Electronic Structure of Ideal Metal/GaAs Contacts

Mark van Schilfgaarde
SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025

N. Newman
Conductus, 969 W. Maude Avenue, Sunnyvale, California 94086
(Received 30 July 1990)

The electronic structure of seven ideal metal/GaAs interfaces is calculated self-consistently, within the local-density approximation. Calculated pinning positions ranged from 0.3 to 1 eV above the valence-band maximum. The metal *d* electrons are found to play a significant role in the electronic structure of the ideal interface, and in determining the Schottky barrier height. These calculations contradict models which invoke intrinsic interface states to explain the experimentally observed Fermi-level pinning.

PACS numbers: 73.20.At, 73.40.Ns

Despite the fact that 100 years have passed since the discovery of the Schottky barrier, there is no satisfactory model which accounts for the observed Fermi-level pinning. Through extensive experimental studies of the Schottky barrier, significant progress has been realized in characterizing the detailed structural and electronic properties of the metal/semiconductor interface.[1] Despite this, theoretical understanding has lagged far behind, particularly with respect to the origin of Fermi-level pinning. Long ago, Bardeen[2] showed that the presence of surface interface states can account for the observed insensitivity of Fermi-level pinning to metal overlayer. While Bardeen suggested crystal imperfections or Tamm states as possible candidates, Heine[3] proposed that interfacial states are an intrinsic property of even an ideal interface, which he described as tails of metallic wave functions tunneling into the semiconductor band gap. Trying to characterize the same phenomenon from a different point of view, Phillips[4] ascribed the pinning to interfacial dipoles arising from polar bonds across the metal-semiconductor junction, and attempted to correlate the pinning position to interfacial heats of formation.

It is now well established that the barrier height of a Schottky barrier—its most important property—is largely insensitive to the metal overlayer for a number of semiconductors, such as GaAs and InP.[5] However, a consensus of opinion as to the origin of this phenomenon is still lacking. Many models have been patterned after these early workers, including chemical bonding models,[4,6,7] native defect models,[8] and, more recently, a universal charge-neutrality-point hypothesis,[9] popularized by Tersoff.[10] To assess the validity of the proposed models, and obtain trends in barrier heights of ideal interfaces, a series of explicit self-consistent, *ab initio* calculations are needed. In this work we present the results of such a series, on seven metal/GaAs interfaces. Because they properly solve the Schrödinger equation [within the local-density-functional approximation (LDA)], they encompass in a rigorous way the effects these models attempt to address. As we show, we find that the intrinsic interfacial models, from the point of view either of Heine or of Phillips, are not consistent with the Fermi-level pinning observed experimentally. Moreover, the currently popular universal charge-neutrality-point argument[10] is inconsistent with the explicit calculations we present here. Particularly, we show that metal *d* electrons can play a significant role in determining the Schottky barrier height of ideal interfaces.

Because explicit, first-principles calculations of Schottky barriers require many atoms, and are therefore difficult to do, only a few have been attempted. Early calculations employed a jellium for the metal[11] or semiconductor,[12] or used a semiempirical tight-binding theory.[13] Zhang, Cohen, and Louie[14] published a local-density-functional calculation of an Al/Si interface which illustrated the important role of Heine's interfacial states, but the cell size was too small to determine the Schottky barrier height. Das *et al.*[15] did succeed in calculating the barrier height of $NiSi_2$ on Si within the LDA. Their calculated value of the barrier height was 0.4 eV below the measured value, but they obtained the experimentally observed difference between junctions with different orientations of metal overlayer.

