Summary Abstract: Are they really Schottky barriers after all?

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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 work function, 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, bandgap, 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]

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

where $\phi_{bn}(\phi_{bp})$ = Schottky barrier height to an n-type (p-type) semiconductor, Φ_M = metal work function, q is the electron's charge, and χ = 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. This idea is shown schematically in Fig. 1 for a general case of several interface phases, a thin native oxide, and a metal overlayer. We should therefore modify the "ideal" surface discussion as follows:

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

where Φ_{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 Φ_{eff} is due mainly to Φ_{anion}, the work function of the anion; we suggest that this occurs as a result of one or both of the

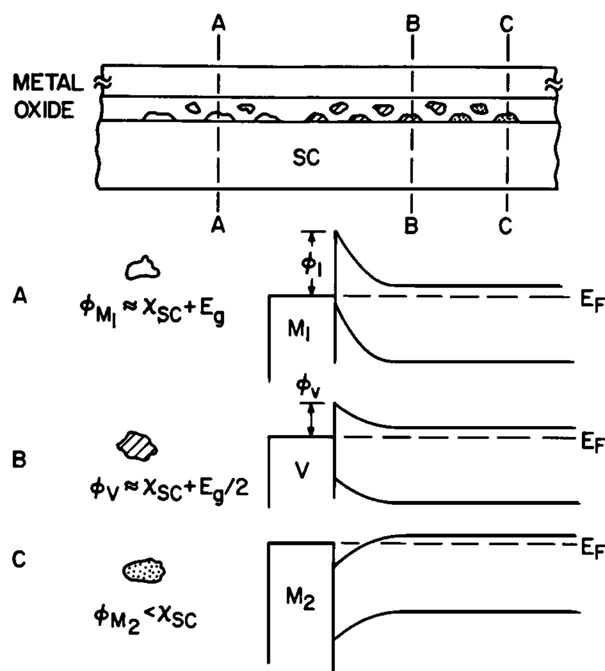

FIG. 1. Schematic representation showing the effects of microclusters of different interface phases on Φ_{eff} (see text), according to the postulates of the effective work function (EWF) theory. Cross sections "A", "B", and "C" show the barrier heights associated with phases M_1, V, and M_2 of arbitrarily different work functions, respectively.

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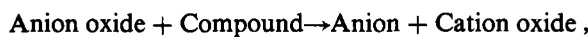
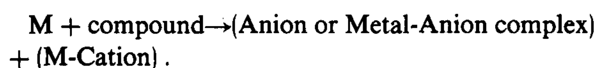
following reactions:



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 material. This is consistent with our model which 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 midgap 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] shows 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).

Thus, the question becomes: Does

$$(E_G/q) + \chi - \phi_{bn} = \Phi_{\text{anion}},$$

and

$$\phi_{bn} + \chi = \Phi_{\text{anion}},$$

for those cases in which a large excess of the anion phase, e.g. As, is expected to exist at the interface? This has been examined in Ref. 12 for previous data on the Au/semiconductor Schottky contact and the EWF model appears to be broadly valid.

The EWF model also explains such departures from "normal" behavior as the Al–AlAs result,[2] also shown in Table I.[12] 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 Φ_{eff} should be dominated by $\Phi_{\text{Al}} = 4.0$–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 Φ_{Al} than to Φ_{As}. Similarily the Ga–GaAs Ohmic contact mentioned earlier can be explained since $\Phi_{\text{Ga}} = 4.36$ eV[14] and $\phi_{bn} = 0$–0.3 (for Ohmic behavior); $\chi_{\text{GaAs}} + \phi_{bn} = 4.1$–$4.4 \approx \Phi_{\text{Ga}}$.

Next, we tentatively suggest that the EWF model may be able to explain the results on Fermi level pinning experiments performed in UHV conditions on cleaved surfaces of III–V materials, e.g., GaAs, particularly those of Spicer *et al.*[13] and Skeath *et al.*.[14] They observe a more or less well defined pinning energy ≈ 0.8 eV above the valence band for (110) n-GaAs for overlayer coverages of 0.1–1.0 monolayers and that the pinning energy is independent of materials (except for Au coverage) for materials such as Cs, Al, Ga, In and O. They interpret this result to mean that the pinning must be due to native defects, i.e., Ga and/or As vacancies, in the surface of the GaAs, which are generated by impingement or adsorption of the coverage material, and thus the pinning energy corresponds to the energy of the defect. We note that the "pinning" position of 0.8 eV is not incompatible with the ideas of the EWF model if the impinging atom were either oxygen or atoms with $\Phi \approx \Phi_{\text{Ga}}$ and it is assumed that the impinging atom knocks out both a Ga and an As atom pairwise from the lattice onto the surface. For this case, Φ_{eff} would be an appropriately weighted average of the work functions of the atomic species in the surface. For the assumptions cited above, an impingement of one Ga atom onto a GaAs surface would result in two Ga "adatoms" and one As "adatom". Since the density of states for Ga is roughly half[15] that of As, a possible averaging scheme (ignoring screening by the substrate) would be

$$\Phi_{\text{eff}} = (2\Phi_{\text{As}} + 2\Phi_{\text{Ga}})/4 \approx 4.5 \text{ eV}.$$

