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Formation of an electric dipole at metal-semiconductor interfaces

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The insensitivity of experimentally observed Schottky barrier height (SBH) to the metal work function, a phenomenon known as Fermi level pinning, has traditionally been attributed to the presence of interface states in the band gap of the semiconductor. A recent theory showed that the polarization of the chemical bonds at metal semiconductor interfaces could quantitatively account for the experimentally observed strength of Fermi level pinning on different semiconductors, without regard to the actual distribution of gap states. This bond polarization theory thus provides a coherent explanation of the Fermi level pinning effect, on the one hand, and the experimentally observed dependence of the SBH on interface structure, on the other hand. The method used in this theory, the electrochemical potential equalization method hitherto employed only in molecular physics, and its limitations are here discussed in detail, especially in the context of application to solid interfaces. Similarities and differences between this theory and the metal induced gap state theory are also discussed.

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I. INTRODUCTION

The formation mechanism of the Schottky barrier height (SBH) at metal-semiconductor (MS) interfaces has been a topic of much interest and debate.[1] There have been many proposals to explain how and why the experimentally observed SBH appears to be essentially independent of the metal work function on some semiconductors. This phenomenon, known as Fermi level (FL) pinning,[2] is usually attributed to the presence of interface states in the bandgap of the semiconductor. Various sources of gap states (GS) have been proposed, including surface states,[3] metal induced gap states (MIGS),[4–6] defect related states,[7–9] and disorder induced gap states (DIGS),[10] each with a slightly different distribution in the proposed density of gap states. However, irrespective of the exact origin of the gap states, these theories are all similar in their assumptions that the distribution of the gap states is a function of only the semiconductor and that the charge neutrality level (CNL) of the gap states essentially determines the SBH.[6,11,12] Because of these assumptions, gap state models predict that the SBH should have only a weak dependence on the metal work function and the structure of the MS interface. A much wider spectrum of experimental behavior has actually been observed concerning the SBH, than is compatible with these assumptions. Beside the FL pinning phenomenon, which gap state models are able to explain, a clear dependence of the SBH on the structure of single crystal MS interfaces has been experimentally observed[13,14] and theoretically demonstrated,[15–17] in apparent disagreement with the concept of gap states and CNL. The assumption that interface gap states depend only on the semiconductor has also been shown to lead to contradiction between the bias dependence of the SBH and the work function dependence of the SBH.[18] In addition, the ubiquitous observation of SBH inhomogeneity at polycrystalline MS interfaces[19,20] also supports the structure dependence of the SBH and runs afoul of the gap states models. If one accepts the notion that the SBH depends on the interface structure, then one needs to answer the question of “why the SBH, which depends so sensitively on the structure of epitaxial interfaces, should appear to assume nearly constant values for polycrystalline MS interfaces?” Recently, a coherent explanation of these seemingly conflicting observations emerged. A theory relating the interface dipole to bond polarization at MS interfaces was able to reproduce semiquantitatively the degree of FL pinning experimentally observed for different semiconductors.[21] Through its emphasis on the bonding at MS interfaces, this theory was also in good agreement with the structure-dependence of the SBH observed at single crystal interfaces and the SBH inhomogeneity observed at polycrystalline MS interfaces. The approach used in this bond polarization theory was an electrochemical potential equalization (ECPE) method[22–24] which has seen much application in the analysis of dipoles of small molecules, but has not previously been applied to the analysis of the electronic structure of crystal interfaces. It is the purpose of this paper to describe the principles and practices of this molecular method and, in particular, to address various issues concerning its application to solid interfaces. Since the SBH problem is, in its very essence, an electrostatics problem, we also include a short introduction on the relationship between bands and electric potential at an interface to lay the framework for subsequent discussion on the formation of the interface dipole. The motivation for the ECPE method, its application to MS interfaces, and its various consequences are discussed in detail. The success of the bond polarization theory in explaining the experimentally observed trends is demonstrated. Its limitations and its relationship with the CNL concept of interface gap states are also discussed.

II. ELECTROSTATIC POTENTIAL AND ENERGY BANDS AT METAL-SEMICONDUCTOR INTERFACES

The SBH of a p-type semiconductor $\Phi_{B,p}^{o}$ is the minimum energy required to excite an electron from the semiconductor valence band and place it across the MS interface at the Fermi level of the metal, as schematically shown in Fig. 1(a). When a semiconductor comes into contact with a metal, the wave functions of the two sides interact and new wave functions are formed in the immediate neighborhood of the inter-

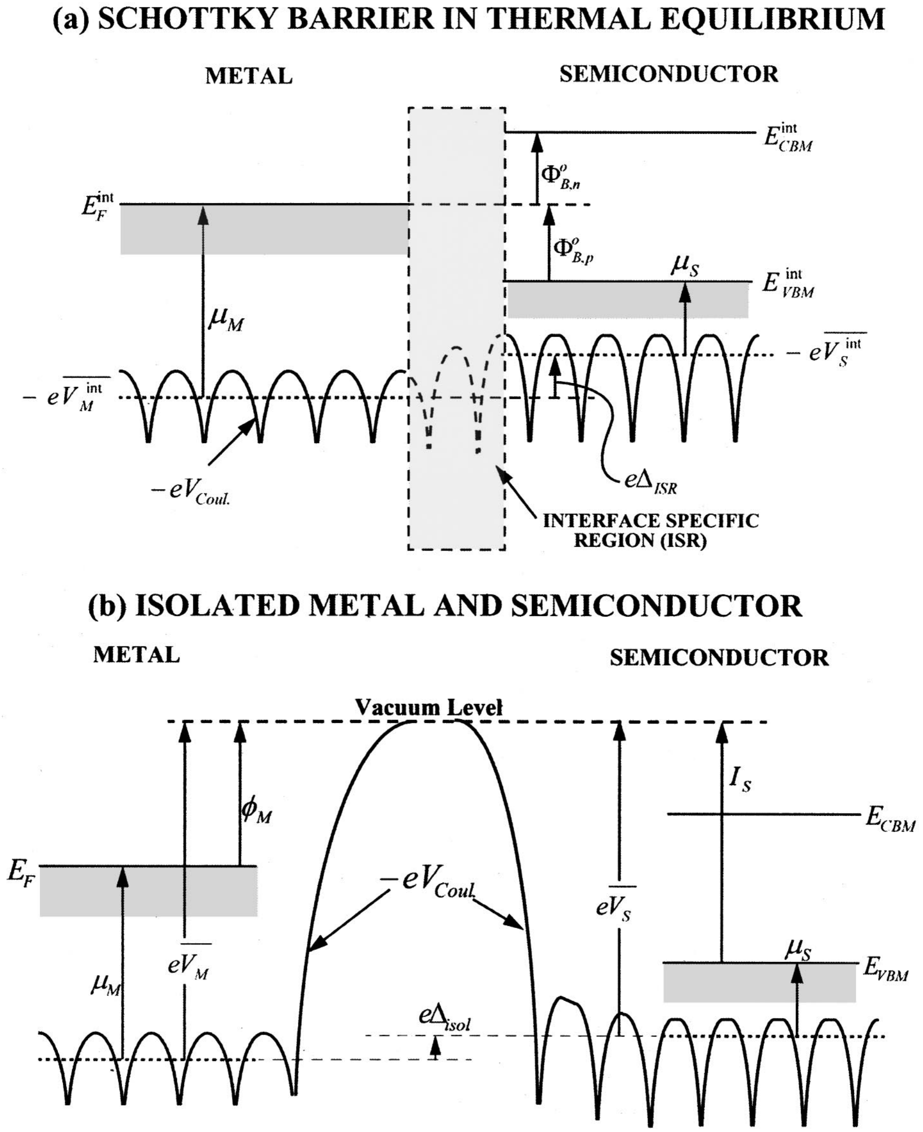

FIG. 1. (a) Energy band diagram and crystal potential distribution at a metal-semiconductor interface, showing the concept of an interface specific region. (b) Band diagrams and crystal potential distribution at the surfaces of isolated metal and semiconductor crystals.

face. For convenience, an interface specific region (ISR) can be imagined which serves as a transition region between the metal and the semiconductor. Within the ISR, the electronic states are neither purely semiconductorlike nor purely metallike, and are characteristic of the interaction between the metal and the semiconductor. The width of the ISR depends on the screening length, and is typically the length of a few lattice spacings for interfaces that are physically abrupt. This width can be much larger for diffuse interfaces. As schematically shown in Fig. 1(a), the bulk bands of the metal and the semiconductor are fully recovered outside the ISR. Also shown in Fig. 1(a) are the rapidly varying "crystal potential" $-eV_{\mathrm{Coul}}$, where V_{Coul} is the electrostatic potential and $-e$ is the electronic charge, and the long-range averages, $-e\overline{V}_M^{\mathrm{int}}$ and $-e\overline{V}_S^{\mathrm{int}}$, of the crystal potential in the metal and the semiconductor, respectively. The superscript "int" is to remind us that these quantities refer to the metal and the semiconductor which have already been joined at an interface. There are a few different proposals on what to use as a long-range potential for a crystal solid, and they differ only by a rigid shift. Here, we can imagine using something similar to the macroscopic averaging technique to obtain the per-cell average.[25] In an isolated bulk crystal, the energetic positions of the electronic bands are uniquely determined once the crystal potential is properly referenced. For a metal, one can define an internal chemical potential as[26]

$$\mu_M = E_F^{\mathrm{int}} + e\overline{V}_M^{\mathrm{int}}. \tag{1}$$

For a semiconductor, one can also define an "internal ionization energy" as

$$\mu_S = E_{\mathrm{VBM}}^{\mathrm{int}} + e\overline{V}_S^{\mathrm{int}}. \tag{2}$$