Schottky barriers were calculated in a supercell geometry of *n* planes of metal followed by *m* planes of GaAs, repeating along the (110) direction. GaAs(110) was selected because it is probably the most intensively studied and best characterized:[1] The (110) surface is nonpolar and can be cleaved. bcc Cr and Fe and fcc Ag, Au, Al, Ga, and Cd were chosen for metal overlayers out of lattice-matching considerations, and also because they are representative of very different kinds of bonding. Our interfaces are constructed as follows. In bcc and fcc, (110) planes in the semiconductor and metal are parallel; in bcc, the [001] directions are also parallel, while in fcc the [001] and [1$\bar{1}$0] directions are parallel. The translation state is established by placing a metal atom in the next Ga site beyond the semiconductor surface. To obtain lattice matching, the lattice constants of

the metals were adjusted. This required an adjustment of less than 1%, except in Cd which was compressed by 2.4%. Although neither Ga nor Cd actually assume an fcc lattice, they were chosen because their energy-band structures are essentially like that of a simple metal, and this feature is preserved in the fcc lattice. The Fe system was calculated nonmagnetically.

We use the method of linear muffin-tin orbitals (LMTO) in the atomic-spheres approximation (ASA), using the local-density functional of von Barth and Hedin.[16] As is customary in the ASA, we fill the interstices in GaAs with empty spheres of equal size to render the sphere packing bcc. The usual LMTO basis set of nine orbitals (*spd*) per atom was used, with the Ga, As, and empty-sphere *d* orbitals folded down (removed from the basis) using a technique essentially equivalent to the Löwdin procedure. Downfolding made a minute change in the energy bands and changed the total energy by 5 mRy/atom. The band gap is calculated to be 0.5 eV, close to the exact LDA result. Size convergence was checked by varying n and m; those reported here used $n=9$, $m=9$ for the fcc metals, and $n=8$, $m=10$ for the bcc. The Fermi level E_F, and thus the p-type barrier height $\Phi_B = E_F - E_v$, can be calculated by its position in the local gap of the GaAs layer farthest from the interface, as Fig. 1 shows. A simpler approach which yields essentially identical results (and is equivalent to the "reference charge density" of Ref. 15) is to obtain Φ_B as the sum of the self-consistent interfacial dipole $\Delta\Phi$ and the difference Φ_0 between the bulk metal Fermi level and bulk semiconductor valence-band edge.[17]

Figure 1 displays the self-consistently calculated density of states (DOS) of Ag and Fe on GaAs, resolved into monolayers parallel to the interface. In all systems studied, DOS far from the interface are essentially like those of the bulk metal or semiconductor. Tails of the metallic wave functions tunneling into the semiconducting band gaps are clearly shown at the interface, decaying in 4 monolayers. The magnitude of this interfacial DOS is large, showing that the metal Fermi level is strongly pinned, as we discuss below; however, the pinning position is different from metal to metal. The DOS of Au/GaAs look essentially similar to Ag, except that the localized resonance indicated in Fig. 1, top, is absent, and the *d*-band width is broader. Al, Cd, and Ga all look essentially identical to each other: They lack the metallic *d* states of the figure and the semiconductor DOS right at the interface is less altered from the bulk DOS than the *d*-metal systems. Cr/GaAs appears approximately similar to Fe.

Table I displays the self-consistently calculated barrier heights Φ_B, together with the experimental data. The calculated barrier heights exhibit a wide range (0.3–1 eV). The Fermi levels of the three "simple" metals Al, Cd, and Ga all pin at approximately the same position in the gap—about 1 eV above E_v, whereas Cr, Fe, Ag, and Au lie much lower in the gap. Also displayed in Table I are the metal work functions and the hypothetical Φ_0 discussed above. The construction for Φ_0 does not allow for any screening at the interface, and is therefore analogous to the "natural" or "unpinned" barrier height in the classical Schottky picture.

