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Surface States and Barrier Height of Metal–Semiconductor Systems*

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The dependence of the barrier height of metal–semiconductor systems upon the metal work function is derived based on the following assumptions: (1) the contact between the metal and the semiconductor has an interfacial layer of the order of atomic dimensions; it is further assumed that this layer is transparent to electrons with energy greater than the potential barrier but can withstand potential across it. (2) The surface state density (per unit area per electron volt) at the interface is a property only of the semiconductor surface and is independent of the metal. The barrier height φ_{Bn} is defined here as the energy needed by an electron at the Fermi level in the metal to enter the conduction band of the semiconductor.

With the above assumptions, the barrier height for n-type semiconductor–metal contacts is found to be a linear combination of the metal work function φ_m and a quantity φ_0 which is defined as the energy below which the surface states must be filled for charge neutrality at the semiconductor surface. The energy φ_0 is measured from the edge of the valence band. For constant surface state density the theoretical expression obtained is

$$\varphi_{Bn}=\gamma(\varphi_m-\chi)+(1-\gamma)(E_g-\varphi_0)-\Delta\varphi_n,$$

where χ and E_g are electron affinity and the band gap of the semiconductor, respectively, $\Delta\varphi_n$ is the image force barrier lowering, and γ is a weighting factor which depends mainly on the surface state density and the thickness of the interfacial layer.

The theoretical expression is compared to the presently available φ_{Bn} vs φ_m data for Si, GaP, GaAs, and CdS, by fitting the data to straight lines using the method of least squares. The best straight-line fit was obtained for the GaP data, with probable error limits on the slope and intercept of ± 0.03 and ± 0.13 eV, respectively.

The parameter γ in the theoretical expression is found to range from 0.07 for GaAs to almost unity for the CdS data reported by Goodman indicating weak and strong dependence of the surface barrier height on the metal work function, respectively.

The value of φ_0 is roughly a third of the respective band gap energies for Si, GaP, and GaAs, and the surface state density for these semiconductors is found to be in the range 10^{13}–10^{14} states/cm^2/eV, for the experiments cited.

Excessive scatter in the data points for the CdS data of Mead and Spitzer casts doubt on the significance of a straight-line fit for this case. The data of Goodman for CdS obey the Schottky theory for a metal–semiconductor barrier, but this agreement requires a value of the electron affinity χ which is different from the vacuum-photothreshold value measured by other authors.

I. INTRODUCTION

IN 1947 Bardeen[1] proposed a theory to explain the rectification characteristic of a metal–semiconductor contact. He showed that if the density of localized surface states having energies distributed in the semiconductor energy gap is sufficiently high, a double layer at the free surface of a semiconductor is formed from a net charge of electrons in surface states and a space charge of opposite sign. He concluded that this double layer will tend to make the work function independent of the height of the Fermi level in the interior of the semiconductor, and the rectification characteristics of a metal–semiconductor contact are then practically independent of the metal. It is well known that such surface states and surface barriers do exist.[2] The surface states can occur either from the termination of the periodic structure of the semiconductor crystal at the surface or from the presence of adsorbed foreign atoms on the surface.

The work of Archer and Atalla[3] on metal contacts on cleaved silicon surfaces seems to indicate that for gold on cleaved silicon, there is good agreement between experiment and the simple theory proposed by Schottky[4] that the barrier height depends only on the work functions of the metal and the semiconductor and is independent of the semiconductor doping. Recently, however, Mead and Spitzer[5] have studied the barrier height of metal–semiconductor systems for 14 elemental

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[1] J. Bardeen, Phys. Rev. **71**, 717 (1947).

[2] R. H. Kingston, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957).

[3] R. J. Archer and M. M. Atalla, Am. Acad. Sci. N. Y. **101**, 697 (1963).

[4] H. K. Henisch, *Rectifying Semiconductor Contacts* (Oxford University Press, New York, 1957), Chap. VII.

[5] C. A. Mead and W. G. Spitzer, Phys. Rev. **134**, A713 (1964).

and III–V semiconductors using cleaved semiconductor surfaces. In all cases, they report that the position of the Fermi level at the surface is essentially independent of the metal work function and is very close to one-third of the band gap from the valence-band edge.

The results of the experiments cited above are evidently quite different; the Schottky model seems to hold for Si–metal systems, but the results for the Mead and Spitzer experiments are in direct conflict with the Schottky theory.

Crowell, Sze, and Spitzer[6] have observed that the temperature dependences of the gold n-type silicon surface barrier height and the silicon energy gap are the same. They also showed that the Fermi level at the metal–semiconductor interface is pinned in relation to the valence-band edge, independent of lattice temperature.

In this paper the dependence of the barrier height on metal work function, surface states, and the thickness of the interfacial layer is derived. An attempt will be made to explain published experimental results in accordance with the derived theoretical expression; additional data on metal-GaP systems are given in Sec. III to confirm the validity of the expression. The temperature dependence of the barrier height is also explained. A discussion of the basic assumptions involved in this treatment is given in Sec. IV.

II. THEORY OF METAL–SEMICONDUCTOR SURFACE BARRIER IN THE PRESENCE OF SURFACE STATES

The energy band diagram of a metal–n-type-semiconductor contact is shown in Fig. 1. The various quantities used in the derivation which follows are defined in this figure. The first quantity which is of interest to us is the energy φ_0; this energy is measured from the valence-band edge at the semiconductor surface and specifies the level below which all surface states must be filled for charge neutrality at the semiconductor surface. The second quantity is φ_{Bn}, the barrier height of the metal–semiconductor contact; φ_{Bn} is the energy needed by an electron at the Fermi level in the metal to enter the conduction band of the semiconductor, and includes the effect of the image force lowering $\Delta\varphi_n$. The interfacial layer will be assumed to have a thickness of a few angstroms and will be assumed transparent to electrons whose energy is greater than the potential barrier.

We first consider a semiconductor with acceptor surface states whose density is D_s states/cm²/eV, and assume, as did Bardeen,[1] that D_s is a constant over the energy range from φ_0 to the Fermi level. The case of a nonuniform density of surface states in the forbidden gap will be considered in Sec. IV.