Note that μ_M and μ_S represent the bulk quantum mechanical contributions, i.e., kinetic energy and exchange-correlation energy, to the Fermi energy and the valence band maximum (VBM) state, respectively. Therefore, they are internal properties of the metal and semiconductor, respectively, and are independent of all interface/surface specifics. In other words, conditions $\mu_M = E_F + e\overline{V}_M$ and $\mu_S = E_{\mathrm{VBM}} + e\overline{V}_S$ hold in general and not just at MS interfaces. These internal quantities can be calculated to high precision, but they are not physically measurable.[27,28] On either side of the ISR, the energetic positions of the bulk bands are completely determined once the (average) crystal potential is known, and vice versa. The electrostatic potential is governed by Poisson's equation and is continuous throughout all space. Its continuity inside the ISR imposes an important constraint on how the two sets of bulk bands on opposite sides of the ISR should line up. The difference between the averaged electric potential across the interface, $e\Delta_{\mathrm{ISR}}=e\overline{V_M^{\mathrm{int}}}-e\overline{V_S^{\mathrm{int}}}$, is sometimes referred to as the interface dipole. However, many different definitions exist for the "interface dipole" and care should be exercised to distinguish them. Because $e\Delta_{\mathrm{ISR}}$ in general depends on the local atomic and electronic structure of the interface, it likely varies laterally at nonepitaxial MS interfaces. Combining Eqs. (1) and (2), one gets

$$\Phi_{B,p}^{o}=E_F^{\mathrm{int}}-E_{\mathrm{VBM}}^{\mathrm{int}}=\mu_M-\mu_S-e\Delta_{\mathrm{ISR}}, \tag{3}$$

which shows that whenever $e\Delta_{\mathrm{ISR}}$ varies, the SBH also varies by exactly the same amount. From Eq. (3), the SBH can be expressed as the sum of $-e\Delta_{\mathrm{ISR}}$ and terms that are related only to the bulk crystals and not the interface. Therefore, as far as the magnitude of the SBH is concerned, the only relevant input from the ISR is $e\Delta_{\mathrm{ISR}}$, which depends on the charge distribution of the entire ISR and not on the electron energy levels *per se*. Note that the fact that the average crystal potential is drawn flat on either side of the ISR in Fig. 1(a) implies that the ISR has no net charge. In general, this is only approximately true, because a small long-range electric field and band bending, negligible on the atomic length scale of Fig. 1(a), may be present in the semiconductor. So, the ISR could have a small net charge, which has been shown not to have a significant effect on $e\Delta_{\mathrm{ISR}}$, through the experimental observation of the independence of the SBH on the semiconductor doping level.[29] From Eq. (3), it is clear that the SBH is directly related to the interface dipole, but is essentially independent of the net interface charge.

The SBH at a MS interface, similar to the band offset at a semiconductor heterojunction and the work function at a free surface, represents a mismatch of certain energy levels across an interface. A popular approach to the analysis of such energy barrier problems has been to place the (bulk) energy levels from both sides of the interface on one absolute and universal energy scale.[30–32] The difference in the energy levels on this scale can be regarded as a pure bulk contribution, which can then be corrected for additional chemical effect at the interface. Since the *p*-type SBH is the energy difference between the Fermi level of the metal and the VBM of the semiconductor, a comparison of these two levels in their respective, isolated, crystals, as shown in Fig. 1(b), has often been used as a reasonable starting point, i.e., a "baseline condition." As shown in Fig. 1(b), this energy difference before the metal and the semiconductor come into contact is

$$E_F-E_{\mathrm{VBM}}=I_S-\phi_M \quad \text{(isolated crystals)} \tag{4}$$

$$=\mu_M-\mu_S-e\Delta_{\mathrm{isol}}, \tag{5}$$

where I_S is the ionization potential of the semiconductor, ϕ_M the work function of the metal, and $e\Delta_{\mathrm{isol}}$ is the difference in the average crystal potentials of the two isolated solids $(e\Delta_{\mathrm{isol}}=e\overline{V_M}-e\overline{V_S})$. If the charge distributions on the two isolated surfaces remain "frozen" when the metal makes contact with the semiconductor, the difference in the average electrostatic potential also remains unchanged because of the principle of superposition. Therefore,

$$e\Delta_{\mathrm{ISR}}=e\Delta_{\mathrm{isol}} \quad \text{(frozen charge)}. \tag{6}$$

Combining Eqs. (3)–(6), one gets

$$\Phi_{B,p}^{o}=I_S-\phi_M \quad \text{(frozen charge)} \tag{7}$$

which is simply the result predicted by the Schottky-Mott model. Because of its frozen-charge assumption, the Schottky-Mott model assumes no MS interaction. An obvious drawback of any noninteracting model is that the expected rearrangement of charge density (and atomic positions) at the interface, which is required by thermodynamics, has been ignored. Even though it may seem less than realistic, the Schottky-Mott model has the advantage that the electrostatic potential is guaranteed to be continuous across an MS interface. Because of this mechanical soundness, the Schottky-Mott condition has served as a convenient baseline to which chemical effects can be added, as in Eq. (9) below, without the fear of violating Poisson's equation.

III. ANALYSIS OF EXISTING SCHOTTKY BARRIER THEORIES

Excluding the latest work on chemical bonding, theories on SBH can be roughly categorized into four groups: noninteracting models, empirical models, *ab initio* calculations, and CNL-based models. Noninteracting models, including the Schottky-Mott theory and the effective work function model,[33,34] essentially ignore any interface interaction, as already discussed. At real MS interfaces, some charge relaxation has to take place, invalidating Eqs. (6) and (7). The net dipole $e\Delta_{\mathrm{Sch}}$, due to the charge rearrangement can be written down from a comparison of Eqs. (3) and (5) as

$$e\Delta_{\mathrm{Sch}}=e\Delta_{\mathrm{ISR}}-e\Delta_{\mathrm{isol}}. \tag{8}$$

Therefore, when the effect of charge rearrangement at the interface is taken into consideration, the SBH is modified from the Schottky-Mott condition to

$$\Phi_{B,p}^{o}=I_S-\phi_M-e\Delta_{\mathrm{Sch}}. \tag{9}$$

The term $e\Delta_{\mathrm{Sch}}$, which is sometimes referred as the interface dipole, and is here called "Schottky dipole" to avoid confusion with other definitions of the interface dipole. This term represents the dipole contribution from the thermodynamic effect, or the chemical effect, associated with the formation of the interface. Different SBH models essentially differ in how they account for $e\Delta_{\mathrm{Sch}}$ at MS interfaces. Empirical correlations of the experimental SBH, including those found with a constant fraction of the bandgap,[2] the heat of formation,[35,36] anion electronegativity,[37] semiconductor ionicity,[38] eutectic temperature,[39] etc., usually have no spe-

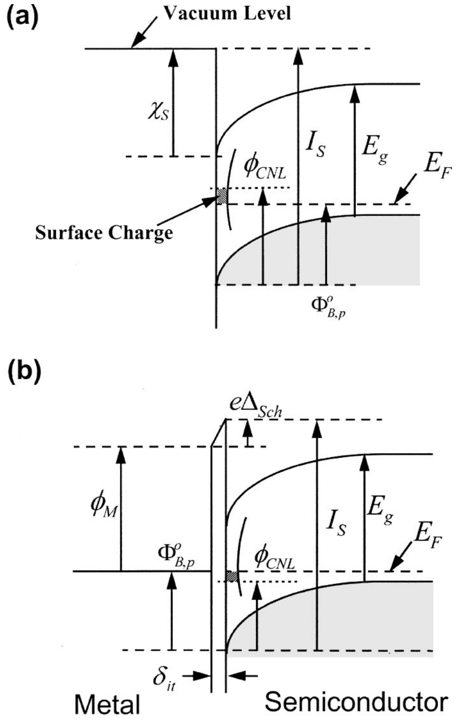

FIG. 2. (a) Band diagram at the surface of a p-type semiconductor with a density of surface states. (b) Band diagram, according to the fixed-separation model of interface gap states, at a metal-semiconductor interface. The shaded areas in (a) and (b) represent the surface charge and the interface charge, respectively.

cific proposals for the formation of $e\Delta_{\mathrm{Sch}}$. Therefore, they tend to be only of limited use to the development of a comprehensive SBH picture. Ab initio calculation is the ultimate method to calculate SBH values.[15,17,25,40–42] However, because the results are numerical solutions, the physics of the SBH formation mechanism is usually buried in the complicated details of the calculated electronic structure. Ab initio calculations can only be performed on simple epitaxial interface structures, and are not expected to be of much help for polycrystalline MS interfaces, which comprise the bulk of the SBH literature.

Theoretical models based on the concept of the CNL of interface gap states have been the most active and popular theories invoked to interpret experimental SBH results in general and the FL pinning effect in particular.[3,6,11,12,43,44] The basic idea of the CNL concept is quite simple and is best illustrated at a free surface, as shown in Fig. 2(a). A distribution of surface-specific states is assumed to be present at the surface and often a substantial density of these states is found in the band gap of the semiconductor. The net charge due to the occupation of the surface states is determined by the position of the Fermi level at the surface, as schematically represented by the hatched area in Fig. 2(a). The charge neutrality level of the surface states is defined as that energetic position which, when coincides with the FL position, would yield zero surface charge. In the absence of an external electric field, the total surface charge is equal in magnitude but opposite in sign to the total charge of the depletion region. Therefore, the presence of surface states can help pin the Fermi level near the CNL, i.e., $\Phi^o_{B,p} \approx \phi_{\mathrm{CNL}}$, where ϕ_{CNL} is the difference between the CNL and the VBM. How strongly the surface Fermi level is pinned depends on the density of the surface states. The difference between the Fermi level position and the CNL is usually quite small. For example, this difference is only $\sim$10 meV, for a surface with moderate surface state density ($\sim 10^{13}\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$) and doping level ($\sim 10^{15}\,\mathrm{cm}^{-3}$).

