Schottky barriers: An effective work function model

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The experimental observations of metallurgical interactions between compound semiconductor substrates and metallic or oxide overlayers have stimulated a new model of Fermi level "pinning" at these interfaces. This model assumes the standard Schottky picture of interface band alignment, but that the interface phases involved are not the pure metal or oxide normally assumed by other models. For both III-V and II-VI compounds, the barrier height to gold is found to correlate well with the anion work function, suggesting the interface phases are often anion rich. This correlation holds even for cases in which the "common anion rule" fails, and explains both successes and failures of this earlier model.

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Metal-semiconductor contacts, while crucial to semiconductor devices and studies, are still not well understood. Models relating Schottky barrier heights to metal workfunction, electronegativity, and heats of condensation and reaction with substrate constituents, as well as semiconductor properties such as surface and interface states, heats of formation, polarizability, ionicity, band gap, and defect energy levels can all be found in the recent literature. Some of these models assume the interface to occur abruptly between the two desired phases, while other models require the occurrence of the metallurgical interactions recently observed. The wealth of models available, and the diversity of assumptions they invoke, imply that the fundamentally important aspects of Schottky barrier formation have not yet been established.

In spite of the rich array of various models there are some notable experimental results which remain unexplained. One is the fact that liquid gallium will make a temporary ohmic contact to lightly doped n-type GaAs under the conditions in which the native oxide to GaAs is disrupted exposing clean gallium to an oxide free GaAs surface.[1] With time and exposure to air the contact will become rectifying as predicted by previous models. The second and more convincing result is the Okamoto *et al.* study[2] of Schottky barrier heights for the Al-(GaAs-AlAs) interface prepared by molecular beam epitaxy. They find barrier heights, particularly to AlAs, which are significantly different from those predicted by previous models and which are significantly different from those for Au-AlAs.[3] We have reexamined earlier models in light of the recent observations of interface intermixing and propose that the simple Schottky picture of work-function matching—if coupled with mixed phases at the interface—appears to account for a large amount of experimental data and suggests directions for research in controlling Fermi level pinning.

Our model begins with that of Schottky,[4] which assumes an ideal metal-semiconductor interface, i.e., one in which the interface is inert and there are no appreciable surface or induced interface states in the semiconductor. The Schottky barrier height is given by[4]

$$\phi_{bn} = \Phi_M - \chi,$$
$$\phi_{bp} = (E_G/q) + \chi - \Phi_M,$$

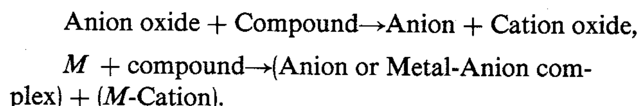
where ϕ_{bn} (ϕ_{bp}) is the Schottky barrier height to an n-type (p-type) semiconductor, Φ_M is the metal work function, q is the electron's charge, and χ is the electron affinity of the semiconductor. Thus, for the ideal case and for a given semiconductor, ϕ_b should be determined by the metal work function. Unfortunately, this is not the case for GaAs and many other semiconductors.[3]

Our model, called the effective work function model (EWF), suggests that the Fermi level at the surface (or interface) is not fixed by surface states but rather is related to the work functions of microclusters of the one or more interface phases resulting from either oxygen contamination or metal-semiconductor reactions which occur during metalization. The theory requires that when a metal is deposited, or an oxide is formed, there is a region at the interface which contains a mixture of microclusters of different phases, each having its own work function. We should therefore modify the "ideal" surface discussion as follows:

$$\phi_{bn} = \Phi_{\rm eff} - \chi,$$

where $\Phi_{\rm eff}$ is an appropriately weighted average of the work functions of the different interface phases. Thus the measured ϕ_{bn} can depend somewhat on the measurement technique, i.e., C-V or I-V.

For most of the compounds under discussion, metalization and/or oxidation results in a condition in which $\Phi_{\rm eff}$ is due mainly to $\Phi_{\rm Anion}$, the work function of the anion; we suggest that this occurs as a result of one or both of the following reactions:



Anion oxide + Compound→Anion + Cation oxide,

M + compound→(Anion or Metal-Anion complex) + (M-Cation).

The condition for driving this reaction to the right and hence generating excess Anion at the interface is that the Gibbs free energy ΔF is negative. Such oxide reactions have been examined,[5] and excess group V anions have been experimentally observed when ΔF is negative, i.e., for GaAs, InAs, and InSb.[6,7] This has not been observed when ΔF is positive, i.e., for GaP.[7] It is interesting to note that for InP, $\Delta F \approx 0$; it has been possible to form metal-oxide semiconductor field-effect transistor (MOSFET) structures using SiO_2, which exhibit a low interface state density[8] on this

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TABLE I.[a] Au Schottky barriers.

