# Schottky Barrier Heights and the Continuum of Gap States

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Simple physical considerations of local charge neutrality suggest that near a metal-semiconductor interface, the Fermi level in the semiconductor is pinned near an effective gap center, which is simply related to the bulk semiconductor band structure. In this way "canonical" Schottky barrier heights are calculated for several semiconductors. These are in excellent agreement with experiment for interfaces with a variety of metals.

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Despite decades of intense study, there exists no quantitative, predictive theory of Schottky barrier heights. Simple models[1-3] and phenomenological theories[4-7] have had some success in explaining barrier formation and chemical trends in barrier heights. Also, a few calculations for model systems[8,9] have yielded reasonable agreement with experiment. In general though, the complexity of real interfaces and the subtlety of the effects involved have frustrated attempts at a truly predictive theory. In view of the intrinsic interest and technological importance of metal-semiconductor (M-S) interfaces, this inability to understand their most crucial electronic characteristic is quite disappointing.

For the more covalent semiconductors, the barrier height is independent of the metal used to within ± 0.1 eV for metals of practical interest.[4] Thus, one hopes for a rather simple explanation of the roughly "universal" barrier heights for M-S interfaces with these semiconductors. Explanations so far have focused on the possible pinning of the Fermi level ($E_F$) by states associated with defects in the semiconductor.[10-12] I argue below that these explanations, while successful in describing surfaces with submonolayer metal coverages, are inappropriate for bulk interfaces.

Here I show that a simple parameter-free model for Fermi-level pinning by metal-induced gap states (MIGS) can predict quantitatively the observed values of the "universal" barrier heights, as well as explaining why more-ionic semiconductors do not exhibit such universality. Such MIGS pinning has been found in numerical calculations by Louie, Chelikowsky, and Cohen[8,9] but the simplicity and generality of the mechanism has not been recognized. In particular, the behavior seen is by no means peculiar to the ideal planar interface as has been suggested.[10] While following Heine[3] in spirit, I stress here the continuum nature of gap states, and the resulting locally metallic character of the semiconductor near the interface.

The various models of Schottky barrier formation are discussed in several excellent reviews.[13,14] The crucial point is simply that the barrier height is determined by the position of $E_F$ within the semiconductor gap. The barrier is the energy needed to excite an electron from $E_F$ to the conduction minimum (for $n$-type semiconductors). Band bending due to doping can be neglected in the region of interest, which extends only ~ 10 Å from the interface.

At a M-S interface there is a continuum of states around $E_F$ because of the metal. As first discussed by Heine,[3] those states within the gap decay exponentially inside the semiconductor, but still have significant amplitude a few layers from the interface. Any deviation from local charge neutrality in this region results in "metallic" screening by the MIGS.

A very small density of MIGS is sufficient to pin $E_F$. With use of Thomas-Fermi screening, a local density of only 0.02 state/atom eV in the gap gives a screening length of about 3 Å. Numerical results of Louie and Cohen[8] show a density much greater than this for the first 6 Å or so at a metal-Si interface.

It is therefore convenient to consider the barrier height as having two contributions—a short-range part, which may be related to surface dipoles,[1] the M-S electronegativity difference,[4] or more subtle details of bonding; and an additional dipole from metallic screening by MIGS, which tends to pin $E_F$ so as to maintain local charge neutrality. Here I argue that whether short-range or screening effects dominate ($E_F$ unpinned or pinned) depends simply on bulk semiconductor properties, as does the barrier height in the pinned limit. Moreover in the strongly pinned limit appropriate to Si, Ge, and GaAs, the pinning occurs relatively deep in the semiconductor.

It is important to remember that the MIGS are actually Bloch states of the bulk semiconductor with complex wave vector.[15-17] The formal properties of gap states have been studied extensively.[15-17] There is a sum rule[18,19] on the density of states (DOS) whereby any weight in gap states must come from the valence and conduction bands. Gap states take their weight primarily from those bands that are nearest in energy (allowing for wave-vector and symmetry selection rules). Charge neutrality thus requires occupation of those MIGS which come primarily from the valence band, while leaving those of mainly conduction-band character empty.

I therefore propose that $E_F$ must fall at or near the energy where the gap states cross over from valence- to conduction-band character. In one dimension this energy corresponds[16] to the branch point $E_B$ of the complex band structure, as discussed by Kohn and Rehr.[15,16] The generalization to three dimensions is discussed below. (Of course, there is no discontinuous change in the character of the wave functions at $E_B$.[19] Rather, states at $E_B$ derive their weight equally from valence and conduction bands. The net effect is still to pin $E_F$ at or near $E_B$.) For covalent semiconductors, $E_B$ is closely related to the surface-state and vacancy levels, explaining why different theoretical approaches[3,12] yield similar results.