The concept of CNL is clearly a sound physical basis for the analysis of the surface Fermi level position with respect to the semiconductor band edges, which is essentially a problem related to the net surface charge. However, the applicability of the CNL concept to interface dipole problems is not immediately apparent. For example, in Fig. 2(a), I_S, being the difference between the VBM of the semiconductor and the lowest energy level of the vacuum, can be regarded as an offset between bands across the semiconductor-vacuum interface. But I_S is related to the surface dipole and does not have an explicit dependence on the net charge stored in surface states. By analogy, the CNL concept may not be directly applicable to the problems of the SBH and the heterojunction band-offset, because both of these problems are essentially ‘‘dipole’’ problems rather than ‘‘Fermi level’’ (net charge) problems. The CNL concept, nevertheless, has been proposed to have a dominant effect on the formation of the SBH and the heterojunction band-offset.[6,12,45] Before we get into the mechanical models of the CNL, it should be pointed out that the CNL is not the neutrality level for the entire interface region, i.e., the ISR. Rather, the CNL refers to that of only the ‘‘semiconductor side’’ of the interface. For this definition to be meaningful, one needs to be able to separate the ISR into two parts, one belonging to the metal and the other belonging to the semiconductor. But, in general, the dissection of the ISR charge distribution into two halves is arbitrary. So, the definition of the CNL is also inherently ambiguous. Note that, in comparison, it is straightforward to identify or calculate a net interface dipole from the actual charge distribution inside the ISR, because for this purpose the charges do not need to be distinguished as to which side of the interface they belong.

There are two different ways to model the interface dipole within the CNL concept. In the first model, which will be called the ‘‘fixed-separation model,’’ the net charge resulting from the gap states is assumed to be positioned at a fixed distance δ_{it} away from the metal.[43,45,46] The dipole formed from this charge and its image charge in the metal is then regarded as the Schottky dipole, $e\Delta_{\mathrm{Sch}}$, at the interface, as shown in Fig. 2(b). The fixed-separation model was envisioned in early SBH studies where an interface dielectric layer was assumed to be present.[43] It is still regularly invoked to analyze SBH even for intimate MS interfaces. With a constant density, D_{gs}, of gap states present near the CNL, the Schottky dipole can be read off of Fig. 2(b) as

$$e\Delta_{\mathrm{Sch}} = \frac{e^2 D_{\mathrm{gs}} \delta_{it}}{\varepsilon_{it}} (\Phi^o_{B,p} - \phi_{\mathrm{CNL}}), \tag{10}$$

where ε_{it} is the permittivity of the interface region, and where we have ignored the space charge of the semiconductor. Because of the explicit dependence of the Schottky dipole on the magnitude of the (final) SBH, this term behaves like a negative feedback, to dampen changes in the metal work function. With the help of Eq. (9), one gets

$$\Phi_{B,p}^{o}=I_S-\phi_M+\frac{e^2D_{\mathrm{gs}}\delta_{it}}{\varepsilon_{it}}(\phi_{\mathrm{CNL}}-\Phi_{B,p}^{o}). \tag{11}$$

Rearranging terms in Eq. (11), one gets

$$\Phi_{B,p}^{o}=\gamma_{\mathrm{gs}}(I_S-\phi_M)+(1-\gamma_{\mathrm{gs}})\phi_{\mathrm{CNL}}, \tag{12}$$

where γ_{gs} is the gap states parameter, given by

$$\gamma_{\mathrm{gs}}=\left(1+\frac{e^2\delta_{it}D_{\mathrm{gs}}}{\varepsilon_{it}}\right)^{-1}. \tag{13}$$

The theoretical prediction γ_{gs} of the fixed-separation model is equivalent to the "interface behavior parameter" $S_\Phi=-(\partial\Phi_{B,p}^{o}/\partial\Phi_M)$ experimentally observed. Different symbols are used here to distinguish their origins. The use of the same set of parameters $(D_{\mathrm{gs}},\phi_{\mathrm{CNL}})$ of the gap states to analyze interfaces formed with different metals underscores a basic assumption of the fixed-separation model, that the distribution of interface gap states, whether these are MIGSs, defect states, or DIGSs in nature, is essentially an innate property of the semiconductor and does not depend on the metal.[6,11] Without this assumption, Eqs. (12) and (13) would still be valid for a given MS system, but they would be useless for systematic SBH data analysis, because for each MS interface a new set of parameters would be required. In cases where the source of the gap states is assumed to be MIGS, the density of the MIGS can be estimated from the complex, one-dimensional band structure of the semiconductor,[45] which leads to

$$\frac{1}{\gamma_{\mathrm{gs}}}-1\propto\left(\frac{\varepsilon_\infty}{\varepsilon_o}-1\right)^2, \tag{14}$$

where $\varepsilon_\infty/\varepsilon_0$ is the optical dielectric constant of the semiconductor. Equation (14) has found some agreement with experimental results,[45,47] as shown in Fig. 4(b) below. As can be seen from Eq. (13), the higher the density of the gap states, the more tightly the Fermi level is pinned. Also from Eq. (13), a larger ε_{it} leads to less pinning. This is an expected result, since the dielectric screening reduces the Schottky dipole and, therefore, weakens the tendency for the Fermi level to be pinned.

An entirely different view is expressed in the second model, here referred to as the "division-by-epsilon" method, concerning how the CNL could lead to Fermi level pinning. It has been argued that the initial difference between the CNL of the semiconductor and the Fermi level of the metal is simply reduced by a factor of the dielectric constant of the semiconductor, or some other appropriate dielectric constant (e.g., $\varepsilon_{it}/\varepsilon_o$), when thermal equilibrium is reached.[12,48] Mathematically, this means

$$\Phi_{B,p}^{o}-\phi_{\mathrm{CNL}}=(I_S-\phi_M-\phi_{\mathrm{CNL}})\frac{\varepsilon_o}{\varepsilon_{it}}. \tag{15a}$$

The left-hand side of Eq. (15a) is the final difference between the E_F and the CNL, while the quantity in the parenthesis is the initial difference. Rearranging Eq. (15a), one gets

$$\Phi_{B,p}^{o}=(I_S-\phi_M)\frac{\varepsilon_o}{\varepsilon_{it}}+\phi_{\mathrm{CNL}}\frac{\varepsilon_{it}-\varepsilon_o}{\varepsilon_{it}} \tag{15b}$$

and

$$e\Delta_{\mathrm{Sch}}=(\phi_M-I_S+\phi_{\mathrm{CNL}})\frac{\varepsilon_{it}-\varepsilon_o}{\varepsilon_{it}}. \tag{15c}$$

From Eq. (15b), it is seen that the Fermi level would be more tightly pinned, if dielectric screening were to increase. Such a dependency is contradictory to the fixed-separation model of gap states. As shown in the Appendix, the fixed-separation model is in agreement with the chemical potential equalization method, which is based on the minimization of the total energy. The basis for the division-by-epsilon model is largely unknown. One notes, simply from the functional form of Eq. (15a), a curious feature of the division-by-epsilon model. Since the quantities I_S, ϕ_M, and, likely, ϕ_{CNL} all contain bulk quantum mechanical contributions and kinetic energy terms, the fact that these terms are also electrically screened seems to contradict our usual understanding of dielectric screening. The combination of chemical and screening effects at MS interfaces leads to chemical trends in general agreement with that predicted by the division-by-epsilon model, as shown in Fig. 4(c) below. Numerical agreement between theory and experiment is not great, however.

IV. POLARIZATION OF CHEMICAL BONDS IN MOLECULES

When an MS interface is formed in thermodynamic equilibrium, chemical bonds are established at the interface. All the electronic properties of the MS interface, including the formation of the electric dipole and the SBH, are the direct result of these interface bonds. However, the study of the electronic structure across any hetero-structured interface is a complicated problem. Topics of this type used to be investigated exclusively through calculations performed in reciprocal space, which is limited to structures which are ordered and periodic. This past decade has seen a clear movement toward studying the electronic structure of materials in real space.[49,50] The phase stability and the electronic and optical properties of solids and molecules have generally found qualitative, or even semi-quantitative, agreement with the simple tight-binding picture of the formation of chemical bonds. The real-space approach is particularly important for MS interfaces where the structure is usually nonepitaxial and essentially random. Furthermore, at a polycrystalline MS interface, the bonding geometry likely changes from place to place, leading to a locally varying interface dipole. The measured SBH then reflects some weighted average of this interface dipole. To explain experimentally observed SBH thus requires some averaging of the electronic structure in real space. All of these conditions suggest the use of properties associated with the individual MS bonds to model the properties of the interface as a whole. In that respect, the methodology and philosophy used by chemical physicists to analyze chemical bonds of small molecules are expected to shed light on the SBH problem at hand. Chemical bonding has long been recognized to be important for the formation of the SBH,[35,36,51] but until very recently,[21] no attempt was made to relate the chemical bonds to the interface dipole in any quantitative way.