Compound	$E_G/q+\chi$	ϕ_{bp}	$\Phi_{Au}=5.1$–5.5 eV[b] $E_G/q+\chi-\phi_{bp}$	Φ_{Anion}
GaP	5.86[c]	0.96[j]	4.9	5.0[r]
InP	5.75[c]	0.85[k]	4.9	5.0[r]
AlAs*	5.6–6.0[d,e]	0.9[l] (1.4)**[m]	4.7–5.1 (4.2–4.6)**	5.0[r](4.8)[s] ($\Phi_{Al}=4.0$–4.3[b,r])
GaAs	5.5[f]	0.5[l]	5.0	5.0[r](4.8)[s]
InAs	5.3[f]	0.3–0.5[n,o]	4.8–5.0	5.0[r](4.8)[s]
AlSb*[g]	5.2[g]	0.54[l]	4.7	4.8[r](4.7)[t]
GaSb	4.76[f]	0.1[l]	4.7	4.8[r](4.7)[t]
InSb	4.77[f]	≈0.1[l]	4.8(77 K)	4.8[r](4.7)[t]
ZnO	7.92[h]	2.7[l]	5.2	7.3[r]
ZnS	7.5[h]	1.6[l]	5.9	5.74[r]
CdS	7.21[h]	1.63[l]	5.58	5.74[r]
GaS*	6.5[i]	0.75[p]	5.75	5.74[r]
ZnSe	6.76[h]	1.31[l]	5.45	5.7[r]
CdSe	6.65[h]	1.21[l]	5.44	5.7[r]
GaSe*	5.4[i]	0.5[p]	4.9	5.7[r]
ZnTe	5.79[h]	0.65[q]	5.14	4.88[r]
CdTe	5.72[h]	0.78[l]	4.94	4.88[r]
GaTe*	4.95[i]	0.45[p]	4.5	4.88[r]

*Does not obey common anion rule.
**Al-AlAs barriers.
[a]Band gaps were taken from A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972), p. 8.
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material. This is consistent with our model that would predict either no or very little excess free phosphorus at the interface. A GaP MOSFET structure with low interface-state densities would be predicted, since no free P is expected at this interface. It should also be noted that for GaAs it is well known that MOSFET structures have notoriously high "interface-state densities" (10^{13}–10^{14} cm^{-2}) and that excess arsenic is usually observed at the interface.[9] Again this is consistent with the model, since the ϕ_{bn} expected for the As-GaAs interface is about 0.8 eV (the usually observed barrier height for most metal depositions as well). Since workers have reported a large density of mid-gap states for MOSFET GaAs structures, the model would ascribe these "states" to arsenic clusters at the interface which act as Schottky barrier contacts with $\phi_{bn}\approx 0.8$ eV embedded in an oxide matrix.

Excess anions can also be generated by reaction of metals with the substrate. For example, it is known that Au deposited on GaAs and GaP results in excess Ga in the Au film.[10] Also preliminary phase diagram data[11] show that an arsenic phase is expected at equilibrium for Au-GaAs and Au-InSb. Thus a knowledge of both oxide and reactive metal chemistry should enable accurate predictions of the transport properties of metal-semiconductor devices (including Schottky barrier heights).

The current status of this model[12] is shown in Table I, which lists the experimentally derived values of ϕ_{bp} and $E_G/q+\chi-\phi_{bp}$ for Au/III-V and Au/II-V contacts. There are three points to note in this table. First, the Schottky model ($E_G/q+\chi-\phi_{bp}=\Phi_{Au}\equiv 5.1$–$5.5$ eV) is not obeyed. Second, the EWF model agrees well, as expected, for these data by assuming Φ_{eff} to be dominated by Φ_{Anion}, i.e., $\Phi_{Anion}=E_G/q+\chi-\phi_{bp}$. Third, the common anion rule[13] is not obeyed for AlAs and AlSb. We believe that the common anion rule followed more directly from the anion than initially suggested; in fact, we believe that this rule followed from the formation of microclusters of anions

at the interface which dominated the Fermi level position determinations cited . The common anion rule asserts that ϕ_{bp} depends only upon the semiconductor anion. Since, in our model, $\phi_{bp} = ((E_G/q) + \chi) - \Phi_{\rm Anion}$, a common anion would lead to a constant ϕ_{bp} only for a constant $E_G/q + \chi$; Table I shows that those cases following the common anion rule also obey that constraint.

The EWF model also explains such departures from "normal" behavior as the Al–AlAs result,[2] also shown in Table I. For the Al-AlAs case, the metalization was performed in an ultrahigh vacuum molecular beam epitaxy system, where the AlAs surface was very clean, and subsequently annealed. Under these conditions, excess As should react with Al rather than forming microclusters of As. Thus, it is expected that $\Phi_{\rm eff}$ should be dominated by $\Phi_{\rm Al} = 4.0$–4.3 eV. We believe that this explanation is correct, since $\chi + \phi_{bn} \approx 4.2$–$4.6$ for this case, which is much closer to $\Phi_{\rm Al}$ than to $\Phi_{\rm As}$. Similarly, the Ga-GaAs ohmic contact mentioned earlier can be explained since $\Phi_{\rm Ga} = 4.36$ eV (Ref. 14) and $\phi_{bn} = 0$–0.3 (for ohmic behavior); $\chi_{\rm GaAs} + \phi_{bn} = 4.1$–$4.4 \approx \Phi_{\rm Ga}$.

The electrical behavior of most covalent semiconductor interfaces is dominated by the apparent pinning of the Fermi energy level at the interface. We are proposing a model of this behavior which assumes work function matching and (typically) mixed phase behavior at the interface; "pinning" normally observed is shown to follow naturally from microclusters of anions at the interface, which are expected from chemical arguments and observed in some recent experiments.

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