¹ make possible the substitution of an array of pseudoatoms for the actual atoms of the lattice. The weak pseudopotentials associated with these pseudoatoms serve as a small perturbation on the free-electron system.

The pseudopotential form factor representing the potential due to a pseudoatom consists of various contributions some of which may change significantly in the junction region. The valence-charge potential arising from the net valence charge on the ion, and the core potential arising from the remainder of the nuclear charge and core electrons are unaffected by the local electron configuration. Other contributions such as the

effect of the orthogonalization hole (the absence of conduction electrons in the core region) can probably be computed in terms of the local electron density. Still other contributions²¹ depend essentially on the electronic wave functions in the vicinity of the atom.

For simplicity we approximate the actual potential by writing it as

$$V_T(\mathbf{r}, E) = V_{p, \text{bulk}}(\mathbf{r}, E) + V_{ec}(\mathbf{r}) + V_d(\mathbf{r}), \quad (3.1)$$

where $V_{p, \text{bulk}}(\mathbf{r}, E)$ is the bulk periodic pseudopotential, $V_{ec}(\mathbf{r})$ is the exchange and correlation potential due to inhomogeneous electron-density effects, and $V_d(\mathbf{r})$ is the Coulomb dipole potential. The last two terms are the analog of the conventional band-bending potential. The validity of a band-bending model of the junction rests on the validity of Eq. (3.1). The justification for such a model usually relies on arguments to the effect that in a material with a large dielectric constant, the last two terms in (3.1) are slowly varying on the distance scale of a single unit cell.

We first ignore the band-bending term and comment on the difficulties inherent in matching the wave function in each of the two materials at the junction. A single Bloch wave in one material must be joined at the junction to an infinite series of Bloch waves in the second material each of which has the same energy,²² i.e.,

$$\psi_E(\mathbf{r}) = \sum_{k_x k_{11}} a_{k_x k_{11}} \psi_{E k_x k_{11}}(\mathbf{r}). \quad (3.2a)$$

For a fixed value of k_{11} in the reduced zone, there are an infinite number of wave functions in the various bands which must be included in the above sum.

In order to obtain a tractable model, we further approximate the Bloch function in each material by a separable form

$$\psi_{k_x k_{11}}(\mathbf{r}) = \psi_{k_{11}}(\mathbf{g}) \psi_{k_x}(x), \quad (3.2b)$$

where \mathbf{g} is a coordinate vector parallel to the junction.

For a wave function with given values of E and k_{11} in the first material there are now at most two terms (values of $\pm k_x$) in the sum of Bloch's waves of the second material which join it at the junction. Unfortunately, the only model in which a separable ψ is rigorously realized is one in which the potential in directions parallel to the boundary is uniform and periodic variations are confined to the direction normal to the junction.

If we now include the band-bending term in the potential, an exact treatment of even the separable model involves a linear superposition of many Bloch waves. The effective-mass approximation^{23,24} (EMA) is a means of avoiding some of the complications of such an exact treatment. When a slowly varying potential

$V(\mathbf{r})$ is imposed on a periodic lattice potential $V_p(\mathbf{r})$, the wave functions within a band (n) are given in the EMA by

$$\psi_{En}(\mathbf{r}) = \sum_{\mathbf{k}} f_{nE}(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r}), \quad (3.3)$$

$$f_{nE}(\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \int e^{i\mathbf{k}\cdot\mathbf{r}} f_{nE}(\mathbf{r}) d^3\mathbf{r}, \quad (3.4)$$

$$[\epsilon_n(-i\nabla) + V(\mathbf{r})] f_{nE}(\mathbf{r}) = E f_{nE}(\mathbf{r}). \quad (3.5)$$

Here $\epsilon_n(-i\nabla)$ is the bulk one-electron energy due to the periodic potential. The $\psi_{n\mathbf{k}}(\mathbf{r})$ are eigenfunctions of the bulk material and Ω is the volume of the system. Equation (3.5) is the periodic-potential form of Eqs. (2.2) in the free-electron model.

