Metal/(100)GaAs interface: Case for a metal-insulator-semiconductor-like structure

J. L. Freeouf and J. M. Woodall
IBM Research Division, P.O. Box 218, Yorktown Heights, New York 10598

L. J. Brillson and R. E. Viturro
Xerox Webster Research Center, Webster, New York 14580

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Various models have been developed to address the problem of "Fermi level pinning," i.e., why the barrier height varies much less than the Schottky metal work function limit. The most widely accepted mechanism is some variant of the metal-induced gap state model. However, recent experimental data on (100)$In_xGa_{1-x}As$ surfaces and interfaces ($0 \leqslant x \leqslant 1$) suggest that the surface or interface Fermi level can assume values which lie well outside the variance associated with Fermi level pinning; in fact, recent data suggest the achievement of the Schottky limit. Furthermore, studies of epitaxially grown layers where dopant incorporation is dependent on an interface Fermi level suggest that such Fermi level positions are not always pinned. In order to account for these recent results, along with the pinned values, we introduce the concept of an insulating layer like surface reconstruction. Recent calculations suggest that reconstructions of the GaAs(100) surface are insulating. Thus, we suggest that the GaAs(100) metal interface is often a metal (M)/surface reconstruction layer (I)/GaAs bulk (S), or MIS-like. This approach attempts to reconcile disparate models of interface behavior by showing the limits of validity of these models with respect to the actual physical structure of the interface in question.

For many years, a major focus of theoretical studies of Schottky barriers[1] has been the problem of "Fermi level pinning," that is, the reduced range of barrier heights available at metal-semiconductor interfaces as compared with the range of metal work functions that would define this range in a simple Schottky[2] picture of these interfaces. Such departures have been associated with intrinsic and/or extrinsic aspects of the interface formation and/or structure. Perhaps the most commonly held view ascribes these limitations to an intrinsic property of these interfaces, namely, the interface states generated by the change in boundary conditions at the interface.[3-7] Alternative models of these issues have concentrated upon extrinsic effects associated with the formation of these interfaces. Chemical reaction[8] has long been noted, and possible implications in defect[9,10] formation within the semiconductor and interface metal work function[11-13] alteration have been discussed at great length.

The present letter is an endeavor to reconcile these apparently disparate views, where such is appropriate. We begin by recognizing that the Fermi level pinning under discussion is apparently not so universal as previously believed.[14] Recent studies of metal deposition at 100 K upon As-capped GaAs(100) surfaces grown by molecular beam epitaxy (MBE), with the As cap removed *in situ*, strongly suggest interface Fermi level motion approaching that suggested by the Schottky picture of Schottky barriers[14]; this Fermi level motion is clearly in excess of that observed on cleaved (110) surfaces, and is clearly inconsistent with models predicting the same pinned position on all surfaces. This result by itself suggests that extrinsic issues play a non-negligible part in at least some of the interfaces under discussion. The discussion must then concern which interfaces are modified by such materials issues, and the mechanism whereby such materials issues may impact the universal results of the theoretical descriptions.

We note the recent efforts of Tersoff[7] to understand the dipole rearrangement at metal-semiconductor interfaces, and the neutrality level at which the Fermi level will normally pin. These results suggest that pinning will be universal, with the proviso that the degree of pinning should scale roughly as ϵ_∞, the high-frequency dielectric constant. This result offers a natural approach to the well known "ionic-covalent" transition[15] between semiconductors exhibiting "pinning" and semiconductors whose barrier height behavior more closely approaches the simple work function matching scheme. Unfortunately, this result offers little guidance for dissimilar behavior at nominally identical interfaces, i.e., interfaces involving the same metal on the same semiconductor. Such discrepancies appeared to offer some reason to question the experimental results, or perhaps to introduce some geometrical structure[16] to the adsorbed metal atoms.