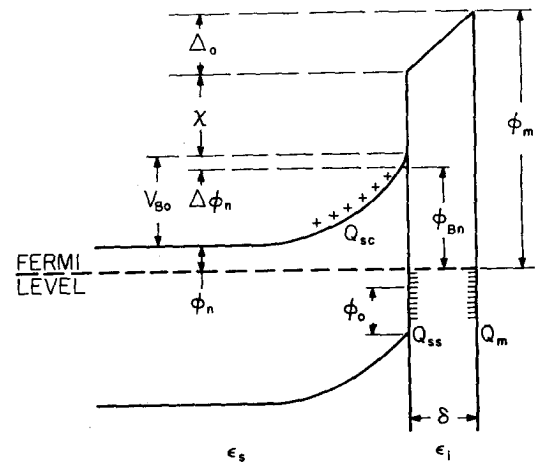

FIG. 1. Energy band diagram of a metal–n-type-semiconductor contact with an interfacial layer. ϕ_m = work function of metal, ϕ_{Bn} = barrier height of metal–semiconductor surface barrier, ϕ_0 = energy level at surface defined in Sec. II, $\Delta\phi_n$ = image force barrier lowering, ϕ_n = energy difference between conduction band and E_F in bulk semiconductor, Δ_0 = potential across interfacial layer, χ = electron affinity of semiconductor, V_{BO} = diffusion potential, ϵ_s = dielectric constant of semiconductor, ϵ_i = dielectric constant of interfacial layer, δ = thickness of interfacial layer, Q_{sc} = space-charge density in semiconductor, Q_{ss} = surface state charge density on semiconductor, and Q_m = surface charge density on metal.

For a uniform distribution the surface state charge density on the semiconductor Q_{ss} is given by

$$Q_{ss} = -eD_s(E_g - \varphi_0 - \varphi_{Bn} - \Delta\varphi_n)\text{C/cm}^2, \qquad (1)$$

where $\Delta\varphi_n$ is the image force barrier lowering[7] and e is the electronic charge. The quantity in parentheses is simply the difference between the Fermi level at the surface and φ_0. D_s times this quantity yields the number of surface states above φ_0 which are full.

The space charge which forms in the depletion layer of the semiconductor can be expressed as an equivalent surface charge density, which is the net charge/cm² looking into the bulk semiconductor from a point just inside the semiconductor surface. The charge is obtained by solving Poisson's equation for the depletion layer of the semiconductor and can be written as

$$Q_{sc} = [2e\epsilon_s N_D(\varphi_{Bn} + \Delta\varphi_n - \varphi_n - kT/e)]^{\frac{1}{2}}\text{C/cm}^2, \quad (2)$$

where N_D is the donor density of the bulk semiconductor. Equation (2) is valid only if there is no inversion layer in the semiconductor; the metal–semiconductor systems considered in this paper all meet this restriction.

The total equivalent surface charge density on the semiconductor surface is given by the sum of Eqs. (1) and (2). In the absence of any space charge effects in the interfacial layer, an exactly equal and opposite charge Q_m develops on the metal surface. For thin interfacial layers, such effects are negligible, and Q_m can

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

[7] S. M. Sze, C. R. Crowell, and D. Kahng, J. Appl. Phys. 35, 2534 (1964).

be written as

$$Q_m = -(Q_{ss}+Q_{sc}) = eD_s(E_g-\varphi_0-\varphi_{Bn}-\Delta\varphi_n) - [2e\epsilon_s N_D(\varphi_{Bn}+\Delta\varphi_n-\varphi_n-kT/e)]^{\frac{1}{2}}. \quad (3)$$

The potential Δ_0 across the interfacial layer with no voltage applied to the junction can be obtained by the application of Gauss' law to the surface charge on the metal and semiconductor:

$$\Delta_0 = -\delta(Q_m/\epsilon_i), \quad (4)$$

where ϵ_i is the dielectric constant of the interfacial layer and δ its thickness. Another relation for Δ_0 can be obtained by inspection of the energy band diagram of Fig. 1:

$$\Delta_0 = \varphi_m - (\chi+\varphi_{Bn}+\Delta\varphi_n). \quad (5)$$

This results from the fact that the Fermi level must be constant throughout the metal–interfacial-layer–semiconductor system at equilibrium.

If Δ_0 is eliminated from Eqs. (4) and (5), and Eq. (3) is used to substitute for Q_m, we obtain

$$(\varphi_m-\chi)-(\varphi_{Bn}+\Delta\varphi_n) = \left[\frac{2e\epsilon_s N_D\delta^2}{\epsilon_i^2}(\varphi_{Bn}+\Delta\varphi_n-\varphi_n-kT/e)\right]^{\frac{1}{2}} - \frac{eD_s\delta}{\epsilon_i}(E_g-\varphi_0-\varphi_{Bn}-\varphi_n). \quad (6)$$

Equation (6) can now be solved for φ_{Bn}. Introducing the quantities V_1, α, and γ:

$$V_1 = 2e\epsilon_s N_D\delta^2/\epsilon_i^2, \quad (7a)$$

$$\alpha = eD_s\delta/\epsilon_i, \quad (7b)$$

$$\gamma = 1/(1+\alpha) = \epsilon_i/(\epsilon_i+e\delta D_s), \quad (7c)$$

we can write the solution to (6) as

$$\varphi_{Bn} = [\gamma(\varphi_m-\chi)+(1-\gamma)(E_g-\varphi_0)-\Delta\varphi_n] + \{\gamma^2V_1/2-\gamma^{\frac{1}{2}}[V_1(\varphi_m-\chi) + (1-\gamma)(E_g-\varphi_0)V_1/\gamma - V_1(\varphi_n+kT/e)/\gamma+\gamma V_1^2/4]^{\frac{1}{2}}\}. \quad (8)$$