There are a few methods of estimating the dipole moment of a molecule. In the simplest case of a heteronuclear diatomic molecule with *s*-valence orbitals, the most intuitive way to calculate the dipole moment is to approximate molecular orbitals by a linear combination of atomic orbitals (LCAO). Relevant to the relative weight of the bonding molecular orbital are the difference in the orbital energies for the individual atoms ΔE and the bond integral β which is negative for *s* electrons. It has been shown that,[50] for a total bond order of 1, the charge transferred from the atom with the higher energy level (atom *A*) to the atom with a lower energy level (atom *B*) is

$$Q_B=\frac{x^2+x(1+x^2)^{1/2}}{1+x^2+x(1+x^2)^{1/2}}=x-x^3+\cdots, \qquad (16)$$

where $x\,(=\Delta E/|\beta|)$ is the normalized atomic energy-level mismatch and Q_B is the number of excess electrons on atom *B*. In the case of a small energy difference in the original atomic levels, the total charge transferred from *A* to *B* is simply $-ex$ and the dipole moment is exd_{AB}, where d_{AB} is the interatomic distance for the *AB* molecule.

A second method which allows all the atomic charges of a large molecule to be estimated simultaneously is the ECPE method.[22–24,52,53] This is the method which has been briefly described in a recent publication.[21] In this scheme, the molecular energy is approximated as a second order Taylor expansion about the neutral atoms. The energy of the *i*th atom in a molecule is[22]

$$E_i(Q_i)=E_i^o+U_iQ_i+\tfrac{1}{2}Y_iQ_i^2+\cdots, \qquad (17)$$

where E_i^o is the ground state energy for the neutral atom, $-eQ_i$ is the net charge, and U_i and Y_i are, respectively, the first and second derivative of the energy of the atom with respect to Q_i, i.e., $U_i=(\partial E_i/\partial Q_i)_{Q_i=0}$ and $Y_i=(\partial^2E_i/\partial Q_i^2)_{Q_i=0}$. For an isolated atom, U_i and Y_i are actually ill-defined because strictly speaking, the energy is only defined for integral Q_i's and is not differentiable around $Q_i=0$. However, within the spirit of the density functional theory,[24,54] and using an ensemble average of the various configurations,[55] these quantities have been argued to be meaningful. Analyses show that U_i is the Mulliken electronegativity ($U_i=\chi_i/2+I_i/2$, where χ_i and I_i are, respectively, the electron affinity and the ionization potential of the atom) and Y_i is the hardness[22,56] of the isolated atom ($Y_i=I_i-\chi_i$). The total energy of a molecule is then the sum of the energies of the individual atoms and the interactions between them. Representing the off-diagonal elements of the hardness matrix with only Coulombic interactions, one writes

$$E_{\text{tot}}(Q_1,Q_2,\ldots,Q_N)=\sum_i^N\left(E_i^o+U_iQ_i+\frac{1}{2}Y_iQ_i^2\right)+\sum_{i\neq j}^N\frac{Q_iQ_jJ_{ij}}{2}, \qquad (18)$$

where J_{ij} is the Coulombic interaction between one electron located at atomic positions *i* and another at the position of the *j*th atom, i.e., $J_{ij}=e^2/(4\pi\varepsilon_o d_{ij})$, where d_{ij} is the distance between these two atoms. In thermal equilibrium, the net charge on each atom will be such that the total energy of Eq. (18) is minimized, while the overall neutrality is maintained, i.e., $\Sigma Q_i=0$. Such a problem is typically solved by Lagrange's undetermined multipliers method, with the "local" electrochemical potential playing the role of the multiplier. By requiring the electrochemical potential for every atom of the molecule to be constant, a set of *Q*'s can be obtained which automatically minimizes the total energy. This method has been shown to predict the correct trend of the observed electric dipoles in molecules. Since the included interaction contains no dipolar or higher-order terms, this method obviously applies only to the situation where the charge on each individual atom is centered on its nucleus. In reality, the electric dipole in molecules can be much more complicated.[23,24,57,58] Additionally, the division of molecular charge distribution into individual atoms can be ambiguous.[58] Its faults notwithstanding, this method is simple and has a sound basis. Its use in the study of MS interfaces is adequate, since one is only interested in explaining the systematic trend of the SBH, rather than determining accurate numerical values for individual SB systems.

V. BONDS AND DIPOLES AT METAL-SEMICONDUCTOR INTERFACES

The charge rearrangement in the ISR of a MS interface is obviously driven by the minimization of interface energy. The bond polarization theory assumes that the most significant charge rearrangement, when a metal comes into contact with a semiconductor, is due to the formation of chemical bonds between the metal and the semiconductor. So the Schottky dipole is assumed to arise from the polarization of interface bonds, which can be estimated by chemical methods described above. Within the simple picture of charge transfer, Eq. (16), one can assume a uniform density N_B of chemical bonds, each with a dipole of exd_{MS}, to be present at a MS interface. Here d_{MS} is the distance between metal and semiconductor atoms at the interface. The electrostatic potential changes by $N_Bexd_{\text{MS}}/\varepsilon_{it}$ across such a dipole layer, and therefore Eq. (9) becomes

$$\Phi_{B,p}^o=I_S-\phi_M+\frac{e^2xN_Bd_{\text{MS}}}{\varepsilon_{it}}. \qquad (19)$$

One recalls that *x* is related to the difference in atomic orbital energies. Its use does not seem appropriate at the MS interface, considering the fact that the atoms involved in the interface bonds are already bonded in their respective crystals. Thus, one can conceivably substitute ΔE with some other parameter that reflects more appropriately the energy mismatch in the highest occupied states across the MS interface. In that respect, the difference between the Fermi level of the metal and the CNL of the semiconductor might take the place of ΔE. Making the switch of $x \rightarrow (\phi_M - I_S + \phi_{\mathrm{CNL}})/|\beta|$ in Eq. (19), one sees that interface bond polarization leads to the expected Fermi level pinning effect

$$\Phi^o_{B,p} = \gamma_B (I_S - \phi_M) + (1-\gamma_B)\phi_{\mathrm{CNL}}, \tag{20}$$

where

$$\gamma_B = 1 - \frac{e^2 N_B d_{\mathrm{MS}}}{\varepsilon_{it}|\beta|}. \tag{21}$$

Equation (20) has the same functional form as that predicted by models of interface gap states, Eq. (12). However, it is not very useful for comparisons with experimental results, because the bond integral β is specific to each MS system. Furthermore, the assumptions on *s*-valence electrons and noninteracting dipoles in this approach are not very realistic. Despite these shortcomings, the chemical trend suggested by Eq. (20) is still a valid one. It is interesting to note that here the Fermi level pinning would be weakened if the dielectric screening ε_{it} were to increase. Such a dependency is in good agreement with the general concept of screening, namely, screening acts in a direction that counters the effect of charge transfer. The charge transfer itself is driven by chemistry, not screening.

To apply the ECPE method to estimate the Schottky dipole at an MS interface, one can regard the entire metal-semiconductor region (ISR) as a giant "molecule."[21] A few planes of atoms each from the semiconductor and metal lattices are included in this molecule, consisting a total of N_M metal atoms and N_S semiconductor atoms. The MS interface is assumed to be atomically abrupt and the two truncated lattices are assumed to form a density of chemical bonds N_B on an atomically flat interface plane, as schematically shown in Fig. 3. In general, N_B need not equal, and is likely less than, the total number of semiconductor (or metal) atoms per unit area of the interface. Lattice mismatch, structure incompatibility, the formation of tilted bonds, etc., all tend to reduce the number of effective bonds formed across an MS interface. To simplify the problem, one assumes that the semiconductor is either an elemental semiconductor or, in the case of a compound semiconductor, consisted of hybrid atoms, i.e., atoms which possess the traits of the compound rather than the individual (anion and cation) atoms. Without loss of generality, one assumes chemical bonds to form in a square array with a lateral dimension of $d_B\,(=N_B^{-1/2})$. The total energy for the ISR can be written down as

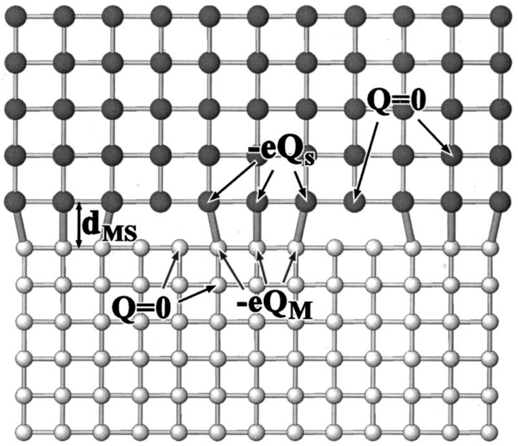

FIG. 3. A cross-sectional view of the model of a metal-semiconductor interface, used in the bond polarization theory. A number of bonds, drawn as thick bars, are assumed to form between the semiconductor (upper half) and the metal (lower half). Charge transfer is assumed to occur only between atoms directly involved in the interface bonds.

$$\begin{aligned} E_{\mathrm{ISR}}(Q_{M_1},\ldots,Q_{M_{N_M}},Q_{S_1},\ldots,Q_{S_{N_S}}) &= \sum_i^{N_M}\left(E^o_M + U_M Q_{M_i} + \frac{1}{2}Y_M Q^2_{M_i}\right) \\ &\quad + \sum_i^{N_S}\left(E^o_S + U_S Q_{S_i} + \frac{1}{2}Y_S Q^2_{S_i}\right) + \sum_{i\neq j}^{N_M}\frac{Q_{M_i}Q_{M_j}J_{M_iM_j}}{2} \\ &\quad + \sum_{i\neq j}^{N_S}\frac{Q_{S_i}Q_{S_j}J_{S_iS_j}}{2} + \sum_{i,j}^{N_M,N_S} Q_{M_i}Q_{S_j}J_{M_iS_j}. \end{aligned} \tag{22}$$