The common pinning position of Al, Cd, and Ga can be understood essentially in terms of the dielectric screening argument of Harrison and Tersoff[18] or the charge-neutrality argument of Tejedor, Flores, and

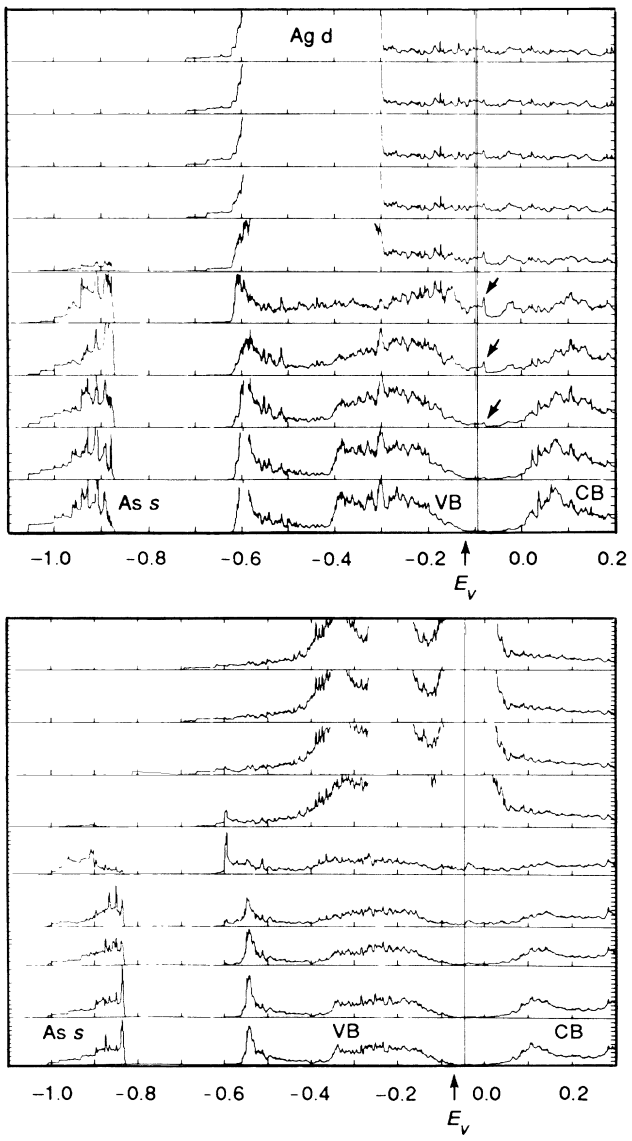

FIG. 1. Densities of states of Ag (top) and Fe (bottom) on GaAs(110), resolved by monolayers parallel to the metal/semiconductor interface. Panels begin uppermost with metallic plane farthest removed from the interface, moving down one plane per panel, through the interface and ending with the most distant semiconductor plane. The density of states (DOS) in each panel ranges from 0 to 10^{15}/eV cm^2. Vertical line marks the Fermi level. The energy scale is in rydbergs.

Louis, and Tersoff.[9,10] Consider the response of an electron gas (initially self-consistent) to a small external step potential ΔV^0 that shifts the potential of the metal side relative to the semiconductor. The electrons respond by screening out ΔV^0, reducing the potential shift to $\Delta V = \Delta V^0/\epsilon$, where ϵ is the effective dielectric constant. We calculated ϵ by shifting the potential on one side of the interface by a small constant, generating the output density ρ_{out} for this potential, and determining what fraction $1/\epsilon$ of the screening charge $\rho_{\text{out}} - \rho_{\text{in}}$ would generate a screening potential that canceled ΔV^0 well away from the interface. We found that $1/\epsilon$ was about 1/30 for all metals except the transition metals Cr and Fe, in which case it was about 1/120. The screening of Φ_0 to the self-consistent barrier height Φ_B is quite analogous, with $1/\epsilon$ a measure of the effective pinning strength, and has been identified[9,10] with the S factor in Schottky-barrier terminology.[5] Now, Al, Ga, and Cd are essentially simple metals, with similar free-electron-like energy bands. Although Φ_0 varies greatly among these three materials, this difference is screened out to make them pin at approximately the same position, in contradistinction to the Schottky picture and work based on it.[19] This explanation is essentially the same as the neutral-point argument,[9,10] except that the strength of the pinning, $1/\epsilon$, is much larger than the value usually quoted for GaAs ($1/\epsilon \approx 0.12$), and therefore cannot be the source of the experimentally observed range in barrier height, as Refs. 9 and 10 assert.