Equation (7a) can be used to calculate V_1 if values of δ and ϵ_i are estimated: For vacuum-cleaved or well-cleaned semiconductor substrates the interfacial layer will have a thickness of atomic dimensions, i.e., 4 or 5 Å. The dielectric constant of such a thin layer can be well approximated by the free-space value, and since this approximation represents a lower limit for ϵ_i, it leads to an overestimation of V_1. For $\epsilon_s \cong 10\epsilon_i$ and $N_D \leq 10^{18}$ cm^{-3}, V_1 is small, of the order of 0.01 eV, and the { } term in Eq. (8) is estimated to be less than 0.04 eV. Neglect of the { } term in Eq. (8) reduces the equation to

$$\varphi_{Bn} = \gamma(\varphi_m-\chi)+(1-\gamma)(E_g-\varphi_0)-\Delta\varphi_n \equiv \gamma\varphi_m+b. \quad (9)$$

If γ and b can be determined experimentally and if χ is known, then using the measured values we can determine φ_0 from the relation

$$\varphi_0 = E_g-(\gamma\chi+b+\Delta\varphi_n)/(1-\gamma), \quad (10)$$

and from (7c) a relation for determining D_s is

$$D_s = (1-\gamma)\epsilon_i/\gamma\delta e. \quad (11)$$

Using the previous assumptions for δ and ϵ_i, Eq. (11) becomes

$$D_s \cong 10^{13}(1-\gamma)/\gamma \text{ states/cm}^2\text{/eV}. \quad (11a)$$

Three special cases of Eq. (9) are of interest:

(1) When $\gamma \to 0$, then

$$\varphi_{Bn} \cong (E_g-\varphi_0)-\Delta\varphi_n. \quad (12)$$

In this case the Fermi level at the interface is "pinned" by the surface states at the value φ_0 above the valence band. The barrier height is independent of the metal work function, and is determined entirely by the doping and surface properties of the semiconductor.

(2) When $\gamma \to 1$, then

$$\varphi_{Bn} \cong (\varphi_m-\chi)-\Delta\varphi_n. \quad (13)$$

This is recognized as the familiar expression (except for the $\Delta\varphi_n$ term) for the barrier height of a simple Schottky barrier where surface effects are neglected.

The barrier height φ_{Bn} of a metal–n-type-semiconductor contact is the threshold for photoemission of electrons from the metal into the semiconductor. The corresponding quantity for a metal–p-type semiconductor is φ_{Bp}, which is the threshold for photoemission of holes from the metal into the p-type semiconductor. If φ_0 is assumed to be independent of doping, then for a given semiconductor φ_{Bn} and φ_{Bp} are related by

$$\varphi_{Bn}+\varphi_{Bp}+\Delta\varphi_n+\Delta\varphi_p = E_g, \quad (14)$$

where $\Delta\varphi_p$ is the image force barrier lowering for the metal–p-type-semiconductor contact. In checking the validity of (14) for cases where both φ_{Bn} and φ_{Bp} have been measured for a particular semiconductor, the image effects should not be neglected as some authors have done.[8,9] In experiments to be cited later in this paper, we find that $\Delta\varphi_n+\Delta\varphi_p$ can exceed 0.1 eV.

(3) The temperature effect on the barrier height: If we assume that the surface state density and the thickness of the interfacial layer are slowly varying functions of the lattice temperature, then γ and φ_0 are essentially independent of temperature. If the temperature variation of the image force barrier lowering can be neglected, we obtain from Eq. (9)

$$\partial\varphi_{Bn}/\partial T = \gamma\partial\varphi_m/\partial T-\gamma\partial\chi/\partial T+(1-\gamma)\partial E_g/\partial T. \quad (15)$$

[8] C. A. Mead and W. G. Spitzer, Phys. Rev. Letters **10**, 471 (1963).
[9] W. G. Spitzer and C. A. Mead, J. Appl. Phys. **34**, 3061 (1963).

If the temperature dependence of $(\varphi_m-\chi)$ and the band gap are approximately equal or if γ is small compared to unity, then from Eq. (15)

$$\partial\varphi_{Bn}/\partial T\cong\partial E_g/\partial T. \tag{16}$$

III. EXPERIMENTAL DETERMINATION OF φ_0 AND SURFACE STATES DENSITY

The Si–metal system studied by Archer and Atalla[3] will be considered first. An attempt is made here to fit the data of the experiments to the theory of Sec. II. The GaAs system studied by Mead and Spitzer[9] and the CdS–metal systems studied by Mead and Spitzer[9] and by Goodman[10] are then investigated.

Also included are the experimental results for metal–GaP systems. The details of these experiments have been previously reported.[11,12]

1. Si–Metal Systems

Archer and Atalla attempted to verify the relation between the barrier height of a metal–silicon junction and the metal–semiconductor work function by using one metal and varying the doping density in the silicon. They proposed the simple Schottky model for the junction which yields Eq. (13). This expression can be rewritten in terms of φ_n and the diffusion potential V_{BO} by using the fact that $\varphi_{Bn}+\Delta\varphi_n=V_{BO}+\varphi_n$ (Fig. 1):

$$V_{BO}=\varphi_m-\chi-\varphi_n. \tag{17}$$

This relation corresponds to the case where the electronic charge due to surface states is entirely negligible. However, the second part of Archer and Atalla's experiment, in which different metals were used in forming the junctions, shows that the metal–semiconductor barrier height measured from the Fermi level in the metal is quite insensitive to the work function of the metal used, indicating that surface states charge is not negligible. The data of Crowell *et al.*[13] for Au, Ag, Cu, and Pd support this observation. Equation (13) should therefore be replaced by Eq. (9), which is rewritten here in terms of φ_n and V_{BO}:

$$V_{BO}=\gamma(\varphi_m-\chi)+(1-\gamma)(E_g-\varphi_0)-\varphi_n. \tag{18}$$

Archer and Atalla obtained the following expression for V_{BO} vs φ_n from a least-squares fit of a straight line to their experimental data:

$$V_{BO}=0.846-1.2\varphi_n. \tag{19}$$

They were not able to explain the fact that Eq. (19) has a slope of 1.2 rather than unity as predicted by Eqs. (17) and (18). They reanalyzed the data by fitting it to a line with slope of unity and minimizing the average deviation of the data from the line, obtaining the relation

$$V_{BO}=0.810-\varphi_n. \tag{20}$$

They compare the intercept of this equation to the intercept of Eq. (17) obtaining

$$\varphi_m-\chi=0.810. \tag{21}$$

The metal used was gold, with $\varphi_m=4.70$ eV,[14] and χ for silicon is 4.05 eV,[15] so that

$$\varphi_m-\chi=0.65 \tag{22}$$

for these materials. The agreement between Eqs. (21) and (22) is fair.