The boundary condition for the ISR naturally requires all Q_{M_i}'s and Q_{S_j}'s to be zero on the extreme outside atomic planes of the ISR. Taking that condition to the limit, we shall assume Q's to be nonzero only for those metal and semiconductor atoms on the immediate interface planes which are directly involved in the bonding (see Fig. 3). Then, from symmetry, each metal atom involved in the bonding contains the same net charge of $-eQ_M$, and every semiconductor atom involved in the bonding contains a net charge of $-eQ_S\,(=+eQ_M)$. As will be discussed, this approximation turns out to be necessary for the use of the electrochemical potential equalization method at MS interfaces. In thermal equilibrium, the electrochemical potential of every atom in the ISR should be equal. The electrochemical potential for a metal atom taking part in the bonding is

$$\begin{aligned} \left.\frac{\partial E_{\mathrm{ISR}}}{\partial Q_{M_i}}\right]_{\mathrm{interface}} &= U_M + Y_M Q_M \\ &\quad + \sum_{n_x,n_y}^{\text{excl. } n_x=n_y=0} \frac{e^2 Q_M}{4\pi\varepsilon_{it} d_B\sqrt{n_x^2+n_y^2}} \\ &\quad + \sum_{n_x,n_y=-\infty}^{\infty} \frac{e^2 Q_S}{4\pi\varepsilon_{it}\sqrt{d^2_{MS}+d^2_B(n_x^2+n_y^2)}}. \end{aligned} \tag{23}$$

The third and fourth terms on the right of Eq. (23) are, respectively, the Coulomb terms due to metal and semiconductor atoms. Keeping only the interactions between charged atoms that are nearest neighbors, these two terms can be simplified to give

$$\left.\frac{\partial E_{\mathrm{ISR}}}{\partial Q_{M_i}}\right]_{\mathrm{interface}} \approx U_M + Y_M Q_M + J_{\mathrm{MS}} Q_S + 4J_{\mathrm{MM}} Q_M, \tag{24}$$

where $J_{\mathrm{MS}}[=e^2/(4\pi\varepsilon_{it}d_{\mathrm{MS}})]$ and $J_{\mathrm{MM}}[=e^2/(4\pi\varepsilon_{it}d_B)]$ are, respectively, the interaction for the bonded metal-semiconductor pair and the metal-metal interaction along the interface plane. The numerals in Eq. (24) reflect the fact that for each metal atom at the interface, there are four metal nearest neighbors and one semiconductor nearest neighbor that are charged. Similarly for a semiconductor atom bonded with metal at the interface, the electrochemical potential is

$$\left.\frac{\partial E_{\mathrm{ISR}}}{\partial Q_{M_i}}\right]_{\text{interface}} = U_S + Y_S Q_S + \sum_{n_x,n_y}^{\text{excl. } n_x=n_y=0} \frac{e^2 Q_S}{4\pi\varepsilon_{it} d_B\sqrt{n_x^2+n_y^2}} + \sum_{n_x,n_y=-\infty}^{\infty} \frac{e^2 Q_M}{4\pi\varepsilon_{it}\sqrt{d_{\mathrm{MS}}^2 + d_B^2(n_x^2+n_y^2)}} \quad (25)$$

$$\approx U_S + Y_S Q_S + J_{\mathrm{MS}} Q_M + 4 J_{\mathrm{SS}} Q_S, \quad (26)$$

where $J_{\mathrm{SS}} = J_{\mathrm{MM}}$. Equating Eqs. (24) and (26) and setting $Q_M = -Q_S$, one obtains

$$Q_S = \frac{U_M - U_S}{Y_S + Y_M - 2J_{\mathrm{MS}} + 4J_{\mathrm{MM}} + 4J_{\mathrm{SS}}}. \quad (27)$$

In the spirit of analyzing charge transfer between two crystals, rather than between atoms, one can let the atoms acquire bulk characteristics. For a bulk metal, the ionization potential and the electron affinity are both identified as the work function of the metal ϕ_M. Thus, $U_M = \phi_M$ and $Y_M = 0$. For a semiconductor, the ionization potential I_S and the electron affinity χ_S differ by its band gap E_g. Therefore, $U_S = I_S - E_g/2$ and $Y_S = E_g$. Also, to account for the fact that the Coulombic interactions take place inside a solid rather than in free space, screening by the respective dielectric medium is also assumed. Equation (27) becomes

$$Q_S = \frac{I_S - \phi_M - E_g/2}{E_g + \kappa}, \quad (28)$$

where κ is the sum of all the hopping interactions, i.e.,

$$\kappa = 4J_{\mathrm{SS}} + 4J_{\mathrm{MM}} - 2J_{\mathrm{MS}}. \quad (29)$$

As will be shown, κ is usually a negative quantity. However, because dielectric screening at the interface is strong, the absolute value of this term is usually smaller than the band gap of typical semiconductors. This interface charge transfer leads to a potential drop of

$$\Delta_{\mathrm{Sch}} = \frac{eQ_S N_B d_{\mathrm{MS}}}{\varepsilon_{it}} = \frac{eN_B d_{\mathrm{MS}}(I_S - \phi_M - E_g/2)}{\varepsilon_{it}(E_g + \kappa)}. \quad (30)$$

Plugging Eq. (30) into Eq. (9) gives

$$\Phi_{B,p}^{o} = \gamma_B(I_S - \phi_M) + (1 - \gamma_B)\frac{E_g}{2}, \quad (31)$$

where

$$\gamma_B = 1 - \frac{e^2 N_B d_{\mathrm{MS}}}{\varepsilon_{it}(E_g + \kappa)}. \quad (32)$$

TABLE I. Numerical values used for the plots in Fig. 4. The interface behavior parameter S_Φ has been converted from least square fitted experimental data (Ref. 59) using the formula $S_X/2.27\,\mathrm{eV} = S_\Phi$.

Semiconductor	$\varepsilon_\infty/\varepsilon_0$	Band Gap (eV)	S_Φ
Ge	16	0.67	0.040
Si	11.8	1.11	0.035
GaAs	10.9	1.35	0.066
CdTe	7.2	1.44	0.070
GaTe	7.1	1.66	0.141
CdSe	5.9	1.74	0.079
GaSe	6.6	2.05	0.251
GaP	9	2.24	0.145
CdS	5.5	2.42	0.308
GaS	6	2.5	0.419
ZnSe	5.9	2.58	0.291
SnO_2	4	3.0	0.366
$SrTiO_3$	4.69	3.15	0.198
ZnO	4.6	3.2	0.419
ZnS	5.5	3.54	0.520
SiO_2	2.34	9.1	0.670

Equations (31) and (32) were derived in an earlier publication.[21] Obviously, Eq. (31) predicts a dependence of the SBH on the metal work function which is similar to that predicted by gap state models, Eq. (12), with $E_g/2$ taking the place of the CNL. However, the "interface parameter" γ_B according to the ECPE method is quite different from that predicted by the gap state models, Eq. (13).

The agreement between Eq. (32) and experimental data was recently demonstrated,[21] and is repeated here to accommodate further discussion and comparison. Experimentally observed S_Φ's[59] are listed in Table I and plotted against the band gap of the semiconductor in Fig. 4(a). However, the experimental data for diamond has been excluded from Fig. 4, because the covalent radius of carbon is considerably smaller than that of other semiconductors, and because conflicting values of S_Φ for diamond exist in the literature.[60] A roughly linear relationship is observed in Fig. 4(a), lending strong support for the validity of the chemical bonding picture of SBH formation. An *x*-axis intercept of 0.68 eV and a slope of $\sim 0.15\ \mathrm{eV}^{-1}$ are deduced from a least square fit, yielding a $d_{\mathrm{MS}}N_B$ product of $8\times10^6\ \mathrm{cm}^{-1}$. In this analysis, the dielectric constant of the ISR, $\varepsilon_{it}/\varepsilon_0$ has been approximated by twice the optical dielectric constant of the semiconductor $\varepsilon_\infty/\varepsilon_0$ as is often done in the literature. Taking d_{MS} to be 0.25 nm, one gets an N_B of $\sim 3\times10^{14}\ \mathrm{cm}^{-2}$, which is a very reasonable estimate of the number of available bonds at an interface. The same set of experimental data is also plotted in Fig. 4(b) in the format $S_\Phi^{-1} - 1$ against the square of the semiconductor polarizability. According to the fixed-separation model of MIGS, Eq. (14), a linear relationship should be observed. A roughly linear relationship can indeed be discerned in Fig. 4(b), even though the scatter of the data is quite significant. A comparison of the experimental data with the prediction of the division-by-epsilon model