We now show that transition and noble metals possess an additional contribution to the barrier height. It arises from charge transfer between the metal d states and the semiconductor, raising the semiconductor bands with respect to the metal and lowering the pinning position within the gap. This is most easily seen in the case of Ag and Au. As a rough model of the interface, consider a three-level system, one level representing the conduction band, another the valence band, and a third an occupied d level on the metal side. A Hamiltonian for this system would take the form

$$\begin{pmatrix} E_c & 0 & V \\ 0 & E_v & V' \\ V & V' & E_d \end{pmatrix}.$$

This Hamiltonian produces two "valence" states, derived from E_v and E_d. Through the coupling V, some conduction-band character is admixed, transferring charge from the d state to the (empty) conduction-band state. (V' further shifts the levels, but is unimportant for charge transfer, since both E_d and E_v are occupied.) As the metal d level becomes more corelike, its extent shrinks, causing V to decrease; in this limit the charge transfer scales as $V^2/(E_c - E_d)$. Contrasting Ag and Cd clearly illustrates this effect. Coupling to the Ag d band is large enough to make a significant dipole, while in Cd, with its semicore d band, the effect is insignificant. To demonstrate conclusively that Ag has a significant d-derived dipole, we shifted the Ag d band downward by 0.3 eV, and reduced its coupling V to $\frac{1}{8}$ of its true value, by artificially adjusting LMTO potential parameters. Repeating the self-consistency procedure, the Fermi level shifted upward in the gap by 0.2 eV. (The interfacial DOS still retained some of the d-derived resonant state shown in Fig. 1, top, so a further shift is expected if the d states were entirely eliminated.) Fe and Cr are more subtle cases, because the d bands span the band gap and are only partially occupied. The detailed calculations (Table I) show, however, that they also depress the Fermi level relative to the simple metal.

Table I shows a lack of correlation between calculated and experimental barrier heights. Theoretically, a calculation using the exact (nonlocal) density functional should yield the correct barrier height for the ideal interface. At present the error due to the LDA cannot be calculated, though the work of Ref. 15 suggests that the errors are a few tenths of an eV. On the experimental side, interfaces have been observed to be reconstructed, chemically reactive, disordered, nonstoichiometric, and/or contain new interface phases.[19,21] Some recent scanning-tunneling-microscopy experiments[22] indicate that the local barrier height of small clusters of Au on GaAs depends strongly on the local environment. Although interpretations of these data are controversial,[23] large variations in barrier height have been reported[24] on samples metallized at low temperature, where interfacial chemical reactions may be minimized. These calculations are so computationally demanding that we have not as yet made any systematic study. However, the purpose of the present work is to address the validity of current models of the barrier height; this we can do by approximating the Schottky barrier by an ideal, epitaxial interface within the LDA.

To summarize, we have shown through explicit local-density-functional calculations that the interfacial states pinning the Fermi level are large, with a range of about four atomic layers; and that d states significantly alter

TABLE I. Calculated and experimental Schottky barrier heights $\Phi_B = E_F - E_v$ for seven metal/GaAs(110) junctions, in eV. Also shown are the metal work functions W and Φ_0. Experimental data were taken from Refs. 7 and 20, converting to $E_F - E_v$ barrier heights measured on n-type GaAs.

Metal	W	Φ_0	Φ_B (calc.)	Φ_B(expt.)
Fe	4.5	0.52	0.34	0.75
Cr	4.5	1.84	0.36	0.78
Ag	4.26	−0.38	0.39	0.56
Au	5.1	0.04	0.29	0.53
Ga	4.2	0.81	0.94	
Al	4.28	0.91	1.05	0.63
Cd	4.22	2.07	1.07	

the electronic structure of the intimate contact and also the barrier height. The S factor as calculated from the interfacial dielectric constant ranged from 1/30 to 1/120; however, because there is no universal pinning position, i.e., "charge-neutrality" point, the identification of the experimentally observed range in barrier height with $1/\epsilon$ is inadmissible. Thus, we conclude that models which invoke intrinsic interface states to explain Fermi-level pinning are not consistent with experimental observations. This strongly suggests that the nonideal nature of the experimentally observed interfaces plays an important role in determining the Schottky barrier height.