Use of Eq. (18) to interpret the experimentally derived Eq. (21) would seem to be more reasonable than the procedure of Archer and Atalla, in light of the fact that surface states are known to be nonnegligible in their experiments. From a comparison of Eqs. (20) and (18) we find

$$\gamma(\varphi_m-\chi)+(1-\gamma)(E_g-\varphi_0)=0.810. \tag{23}$$

The values for γ and φ_0 can be obtained as follows: Archer and Atalla measured V_{BO} for various metals on n- and p-type silicon. Their results were presented as a plot of V_{BO} vs $\varphi_m-(\chi+\varphi_n)$, and for each experimental point, the metal used to form the contact was specified. We have calculated the value of φ_{Bn} corresponding to each of Archer and Atalla's experimental points, and the results of these calculations are plotted in Fig. 2. The photothreshold data of Crowell *et al.*[13] are shown for comparison.[16] A least-square straight line fit to Archer

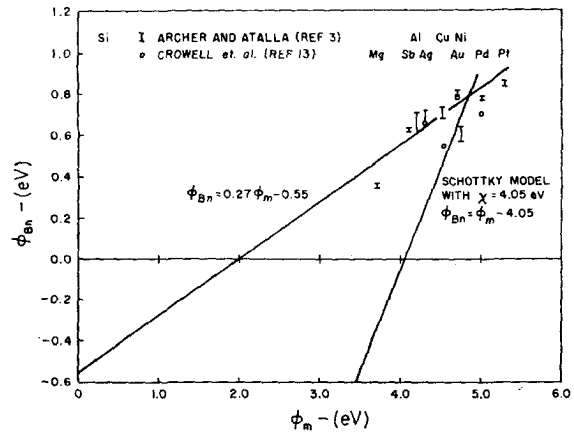

FIG. 2. Least-squares straight-line fit to the silicon φ_{Bn} vs φ_m data calculated from the results of Archer and Atalla (Ref. 3); vertical lines indicate range of φ_{Bn} values for each metal. The photothreshold measurements of Crowell *et al.* (Ref. 13) are shown for comparison.

[10] A. M. Goodman, J. Appl. Phys. **35**, 573 (1964).
[11] M. Cowley and H. Heffner, J. Appl. Phys. **35**, 255 (1964).
[12] S. M. Sze, J. L. Moll, and T. Sugano, Solid State Electron. **7**, 509 (1964).
[13] C. R. Crowell, W. G. Spitzer, L. E. Howarth, and E. E. LaBate, Phys. Rev. **127**, 2006 (1962).
[14] J. C. Reviere, Proc. Phys. Soc. (London) **870**, 676 (1957).
[15] F. G. Allen and G. W. Gobeli, Phys. Rev. **127**, 150 (1962).
[16] The data of Crowell *et al.* were obtained from samples prepared by cleaving Si in vacuum, and subsequently evaporating metals onto the cleaved surface. Using the same cleavage apparatus,

TABLE I. Experimental values for metal–GaP barrier heights.

Metal	V_0 (intercept of $1/C^2$ vs V plot)	φ_{Bn} (capacitance)	φ_{Bn} (photoresponse)	φ_{Bn} (capacitance)–φ_{Bn} (photoresponse)
Copper	1.3	1.34	1.20±0.02	0.14
Aluminum	1.10	1.14	1.05±0.005	0.09
Gold	1.30	1.34	1.28±0.02	0.06
Platinum	1.48	1.52	1.45±0.03	0.07
Magnesium	1.05	1.09	1.04±0.005	0.05
Silver	...	...	1.20±0.02	...

and Atalla's data yields

$$\varphi_{Bn}=0.27\varphi_m=0.55 \tag{24}$$

with probable error limits on the slope and intercept of ±0.05 and ±0.22 eV, respectively. Comparing this expression to Eq. (9), and using Eqs. (10) and (11a), we obtain

$$\gamma=0.27\pm0.05,$$
$$\varphi_0=0.30\pm0.36 \text{ eV},$$
$$D_s=(2.7\pm0.7)\times10^{13} \text{ states/cm}^2\text{/eV},$$

where the error limits in φ_0 and D_s are calculated on the basis of the error limits in the slope and intercept of (24). Using the above values for γ and φ_0, and the values of φ_m, χ, and E_g for Au and Si, we find

$$\gamma(\varphi_m-\chi)+(1-\gamma)(E_g-\varphi_0)=0.76\pm0.26. \tag{25}$$

Equation (25) is in satisfactory agreement with (23) in view of the uncertainties in γ and φ_0.

It has been shown experimentally[6] that the height of a gold–n-type-silicon barrier has the same temperature dependence as the silicon energy gap. Therefore, the Fermi level at the metal–semiconductor interface is pinned with respect to the valence-band edge (in the temperature range 100° to 400°K); in other words, the relation $\partial\varphi_{Bn}/\partial T=\partial E_g/\partial T$ holds. In order to explain this equality we have to consider the temperature dependence of E_g, φ_m, and χ. In the above temperature range, $\partial E_g/\partial T$ for Si has been measured by Macfarlane *et al.*[17] to be approximately -2.4×10^{-4} eV/°K. $\partial\chi/\partial T$ is determined by Allen[18] to be of the order of $+10^{-4}$ eV/°K. The temperature dependence of the metal work function has been discussed by Herring and Nichols[19] to be of the order of 10^{-5} to 10^{-4} eV/°K. $\partial\varphi_m/\partial T$ for freshly evaporated films of silver has been determined by Crowell and Armstrong[20] to be -1.3×10^{-4} eV/°K. Since gold is a monovalent metal similar to silver, $\partial\varphi_m/\partial T$ for gold films can be assumed to be about -10^{-4} eV/°K. Thus the sum of $\partial\varphi_m/\partial T$ and $-\partial\chi/\partial t$ is very close to $\partial E_g/\partial T$, and we obtain the relation as shown by Eq. (16).

