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Theory of metal-semiconductor interfaces

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We present a microscopic model for the formation of Schottky barriers at metal-semiconductor contacts. The theory proposes that Schottky barriers are determined by "metal-induced gap states" at the semiconductor surface, which are dangling-bond derived resonances. The dangling-bond character of these states implies that the energies of surface states at clean semiconductor surfaces *are* very important in Schottky-barrier formation. This work introduces an ionicity parameter, obtained from atomic-term values, to quantitatively characterize the well-known transition from covalent to ionic behavior at metal-semiconductor interfaces. This model directly associates this transition with a truly fundamental change in the electronic structure of the semiconductor substrate and provides a natural interpretation of strong Fermi-level pinning at metal contacts to covalent materials with large optical gaps and low bond polarizabilities.

I. INTRODUCTION

In the past, the phenomenon of Schottky-barrier formation at metal-semiconductor contacts has elicited a great deal of experimental as well as theoretical interest.[1-14,18,19] It was originally observed that Schottky-barrier heights for covalent semiconductors, like Si, are rather independent at the electronegativity of the overlayer metal. The classical theoretical explanation for this phenomenon involves screening through an interface dipole layer.[3,4] More recently, it has been experimentally determined that the degree of Fermi-level stabilization at such interfaces evolves quite quickly from covalent behavior (a pinned Fermi level) to ionic behavior (an unpinned Fermi level) as a function of semiconductor "ionicity".[5] This intriguing observation has led to a number of theories of Schottky-barrier formation which have involved band bending, interface bond polarizabilities, many-body effects, etc., to explain the experimental trend.[6-8] In addition, recent scattering experiments at these interfaces[9-11,13] have led to the diverse conclusions (a) that some surface states are well correlated with Schottky-barrier heights, (b) that *new* metal-interface-derived states dominate the formation of barriers, and (c) that chemical bonds in the interface region are primarily responsible for the observed Schottky-barriers.

In this paper we present a new theory of the covalent-ionic transition at metal-semiconductor interfaces. In this theory we again attribute Fermi-level stabilization to the formation of a dipole layer at the interface. We propose that the dipole layer is due to the filling of *dangling-bond-derived* states which are resonantly broadened in the presence of a metal overlayer. A simple description of the metal-semiconductor interface directly identifies the "covalent-ionic" transition in these materials with a very fundamental transition in the electronic character of the compounds. Specifically, we find a fundamental transition in the character of the band gap in these materials which accounts for this transition in interface behavior. We introduce a new ionicity parameter which characterizes the transition and allows a systematic quantitative description of the "covalent-ionic" interface transition.

We finally reconcile several models of Schottky-barrier formation by noting that the barrier occurs through new interface "induced" states which are derived from (and hence characteristic of) the surface states at the clean semiconductor surface and depend strongly on the energies of the clean states.

In this paper we proceed as follows. In Sec. II, we briefly discuss the experimental observations of Kurtin *et al.*[5] which gave evidence of the covalent-ionic transition at these interfaces. In Sec. III, we examine the effects of ionicity on the nature of the band gap to a wide range of binary compounds. Here we extract an ionicity parameter to characterize a fundamental transition in the nature of the band gap. Section IV deals with the energies of the surface states which reside in these gaps and are shown to be related straightforwardly to this ionicity parameter. In Secs. V and VI the effects of a metal overlayer on these clean surface states are discussed in some detail. We also present a comparison of our Schottky-barrier calculation with the original observations of Kurtin *et al.* Finally, in Secs. VII–X, we discuss the parameter dependence of the theory, related scattering experiments, the relation of this model to previous theoretical work, and possible extension of the theory. A summary is presented in Sec. XI.

II. IONICITY AND THE INDEX OF INTERFACE BEHAVIOR

In general, when a metal and a semiconductor are not in mechanical contact, their respective Fermi levels lie at different energies relative to the vacuum. That is, their work functions generally differ. When a metal and semiconductor are then brought into *intimate* mechanical contact, in which transfer of electrons is possible, thermodynamic equilibrium is achieved when the Fermi levels in the two materials are equilibrated. For a static model of the band gap of a doped semiconductor at such an interface (which assumes there are no surface or interface-derived band-gap states) this equilibration involves a transfer of electrons into (or out of) impurity states within several hundred angstroms of the surface. This induces some surface band bending which is then primarily responsible for matching the Fermi levels at the interface. Following such an argument one concludes that the Schottky barrier Φ_B (i.e., the energy from the Fermi level to the conduction-band minimum at the interface) equals the difference between the work functions of the separated metal Φ_M and that of the clean semiconductor Φ_S. That is,

$$\Phi_B = \Phi_M - \Phi_S . \tag{1}$$

However, in Fig. 1, we show a plot of experimental Schottky-barrier values[12] for four semiconductors in contact with metals of varying electronegativity E_M (the electronegativity is linearly related to the metallic work function). One generally notes a linear correlation between the barrier heights and the metal electronegativity, but the slopes are *not* uniform and poorly fit the static prediction of Eq. (1). To quantitatively describe the phenomenon one generalizes Eq. (1)

$$\Phi_B = S E_M + \Phi_0 , \tag{2}$$

where S is a number characteristic of the *semiconductor substrate* and is labeled the index of interface behavior. For the data in Fig. 1, $S=1$ for ZnS (curve d) and $S \approx 0$ for Si (curve a).

In 1969 Kurtin, McGill, and Mead[5] compiled such Schottky-barrier measurements for a number of binary semiconductor-to-metal contacts. Ordering the ionicity of their semiconductors by the difference (ΔE) between the Pauling electronegativities of the binary constitutents, they plotted the index S against semiconductor "ionicity." Their results are reproduced in Fig. 2. Here we see a striking transition from S near zero to S near unity which occurs for electronegativity differences at roughly 0.8. However, several features of this curve should be emphasized.