The electron density in the EMA may be obtained from the following considerations. Using Eq. (3.3)

$$\rho_n(\mathbf{r}) = \sum_E |\psi_{En}(\mathbf{r})|^2 = \sum_{\mathbf{k}\mathbf{k}'E} f_{nE}(\mathbf{k}) f_{nE}^*(\mathbf{k}') \times \psi_{n\mathbf{k}}(\mathbf{r}) \psi_{n\mathbf{k}'}^*(\mathbf{r}). \quad (3.6)$$

Near \mathbf{k}' , $\mathbf{k}=0$, we may write

$$\begin{aligned} \rho_n(\mathbf{r}) &\cong |u_{n0}(\mathbf{r})|^2 \sum_{\mathbf{k}\mathbf{k}'E} f_{nE}(\mathbf{k}) f_{nE}^*(\mathbf{k}') e^{i\mathbf{k}\cdot\mathbf{r} - i\mathbf{k}'\cdot\mathbf{r}} \\ &= |u_{n0}(\mathbf{r})|^2 \sum_E |f_{nE}(\mathbf{r})|^2, \end{aligned} \quad (3.7)$$

where the Bloch function $u_{n\mathbf{k}}(\mathbf{r})$ factors out, giving a rapidly oscillating contribution to the density. We define the effective density, to be used in Poisson's equation, to be equal to an average over the unit cell, and therefore

$$\begin{aligned} \rho_n(\mathbf{R}_m) &= \sum_E \int \frac{d^3\mathbf{y}}{B} |\psi_{En}(\mathbf{R}_m + \mathbf{y})|^2 \\ &= \sum_{\mathbf{k}\mathbf{k}'E} f_{nE}(\mathbf{k}) f_{nE}^*(\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_m} \\ &\quad \times \frac{1}{B} \int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{y}} u_{n\mathbf{k}}(\mathbf{y}) u_{n\mathbf{k}'}^*(\mathbf{y}) d^3\mathbf{y}, \end{aligned} \quad (3.8)$$

where B is the volume of the unit cell, $\mathbf{r} = \mathbf{R}_m + \mathbf{y}$, and \mathbf{R}_m is a lattice site.

The integral can be expanded in a series in $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, which for $\mathbf{k} = \mathbf{k}'$ gives unity, so that

$$\begin{aligned} \rho_n(\mathbf{R}_m) &= \sum_{\mathbf{k}\mathbf{k}'E} f_{nE}(\mathbf{k}) f_{nE}^*(\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_m} \left[1 + O\left(\frac{q}{G}\right) \right] \\ &\cong \sum_E |f_{nE}(\mathbf{R}_m)|^2, \end{aligned} \quad (3.9)$$

where G is a reciprocal lattice vector. In averaging over the unit cell, we have averaged out the variation in density associated with the chemical bonding in the semiconductor.²⁰ The electrostatic effects treated here, however, vary with a characteristic distance of several

²² V. Heine, Proc. Phys. Soc. (London) 81, 300 (1963).

²³ J. C. Slater, Phys. Rev. 76, 1592 (1949).

²⁴ D. J. BenDaniel and C. B. Duke, Phys. Rev. 152, 683 (1966).

Bohr radii, which in a semiconductor is much larger than a typical cell dimension. Equation (3.9) is the periodic-potential analog of Eqs. (2.6)–(2.9) in the free-electron model. We already have discussed the physical consequences of the averaging over the single-cell density variations at the end of Sec. II C.

In order to calculate the electron density, we require the wave functions for all values of the energy spectrum of the bulk materials. Only when (i) $\epsilon_n(-i\nabla)$ in both materials can be represented as an expansion about critical points in the energy spectrum, and (ii) continuity of k_{11} is possible for all electron states in the energy band considered, can simple relationships be obtained between the values of f and df/dx in the metal and semiconductor at the interface. Then

$$f^{sc}(x=0) = f^m(x=0), \quad (3.10)$$

$$\frac{1}{m_{sc}} \frac{df^{sc}}{dx}(x=0) = \frac{1}{m_m} \frac{df^m}{dx}(x=0). \quad (3.11)$$

The latter relationship guarantees current conservation.²⁴

From the above discussion we see that practical calculations require a large number of simplifications and approximations, many of which cannot be justified *a priori*. Treatment of the periodic potential in a simple manner requires the approximation of a separable wave function. Consideration of band bending requires the use of the EMA in situations for which it cannot be justified adequately. By using these approximations, Eq. (3.3) may be rewritten as

$$\psi_{En}(\mathbf{r}) = \left[\sum_{k_x} f_{nE}(k_x) \psi_{nk_x}(x) \right] \psi_{nk_{11}}(\phi). \quad (3.12)$$

The variation associated with k_{11} is treated exactly at the interface and the variation associated with k_x is treated within the EMA. We examine this model in the next section in order to estimate the modifications of the predictions of the free-electron model by a lattice potential.