By finding the branch point in the complex energy bands, we immediately have a "canonical" barrier height for the given semiconductor. The barrier heights which are determined in this way from the bulk band structure of several semiconductors are in excellent agreement with experimental values for interfaces with a variety of metals.

The expected behavior can be seen in the self-consistent calculation of Louie and Cohen[8] for a "jellium"-Si(111) interface. At Si atoms a few layers from the metal, states "spill over" into the gap from the conduction and valence bands above and below. In between there is a minimum in the calculated local DOS, presumably at $E_B$ (where the MIGS decay length is shortest). The Fermi level is pinned precisely at this minimum; this is viewed as a natural consequence of the principle of local charge neutrality.

One begins by defining the cell-averaged real-space Green's function,

$$G(\vec{R},E) = \int d^3r \sum_{nk} \frac{\psi_{nk}^*(\vec{r})\psi_{nk}(\vec{r}+\vec{R})}{E-E_{nk}} = \sum_{nk} \frac{e^{i\vec{k}\cdot\vec{R}}}{E-E_{nk}}, \qquad (1)$$

where $\vec{k}$ is the Bloch wave vector, $n$ is the band index, and $\psi$ and $E$ are the corresponding wave function and energy.

In one dimension, for sufficiently large $R$, $G(R,E)$ changes sign at the energy of the branch point.[17] In higher dimensions we pick a direction by specifying $\vec{R}$; then for each $k_\parallel$ there is a branch point as the longitudinal wave vector is varied. By integrating over the entire Brillouin zone, for large $\vec{R}$ we automatically pick out the contribution to $G(\vec{R},E)$ with longest range.

For an ideal interface, $\text{Im}(\vec{k})$ must be normal to the interface. It would therefore appear that we should pick $\vec{R}$ in that direction. However, for a disordered interface it seems preferable to assume that all directions are permitted, as in an impurity problem. Then the direction which gives the most slowly decaying MIGS is the important one. Experimentally there appears to be no dependence of barrier height on orientation for interfaces prepared in the usual manner. On the other hand, there is evidence of strong orientation dependence for ideal epitaxial interfaces,[20] consistent with the model here but not with defect models.

Fortunately, the appropriate choice of direction is obvious. The fcc (cell) nearest-neighbor lattice vector is $(a/2)(110)$. This is also the direction along the chains of bonded atoms in the diamond and zinc-blende structures. Numerical calculations have shown that charge disturbances propagate farthest along these (110) chains.[21] We therefore consider $\vec{R}_m = m(a/2)(110)$. For various $\vec{R}_m$ ($m = 1, \ldots, 10$) we calculate $G(\vec{R},E)$ and locate the energy in the gap where this changes sign. This energy approaches a constant value for large $\vec{R}_m$ ($m > 3$). The direction dependence is discussed below.

In general, $E_F$ must depend on the details of the interface, since the density of MIGS is determined by the boundary condition. For example, if the metal continuum were replaced by a few discrete levels in the gap (e.g., defect levels), then $E_F$ would be pinned at one of these levels, possibly quite far from $E_B$. Such an effect has been seen at surfaces.[10] If, however, the metal DOS is relatively featureless throughout the gap, and the MIGS penetrate deep enough to screen the interface, then the position of $E_F$ in the semiconductor gap will be determined primarily by the complex band structure. We ignore conservation of $k_\parallel$ across the interface, since microscopically M-S interfaces are disordered.[20]

The calculation was carried out using energy bands obtained with the linearized augmented plane-wave method, summing 152 points in the irreducible wedge of the bulk Brillouin zone. Because the local density approximation used for correlation and exchange gives poor values for the absolute gap but good dispersions, I rigidly shift the conduction bands to give the correct room-temperature energy gap, following Baraff and Schluter.[22] I stress that it is unimportant how the band structure used in (1) is obtained, as long as it is reasonably accurate.

The results are tabulated in Table I, which gives the calculated barrier height for $n$-type semiconductors, i.e., the difference between the inferred Fermi level and the conduction-band minimum; and the asymptotic charge decay length $\lambda$ for states at this energy. Results are numerically accurate to better than 0.05 eV (0.4 for ZnS) and 0.5 Å, respectively.

Only results for (110) lattice vectors are given in Table I. The (100) and (111) directions require much larger wave-vector samples for good convergence. Preliminary results with a 1186-point sample indicate a smaller barrier for Si(100), suggesting a possible explanation for new experimental results on orientation dependence for epitaxial films.[20] Results also confirm that the (110) direction gives the longest decay length, justifying the choice of (110) to determine the barrier height for disordered interfaces.