(a) $S=1$ does *not* describe a static semiconductor band gap in which there is *no* Fermi-level stabilization. From Eq. (1) $d\phi_B/d\phi_M = 1$ for such a system, and ϕ_M may be empirically related to E_M by the relation

$$\phi_M = A E_M + B . \tag{3}$$

Hence,[14] $S = A \approx 2.3-2.5$ would describe the ionic free-Fermi-level limit for their interfaces, a limit not achieved in Fig. 2.

(b) A re-evaluation of the original data of Kurtin *el al.* has recently been undertaken by Schlüter. This work finds that there may be some error (roughly 20%) in the original estimates of S, and that some S values near the saturation limit of 1 actually tend to lie a bit higher.

(c) Even with the corrections of (a) and (b) one sees a sharp transition near $\Delta E = 0.8$ from a regime in which S is small and rather insensitive to the electronegativity to a regime in which S increases sharply with electronegativity. It is not immediately apparent why such a sharp transition should occur at such an arbitrary electronegativity difference.

(d) In their original work Kurtin *et al.*[5] correlated this transition with sharp changes in the behavior of two other electronic properties at the same electronegativity difference. This implies that this transition is not limited to the interface

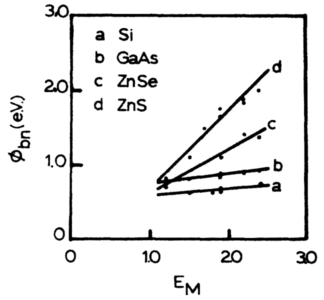

FIG. 1. Dependence of Schottky-barrier heights ϕ_{bn} on metal electronegativity for four representative semiconductors.

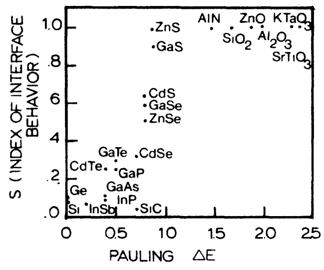

FIG. 2. Dependence of the index of interface behavior S on semiconductor ionicity. The ionicity is ordered by the difference in Pauling electronegativity.

system, but reflects a more fundamental change in the electronic structure of the semiconductor substrates.

The theory which we will now develop directly associates the transition in interface behavior with a very fundamental transition in the electronic structure of these solids.

III. COVALENT AND IONIC GAPS

We note first of all that the deviation of all of the compounds of Fig. 2 from the static interface behavior described by Eq. (1) is attributable to the presence of surface or interface states in the semiconductor band gap. Thus, the dependence of the *character* of the band gap on semiconductor ionicity is of central importance to this problem, and is described in this section.

In Fig. 3 we schematically show the broadening of the atomic valence s and p levels into semiconductor bulk bands for a number of systems. This diagram refers only to the tetrahedrally coordinated semiconductors. In each panel we denote an energy χ which measures the energy from the anion valence p state to the cation valence s state.

The first panel corresponds to the homopolar crystals C, Si, Ge, and α-Sn. By definition there are n-fold degenerate atomic s and p states in the atomic limit as shown. The energy χ is negative since the valence p state is less strongly bound than the valence s state. The introduction of crystalline interactions then broadens these states into bands as shown. Here one immediately notes an interesting trend. If one does not include s-p mixing in the problem, there is no band gap. This is the case for the column labeled $V_{sp}=0$. Near the Fermi level we see overlapping degenerate s- and p-derived bands. The introduction of an sp interaction then strongly mixes these states, removes this degeneracy, and opens a band gap, as shown in the third column.

In the second panel we treat a class of heteropolar solids. Here we require two different atomic constituents, and this introduces a slight splitting in the atomic valence s and p levels. The respective cation levels are slightly higher in energy then the anion levels. However, as shown in the first column, the energy χ is still negative, i.e., the valence anion p state is less strongly bound than the valence cation s state. We note, however, that near the Fermi level this system behaves much like the homopolar solid. That is, in the absence of an sp interaction we have no band gap. Again, one observes s- and p-derived bands overlapping near the Fermi level. The introduction of an s-p interaction then strongly mixes these states and opens a band gap as in the homopolar crystal. This class of solids is labeled heteropolar but covalent because of this identification with the homopolar regime.

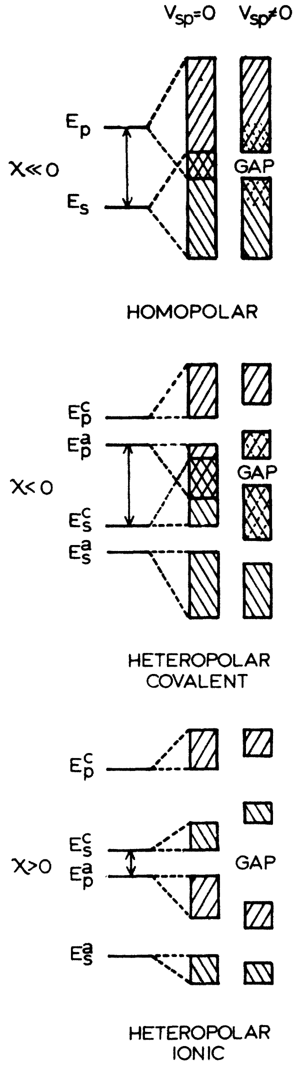

FIG. 3. Schematic evolution of atomic states into bulk semiconductor bands for tetrahedrally coordinated systems. Results are shown for several cases both with and without hybridization interaction (V_{sp}).

As we move to more and more heteropolar solids the energy χ increases and eventually turns positive. This situation is shown in the third panel where the cation s level is less strongly bound than the anion p level. In this case we see that even in the absence of the sp interaction the Fermi level falls in a forbidden gap and this gap *increases linearly with the energy* χ. The introduction of an sp interaction then serves to widen this gap (in fact, this mixing can generally be treated in perturbation theory) so that the total gap is strongly dependent on the energy χ. This strong scaling of the gap with the energy χ is a fundamental characteristic of the heteropolar ionic regime and occurs for positive values of the ionicity parameter.