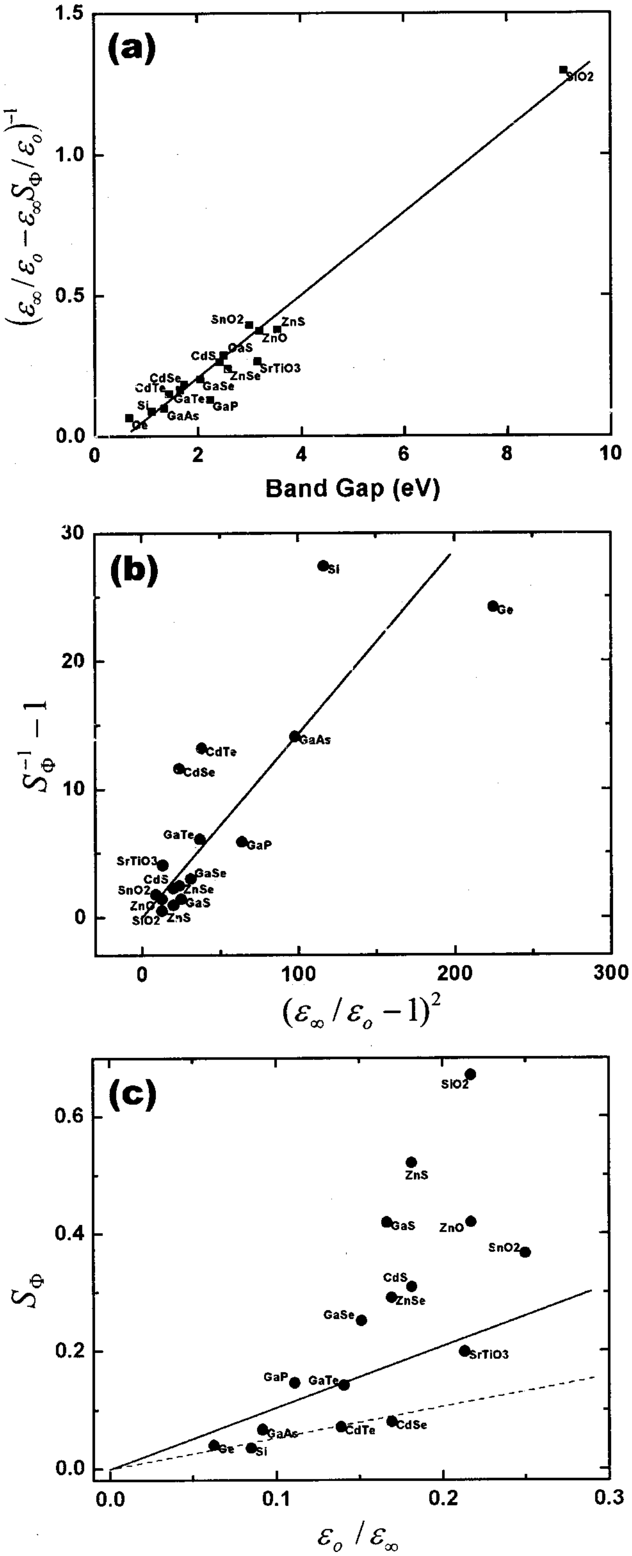

FIG. 4. Experimentally observed interface behavior parameter (Ref. 59) (a) plotted as $(\varepsilon_\infty/\varepsilon_0-\varepsilon_\infty S_\Phi/\varepsilon_0)^{-1}$ against the band gap of the semiconductor, as suggested by the bond polarization theory. (b) plotted as $S_\Phi^{-1}-1$ against the square of the polarizability of the semiconductor $(\varepsilon_\infty/\varepsilon_0-1)^2$, as suggested by MIGS theory (Ref. 45). (c) plotted against the inverse of the dielectric constant as suggested by the division-by-epsilon model of MIGS (Ref. 12).

of MIGS, Fig. 4(c), also reveals clear discrepancies. In Fig. 4(c), the solid line and the dashed lines correspond to the predictions of the divison-by-epsilon model with $\varepsilon_{it}=\varepsilon_\infty$ and $\varepsilon_{it}=2\varepsilon_\infty$, respectively.

VI. RELATIONSHIP BETWEEN CHEMICAL BONDS AND METAL INDUCED GAP STATES

The present results show that the polarization of interfacial bonds can quantitatively account for the Fermi level pinning phenomenon experimentally observed at polycrystalline MS interfaces. Traditionally, the Fermi level pinning effect has been attributed to the presence of MIGS. Since the dependence of the SBH on the metal work function is predicted in very similar fashions by the bond polarization theory and the fixed-separation model of MIGS, it is worthwhile to explore possible connections between these two theories. We will first examine the similarities. Both theories recognize that, due to the requirement on the minimization of total energy, the charge density at a MS interface needs to relax from the frozen distributions assumed in the Schottky-Mott model. This charge relaxation is assumed by both theories to be the source of the additional interface dipole, the Schottky dipole, and the origin of the Fermi level pinning effect. So, both theories try to estimate the optimum amount of charge transfer which minimizes the energy. That the interface energy is indeed minimized in the bond polarization theory has been explicitly demonstrated through the use of the Lagrange's multipliers method. Since the fixed-separation model of MIGS specifically works with the Fermi level, it also should lead to a minimized interface energy, albeit only implicitly. The fact that the fixed-separation model of MIGS is also based on the ECPE method is explicitly demonstrated in the Appendix. Therefore, the MIGS fixed-separation theory and the bond polarization theory deal with the same phenomenon, charge transfer at MS interface; the two theories are also based on the same principle, the minimization of interface energy. However, there are significant differences in the assumptions and methodologies used in these theories.

The biggest difference between these two theories is probably the "basis set" used in the analysis. As an example of the significance of the basis set, we first look at the analogous case of molecular states vs atomic states in molecules. In the analysis of molecular dipole, the basis set used in the ECPE theory, Eq. (17), is the isolated atomic levels prior to the formation of molecules. The eventual charge distribution in the molecule is expanded in the basis set of atomic states, whose spherical distribution around each nucleus validates the use of point charges to represent atomic charges and the neglect of off-diagonal terms.[22,52] This approach rightfully ignores the details of how molecular orbitals are actually formed. Even though the "density of states" projected onto each atom will change upon the formation of molecules, this change is a derivative of, and can be predicted from, the distribution of the initial energy levels. Therefore, the energy levels of an oxygen atom can be used to analyze dipoles of all small molecules containing oxygen, e.g., CO and NO. Alternatively, one can use the molecular states as the basis set to analyze the molecular dipole. This involves first solving for the molecular orbitals, with, for example, the LCAO approach, and then calculating the dipole moment from the sum of charge densities of all the occupied molecular orbitals. Irrespective of which basis set (atomic or molecular) is used, similar dipole moment should be obtained for the molecules. For systematic studies, however, the use of the molecular states as the basis set is inconvenient because the basis set changes with molecules and needs to be solved for different molecules. In other words, one cannot use the orbitals of a CO molecule to analyze the dipole moment of an NO molecule. The bond polarization theory is, in spirit, similar to the analysis of molecular dipoles in terms of atomic states, while the MIGS fixed-separation theory is similar to the approach based on molecular states. The use of the bulk band structure of the isolated semiconductor and metal crystals, as done in the bond polarization theory, gives some credence to the procedure of obtaining the dipole by multiplying the charge on each atom with the interatomic distance. In the MIGS theory, however, the basis set is the MIGS. In an attempt to perform systematic analysis, the MIGS theory has to assume that the distribution of MIGS is independent of the metal. This is not appropriate, since calculations already showed that the actual distribution of MIGS depends on the metal.[15,17,61] In the bond polarization theory, it is natural to analyze the SBH's observed for different metals with similar N_B and d_{MS}, because these are only geometrical parameters.

Another difference between the two theories is the discreteness of the individual bonds in the bond polarization theory vs the smeared-out charge distribution in the MIGS theory. One consequence of this difference is clearly illustrated in the Appendix for the fixed-separation model of MIGS the charge transfer is constrained to take place between imaginary planes. This constraint reduces the interface electrostatics from a three-dimensional problem [see Eqs. (23) and (25)] for the bond polarization theory, to a one-dimensional problem for the fixed-separation model of MIGS. The one-dimensionality of the fixed-separation model allows the Coulomb interaction to be expressed in a closed form, Eq. (A3), which leads to a Schottky dipole, Eq. (10), that is proportional to the *final* difference between the characteristic energy levels of the metal and the semiconductor. Therefore, this term works like a negative feedback in a unity-gain amplifier, with the resulting overall gain quite predictably given by Eq. (13), in a form of $(1+F)^{-1}$, where F is the transmission factor of the feedback circuit. To see the analogy with a feedback circuit explicitly, one can rearrange terms of Eq. (12) into

$$\Phi_{B,p}^{o}-\phi_{\mathrm{CNL}}=\gamma_{\mathrm{gs}}(I_S-\phi_{\mathrm{CNL}}-\phi_M). \tag{33}$$

The left hand side of Eq. (33) is analogous to the output of the circuit, whereas the quantity in the parenthesis on the right hand side of Eq. (33) is the initial input. In contrast, the Schottky dipole in the bond polarization theory, Eq. (30), is proportional to the *initial* energy difference, which means that the equivalent circuit is a (positive) feedback amplifier that operates in reverse. So the difference in the functional forms of γ for the two theories, i.e., Eqs. (13) and (32), can be attributed to the different dimensionalities of the two theories. However, since both theories are linear theories, their distinction is only reflected in the range of achievable γ values.

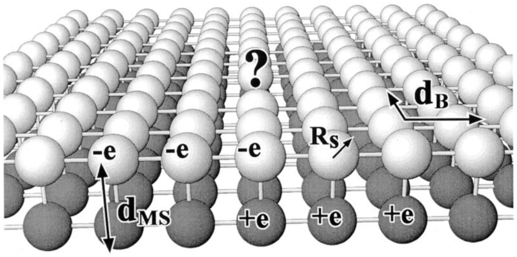

FIG. 5. Schematic of two parallel sheets of charges, arranged in a square array, with one of the charges on the top sheet, marked by a question mark, missing.

