Comment on "Electronic Structure of Ideal Metal/GaAs Contacts"

In a recent Letter, van Schilfgaarde and Newman [1] (vSN) presented the results of a first-principles local-density functional (LDF) calculation of the Schottky-barrier heights (Φ_B) between p-type GaAs and various epitaxial metal contacts. Our objectives in this Comment are to note some limitations of the calculational procedure and to extend the interpretation of Ref. [1].

A limitation of any LDF calculation of semiconductor ground-state properties is that the gap between filled and empty single-particle eigenvalues is reduced relative to the actual gap by roughly a factor of 2 [2,3]. Specifically, vSN obtain a band gap of 0.5 eV for GaAs, as is appropriate to this approximation. Since the calculated barrier heights for Ga, Al, and Cd are roughly 1 eV, double this calculated gap, they lead to inverted interfaces. The charge transfer into conduction-band states alters the band lineup from that expected in the absence of conduction-band states available for occupancy. Thus, the results presented by vSN should differ from those expected from a calculation containing the correct band gap. In particular, the charge contained in GaAs conduction-band states [4] with the Fermi level 0.5 eV above E_c is about $3\times10^{20}/\mathrm{cm}^3$. This is enough charge density to obtain substantial band-bending changes between monolayers, since the Debye length at such a charge density is several angstroms.

A second limitation of the vSN calculation is the failure to impose boundary conditions which guarantee thermodynamic equilibrium at the junction. In particular, the equal pressure condition requires that the atoms on each side of the junction be at their equilibrium position before the interface charge transfer is evaluated [5]. The epitaxial conditions imposed by vSN do not satisfy this condition, so their results apply to nonequilibrium junctions. Furthermore, the structure imposed by vSN was apparently not the distorted, relatively constant-volume structure to be expected from the uniaxial strain imposed by lattice matching, but rather a symmetry-preserving compression by up to 2% in lattice constant. Use of this boundary condition not only distinguishes the calculation from any observable situation, but also suggests that the work functions of the metals measured experimentally need have no relationship to those hydrostatically compressed versions for which a barrier height is calculated.

It should be noted that the calculations of vSN lead to barrier heights that are as consistent with a Schottky model as with either the experimental values of Φ_B or the results of intrinsic interface models [6]. Specifically, the Schottky model describes all calculated barriers except those for the low-work-function d-electron metals, for which vSN noted special bonding effects. The contrary conclusion of vSN was due to the mistaken use of an arbitrary internal potential, rather than the appropriate external work function, to establish correlations with Φ_B. The results of vSN show that the dipole at the metal/semiconductor interface varies to screen out changes in the internal potential at the interface; this would be a test of the Schottky model *only* if the dipoles at the metal/vacuum and semiconductor/vacuum interfaces are invariant of these changes, but they are not [5].

vSN did note strong disagreement between their calculated and experimental barrier heights, and concluded that experimental barriers must correspond to junctions which exhibit imperfect ("nonideal") atomic structure relative to their model epitaxial, defect-free geometry. This conclusion was reached earlier by many investigators [5–9]. Indeed, this result was previously proposed on the basis of a calculation [5] which neglected band-structure effects and predicted barrier heights in agreement with the Schottky model. In both calculations the predicted barrier heights depend strongly upon the metal. The experimental barrier heights are much less dependent upon the metal than are the calculated barrier heights; this is normally called "Fermi-level pinning" [5–8]. Since this "pinning" is not shown by the calculations of vSN, its origin must not be included in their calculations.

In summary, the calculations of vSN are performed away from mechanical equilibrium, predict inverted interfaces which should distort the interface potentials, and lead to results as consistent with the Schottky model as with any other model of Schottky barriers.

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