Figure 3 thus describes the evolution of the band gap with semiconductor ionicity. We generally identify two regimes. In the first, or covalent regime, the gap is not terribly sensitive to the semiconductor ionicity. The gap is formed from strong *s-p* mixing of degenerate states at the Fermi level. In other words, the hybridization interaction is responsible for the band gap. This regime occurs not only for homopolar crystals but for a *wide range* of heteropolar substances. In the second, or ionic regime, we see that the gap is *very* sensitive to semiconductor ionicity. Here the gap is actually dominated by *"unperturbed" self-energy differences*, and hybridization plays a secondary, perturbative, role. In such systems we observe significant charge transfer across the gap from the cations to the anions.

Importantly, the transition between these regions is characterized by the sign of the ionicity energy χ. The transition in the character of the band gap is quite clearly evident in the experimental data. This is demonstrated in Figs. 4(a) and 4(b). In Fig. 4(a) we plot the average optical gap or Phillips gap[15] against the ionicity parameter χ for tetrahedrally coordinated semiconductors. We see a "main sequence" of compounds from Ge to CuCl for which the gaps tend to increase significantly for positive values of χ. However, we also note significant deviations from the trend, i.e., the lighter elements fall well off this mean sequence.

However, these deviations follow directly from the variations in bond lengths of these semiconductors. That is, the lighter elements tend to bond with shorter bonding radii and hence interact more strongly, widening the observed gaps. This effect can *quantitatively* be taken into account by tabulating the average gaps and the ionicity parameter χ in units of the "bonding" interaction which varies, following Phillips, with the bond length d as

$$V \propto d^{-2.5} . \tag{4}$$

This scheme allows a quantitative comparison of the relative contributions of the covalent interaction (V) and the ionicity (χ) to the average gap ($\bar{E}_g$), for compounds with varying bond lengths. Thus we scale the gap values and the ionicity value to a standard bond length of 2.45 Å, that is, we define

$$\bar{E}_g^{\text{scaled}} = \bar{E}_g (d/2.45\ \text{Å})^{-2.5} , \tag{5}$$

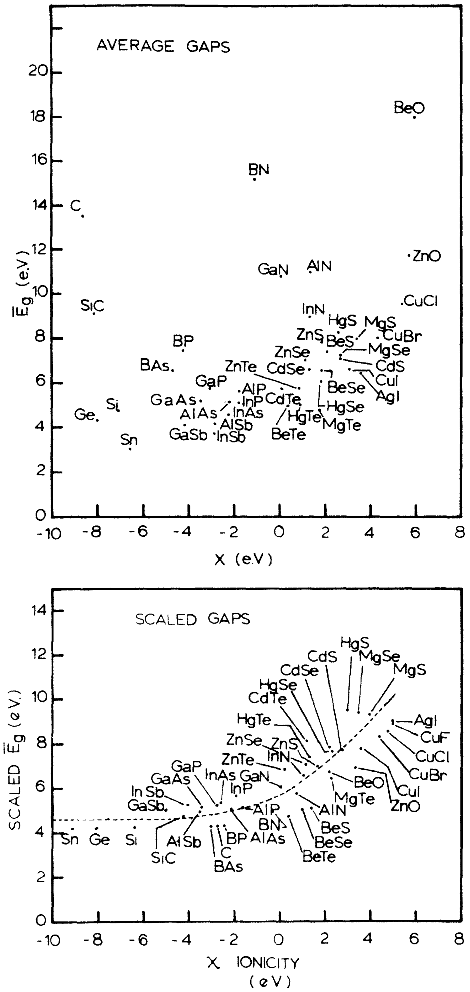

FIG. 4. (a) Dependence of average (optical) gap on the ionicity parameter χ; (b) same data as (a), where $\bar{E}_g$ and χ are now scaled to a uniform bond length.

and

$$\chi^{\text{scaled}} = \chi (d/2.45\ \text{Å})^{-2.5} . \tag{6}$$

In Fig. 4(b) we have plotted the scaled gaps against the scaled ionicities. The scatter of Fig. 4(a) is clearly removed; the points fall on or near the smooth dotted curve. This plot then clearly demonstrates the relevant chemical trends in the average gaps. When χ is large and negative, the dotted curve is quite flat, indicating an insensitivity of the gaps to the ionicity. As χ approaches zero the gaps increase slightly. Finally, for χ positive we observe a regime in which the gaps increase quite rapidly with χ. For large values of the ionicity, χ dominates the observed gaps. We emphasize that this is a transition from a covalent regime in which the gaps are relatively insensitive to χ to an ionic regime in which the gaps are very sensitive to χ. The transition is observed to occur near $\chi = 0$, as we have previously argued.

In addition, we should point out that this transition is evident in other fundamental aspects of the crystalline band structure. Most importantly, the transition from $\chi < 0$ to $\chi > 0$ marks a saturation in the anion *p* character of the valence band and the cation *s* character of the first conduction band. This is physically sensible since we have noted that $\chi > 0$ marks the onset of a regime in which these bands are separable in terms of their atomic character, and their interactions may be easily represented in a perturbation expansion.

IV. SURFACE STATES IN THE OPTICAL GAP

The dependence of the average gaps on ionicity outlined in Sec. III can be used to provide some information about the surface states which reside in these gaps at a clean semiconductor surface. This connection is central to the development of this interface theory. One can argue that the energy separation of surface states in the fundamental gap represents a "surface gap" which will follow the same chemical trends as the bulk optical gap. This can be traced to the fact that in the limit in which $V_{sp} = 0$, surface-derived states always fall within the allowed bulk bands calculated in this limit. At the real surface these states will then generally fall in some gap due to variations in hybridization (i.e., smaller *s-p* mixing) at the surface. For *covalent* materials these surface states occur near the middle of the optical gap which has been directly opened by the *s-p* interactions. For ionic materials, however, these surface states will occur much closer to optical-gap edges, since hybridization interactions are of only secondary importance in the formation of this class of gap.