B. Model Metal-Semiconductor Junction

As we previously emphasized, the approximations required to obtain a manageable model of a metal-semiconductor junction are sufficiently severe that such a model cannot be expected to give a quantitative description of the experimental results. However, let us define a given model band structure in order to illustrate certain qualitative conclusions which will be relevant in discussions of actual junctions. The band structure adopted, consistent with the requirements of Sec. III A, is one in which the motion parallel to the interface is that of a free electron and which exhibits an energy gap in its band structure in the direction normal to the plane

of the junction. That is,

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k_{11}^2}{2m_0} + \frac{\hbar^2 k_x^2}{2m_{L1}} \theta(E_0 - E) + \left(E_1 - \frac{\hbar^2 k_x^2}{2m_{L2}} \right) \theta(E - E_0) \\ \times \theta(E_2 - E) + \theta(E - E_2) (E_1 + E_g + \hbar^2 k_x^2 / 2m_{L3}), \quad (3.13)$$

with

$$E_0 = \hbar^2 k_1^2 / 2m_{L1} = E_1 - \hbar^2 k_1^2 / 2m_{L2}, \\ E_2 = E_1 + \hbar^2 q_1^2 / 2m_{L2} = E_1 + E_g - \hbar^2 q_1^2 / 2m_{L3}, \quad (3.14)$$

where m_0 is the free-electron mass, $k_1 = iq_1$, E_1 is the energy at the top of the valence band, and E_g is the size of the energy gap.

Nonlocalized states appear in the energy gap of this model structure because all motion parallel to the plane of the junction is unbounded. Both the spectrum as a function of k^2 and the density of states are shown in Fig. 11. The band gaps of typical semiconductors range from 0.5 to 3.5 eV; their electron affinities χ , the bulk separation energy as measured from the bottom of the conduction band, from 3 to 5 eV; their valence band widths from 5 to 15 eV.^{4,25,26} The parameters of the model may be chosen to simulate actual semiconductors.

Using the model for the semiconductor, the solutions to the Schrödinger equation (2.2a) must be obtained separately for each of the six regions indicated in Fig. 12. We have obtained these solutions and the resulting expressions for the electron density analogous to Eqs. (2.6)–(2.9) in the free-electron model. The length of these formulas, together with the approximate nature of the model, leads us to discuss in the remainder of this

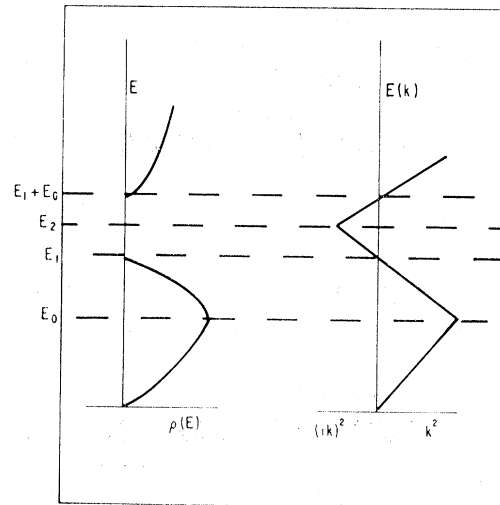


FIG. 11. The density of states and energy spectrum as a function of k^2 for the model of a semiconductor given by Eqs. (3.13) and (3.14).

²⁵ M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

²⁶ R. K. Swank, Phys. Rev. **153**, 844 (1967).

