Exchange-Correlation Potentials in Schottky Barriers and Heterojunctions

In a recent Letter[1] Das *et al.* presented local-density-approximation (LDA) calculations for two $NiSi_2/Si$ interfaces. The p-type Schottky-barrier heights were found to be much too small: 0.12 and -0.02 eV rather than the experimental values of 0.52 and 0.38 eV. They attributed the error to the use of the LDA, and gave a formula [their Eq. (1)] for the barrier height: $B = B_{\rm DFT} + \Delta V_{\rm xc}$, where B is the true barrier height $E_F - E_v(i)$ [where E_F is the metal Fermi energy and $E_v(i)$ the valence-band edge near the interface], $B_{\rm DFT}$ is the corresponding barrier height in terms of the exact density-functional-theory (DFT) eigenvalues, and $\Delta V_{\rm xc}$ is the difference between the vacuum exchange-correlation potentials on either side of a thick slab containing the metal and semiconductor.

We believe the interface with the vacuum to be irrelevant to the Schottky barrier. In any case, $V_{\rm xc}$ outside each vacuum interface is shown to vanish.[2] In general, however, $E_F - E_v(i)$ is not the same as $E_F^{\rm DFT} - E_v^{\rm DFT}(i)$. Figure 1 shows qualitatively the relation of the spatial variation of the quasiparticle (or true) band edges to that of the DFT values for both p- and n-type Schottky barriers. In the metal bulk, the exchange-correlation potentials are the same in both cases and E_F and $E_F^{\rm DFT}$ coincide. In the semiconductor bulk, the exchange-correlation potential takes the values $V_{\rm xc}^-(\mathbf{r})$ and $V_{\rm xc}^+(\mathbf{r})$ for p- and n-type barriers, where $\Delta = V_{\rm xc}^+ - V_{\rm xc}^-$ is the discontinuity on addition of an electron.[3,4] For the p-type barrier, $E_v^{\rm DFT} = E_v$ in the bulk, and for the n-type barrier, $E_c^{\rm DFT} = E_c$. In the depletion region, the band-electron density in a small neighborhood is the same as in the bulk semiconductor, but $V_{\rm xc}$ differs from $V_{\rm xc}^-$ by an amount smaller than Δ, so that the DFT band edges do not follow the true band edges. In particular, on the semiconductor side of the interface, $V_{\rm xc}$ must differ from $V_{\rm xc}^-$ by the same amount for the p- and n-type cases, since the electron density produced by the filling of the Kohn-Sham metal-induced gap states correctly reproduces the interface band-electron density, which is independent of the semiconductor doping. Therefore the DFT barrier is too small by an amount Γ_p for the p-type and by Γ_n for the n-type barrier, with the discrepancies adding up to Δ.

It is likely that Γ_p and Γ_n are of similar size (and therefore of order $\Delta/2$) in many systems. For example, this is implied by assuming that the density of gap states is roughly uniform throughout the gap in both DFT and the quasiparticle spectrum, and that the occupation preserves local charge neutrality. Such a model does not imply charge transfer, and is invoked simply to illustrate the fact that Γ_p is not necessarily zero.

Finally, we note that identical considerations apply to the band offsets between two semiconductors A and B: The DFT valence- and conduction-band offsets are in error by amounts Γ_v and Γ_c, respectively, which sum to the difference between the discontinuities, $\Delta_A - \Delta_B$. We believe that the success of LDA calculations of the valence-band offsets[5] reflects the similarities of the values of Δ for the component semiconductors.[4]

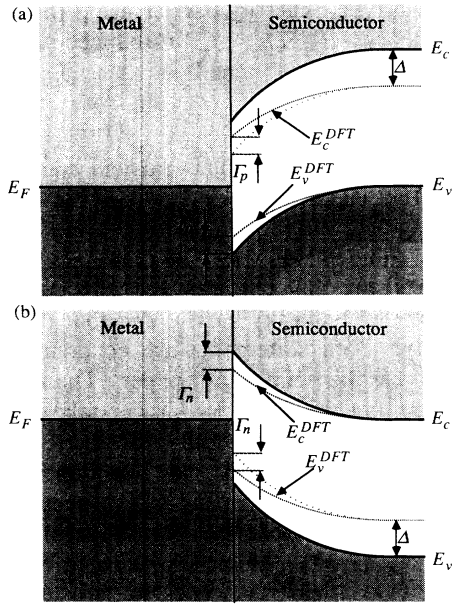

FIG. 1. (a) The quasiparticle and DFT band edges as a function of position in a p-type Schottky barrier. A slow variation of $V_{\rm xc}$ within the depletion layer bends the DFT bands relative to the quasiparticle bands by an amount Γ_p. (b) An n-type Schottky barrier: The DFT bands are bent by Γ_n $(=\Delta - \Gamma_p)$ so that they are pinned exactly as in (a).

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