We offer an alternative approach, namely, that the semiconductor surface reconstruction may alter the pinning behavior from that expected of the bulk semicoductor. According to Tersoff,[7] a material with a small ϵ_∞ (which suggests a large forbidden band gap) would demonstrate reduced pinning. We suggest that the surface reconstruction exhibits such a small dielectric constant and is stable under metal deposition. The thickness of this altered layer need only be one monolayer[17] to strongly alter the interface properties, since the relevant screening length is of the order of the relevant bond length. This distance is *not* the same as a tunneling length, as can be seen by the reduced "pinning" at silicon diodes with interlayers of oxide or nitride.[18] The implications of such a proposal are profound: all interfaces with

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a semiconductor terminated by such a reconstructed layer will exhibit the electronic behavior of a material having the properties of that layer; these interfaces will therefore not exhibit the Fermi level pinning expected of the bulk material. Interfaces in which this interface reconstruction layer has not been formed, or in which it has been destroyed, will pin as the previous model suggests. The results will be the current experimental situation: different answers for similar metal/semiconductor interfaces.

It is well known that semiconductor surfaces reconstruct[19] to minimize their total energy. The cleaved (110) surface reconstruction has been well understood for about ten years now; it involves a simple rotation of the cation—anion bonds and a concomitant raising (lowering) of the anion (cation). Such a reconstruction appears unlikely to persist under a metal, since total energy calculations suggest that it is no longer the lowest energy configuration,[20] and since no long-range (diffusion) motions are required to recover the bulk structure. More complicated surfaces, such as the 2×4 surface reconstructions of the (100) surface of these materials, have proven far more difficult to solve. However, some recent energy-minimization calculations of Chadi[21,22] appear both intuitively attractive and consistent with experimental studies. These results suggest that the stable (100) surface of GaAs involves a large ordered fraction of the surface to consist of As vacancies, and dimer ordering of the remaining surface atoms.[22] The calculation also predicts a forbidden band gap significantly larger[23] than that of bulk GaAs, which at least suggests a smaller dielectric constant and therefore less pinning than expected for bulk GaAs.

Should such a surface reconstruction prove stable under metal deposition, one might well expect different behavior from that anticipated for bulk GaAs. The situation is analogous with a metal-insulator-semiconductor (MIS) structure, where the Fermi level of neither the metal-insulator interface nor the insulator-semiconductor interface is pinned. The result is a structure in which the flatband potential depends strongly upon the metal work function. When the insulator is also sufficiently thin so as to permit tunneling (as is the case for our surface reconstruction), the result behaves electrically as a Schottky barrier with barrier height more dependent upon metal work function than expected for the abrupt (pinned) interface.[18] The results of Ref. 14 bear such a relationship to the rest of the literature upon GaAs Schottky barrier heights, namely, they exhibit significantly greater Fermi level motion than expected under the models of the Tersoff–Tejedor–Louie approach.[5–7] The results for GaAs[14] even approach the Schottky limit, in which the metal-dependent barrier height change approaches the change of the metal work function. We note that the strongest theoretical argument against the Schottky model[2] was the certainty[3] of metal work function alterations induced by the changes in boundary conditions imposed by interfacing with a semiconductor rather than with vacuum. The recent results are consistent with calculations demonstrating that such "certain" changes are in fact small[24]—at least for the situations simulated in that study.

This picture is certainly consistent with the recent "unpinned" results; however, one must maintain contact with the rest of the picture, namely, the many cases in which Fermi level pinning is a fact of life.[1] For the (100) surface, at least two possibilities exist: (1) the reconstruction is disrupted[8,10] or was never formed, and (2) one of the extrinsic mechanisms (e.g., anion clusters[12,13]) forms on top of this reconstruction. For the (110) surface, the insulating layer appears unstable; this does not preclude the extrinsic mechanisms from playing a role, but the intrinsic approaches of metal-induced gap states may also play a significant role. We emphasize, however, that such pinning occurs even for insulators upon GaAs surfaces, and suspect that extrinsic mechanisms are required in at least some of these instances.