These ideas can be made more quantitative as follows. We assume, as shown in the right-hand side of Fig. 5, a one-osillator model for the optical band gap. If we cleave the infinite crystal, the surface will be characterized by dangling-bond states separated by an energy Δ. This is shown in the left-hand side of Fig. 5. If we then rejoin the cleaved crystal halves, the interaction between the dangling-bond states at the surface must recover the original gap. Now the gaps plotted in Fig. 4(b) have been scaled to a uniform bond length; that is, the magnitude of the bonding interactions *V* between the dangling-bond states for these compounds is constant along this scaled curve. We can obtain *V* from the homopolar limit in which $\Delta = 0$ by symmetry. This leads to a value for *V* of roughly 4.6 eV. This finally allows us to obtain Δ as a function of χ in a one-oscillator model from

$$\Delta(\chi) = [E_g^2(\chi) - V^2]^{1/2} . \tag{7}$$

Note that the separation of the optical gap into an interaction term (*V*) and a self-energy term (Δ) closely parallels the separation of $\bar{E}_g$ into E_h and *C* in the Phillips-Van Vechten ionicity scheme.[15] However, we employ relation (7) to provide the important connection between the energy χ and the surface-state energy difference Δ. χ itself has no counterpart in the Phillips-Van Vechten theory. Using the data of Fig. 4(b) and Eq. (7) we obtain the dependence of Δ on χ shown on the right-hand side of Fig. 6. This curve shows some noteworthy trends. When χ is large and negative, Δ is zero and is independent of χ. This reflects the fact that the dangling-bond states are not separated in energy at unreconstructed homopolar surfaces. As χ approaches zero, Δ increases slightly; however, even for χ as large as zero, Δ is less than half the full optical gap. For χ greater than zero, Δ increases much more quickly; by $\chi = 4$ eV, Δ accounts for almost 90% of the bulk optical gap. For very large values of the ionicity, χ dominates both Δ and $\bar{E}_g$. We again emphasize that a covalent surface is characterized by states near the mid-optical gap; the ionic surface localizes surface states closer to the optical gap edge.

Some further remarks about the surface-state

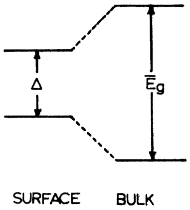

FIG. 5. Schematic "one-oscillator" gap model used to relate surface-state separation Δ and average gap $\bar{E}_g$.

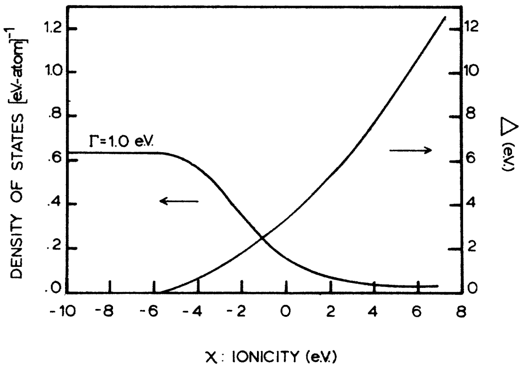

FIG. 6. (Right-hand scale) Δ, the separation of surface states in the optical gap as a function of ionicity; (left-hand scale) the density of midgap resonant states ($\Gamma = 1.0$ eV) as a function of ionicity.

model are useful. First, one should note the quantitative reliability of using this one-oscillator argument for estimating surface-state separations. Detailed surface-state calculations using a self-consistent pseudopotential are available for Si, GaAs, and ZnSe.[16] The values of Δ obtained from our model for these compounds (0 eV,~1 eV,~5 eV, eV, respectively) agree to within a half volt with values obtained from these detailed treatments of these surfaces. In general, we expect agreement to within a volt to be satisfactory for this application.

Secondly, there is some arbitrariness in the choice of V from Fig. 4(b). However, we have found that a reasonable variation in the choice of V affects the ultimate results here only slightly.

Thirdly, we should emphasize that this model requires surface-derived states within the *optical* gap. Only for the very covalent materials are these states generally found within the thermal gaps at the semiconductor surface.

V. METALLIC OVERLAYERS AT THE SEMICONDUCTOR SURFACE

In this section we examine the fate of these surface states in the presence of a metal overlayer. There are two fundamental approximations made in this treatment. Firstly, we assume that at the clean surface the surface states are dispersionless in the two-dimensional Brillouin zones. That is, we approximate the surface states by discrete states. In fact, more detailed calculations of these states show a dispersion of a volt or less, so that this approximation is physically reasonable. Secondly, we assume a *weak* interaction of the dangling-bond states with the metal overlayer. Thus the possibility of surface *bonds* between semiconductor and metal adatoms is not included. This approximation is physically rooted in the spirit of the linear interface expression of Eq. (2) in which S is a function of only the semiconductor substrate. We note that at submonolayer coverages one's physical intuition strongly suggests that chemical bonds dominate the interface properties. At higher coverages the situation is not so clear. We note, first of all, that recent jellium semiconductor-interface calculations using a pseudopotential formalism have yielded barrier heights in reasonable agreement with experiment. We note secondly that experimental energy-loss measurements do not show a measurable energy shift between interface states in the presence of a metallic overlayer and the clean-semiconductor surface states. Proper chemical bonds at the interface should have a stronger effect on such surface features. Finally, modelling the metal overlayer by a jellium potential allows us to focus on the effect on *only* the semiconductor ionicity at these interfaces.