2. GaP–Metal Systems

The GaP–gold barrier height has been determined by both differential capacitance and photothreshold measurements and the details of these experiments have been presented.[11,12] Using similar techniques, the barrier heights for GaP–aluminum, platinum, copper, and magnesium diodes have been measured. The experimental results for all five metals are presented in Table I (with an additional photothreshold value for silver).

The last column in Table I shows the difference in the values of φ_{Bn} determined by the capacitance and photoresponse methods. The value for φ_{Bn} (capacitance) was calculated using the relation

$$\varphi_{Bn}(\text{capacitance})=V_0+\varphi_n+kT/e-\Delta\varphi_n, \tag{26}$$

where the kT/e term is a correction due to the reserve layer in the semiconductor.[4] The presence of this term in the capacitance relation (26) and in Eq. (2) is discussed by Goodman.[21] The value for φ_n was determined to be 0.06 eV, from a calculation using the known donor density in the GaP samples and taking the density-of-states effective mass m^* to be 0.09 m.[22]

There is a consistent discrepancy between the values of φ_{Bn} determined from the capacitance and photoemission measurements: φ_{Bn} (capacitance) is always larger than φ_{Bn} (photoresponse) by an amount of the order of 100 MeV. We offer the following explanation for this phenomenon: Goodman[21] finds that in the presence of an interfacial layer between the metal and semiconductor, two correction terms arise in the equation relating the intercept of the $1/C^2$ plot and the diffusion potential V_{BO}. In terms of our notation it can be verified that Goodman's result takes the form

$$\varphi_{Bn}(\text{capactiance})=V_0+\varphi_n+kT/e-\Delta\varphi_n-V_1/4-[V_1V_{BO}]^{\frac{1}{2}}. \tag{27}$$

Archer and Atalla cleaved the Si in a stream of evaporating metal. Since both experiments were done in a vacuum of 10^{-6} Torr, it would seem that the method of Archer and Atalla produced diodes with less interfacial contamination. For this reason, the data of Archer and Atalla are used in this paper.

[17] G. G. Macfarlane, T. P. Mclean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957).

[18] F. G. Allen, J. Phys. Chem. Solids **8**, 119 (1959).

[19] C. Herring and M. H. Nichols, Rev. Mod. Phys. **21**, 185 (1949).

[20] C. R. Crowell and R. A. Armstrong, Phys. Rev. **114**, 1500 (1959).

[21] A. M. Goodman, J. Appl. Phys. **34**, 329 (1963).

[22] L. L. Chang and G. L. Pearson, J. Phys. Chem. Solids **25**, 23 (1964).

Since the diffusion potential V_{BO} is approximately 1 V for all the GaP diodes, it is evident that a value of about 0.01 eV for V_1 explains the discrepancy between φ_{Bn}(capacitance) and φ_{Bn}(photoresponse). This is in good agreement with the estimate made for V_1 in Sec. II.

A straight-line least-squares fit to the photoresponse data of Table I has been made in Fig. 3. The resulting line obeys the equation

$$\varphi_{Bn}=0.27\varphi_m-0.01. \tag{28}$$

The probable errors in the slope and intercept of Eq. (28) are ± 0.05 and ± 0.13 eV, respectively. By comparing Eq. (9) and (27), using the known value for E_g and estimating χ(GaP) to be 4.0 eV, we obtain

$$\gamma=0.27\pm 0.05$$
$$\varphi_0=0.66\pm 0.2 \text{ eV},$$
$$D_s\simeq(2.7\pm 0.4)\times 10^{13} \text{ states/cm}^2\text{/eV}.$$

Equation (14) can be checked for GaP–Au diodes by use of the value of φ_{Bp} obtained by Crowell *et al.*[23] They obtained a value of 0.715 ± 0.035 eV by measuring the threshold for photomission of holes in p-type GaP–Au diodes. $\Delta\varphi_p$ for their diodes was determined[7] to be 0.069 eV, and $\Delta\varphi_n$ for the diodes used in the present work is 0.078 eV. From these numbers and Eq. (4), $E_g=2.14\pm 0.04$ eV, compared to 2.24 eV for the room-temperature bandgap energy of GaP.

The Schottky relation, Eq. (13), for GaP is shown in Fig. 3 for comparison with the fitted line, showing clearly that the GaP–metal system is not described by this relation.

3. GaAs–Metal and CdS–Metal Systems

Mead and Spitzer[9] have obtained photothreshold data for CdS and GaAs diodes prepared using vacuum-cleaved semiconductor substrates. In Figs. 4 and 5, we show their data fitted to straight lines, in the same way as for Si and GaP, with the following results: For GaAs,

$$\varphi_{Bn}=0.074\varphi_m+0.49 \tag{29}$$

with probable error limits in slope and intercept of ± 0.05 and ± 0.24, respectively. Taking the electron affinity to be 4.07 eV for (110) GaAs,[24] we obtain

$$\gamma=0.074\pm 0.05,$$
$$\varphi_0=0.53\pm 0.33 \text{ eV},$$
$$D_s=(1.25\pm 1.0)\times 10^{14} \text{ states/cm}^2\text{/eV}.$$

Using the most probable value of φ_0 to calculate the quantity $E_g-\varphi_0$ for GaAs, we obtain $E_g-\varphi_0\simeq 0.91$ eV. This is approximately equal to the barrier height measured by the photoelectric method for most of the metals used, indicating that the GaAs–metal system is closely described by the limiting case of $\gamma\to 0$ as given by Eq. (12). The relatively weak dependence of φ_{Bn} on φ_m for GaAs is also apparent from inspection of Fig. 4.