It should be noted that to date the work function dominated observations of Ref. 14 have been restricted to epilayer GaAs samples grown by MBE on nominally (100) oriented (as opposed to the commonly used "tilted off axis" by a few degrees) substrates in which the growth was terminated by an As cap.[25] We speculate on the possible role of exactly oriented (100) layers in the achievement of work function dominated barrier heights. Let us assume that either Ga or As atomic sites at steps on (100) surfaces are Fermi level pinning sites. The unit cell size for unreconstructed (100)GaAs is 0.4 nm. Thus, for a terraced (100)GaAs surface there will be 2.5×10^{7} pinning sites per centimeter of straight-lined steps. Let us also assume using Ref. 24 that the maximum allowed density of pinning sites which will not affect work function dominance is less than or equal to 10^{12} cm^{-2}. To meet this criterion, the step spacing should be no less than 250 nm. This translates into a maximum allowed substrate misorientation of about 0.065°. If surface step density is an important factor in the achievement of work function dominated barriers, an obvious experimental test is the comparison of barrier height variation with metal work function between on- and off-axis substrates.

There are also data from previously published work on Ge-doped GaAs by the liquid phase epitaxy (LPE) method which can be interpreted based upon reduced Fermi level pinning. It has been shown that when Ge-doped GaAs is grown from Ga-rich melts[26] the Ge acts predominately as a shallow p-type dopant whereas when Ge-doped GaAs is grown from Au-rich melts Ge is predominately a shallow n-type dopant.[27] It has also been shown[28] that the electrical behavior of amphoteric dopants, e.g., Ge or Si in GaAs, can be described by the equation:

$$N_d^+/N_a^- = K(T)P_{\mathrm{As}_2}(n_i/n)^2,$$

where the left-hand expression is the ratio of the ionized dopant on donor sites (on Ga vacancies) to acceptor sites (on As vacancies), $K(T)P_{\mathrm{As}_2}$ is the stoichiometry of the crystal, i.e., whether the growth environment is Ga or As rich, and n_i/n is a measure of the Fermi level during growth. It can be shown that the change in Ge doping behavior between Refs. 26 and 27 cannot be explained just by melt stoichiometry variation. Therefore, we qualitatively suggest that the n- or p-type dependence of Ge doping upon melt composition is due mainly to the location of the Fermi level at the melt/GaAs interface during growth. This can be seen

by inspection of the equation. Largely uncompensated p-type doping will occur when the equation is $\ll 1$. For a given or slowly varying melt stoichiometry, this will occur when $n \gg n_i$ or when the interface Fermi level is near the GaAs conduction-band edge. A Schottky picture would predict this behavior for a low work function metal such as gallium, the melt in Ref. 26. Likewise, largely uncompensated n-type doping will occur when $n_i \gg n$, or when the interface Fermi level is near the GaAs valence-band edge, as the Schottky model would predict for high work function metals such as gold, the melt in Ref. 27. A work function (Schottky) model of interfacial Fermi level position coupled with this equation thus predicts that growth from Ga-Ge solutions would result in more p-type (or less n-type) doping than growth from Au-Ge, as is observed. Therefore, we suggst that the interface Fermi level follows the work function of the melt during LPE growth on (100)GaAs.

This is in sharp contrast to the case of Si-doped (100)GaAs by MBE.[29] For this case it was shown that the most plausible explanation was that the above equation is applicable but that the Fermi level is pinned near mid-gap during growth. Since we know that some of the (100) reconstructions which are unpinned are found for the MBE condition, we speculate that pinning during MBE growth may be due to the dynamically changing surface reconstructions which must occur during layer-by-layer growth. In addition, the stability of any reconstruction under the elevated temperature growth conditions may well be substantially reduced compared to the lower temperatures typically explored in Fermi level pinning studies.

In conclusion, we have suggested a mechanism to reconcile the widely accepted metal-induced gap state model[3-7] for Fermi level pinning with a body of experimental data[14] that appeared to contradict the model, in that samples predicted to pin instead obeyed the Schottky model[2] for work function dependent barrier height.[12,13,24] We have also pointed out many situations in which Fermi level pinning occurs, but to which the simple charge neutrality level model cannot apply[9,24] without some extrinsic additional mechanisms,[10,12] which we also summarize. Our suggestion is subject to theoretical tests concerning the stability of the reconstruction as well as the pinning behavior of such a material; experimental studies of the stability are also crucial. Other experimental tests of these suggestions include substrate orientation dependence of pinning and of compensation during different forms of epitaxial growth.

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