At the clean semiconductor surface, a surface state is an eigenstate of the full Hamiltonian which decays evanescently both into the semiconductor bulk and into the vacuum. With a metal overlayer at the surface, we note that the pure surface state is not an eigenstate of the full Hamiltonian, but is matched to propagating waves in the metal potential, if states at the same energy with the proper symmetry exist in the metal. However, if we assume that the interaction of the metal potential with the original clean surface state is weak, this full Hamiltonian can be treated in perturbation theory. That is, we assume that the clean surface state is *close* to an eigenstate of the full interface potential, and that electrons will "leak out" of such states into the metal as a function of time. We can then estimate the average residence time in the "surface states" in a golden-rule type of calculation, providing an estimate of the lifetime broadening of the original surface states.

We have explicitly performed such a transition calculation for an Al-Si(111) interface. In first-order perturbation theory, we write the dangling-bond-state lifetime τ

$$1/\tau = (2\pi/h)\,|H_{if}|^2\rho_f \tag{8}$$

Here, H_{if} represents a matrix element across the perturbing potential (the Al potential as approximated by a jellium potential) between the initial states (the dangling-bond wave function) and the final state (a plane wave at the same energy in the metal). The initial-state wave function is taken from the self-consistent pseudo wave function of Appelbaum and Hamann[17] for the clean unreconstructed Si(111) surface. Their wave function is actually modelled to a convenient analytic form to allow closed-form solution of the necessary integrals. The selection of a jellium potential to model the Al overlayer allows a particularly straightforward expression for H_{if}. Since

$$H_{if} = \langle\psi_i|H'|\psi_f\rangle\,, \tag{9}$$

and

$$H'|\psi_f\rangle \approx \phi_M|\psi_f\rangle\,, \tag{10}$$

where ϕ_M is an internal work function of the metal (i.e., position of the Fermi level below vacuum, typically 4.0–4.5 eV) we have

$$H_{if} \approx \phi_M\langle\psi_i|\psi_f\rangle\,. \tag{11}$$

Here $\langle\psi_i|\psi_f\rangle$ represents a Fourier transform of the *tail* of the dangling-bond wave function, i.e., the part which extends into the jellium region. Here, we choose the jellium edge to lie at a half bond length from the surface Si atom. Putting these pieces together, we obtain a value for the resonant linewidth Γ ($\Gamma = h/\tau$) for such a state

$$\Gamma \approx 1 \text{ eV}. \tag{12}$$

As a consequence, dangling-bond states which had previously been characterized by a well-defined energy are significantly broadened in the presence of a metallic overlayer. This generally leads to a nonzero density of states in the semiconductor band gap at the Fermi level.

Using this model for the Al-Si(111) interface we compute a density of midgap states of ≈ 0.64 states/eV surface Si atom,[12] a result in excellent agreement with the detailed calculation of Louie, Chelikowsky, and Cohen[12] at this interface. If we take the density of these resonant states at the *mid-optical gap* to be representative of the density of states at the Fermi level, and extrapolate the value of the resonant linewidth (~1 eV) to *all ionicities*, we obtain the density of states at the Fermi level as a function of ionicity given on the left-hand scale of Fig. 6. This curve shows several interesting trends. When χ is large and negative, the density of states is "large" and rather insensitive to χ. As χ approaches zero, the density of states drops dramatically and levels off near zero for positive values of the ionicity. We again see a transition from a covalent regime ($\chi < 0$), where there is a large density of states at the Fermi level to an ionic regime ($\chi > 0$), where there are almost no semiconductor-derived states at the midgap. Again, the transition is characterized by the sign of the ionicity parameter.

VI. FERMI-LEVEL STABILIZATION AT METAL-SEMICONDUCTOR INTERFACES.

The resonant broadening of the "clean" surface states in the presence of the metal overlayer results in a nonzero density of states at the Fermi level in the semiconductor band gap. These states then provide some degree of Fermi-level stabilization at these interfaces. Here we derive an expression which quantitatively describes this Fermi-level stabilization, and calculate the index of interface behavior using the results of Sec. V.

Assume a metal and semiconductor are brought into intimate contact, and their respective Fermi levels differ. A transfer of charge per unit surface σ across the interface will result in a movement of the semiconductor Fermi level by $\Delta\epsilon$, where

$$\Delta\epsilon \approx \sigma/eD_S(\epsilon_F)]\,. \tag{13}$$

Here $D_S(\epsilon_F)$ is the density of semiconductor-derived states per unit area at the Fermi level. Expression (13) is a linear approximation to an exact integral expression for $\Delta\epsilon$, and the approximation is good for small values of $\Delta\epsilon$. If the states which characterize $D_S(\epsilon_F)$ are well localized near the interface, the effect of the transfer of charge σ is to create a dipole layer at the interface which physically results in a large change in the electrostatic potential across the interface region. If the decay length of the states at the Fermi level into the semiconductor bulk is given by δ_S, then the change in electrostatic potential across the interface is given by $\Delta\Phi_D$, where

$$\Delta\Phi_D = 4\pi e\sigma(\delta_S + \delta_M)\,. \tag{14}$$

Here δ_M is a typical screening length in the metal ($\delta_M \approx 0.5$ Å). The effect of the dipole potential is to impede the transfer of charge. The system then equilibrates when the combined effects of Eqs. (13) and (14) account for the work function mismatch, that is,

$$\phi_M - \phi_S = 4\pi e\sigma(\delta_S + \delta_M) + \sigma/eD_S(\epsilon_F)\,. \tag{15}$$

The Schottky barrier Φ_B measures the degree of band bending in the semiconductor required to stabilize the Fermi level. That is, the Φ_B measures the work function mismatch *minus* the electrostatic stabilization provided by the interface dipole. From Eqs. (14) and (15) we conclude that

$$\Phi_B = (\phi_M - \phi_S)\left(\frac{1}{1 + 4\pi e^2(\delta_S + \delta_M)D_S(\epsilon_F)}\right). \tag{16}$$