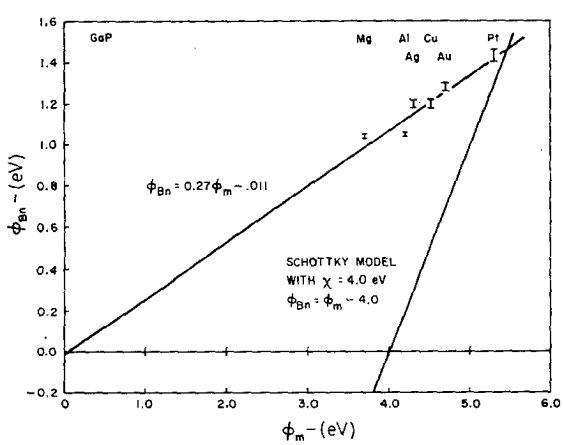

FIG. 3. Least-squares straight-line fit to GaP φ_{Bn} vs φ_m data obtained in the present work.

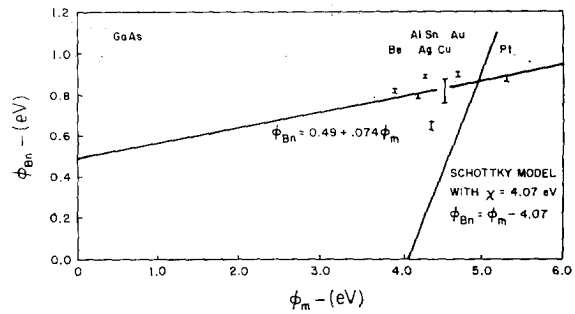

FIG. 4. Least-squares straight-line fit to the GaAs φ_{Bn} vs φ_m data of Mead and Spitzer (Ref. 9, Table III).

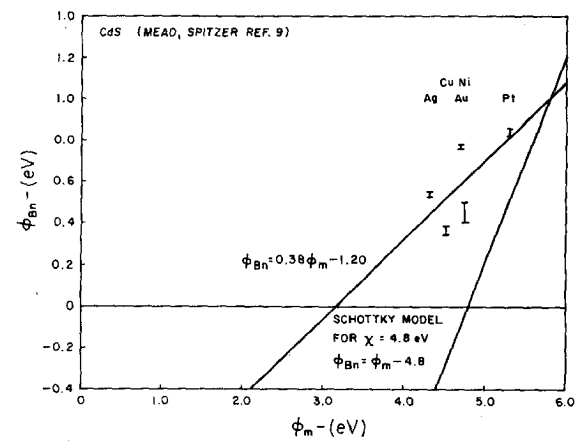

FIG. 5. Least-squares straight-line fit to the CdS φ_{Bn} vs φ_m data of Mead and Spitzer (Ref. 9, Table I).

[23] C. R. Crowell, W. G. Spitzer, and H. G. White, Appl. Phys. Letters, **1**, 3 (1962).

[24] G. W. Gobeli and F. G. Allen, "Photoelectric Threshold and Work Function of III-V Semiconductors," to be published in *Physics of III-V Compounds*, edited by R. K. Willardson and A. C. Beer. Also Phys. Rev. **137**, A245 (1965).

TABLE II. Summary of barrier height data and calculations for Si, GaP, GaAs, and CdS. Entries in the last column are calculated using most probable value of φ_0.

Semiconductor	γ	b(eV)	χ(eV)	$D_s\times10^{-13}$ (eV^{-1} cm^{-2})	φ_0(eV)	φ_0/E_g
Si	0.27±0.05	−0.55±0.22	4.05	2.7±0.7	0.30±0.36	0.27
GaP	0.27±0.03	−0.01±0.13	4.0 (est.)	2.7±0.4	0.66±0.2	0.294
GaAs	0.07±0.05	+0.49±0.24	4.07	12.5±10.0	0.53±0.33	0.38
CdS (Mead, Spitzer)	0.38±0.16	−1.20±0.77	4.8	1.6 ±1.1	1.5 ±1.5	0.6
CdS (Goodman)	0.84±0.05	−3.3 ±0.23	4.8	0.2 ±0.07	−2.1 ±1.5	···

Equation (14) can be checked for GaAs–Au and GaAs–Al diodes, using the photothreshold data of Spitzer and Mead.[9] For GaAs–Au, $\varphi_{Bn}+\varphi_{Bp}+\Delta\varphi_n+\Delta\varphi_p$ is found to be 1.42 eV at 300°K compared to the accepted value of 1.40 eV for the 300°K GaAs band gap.[25] Taking averages of the φ_{Bn} and φ_{Bp} data (at 300°K) from Mead and Spitzer's experiments on GaAs–Al also gives $E_g\approx1.42$ eV.

For the φ_{Bn} vs φ_m data of Mead and Spitzer for CdS we obtain from the least-squares analysis

$$\varphi_{Bn}=0.38\varphi_m-1.20, \tag{30}$$

with error limits of ±0.16 and ±0.77 eV in slope and intercept, respectively. The data and the fitted line are shown in Fig. 5. Taking χ for CdS to be 4.8 eV,[26] we find

$$\gamma=0.38\pm0.16,$$
$$\varphi_0=1.5\pm1.5 \text{ eV},$$
$$D_s=(1.6\pm1.1)\times10^{13} \text{ states/cm}^2\text{/eV}.$$

Goodman[10] has determined φ_{Bn} for contacts prepared by evaporating various metals on chemically cleaned CdS single crystals. He finds that the φ_{Bn} vs φ_m variation in this case is well described by the Schottky relation [Eq. (13) without the $\Delta\varphi_n$ term] with χ taken to be 4.0 eV. This is not consistent, however, with the measured value of χ(CdS)=4.8 eV reported by Kindig and Spicer.[26] Figure 6 shows the data fitted to a straight line by the least-squares method; this line does not differ significantly from the Schottky relation line shown for comparison with $\chi=4.0$ eV. The Schottky relation for $\chi=4.8$ eV is also shown.