This work was supported by ONR Contract No. N00014-89-K-0132 and by AFOSR Contract No. F49620-86-K-0018. Thanks go to W. Harrison for valuable discussions concerning d-electron bonding, and to him, W. Spicer, and E. Weber for reviewing the manuscript.

[1]See, for example, Proceedings of the Seventh through Sixteenth Annual Conferences on the Physics and Chemistry of Semiconductor Interfaces, 1980–1989 (J. Vac. Sci. Technol. B).

[2]J. Bardeen, Phys. Rev. **71**, 717 (1947).

[3]V. Heine, Phys. Rev. **138**, A1689 (1965).

[4]J. C. Phillips, J. Vac. Sci. Technol. **11**, 947 (1974); J. M. Andrews and J. C. Phillips, Phys. Rev. Lett. **35**, 56 (1974).

[5]E. H. Rhoderick, *Metal-Semiconductor Contacts* (Clarendon, Oxford, 1980).

[6]L. J. Brillson, Phys. Rev. Lett. **40**, 260 (1978).

[7]A. B. McClean and R. H. Williams, J. Phys. C **21**, 783 (1988).

[8]W. E. Spicer, I. Lindau, P. R. Skeath, C. Y. Su, and P. W. Chye, Phys. Rev. Lett. **44**, 420 (1980).

[9]C. Tejedor, F. Flores, and E. Louis, J. Phys. C **10**, 2163 (1977).

[10]J. Tersoff, Phys. Rev. B **32**, 6968 (1985); Phys. Rev. Lett. **52**, 465 (1984).

[11]S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B **15**, 2154 (1977).

[12]C. B. Duke and C. Mailhiot, J. Vac. Sci. Technol. B **3**, 1170 (1985).

[13]F. Guinea, J. Sanchez-Dehesa, and F. Flores, J. Phys. C **16**, 6499 (1983).

[14]S. B. Zhang, M. L. Cohen, and S. G. Louie, Phys. Rev. B **32**, 3955 (1985).

[15]G. P. Das, P. Blöchl, O. K. Andersen, N. E. Christensen, and O. Gunnarsson, Phys. Rev. Lett. **63**, 1168 (1989).

[16]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[17]There is a common reference potential within the ASA (the Madelung potential), by which energy bands obtained from separate bulk calculations can be aligned. This provides a convenient definition of the "natural" or "unpinned" barrier height Φ_0 in the classical Schottky picture.

[18]W. A. Harrison and J. Tersoff, J. Vac. Sci. Technol. B **4**, 1068 (1986).

[19]J. L. Freeouf and J. M. Woodall, Appl. Phys. Lett. **39**, 727 (1981).

[20]N. Newman, M. van Schilfgaarde, T. Kendelwicz, M. D. Williams, and W. E. Spicer, Phys. Rev. B **33**, 1146 (1986).

[21]See, for example, Z. Liliental-Weber, J. Washburn, N. Newman, W. E. Spicer, and E. R. Weber, Appl. Phys. Lett. **49**, 1514 (1986).

[22]R. M. Feenstra (private communication).

[23]M. Hecht, J. Vac. Sci. Technol. B **8**, 1018 (1990).

[24]See, for example, R. E. Viturro, S. Chang, J. L. Shaw, C. Mailhiot, L. J. Brillson, A. Terrasi, Y. Hwu, G. Margaritondo, P. D. Kirchner, and J. M. Woodall, J. Vac. Sci. Technol. B **7**, 1007 (1989).