The index of interface behavior S is empirically defined

$$S = \frac{d\Phi_B}{dE_M} = \frac{d\phi_B}{d\phi_M}\,\frac{d\phi_M}{dE_M}\,. \tag{17}$$

Here E_M is the metal electronegativity, and $d\phi_M/dE_M$ is empirically found to be ≈ 2.3. Thus,

$$S \approx 2.3/[1 + 4\pi e^2(\delta_S + \delta_M)D_S(\epsilon_F)]\,. \tag{18}$$

An interesting point should be emphasized here. Equation (15) and the empirical relation between ϕ_M and E_M involve *measured* metal work functions. These quantities implicitly contain the effects of the surface dipole associated with the clean-metal surface. The interface screening described by Eq. (18) thus refers to screening *exclusive* of that which would occur at either clean surface. To be more specific, one will generally find states in the semiconductor region with energies within the band gap. Some of these states are associated with the metal surface; that is, in the *absence* of the semiconductor, there is a nonzero "local" density of states within an angstrom or so of the surface in the same energy interval. These states give rise to the clean metal surface dipole. The states which enter the screening expression (15) are then truly interface-*induced* states, states exclusive of these clean metal-associated states. These induced states are characterized by the dangling-bond resonances discussed in Sec. V. These induced states are typically peaked on the semiconductor surface layer, and thus the decay length δ_S typically measures the screened length from the surface atoms to the edge of the metal.

One may alternatively formulate this problem and Eq. (15) in terms of an *internal* work function, which excludes the effect of the metal-surface dipole. For this case, Schlüter[14] has pointed out that $d\phi_M/dE_M \approx 2.8-3.0$. In this formulation, D_S would include screening from *all* states in the semiconductor band gap. For large ionicities (large χ in Fig. 6) the density of metal-surface-derived states *dominates* the density of gap states, and the typical decay lengths of these metal-associated states into the semiconductor is small (roughly 0.5 Å). Therefore, in this formulation one expects δ_S to decrease as a function of increasing ionicity; the system evolves from a covalent regime in which the dangling-bond-derived states (larger δ_S) dominate the interface screening to an ionic regime where one observes only the screening associated with the clean metal surface (shorter δ_S). Also in this formulation, the density of screening states falls off with semiconductor ionicity. Interestingly, since there is only roughly 20% change in the value for $d\phi_M/dE_M$ in the two definitions of ϕ_M, a simple superposition argument, requires that the screening *strength* $(\delta_S + \delta_M)D_S$ of Eq. (18) as calculated by either method will roughly agree.

Finally, we can use Eq. (18) to calculate S as a function of the ionicity parameter χ. As previously discussed, δ_M is taken to be ≈0.5 Å, δ_S assumed to be roughly 1.2 Å and independent of χ, and finally, $D_S(\epsilon_F)$ is taken from the data plotted in Fig. 6. In Fig. 7 we present the results for S as a function of χ. The plot shows two distinct regimes. In the covalent regime, where χ is negative, S is small and insensitive to χ. In the ionic regime, where χ is positive, S is observed to increase rapidly as a function of χ. This is due to the rapid separation of the dangling-bond states in this regime, a fundamental characteristic of the ionic class of gaps previously discussed. The transition from covalent to ionic behavior is characterized by the sign of χ.

The experimental data are also plotted on this curve. The dark circles are the original data of Kurtin, McGill, and Mead[5], the open circles are data due to a recent recompilation of the original experimental work by Schlüter.[14] We note reasonably good agreement between experiment and this interface model. The most glaring deviations from the model predictions occur for the Cd compounds, possibly attributable to the occurrence of interface bonds or atomic distortions at the interface. Such nonideal interface behavior in these compounds has been previously both suggested theoretically[8] and observed experimentally.[13]

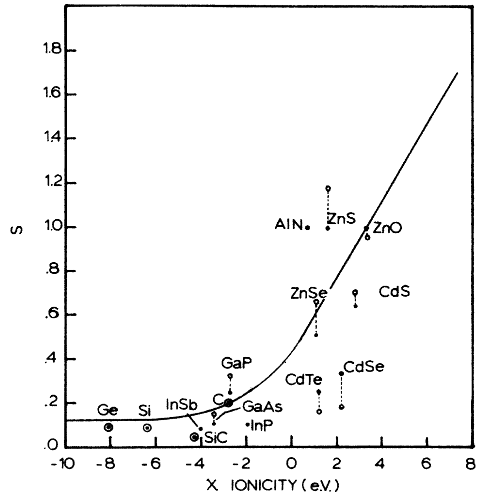

FIG. 7. Dependence at the index of interface behavior S on the semiconductor ionicity parameter χ. The theoretical values follow the dark curve. The filled and open circles are experimental values for S as explained in the text.

A very important prediction of the model is that C and SiC are expected to behave *covalently* at metal interfaces. This is interesting because both are large-gap materials with low polarizabilities. Their large gaps, however, are directly attributable to *short* bonding radii; the gaps are *covalent* in character. This requires a large density of dangling-bond-derived resonant states near the Fermi level in the presence of the metal overlayer. This, in turn, accounts for the covalent behavior of these substances at such interfaces. As shown, this result is in agreement with experimental measurements for metal interfaces to both diamond and SiC. We note however, that the measurement quoted for diamond has elicited some controversy involving the surface dielectric properties of the crystal.

VII. PARAMETER DEPENDENCE OF THE THEORY

This theory of these interfaces which has been developed in the previous sections involves no adjustable parameters; that is, no quantities are fit to the experimental interface data. However, the actual calculation of several quantities in the theory involves several *specific* physical assumptions, and it is important to see how these assumptions affect the final results. The most important of these assumptions involve the calculation of the resonant linewidth Γ, and the assumption that Γ is constant over a wide range of ionicities.