There are potential complications due to the functional form of Eq. (32). Specifically, γ_B can become negative for narrow band-gap semiconductors. Being the sum of all Coulomb interactions, κ varies with bonding geometry in two dimensions. To better handle this term, we return to the unabridged expressions for the chemical potentials, Eqs. (23) and (25), to write

$$\kappa=2\sum_{n_x,n_y}^{\text{excl}\ n_x=n_y=0}\frac{e^2Q_S}{4\pi\varepsilon_{it}d_B\sqrt{n_x^2+n_y^2}}-2\sum_{n_x,n_y=-\infty}^{\infty}\frac{e^2Q_S}{4\pi\varepsilon_{it}\sqrt{d_{MS}^2+d_B^2(n_x^2+n_y^2)}}. \tag{34}$$

The terms on the right hand side of Eq. (34) can be identified as the Coulomb potential energy experienced by a test charge of $2eQ_S$, when it is placed on the only vacant site of an otherwise perfectly arranged pair of parallel sheets of charges, as illustrated in Fig. 5. The two sheets, separated by a fixed distance of d_{MS}, contain a square array of unit charges, each of $+e$ and $-e$ respectively, with a mesh dimension of d_B. The numerical value of Eq. (34) obviously depends on d_B and d_{MS}. In the limit $d_{\mathrm{MS}}\gg d_B$, the charges become smeared out, leading to the one-dimensional result of Appendix. In the other limit, $d_B\gg d_{\mathrm{MS}}$, bonds become independent, and the Coulomb interaction for diatomic molecules is recovered.[22,62] For real MS interfaces, one expects d_{MS} to be comparable to d_B, which means that κ can only be estimated numerically. If one assumes $d_{\mathrm{MS}}=0.25\,\mathrm{nm}$ as before and uses $d_B(=N_B^{-1/2})=0.57\,\mathrm{nm}$, as determined from the linear fit of Fig. 4(a), a κ of ~ -0.76 eV is calculated. This compares very favorably with the intercept of 0.68 eV determined from the linear fit, lending further support for the bond polarization theory. With this estimated value of κ, the interface parameter, γ_B, can become negative according to the bond polarization theory, for semiconductors with a band gap smaller than $\sim$1.3 eV. The MIGS on narrow gap semiconductors have long decay lengths, which means that the limitation of charge transfer to one atomic plane is inappropriate for narrow gap semiconductors. Charge transfer involving two or more layers of atoms needs to be considered to estimate the interface dipole under these circumstances, invalidating the present method. It should also be kept in mind that the higher order terms ignored in our derivation may bear heavily on the interface dipole for narrow-gap semiconductors. What Eq. (32) suggests is that the present approach is only valid for semiconductors with large band gaps, where the monopole representation is a reasonable approximation. Even though the present theory is, strictly speaking, not applicable to narrow-gap semiconductors, the suggestion that γ_B can become negative is not necessarily preposterous. This is because, as explained, the Schottky dipole does not operate as a negative feedback in three dimensions. A negative γ_B is consistent with localized and essentially independent bonds at the interface. As a matter of fact, a negative S_Φ has been observed experimentally on MoS_2, a narrow-gap semiconductor.[63]

The third difference between the bond polarization theory and the MIGS fixed-separation theory concerns the length of charge transfer at the interface. In the bond polarization theory, the charge transfer is associated with bond formation and, therefore, d_{MS} is assumed to be the length of one atomic plane, $\sim$0.25 nm. In the MIGS picture, the density of interface charge decays exponentially with some "penetration depth." In the original jellium calculations,[5] the penetration depth was found to be as short as 0.1 nm for ionic semiconductors and $\sim$0.3 nm for covalent semiconductors. Such a length for the charge transfer is obviously characteristic of bond formation at the interface, which involves interactions between the metal and the semiconductor. However, the capability of the MIGS model to analyze SBH systematics relies on the assumption that the distribution of MIGS is independent of the metal. To be consistent with this assumption, the scenario is usually created in the MIGS model that the MIGS charge resides at the tail end of metal wave functions which tunnel into the semiconductor. Typically, δ_{it} in the fixed-separation model of MIGS is assumed to be $\sim$0.5–2 nm.[45] With the spatial extension of their exponential tails into the semiconductor, MIGS's were often assumed to lead to band bending in the semiconductor as far as 5–10 nm away from the MS interface.[64,65] As a result of such large distances, the charge transfer in the MIGS theory is envisioned to take place passively, between the metal and some preexisting MIGS's in the semiconductor. The bond polarization theory views the creation of all interface states (including MIGS) as a result of active interaction involving both the metal and the semiconductor.

VII. DISCUSSIONS

In the present method of deducing the interface dipole, we have arbitrarily imposed the constraint that the charge transfer at the interface is limited to those atoms on the immediate interface planes. This approximation seems to capture the essence of the interface chemistry while still keeping the problem tractable at the intended level of sophistication. To see the consequence of this assumption, one writes down the electrochemical potential for a semiconductor atom in the ISR, but not directly involved in the interface bonding

$$\left.\frac{\partial E_{\mathrm{ISR}}}{\partial Q_{S_i}}\right]_{\mathrm{interior}} = U_S + \sum_{n_x, n_y=-\infty}^{\infty} \frac{e^2 Q_S}{4\pi\varepsilon_{it}\sqrt{d_B^2(n_x^2+n_y^2)+d_\perp^2}} + \sum_{n_x, n_y=-\infty}^{\infty} \frac{e^2 Q_M}{4\pi\varepsilon_{it}\sqrt{(d_{\mathrm{MS}}+d_\perp)^2+d_B^2(n_x^2+n_y^2)}}, \tag{35}$$

where $d_\perp$ is the distance between this atom and the first semiconductor plane at the interface. Writing down a similar expression for a metal atom which is not on the interface plane and making use of the physical meaning of the Coulombic terms, one obtains the following result:

$$e\Delta_{\mathrm{Sch}} = I_S - \phi_M - \frac{E_g}{2}, \tag{36}$$

which simply states that the SBH should be one half of the band gap

$$\Phi_{B,p}^{o} = \frac{E_g}{2}. \tag{37}$$

This result apparently contradicts Eq. (31) obtained earlier. This disagreement actually has little to do with the approximation that was made on the limited range of the charge transfer, but is related to the presence of an energy gap in the semiconductor. One notes that even if the charge transfer were not limited to the immediate planes of the interface, Eq. (37) would still be obtained by equating the electrochemical potentials of atoms far from the interface.

To understand the crux of the problem, we take a closer look at the ECPE technique. An inherent assumption of this method is that the energy at each atomic site is analytical near zero net charge.[54] This assumption breaks down when a band gap is present. One notes that a semiconductor at low temperatures will remain essentially uncharged irrespective of the exact position of the Fermi level, so long as the Fermi level is positioned inside the band gap. Because Y_S, the hardness of an atom, is proportional to the inverse of the density of states near the CNL of the atom, it becomes indefinable when the hardness concept is applied to a semiconductor. Inside a band gap, the density of states is zero, resulting in a singularity in Y_S at $Q_S = 0$. Therefore, strictly speaking, the ECPE method cannot be used for a semiconductor or any other material with zero density of states at its CNL position. What saves this method and still makes it a valuable technique to estimate the interface dipole semiquantitatively, if not with great precision, is the fact that MIGS's are present at the semiconductor atoms immediately in contact with the metal. In other words, the electrochemical potential for the semiconductor atoms involved in the interfacial bonding, Eq. (25), is well defined and, therefore, can be used to analyze the transfer of charge between this layer of atoms and the metal. The chemical shift between the first layer of semiconductor atoms and the second or third layer of semiconductor atoms, which is expected to be small anyway, cannot be deduced using the ECPE method. Therefore, the assumption that only the first layer of semiconductor atoms is involved in the charge transfer is an important condition for the use of the ECPE method at MS interfaces.

The ECPE method is originally based on atomic orbital energies which are all referenced to the same vacuum level, i.e., the U_i's in Eq. (22) are uniquely defined for isolated atoms. When these quantities are translated into equivalent, crystal-related quantities, e.g., from Eq. (27) to Eq. (28), there may be some ambiguity as to which crystal-related quantities should be adopted. In writing down Eq. (28), we have used the experimental metal work function ϕ_M and semiconductor ionization potential I_S to represent the ability of individual atoms to attract electrons. Both ϕ_M and I_S contain surface terms which depend on the structure of the free surface and do not appear relevant to the interface charge transfer.[27,28,66] It is worth pondering whether the surface contributions should be subtracted out of I_S and ϕ_M, before they are used for the assessment of the interface dipole. The relevant question here is which set of initial charge distributions best represents the actual charge distribution at MS interfaces. It seems that the experimental ϕ_M and I_S should be used. Their use would be consistent with the highly successful, empirical treatment of the heat of formation of metallic alloys using the work functions of the individual metals.[67,68] In addition, the charge distribution at a real surface satisfies physical laws and is analytical. This characteristic obviates the need for corrections due to the disparity in the charge densities on the abruptly terminated surfaces. Similar corrections were shown to be necessary to account for the difference in the charge densities on Wigner-Seitz cell boundaries, when the heats of formation of metallic alloys were modeled.[67–69]

In the transition of Eq. (27) to Eq. (28), U_S has been identified as $I_S - E_g/2$ in analogy with the corresponding quantity for the individual atom $(=[I+\chi]/2)$. The later term is the de facto CNL of an individual atom. Because of the significant differences between atomic levels and semiconductor band structures, U_S needs not be immediately identified with the midgap energy. Well-known proposals for the CNL include the branch point of the band gap,[70] the hybrid energy (of the sp^3 orbitals of the semiconductor atoms),[12] and the dielectric midgap energy.[71] It seems that in making the transition from atomic levels, on which the molecular picture is based, to the MS interface, there is some freedom as to how to choose this charge neutrality level. Some thought could also go into the choice of the bulk-equivalent of Y_S, the atomic "hardness" which is a measure of the repulsion between electrons in the same atom. A direct translation identifies the band gap of the semiconductor as Y_S. As already mentioned, Y_S is actually ill defined for an unperturbed semiconductor because of the presence of its band gap. At the interface, the singularity is removed because of MIGS, but the question remains as to whether E_g best represents the hardness of interfacial semiconductor. A possible replacement of this term is the square-root of the second moment of atomic bonds in the moments theory.[50,72] But one notes that E_g already gives excellent correlation with the experimentally observed S_Φ.