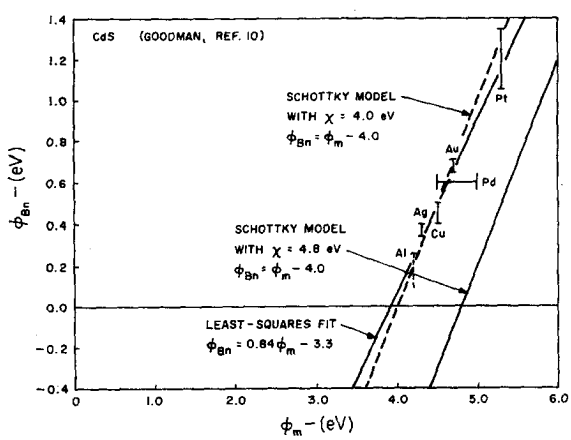

FIG. 6. Least-square straight-line fit to Goodman's φ_{Bn} vs φ_m data for chemically cleaned CdS (Ref. 10, Table VI). The Schottky relations for $\chi=4.0$ eV and $\chi=4.8$ eV are shown for comparison.

The experimental and calculated data for the Si, GaP, GaAs, and CdS–metal systems are summarized in Table II. The ratio φ_0/E_g has been calculated in each case on the basis of the most probable value for φ_0.

IV. DISCUSSION

It has been shown in Sec. III that Eq. (9) provides a reasonable explanation for the φ_{Bn} vs φ_m data for metals on Si, GaP, and GaAs. It is also found in the case of Si that Eq. (9) is compatible with the V_{BO} vs φ_n data obtained by Archer and Atalla. The significance of the calculated value of φ_0 and D_s for Si, GaAs, and CdS is questionable due to the large probable error in these quantities (Table II). The GaP data seems to give the best "fit" to a straight line, and the calculations of φ_0 and D_s can probably be considered reliable for this case. The model chosen for the derivation of Eq. (9) is a highly idealized one, and the fitting of experimental φ_{Bn} vs φ_m data to this equation is a procedure which merits the further discussion which follows.

As pointed out in Archer and Atalla's paper,[3] the vacuum values of χ and φ_m may not be the appropriate values to use in Eq. (9) to calculate $\varphi_m-\chi$ for an intimate metal–semiconductor contact, due to dipole interactions between the semiconductor and the different metals. Since the dipole interactions may differ from metal to metal, there may be a nonsystematic variation between the metal and the semiconductor work functions for the vacuum and intimate contact cases. This effect might partially account for the scatter in the experimental points for Si, GaAs, and for the CdS data of Mead and Spitzer. It is interesting in this connection to note that the greatest amount of scatter in the φ_{Bn} vs φ_m data is observed for the cases where the semiconductor surface was cleaved in vacuum, i.e., the Si–metal and GaAs–metal systems, and the CdS–metal system studied by Mead and Spitzer. In contrast, the GaP–metal system and the CdS–metal system studied by Goodman have a relatively small amount of scatter. This difference might be explained on the basis that the presence of a somewhat thicker interfacial layer on the

[25] C. Hilsum and A. C. Rose-Innes, *Semiconducting III–V Compounds* (Pergamon Press, New York, 1961), p. 59.
[26] N. Kindig and W. E. Spicer, Bull. Am. Phys. Soc. 9, 573 (1964).

chemically cleaned semiconductor surfaces decreases the importance of dipole interactions between metal and semiconductor.

The assumption of a uniform (constant) density of surface states in the forbidden gap is difficult to justify, and in fact may not be valid. Experimental evidence does exist, however, in support of a uniform or near-uniform distribution of surface states in germanium and silicon.[27-29] For a nonuniform distribution of surface states in the forbidden gap, Eq. (1) should be replaced by

$$Q_{ss}=-e\int_{\varphi_o}^{\infty}\frac{1}{1+\exp[(E-E_F)/kT]}D_s dE, \quad (31)$$

where E_F, the Fermi energy, is given according to Fig. 1 by

$$E_F=E_g-\varphi_{Bn}-\Delta\varphi_n. \quad (32)$$

An adequate approximation to Q_{ss} can be obtained by taking the limit of Eq. (31) as $T\rightarrow 0$:

$$Q_{ss}\approx -e\int_{\varphi_o}^{E_g-\varphi_{Bn}-\Delta\varphi_n} D_s dE. \quad (33)$$

The development leading to Eq. (6) can now be repeated in terms of Eq. (33) to give

$$\frac{\epsilon_i}{\delta}(\chi+\varphi_{Bn}+\Delta\varphi_n-\varphi_m)=e\int_{\varphi_o}^{E_g-\varphi_{Bn}-\Delta\varphi_n} D_s dE - [2e\epsilon_s N_D(\varphi_{Bn}+\Delta\varphi_n-\varphi_n-kT/e]^{\frac{1}{2}}. \quad (34)$$

Taking the derivative of Eq. (34) with respect to φ_m yields

$$\frac{\epsilon_i}{\delta}\left(1-\frac{\partial\varphi_{Bn}}{\partial\varphi_m}\right)=e\frac{\partial\varphi_{Bn}}{\partial\varphi_m}D_s(E_g-\varphi_{Bn}-\Delta\varphi_n) + \frac{1}{2}\frac{\partial\varphi_{Bn}}{\partial\varphi_m}\left[\frac{2e\epsilon_s N_D}{(\varphi_{Bn}+\Delta\varphi_n-\varphi_n-kT/e)}\right] \quad (35)$$

or

$$D_s \text{ (at the Fermi level)}=\frac{1-\partial\varphi_{Bn}/\partial\varphi_m}{\partial\varphi_{Bn}/\partial\varphi_m}\frac{\epsilon_i}{\epsilon\delta}\frac{1}{2e} \times\left[\frac{2e\epsilon_s N_D}{(\varphi_{Bn}+\Delta\varphi_n-\varphi_n-kT/e)}\right]^{\frac{1}{2}}. \quad (36)$$

Based on the same assumptions for ϵ_i, δ, and ϵ_s as given in Sec. II, and for $N_D\leq 10^{18}$, the second term on the right-hand side of Eq. (36) is of the order of 2×10^{12} states/cm^2/eV or less. For $\partial\varphi_{Bn}/\partial\varphi_m$ equal to 0.5 or smaller the first term of Eq. (36) is always the dominant term, and if $\partial\varphi_{Bn}/\partial\varphi_m$ does not vary greatly, D_s will then be essentially a constant.