In Sec. V we estimated Γ with a first-order golden-rule calculation. There we assumed a jellium potential to describe the Al overlayer. The edge of the jellium potential was set a half bond length (1.2 Å) from the surface Si atoms. The effect of shifting the edge is given in Fig. 8. We see that as the overlayer is separated from the semiconductor Γ drops corresponding to the reduced strength of the perturbation matrix element in the configuration. Similarly Γ rises exponentially as the overlayer is brought into closer proximity to the surface atom. We estimate that errors in (a) the estimated position of the jellium edge, (b) the detailed modelled form of the jellium-edge potential (i.e., a square well), and (c) the modelled form assumed for the dangling-bond wave function would affect the estimate of Γ by less than 50%. That is, we expect values of Γ between 0.5 and 1.5 eV to be physically sensible for this calculation.

We have investigated the effects of variations of Γ on the estimates we have made for the densities of states at the Fermi level. The results are shown in Fig. 9. The curves on the left correspond to calculations of the densities of midgap states for the resonant widths shown. We see that as the values for Γ decrease, the values for the density of states increase in the covalent regime ($\chi < 0$), and decrease in the ionic regime ($\chi > 0$). The curves all cross between $\chi = -4$ eV and $\chi = 0$. The greatest sensitivity of the density of states on Γ occurs for the very covalent regime. Fortunately, for these very covalent systems, the density of midgap states is so large that S depends only *weakly* on the exact value of the density of states. That is, the variation observed in the density of states for covalent systems as a function of Γ is not large enough to *unpin* the Fermi level in these systems. This effect is shown in detail in Fig. 10 where we have plotted S as a function of ionicity χ, for various values of Γ. One sees essentially no significant variation in the character of these curves; and in fact very little quantitative deviation. As Γ decreases, the transition sharpens slightly and shifts to slightly more negative values of the ionicity parameters. This result shown in Fig. 10 is significant, since we see that *more detailed* calculations of the effect of the metal over-

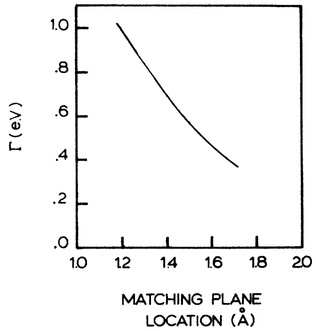

FIG. 8. Effect of shifting the jellium edge on the calculated resonant width Γ. A matching plane location of ~1.2 Å corresponds to placing the jellium edge a half bond length from the surface.

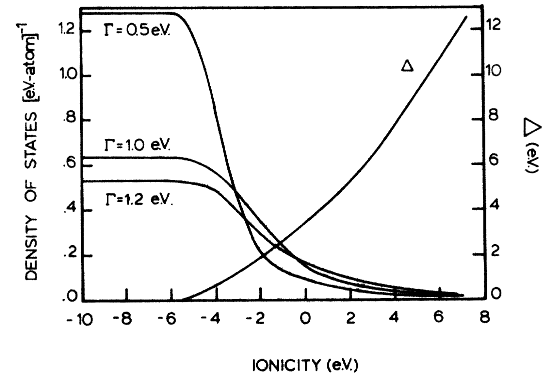

FIG. 9. (Right-hand scale) Δ, the separation of surface states in the optical gap as a function of ionicity; (left-hand scale) the density of midgap resonant states for several widths Γ as a function of ionicity. Note that significant changes occur only for the extremely covalent regime.

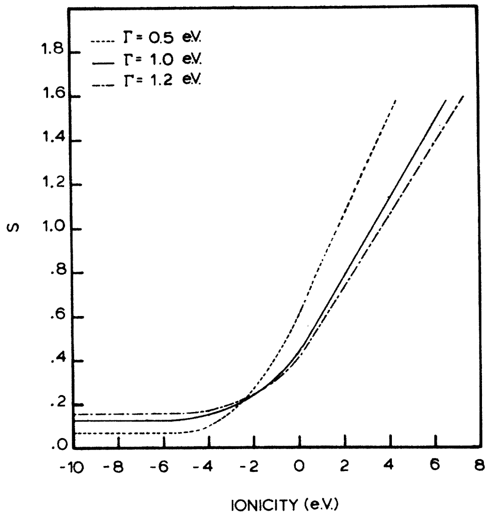

FIG. 10. Theoretical calculations of S vs the ionicity parameter χ for several resonant linewidths Γ. It is significant that the general trends (and, in fact, even the quantitative changes in S) are not extremely sensitive to Γ.

layer on the dangling-bond states will generally lead to the same conclusions about the changes in the index of interface behavior with ionicity.

VIII. SPECTROSCOPIC DATA

The earliest stages of Schottky-barrier formation at semiconductor surfaces have been experimentally studied in recent years. Direct information about metal-semiconductor surface and interface states have been obtained through partial-yield spectroscopy (PYS) and energy-loss spectroscopy (ELS). It is useful to compare these results and experimental conclusions with the model being proposed here.

Partial-yield spectroscopy of Pd overlayers on the (110) surfaces of III–V semiconductors by Eastman and Freeouf (EF) has provided an interesting result. They found that the Schottky-barrier pinning positions for these materials were correlated with the observed positions for the empty cation-derived states on the clean surface. These observations are complicated by excitonic shifts of the observed empty surface-state energies as well as a covalent reconstruction of the (110) surface in which the cations are displaced towards the bulk. The effect of the surface exciton is to lower the apparent energies of the cation dangling-bond states, casting doubt as to their connection with the eventual Schottky-barrier height. However, our interface model emphasizes the importance of these clean surface states for Schottky-barrier formation, although the connection is not direct as EF have proposed. We propose that the clean dangling-bond states are indeed altered by the metal overlayer, inducing a density of interface states at the Fermi level. However, our perturbative treatment of the metal adlayer implies that the clean surface-state energies are important in determining the density of interface-induced states at a Fermi level. In fact it is the rapid separation of the energies of the "dangling-bond" states with semiconductor ionicity for $\chi > 0$ which causes the marked increase in S as previously discussed.