Also shown are experimental Schottky barrier heights.[23-25] I give both the range for a number of "ordinary" metals, and specific values for Au and Al, which have been extensively studied and represent the normal range in metal electronegativity. [$C/V$ measurements for intimate contacts were chosen where available (for Si and GaAs).] In all cases the theoretical value falls within the scatter of barrier heights for typical metals. The decay lengths found here are consistent with those calculated by Louie, Chelikowsky, and Cohen for semiconductor-jellium interfaces.[9] For the elemental semiconductors the measured barriers are smaller (larger) than given by the theory for metals with lower (higher) electronegativity than the semiconductor. Thus, the deviations from the canonical barrier heights calculated here may be attributed, at least in part, to the M-S electronegativity difference (cf. Ref. 4).

TABLE I. Schottky barrier heights.

| | Gap (eV) | Barrier heights (eV)<br>Au | <br>Al | <br>Other | <br>Theory | $\lambda$ (Å) |
|---|---|---|---|---|---|---|
| Si [a] | 1.12 | 0.83 | 0.70 | 0.70–0.82 | 0.76 | 3.0 |
| Ge [b] | 0.66 | 0.59 | 0.48 | 0.38–0.64 | 0.48 | 4.0 |
| GaAs [c] | 1.42 | 0.94 | 0.78 | 0.71–0.94 | 0.74 | 3.0 |
| ZnS [b] | 3.60 | 2.00 | 0.80 | 0.80–2.00 | 1.40 | 1.5 |

[a] Ref. 23. [b] Ref. 24. [c] Ref. 25.

In fact, the predicted barrier heights are in as good agreement with experiment as any calculations reported to date, despite the fact that no allowance has been made for the properties of the metal or the geometry of the interface. I believe that this strongly supports the correctness of the underlying physical idea, that is, the necessity of occupation of the MIGS according to their degree of valence or conduction character in order to maintain layer-by-layer charge neutrality.

Large-gap ionic semiconductors have barrier heights which vary considerably depending upon the metal used.[4] Results in Table I suggest an explanation consistent with that of Louie, Chelikowsky, and Cohen.[9] The short decay length of MIGS in midgap for ZnS results in a negligible DOS in the gap except very near the interface. The MIGS are therefore unable to screen the effect of the metal electronegativity.

If, however, the MIGS decay length is large, the pinning is metallic (Thomas-Fermi-like), and any deviation of $E_F$ from its canonical position is screened exponentially with distance from the interface. The screening is cut off effectively at the MIGS decay length. Reexamining results of Louie and Cohen[8] for jellium-Si(111) in this light clarifies the mechanism at work there. The first Si layer sees a self-consistent potential significantly lowered by proximity to the metal, and the corresponding local DOS is shifted downward in energy (i.e., $E_F$ is near the local conduction minimum). However, band bending (screening by MIGS) between the first and second double layer restores $E_F$ to its canonical midgap position in the Si by moving the conduction minimum up 0.3–0.4 eV. Thus even for the ideal planar interface, pinning takes place far inside the Si, explaining the relative insensitivity to interface details.

Other models of barrier formation have been proposed based on pinning by defect levels.[10-12] At the free surface a very small number of states in the gap (defect or intrinsic surface states) can pin the Fermi level.[2] Since the screening length is hundreds or thousands of angstroms (depending on doping), any charging gives rise to an enormous dipole, which shifts $E_{\mathrm{F}}$ so as to maintain neutrality. At a M-S interface, however, the metal will screen any defects nearby. Since the screening charge is only a few angstroms away, each defect contributes at most a modest local dipole. Defects are therefore orders of magnitude less effective at pinning $E_{\mathrm{F}}$ at a M-S interface than at a surface.

Experimentally there is evidence for defect pinning of $E_{\mathrm{F}}$ on surfaces with submonolayer metal coverage.[10] However, results of these experiments are inconsistent with bulk barrier-height measurements[24,25] and must reflect a different mechanism than the true bulk interface. In particular, submonolayer metal coverages neither screen the defect charge effectively nor provide a continuum of states in the gap. The metal atoms themselves are in effect merely local defects.

Defect models of Schottky barrier formation, while appropriate for bare surfaces, have not established any direct relevance to bulk M-S interfaces. In contrast, the continuum model described here is specifically appropriate to bulk M-S interfaces; it has immediate predictive value, and is in excellent agreement with experiment.

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