A high density of defects anywhere in a semiconductor can pin the local Fermi level.[3,7,73] When defects are present near an interface, it has been customary to model the interface dipole by placing the defects at some characteristic distance away from the metal,[45,46] in exactly the same way as was done in Fig. 2(b), with the exception that the interface gap states now have peak(s) in their distribution. In the interior of a semiconductor, defects have precise, characteristic energy levels. Inside an ISR, however, structural imperfections are rather ill defined since the entire ISR can be viewed as one large defect. The thermodynamically preferred atomic structure of the ISR may differ significantly from that formed by slapping two perfect crystals together. The bonding configuration of the entire ISR is responsible for the formation of the dipole across the ISR.[15,17,74] It is apparent that if defects are present near the interface but outside the ISR, they will provide an additional dipole as per Fig. 2(b). However, it is also apparent that the interface dipole due to chemical bonds is always present and is the proper baseline to which other effects can be added. How much defects can influence the final SBH magnitude depends on the density, energy, and location of the defects. Except in extreme conditions the effect due to defects should be small, especially since the bond polarization theory, even without the assumption of defects, seems to have captured the essence of the experimentally observed Fermi level pinning phenomenon already.

When a metal forms an intimate contact with a semiconductor, chemical bonds have to form. The charge rearrangement associated with the formation of the chemical bonds is a complicated problem, which obviously should depend on the atomic structure of the MS interface. Indeed, experimental results obtained from nearly perfect epitaxial MS interfaces[13,75] and theoretical calculations[15,17] have established the critical dependence of the SBH on the details of the interface atomic structure. At an ordinary, polycrystalline MS interface, the bonding geometry changes from place to place, leading to non-periodic and inhomogeneous interface structures and, likely, inhomogeneous SBH. Clear evidence for the existence of SBH inhomogeneity has recently been observed from virtually all types of nonepitaxial MS interfaces.[19,20,76] With the dependency of the SBH on the interface structure firmly established experimentally, the explanation of the phenomenon of Fermi level pinning may seem to be a daunting task. There is little hope of numerically calculating the SBH for a large number of interface structures, and explaining why the average SBH should appear to be independent of the metal. However, precisely because of the inhomogeneity and the randomness of the interface structure, the experimentally observed, "average" SBHs are expected to display trend which is not sensitive to any of the particular structures of the MS interface, but rather reflects the all-important chemistry at the interface. The present bond polarization theory in real space, even with its known deficiencies, is ideally suited to reveal the chemical trend of interface bonding. The present results show that the polarization of the chemical bonds at MS interfaces leads to a weakened dependence of the SBH on the work function and a natural tendency for the SBHs to converge toward one half of the band gap, both of which are in agreement with experimental results. The excellent agreement of experimental data with the present theory suggests that interface bonding is a primary mechanism of SBH formation.

In summary, simple formulas have been derived for the dipole layer at metal semiconductor interface due to chemical bonding. This contribution leads to an insensitivity of the Schottky barrier height to the metal work function, in good agreement with experimental results. The dependence of experimentally observed interface parameters on different semiconductors is also well explained by this theory. The method used in this theory, the electrochemical potential equalization method, is discussed in detail, especially in the context of application to interfaces. Chemical bonding is likely the primary mechanism for the observed Fermi level pinning phenomenon at MS interfaces. This Schottky barrier mechanism is also in excellent agreement with the structure dependency observed for epitaxial Schottky barriers and the barrier height inhomogeneity observed at polycrystalline metal-semiconductor interfaces.

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APPENDIX: ANALYSIS OF FIXED-SEPARATION MODEL BY ELECTROCHEMICAL POTENTIAL EQUALIZATION METHOD

In the fixed-separation model of gap states, the transfer of charge is assumed to take place between two artificial planes, rather than between atoms as in the bond polarization theory. One plane represents the semiconductor and it has a CNL and a nonzero density of states D_{gs} near its CNL. The other plane represents the metal, and is assumed to have an infinite density of states around its Fermi level. These two planes are assumed to be parallel to each other and separated by a gap of δ_{it}. To predict the charge transfer, by the electrochemical potential equalization method, in the geometry of the fixed-separation model, one writes down the total energy of the system in an expansion. For an isolated semiconductor "plane" (an *S* plane) with an area *A* which is large compared with atomic dimensions, the energy can be written down, in analogy with Eq. (17), as

$$E_{S\text{-plane}}(Q_{S\text{-plane}})=E^{o}_{S\text{-plane}}+(I_S-\phi_{\mathrm{CNL}})Q_{S\text{-plane}}+\frac{Q^2_{S\text{-plane}}}{2AD_{\mathrm{gs}}}+\cdots, \tag{A1}$$

where $Q_{S\text{-plane}}$ is the number of surplus electrons on the *S*-plane. For the isolated metal plane (*M*-plane), a similar expression can be written down

$$E_{M\text{-plane}}(Q_{M\text{-plane}})=E^{o}_{M\text{-plane}}+\phi_M Q_{M\text{-plane}}+O(Q^3_{M\text{-plane}}). \tag{A2}$$

In analogy with Eq. (18), the total energy of the parallel-plate "molecule" is

$$\begin{aligned}E_{\mathrm{tot}}(Q_{M\text{-plane}},Q_{S\text{-plane}})&=E_{S\text{-plane}}(Q_{S\text{-plane}})+E_{M\text{-plane}}(Q_{M\text{-plane}})\\&\quad-\frac{e^2\delta_{it}Q_{S\text{-plane}}Q_{M\text{-plane}}}{2\varepsilon_{it}A},\end{aligned} \tag{A3}$$

where the last term is the electrostatic energy stored in the parallel-plate capacitor $[=\int(dr/2)/\mathbf{E}\cdot\mathbf{D}]$. The electrochemical potential for the *M* plane is, therefore,

$$\frac{\partial E_{\mathrm{tot}}}{\partial Q_{M\text{-plane}}}=\phi_M-\frac{e^2\delta_{it}Q_{S\text{-plane}}}{2\varepsilon_{it}A}. \tag{A4}$$

Equating this with the following expression for the chemical potential of the *S* plane,

$$\frac{\partial E_{\mathrm{tot}}}{\partial Q_{S\text{-plane}}}=I_S-\phi_{\mathrm{CNL}}+\frac{Q_{S\text{-plane}}}{AD_{\mathrm{gs}}}-\frac{e^2\delta_{it}Q_{M\text{-plane}}}{2\varepsilon_{it}A}, \tag{A5}$$

and applying the condition that $Q_{S\text{-plane}}=-Q_{M\text{-plane}}$, one gets

$$\frac{Q_{M\text{-plane}}}{A}=\frac{I_S-\phi_M-\phi_{\mathrm{CNL}}}{\dfrac{e^2\delta_{it}}{\varepsilon_{it}}+\dfrac{1}{D_{\mathrm{gs}}}}. \tag{A6}$$

The charge per unit area on the *M*-plane is $-eQ_{M\text{-plane}}/A$. The potential drop across a parallel-plate capacitor with this charge density and with a gap of δ_{it} is

$$\Delta_{\mathrm{Sch}}=\left(\frac{e\,\delta_{it}}{\varepsilon_{it}}\right)\frac{I_S-\phi_M-\phi_{\mathrm{CNL}}}{\dfrac{e^2\delta_{it}}{\varepsilon_{it}}+\dfrac{1}{D_{\mathrm{gs}}}}. \tag{A7}$$

Therefore, the *p*-type SBH in the fixed-separation model can be written down using Eqs. (9) and (A7)

$$\begin{aligned}\Phi^{o}_{B,p}&=I_S-\phi_M-\left(\frac{e^2\delta_{it}}{\varepsilon_{it}}\right)\frac{I_S-\phi_M-\phi_{\mathrm{CNL}}}{\dfrac{e^2\delta_{it}}{\varepsilon_{it}}+\dfrac{1}{D_{\mathrm{gs}}}}\\&=\gamma_{\mathrm{gs}}(I_S-\phi_M)+(1-\gamma_{\mathrm{gs}})\phi_{\mathrm{CNL}},\end{aligned} \tag{A8}$$

where

$$\gamma_{\mathrm{gs}}\equiv\left(1+\frac{e^2\delta_{it}D_{\mathrm{gs}}}{\varepsilon_{it}}\right)^{-1}. \tag{A9}$$

Obviously, the main results of the fixed-separation model have been reproduced by the ECPE method. This exercise shows that the foundation for the fixed-separation model of the MIGS is the minimization of total energy, same as the bond polarization theory. But more importantly, the derivation above exposes a significant difference, in dimensionality, between the fixed-separation model and the bond polarization theory.

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