Secondly, energy-loss spectroscopy studies of metal overlayers on Si(111), Ge(111), Ge(100), and GaAs($\overline{111}$) have been reported by Rowe, Christman, and Margaritondo (RCM).[11] On these surfaces ELS shows that metal overlayers remove (or substantially reduce) semiconductor surface-derived features and that states appear *at the same energy* as the clean semiconductor surface states, but on the metal adatoms. Note first of all that the absence of a (110) buckled reconstruction for these surfaces causes the surface atoms to interact more strongly with the metal adatoms. This stronger interaction implies a wider broadening, and hence the apparent strength of surface features localized on the semiconductor should be *signficantly reduced.* More importantly, the interaction between dangling bonds and metal adatoms will project some surface-state character onto the adsorbed metal atoms. This would account for the enhancement in the loss feature observed in ELS associated with transitions from the metal-core states. Note that these so-called "extrinsic" metal features are in fact *very well correlated* in energy with the *intrinsic semiconductor* surface-state energies. In fact, this correlation argues against any direct surface state to metal adatom chemical bonding which would result in bonding and antibonding states occurring elsewhere in the spectrum. Further, the ELS results for (110) surfaces show a persistence of some surface-cation-derived features in agreement with the structural reconstruction proposed to this surface.

Finally, ELS measurements on Al-CdSe and Al-CdS interfaces reported by Brillson[13] have yielded evidence of extrinsic gap states *not* correlated with intrinsic clean surface states. However, it has been noted that the Cd compounds deviate from the systematic increase of S with semiconductor ionicity, and presumably this observation could be the basis for this anomaly. Note that the presence of proper chemical bonds at the interface is not in the spirit of the linear interface theory presented here and elsewhere. (That is, occurrence of chemical "bonding" states in the gap would cause barrier heights to depend on the chemical nature of the adsorbed metal, even for a very covalent substrate.[9]) We attribute Fermi-level stabilization to interface-induced states, which *are* well correlated with intrinsic clean surface states, in the sense that their energies are important for the determination of the density of interface states. This simple model of interface interactions provides an interpretation of the enhancement of "surface" features in the adsorbed metal in ELS, the reduction in strength of surface features on the semiconductor surfaces in the presence of the metal, and the nature of the correlation of Schottky-barrier height with surface-state positions.

IX. RELATION TO PREVIOUS THEORETICAL WORK

The intriguing observation of Kurtin, McGill, and Mead has elicited a great deal of theoretical work in recent years. We should emphasize two principal novel features of our work.

First, an interesting feature of the covalent-ionic transition is that it occurs at such an apparently arbitrary value of the ionicity (see Fig.

2). Our treatment of band gaps in Sec. III shows that this critical ionicity corresponds to a fundamental transition in the substrate electronic structure. In fact, the transition is characterized by the sign of the ionicity parameter. Furthermore, the transition is so fundamental that it should be apparent in a number of semiconductor electronic properties.

Secondly, several other treatments have associated this transition with the size of the band gap. We note that there is *generally* a good correlation between larger gaps and more ionic behavior. However, for this reason the reported covalent behavior of large gap but covalent materials (C, SiC) is an important test for these interface models. Our work theoretically associates the compounds with their observed covalent character.

Thirdly, we should relate this work to the self-consistent pseudopotential[12] calculation for several interfaces by Louie, Chelikowsky, and Cohen. These calculations treat intimate Al-jellium–semiconductor contacts for several semiconductors. The idealized model we have proposed here provides a simple physical interpretation of their detailed calculation. We note generally good agreement between the two theories, but note a difference in our identification of "interface" screening states as detailed in Sec. VI.

X. EXTENSIONS OF THE THEORY

The interface theory, as presented in this paper, refers only to tetrahedrally coordinated semiconductor substrates. Here we briefly comment on the extension to *other* structures.

We generally define an ionic gap as one which depends strongly on the electronegativity difference of the constituent elements. When dangling-bond defects are present these gaps are characterized by defect states *near the gap edges.* As a direct consequence the defect-state separation depends *strongly* on the identity of the constituent elements. Furthermore, for *tetrahedrally coordinated* structures such "ionic" gaps occur for *positive* values of the ionicity parameter which we have defined. This is not necessarily true in other structures. For instance, the electron-rich III–VI layered structures involve little s-p hybridization, possess a gap which is ionic by the above definition, and in fact behave rather ionically at interfaces to metals. However, the ionicity parameter χ is negative for several of these compounds. This merely reflects that χ is an inappropriate index of ionicity for a geometry where sp_3 hybridization is irrelevant. One could, however, construct a similar scale to describe the covalent-ionic transition in these and other structures.

XI. SUMMARY

We have proposed a simple model for the formation of Schottky barriers at intimate metal-semiconductor contacts. This theory, while simple: (a) predicts the onset of an empirically observed transition in interface behavior; (b) characterizes the quantitative increase of S with semiconductor ionicity; (c) theoretically directly identifies this transition with a very fundamental transition in the electronic structure of the substrate, clarifying the nature of this covalent to ionic transition, and introduces an ionicity parameter to characterize this transition; (d) explains the covalent behavior of materials like C and SiC which possess large gaps, a trait commonly associated with ionic behavior at the interface; (e) provides a simple physical interpretation of some detailed self-consistent pseudopotential calculations at these interfaces; and (f) interprets several spectroscopic studies of these interfaces.

The principal shortcoming of the theory is that proper chemical bonding at the interface is not considered. Although we have pointed out that spectroscopic data for metal coverages with $\gtrsim 3$ overlayers argue *against* such bonds, they are probably important in the earliest stages of Schottky-barrier evolution (i.e., less than monolayer coverage), and their effect at such coverages may be a tractable theoretical problem.

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