It is perhaps just possible to decide that a better fit to the silicon data of Fig. 2 is provided by a curved line whose slope is about the same as the line shown on the graph near the Pt and Pd points, becoming less steep from Ni to Al, and becoming steeper in the region between Sb and Mg. If this is the case, then according to Eq. (36) the surface states density D_s in the forbidden gap of silicon is somewhat greater in the vicinity of 0.35 eV above the valence band edge. This could correspond to the band of surface state levels 0.4 to 0.6 eV above the valence band edge postulated by Allen and Gobeli[15] as an explanation for their photoemission data. The same authors point out that a discrete surface state level 0.45 eV above the valence band edge is also consistent with their data.

The interfacial layer thickness δ between metal and semiconductor atoms is dependent on both the exposure time of the semiconductor surface to the residual gases and the manner in which the first layer of metal atoms "sits" on the semiconductor surface. It is reasonable to assume that the value for δ varies $\pm 50\%$ about some mean value for cleaved surfaces; such a variation will be averaged out to some extent in the least-squares analysis of the data, and in any case the qualitative features of the model based on constant δ will still be observed. Since the residual pressure in the vacuum system is about 2×10^{-7} to 10^{-6} Torr in the previously cited experiments,[3,5] a monolayer can form on the cleaved surface in less than one second to a few seconds depending on the sticking coefficient of the residual gases.[30] For etched and protected surfaces such as those used in the GaP experiments, it is likely that a monolayer or more of adsorbed residual gas forms the interfacial layer.

The potential Δ across the interfacial layer varies from 0.01 to about 1 V, depending mainly on the metal work function; this results in a field of 10^5 to 10^7 V/cm in the layer. It is well known that SiO_2 films can withstand fields exceeding 10^7 V/cm, but due to the different nature of the interfacial layer for an intimate contact, higher fields may exist in the layer.

The most probable values for the surface-state neutrality level φ_0 as derived from the least-squares analysis for GaP, GaAs, and Si are roughly a third of the respective band gaps. This seems to be consistent with the findings of Mead and Spitzer,[5] since if D_s has a high value, as is apparently the case for GaAs, the Fermi level tends to become pinned at the surface φ_0 eV above the valence band, producing a barrier height of $E_g-\varphi_0$ or about $\frac{2}{3}E_g$. Allen and Gobeli,[15] who propose a surface state distribution different from ours for Si, find the surface state neutrality for cleaved (111) Si "free" surfaces to be about 0.3 eV above the valence band edge. This value has been verified by Kawaji

[27] W. Shockley and G. L. Pearson, Phys. Rev. **74**, 232 (1948).
[28] W. H. Brattain and W. Shockley, Phys. Rev. **72**, 365 (1947).
[29] H. C. Montgomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).
[30] J. H. de Boer, *The Dynamical Character of Adsorption* (Clarendon Press, Oxford, England, 1953), Chap. 2.

and Takashima,[31] and by Handler.[32] More recent work by Gobeli and Allen[24] indicates that the surface neutrality level for the cleaved (110) GaAs surface is about 0.76 eV, which does not correspond to the position of the Fermi level in metal-GaAs contacts. Fischer[33] has performed preliminary photoemission measurements on cleaved GaP (110) surfaces following the procedures described in Ref. 24. Tentative results of this work indicate an electron affinity of approximately 3.45 eV and a surface state neutrality level of about 0.94 eV for the (110) GaP surface. It is not clear that these results can be applied in the present work, however, since the GaP diodes described here were prepared using chemically cleaned (111) GaP surfaces.

The results of Mead and Spitzer[9] and of Goodman[10] for CdS present some difficulties when compared to the theory. In view of the large amount of scatter in Mead and Spitzer's experimental points for CdS, and the concomitant probable errors in the slope and intercept of the fitted line, it is doubtful that any significant conclusions can be drawn regarding the effect of surface states on the potential barrier in this case. The results presented by Goodman appear to obey the Schottky relation, indicating little or no dependence of surface barrier height on surface states, but the value of χ required for agreement with the Schottky relation is in poor agreement with the reported value determined by another method.[26] We have no explanation for this behavior. It seems clear, however, that the chief reason for the difference in results of the experiments of Goodman and of Mead and Spitzer for CdS is the different method of semiconductor surface preparation, and it could be conjectured that the additional interfacial layer thickness for Goodman's diodes had a "smoothing" effect on the φ_{Bn} vs φ_m data, due to the partial elimination of dipole interactions.

It should be clear at this point that the conclusions regarding the surface states density and distribution drawn on the basis of the preceding work are valid only for the specific methods of surface treatment used in the experiments cited. For cleaved surfaces, it is possible that the surface states can be attributed to "dangling bonds"; modification of this scheme by adsorbed gas molecules is expected in the case of chemically cleaned substrates.

The available data for GaP and GaAs provide excellent verification of Eq. (14) if the image corrections are included. The values for φ_{Bn} and φ_{Bp} were taken to be the appropriate photothresholds, since these provide the most direct determinations of φ_{Bn} and φ_{Bp}; the capacitance values of φ_{Bn} and φ_{Bp} are uncertain to the extent that the magnitude of the correction terms of Eq. (27) are not known accurately.

Using the values of γ and V_1 obtained from the data, we have found that for any reasonable value of $E_g - \varphi_0$, the terms involving V_1 in Eq. (8) are unimportant, thus justifying the use of the approximate form, Eq. (9).

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[31] S. Kawaji and Y. Takashima, Surface Sci. 1, 119 (1964).
[32] P. Handler, Appl. Phys. Letters 3, 96 (1963).
[33] T. E. Fischer, Bell Telephone Laboratories, Murray Hill, New Jersey (private communication).