Therefore, $\phi_{bn} \approx 4.5 - 4.0 \approx 0.5$ eV, and $E_F \approx 0.9$ eV from the valence band, as reported in Ref. 13. UPS should observe such an averaged band bending if the Ga and As atoms do not cluster into well-defined separate regions of lateral dimensions comparable to or larger than the Debye length of the substrate (≈ 30 Å for Ref. 13). A cluster size larger than this value would result in UPS observations of two well-defined but different band-bending values, whereas cluster sizes less than this should result in an averaging similar to that discussed above.[16] Thus, apparent pinning may in fact merely be a "Schottky barrier" determined by the "average" work function of the adatoms or microclusters. Since for n-type GaAs with doping of 10^{17}–10^{18} cm^{-3} the necessary surface charge to create a band bending of 0.6–0.8 eV is only $\approx 10^{12}$ cm^{-2}, 0.1 monolayers ($\approx 10^{14}$ atoms cm^{-2}) is more than sufficient to absorb the charge. If the 0.1 monolayer is composed of either single atoms or clusters, charge transfer between the various isolated adatoms and clusters can occur via the large Debye lengths in the semiconductor (> 30 Å).

For the case of Au on GaAs,[14] and coverages of 0.1–10 monolayers, the measured surface Fermi energy varies continuously from the previously reported 0.8 eV position for 0.1 monolayer to ≈ 0.3 eV at 10 monolayer coverage. This result is hard to explain by the adatom induced defect model; however, the EWF model suggests that as the Au coverage increases, Au becomes the "dominant" species, and $\Phi_{\text{Au}} = 5.1$–$5.2 \approx \Phi_{\text{eff}}$. Hence, $\Phi_{bn} \approx 1.1$ eV would be the expected result of Ref. 14. Furthermore, at large coverages, the

pinning position acts as expected of Schottky barriers, i.e., the position is independent of bulk doping.

Finally, we ask the question: if there are $\approx 10^{12}$ defects cm^{-2} ($> 10^{19}$ cm^{-3}) which pin the Fermi level mid gap, how can workers grow GaAs with slightly compensated carrier concentrations of only 10^{14} cm^{-3} by MBE? By what mechanism do the $\approx 10^{12}$ defects cm^{-2} get reduced to $\approx 10^{7}$ during growth? We note again that since the EWF model does not posit defects within the semiconductor it allows for the straightforward growth of low defect density crystal layers via vapor deposition as in MBE.

[1]J. M. Woodall, C. Lanza, and J. L. Freeouf, J. Vac. Sci. Technol. **15**, 1436 (1978).
[2]K. Okamoto, C. E. C. Wood, and L. F. Eastman, Appl. Phys. Lett. **15**, 636 (1981).
[3]C. A. Mead and W. G. Spitzer, Phys. Rev. **134**, A713 (1964).
[4]W. Schottky, Phys **118**, 539 (1942).
[5]J. L. Freeouf, J. M. Woodall, and L. M. Foster, Bull. Am. Phys. Soc. **26**, 285 (1981).
[6]R. L. Farrow, R. K. Chang, S. Moroczkowski, and F. H. Pollak, Appl. Phys. Lett. **31**, 768 (1977).
[7]G. P. Schwartz, G. J. Gualtieri, J. E. Griffiths, C. D. Thurmond, and B. Schwartz, J. Electrochem. Soc. **127**, 2488 (1980).
[8]L. G. Meiners, D. L. Lile, and D. A. Collins, J. Vac. Sci. Technol. **6**, 1458 (1979).
[9]H. H. Wieder, J. Vac. Sci. Technol. **15**, 1498 (1978).
[10]A. Hiraki, K. Shuto, S. Kim, W. Kammura, and M. Iwami, Appl. Phys. Lett. **31**, 611 (1977).
[11]R. W. Williams (private communication).
[12]J. L. Freeouf and J. M. Woodall, Appl. Phys. Lett. **39**, 727 (1981).
[13]W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, J. Vac. Sci. Technol. **17**, 1019 (1980).
[14]P. Skeath, C. Y. Su, I. Hino, I. Lindau, and W. E. Spicer, Appl. Phys. Lett. **39**, 349 (1981).
[15]A. Williams (private communication).
[16]J. L. Freeouf, T. N. Jackson, S. E. Laux, and J. M. Woodall, Appl. Phys. Lett. **40**, 634 (1982).