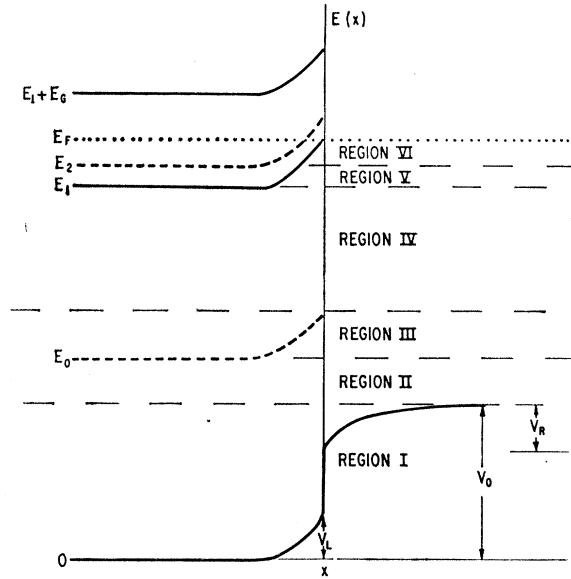


FIG. 12. The energy bands and band-bending potential in the model of the metal-semiconductor junction specified by Eqs. (2.2a), (2.4), (3.13), and (3.14).

section selected aspects of the results rather than giving them in full.

In each of the six regions E_x has a restricted range of variation and the expression for the density is of the form

$$n(x) = \sum_i \int dE_x |\psi_{E_x^i}(x)|^2 W(E_x), \quad (3.15)$$

where the sum over i includes degenerate wave functions, and the weighting factor $W(E_x)$ gives the number of filled states in the energy band associated with k_{11} for a fixed E_x . For the separable model considered, $W(E_x)$ is the same for both materials:

$$W(E_x) = \int_0^{E_F - E_x} \rho_{11}(E) dE, \quad (3.16)$$

in which $\rho_{11}(E)$ is the two-dimensional density of states associated with motion parallel to the junction. Consideration of tight-binding expressions for $\rho_{11}(E)$ indicates that $W(E_x)$ is constant for small values of E_x and tends to zero as $E_x \rightarrow E_F$. In the particular model considered

$$\rho_{11} = m_0/2\pi\hbar^2, \quad (3.17a)$$

$$W(E_x) = (m_0/2\pi\hbar^2)(E_F - E_x). \quad (3.17b)$$

Since states in the energy gap are lightly weighted, their contribution to the charge density responsible for the potential barrier is relatively small. The charge contribution from the gap may be of long range since for narrow band gaps the characteristic decay length q_1^{-1} may be longer than the scale length associated with valence-band contributions. However, the value of the potential at the interface is affected only slightly by the

small amount of charge due to the evanescent states in a small band-gap semiconductor. It is principally determined by the short-range charge deviations due to oscillatory states in the metal and the semiconductor, and evanescent states in the metal. Only as the energy gap of the semiconductor becomes comparable to the metal's conduction-band width does the evanescent component in the semiconductor play an important role in fixing the barrier height of the interface. In this case the states in the semiconductor gap serve as the analog of the vacuum in a metal-vacuum interface, and bring the effective metallic work function closer to its value at a metal-vacuum interface.

The band structure within the valence band is reflected in a new characteristic length for oscillations of the charge variation. We expect that k_1^{-1} serves as a characteristic decay length for the charge oscillations calculated in Sec. II. In addition, the matching of the wave function along the line $E_0(x)$ introduces reflected waves which may lead to charge deviations further from the interface than are present in a totally free-electron model. These reflected waves are, however, artifacts of the particular band structure chosen.

C. Summary

Our main conclusions about metal-semiconductor contacts are: (a) the bulk one-electron separation energies of the composite materials dominate the features of the junction potential; (b) for narrow band gap semiconductors, the nearly-free-electron (NFE) model of the interface, adjusted to give the bulk separation energy in the semiconductor, may provide a semiquantitative description of the junction potential; (c) the main limitation on the applicability of the NFE model to the description of metal-semiconductor contacts lies in its inability to simply describe the "chemical-bonding" charge accumulation in the bulk semiconductor; and (d) to the extent that the NFE model provides a qualitative description of a bimetallic or metal-semiconductor contact, all of the "band-bending" effects associated with the difference in the bulk one-electron separation energies of the composite materials are adequately described by alterations in the "bulk" electronic charge density near the interface. It is not necessary to introduce specifically surface properties like surface states to describe the junction potential.

As Heine⁶ has noted, the evanescent charge contributions due to electron states in the semiconductor and in the metal are the analog of the surface states originally introduced¹⁶ to explain deviations from the Mott-Gurney model. In our model, all the electron states of the system, not just the evanescent ones, are determined by and determine the junction characteristics. Although surface states associated with impurities may exist in some junctions, their introduction in the situations we have considered is both unnecessary and incorrect.