RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 8 15 MARCH 1989-I

Band bending and the apparent barrier height in scanning tunneling microscopy

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(Received 21 November 1988)

We consider the influence of tip-induced band bending on the apparent barrier height deduced from scanning tunneling microscopy (STM) experiments at unpinned semiconductor surfaces. Any voltage applied to a probe tip appears partly in the vacuum gap as an electric field at the semiconductor surface and partly in the semiconductor interior as band bending. The fraction appearing in each region is a function of gap spacing so that modulation of the tip-sample separation inevitably modulates the induced surface potential in the semiconductor. At finite temperature, the height and shape of this barrier determine the probability that an electron will reach the semiconductor surface where it can subsequently tunnel through the vacuum gap. Since the surface potential decreases with increasing tip-sample separation, STM measurements of the tunneling barrier at unpinned semiconductor surfaces will yield unusually low values. Detailed numerical calculations of the effect for passivated n-type Si(111) show it to be of observable magnitude. This mechanism may be distinguished from other recently proposed barrier-lowering mechanisms in that it is doping dependent, potentially long range, and possesses a unique voltage signature.

A number of semiconductor surfaces, including the cleavage face of GaAs (Ref. 1) and Si surfaces passivated by novel methods,[2] have unusually low defect densities resulting in Fermi levels which are not pinned at the vacuum-semiconductor interface. The importance of tip-induced band bending in the tunneling current-voltage characteristics of such systems has recently been demonstrated in scanning tunneling microscopy (STM) experiments on the H-terminated Si(111) surface.[3] We consider here the influence of this effect on the apparent barrier height deduced via tunneling microscopy.

The apparent barrier height has been a subject of great experimental and theoretical interest. Elastic deformation of the sample surface during macroscopic tip-sample contact can lead to anomalously low values in experiments on layered compounds,[4] while density-functional calculations have demonstrated how a physical collapse of the tunnel barrier may accompany the transition from tunneling to single-atom contact in experiments on metals.[5] We propose a novel barrier-lowering mechanism particular to a large class of semiconductors,[1] whose physical basis is altogether different.

The theory of planar metal-insulator-semiconductor (MIS) structures serves as our starting point.[6] Tip-induced band bending at an ideal, unpinned semiconductor surface is illustrated in Fig. 1 for an n-type sample in the depletion regime at zero external bias. The field in the vacuum, as well as that in the space charge region of the semiconductor, arises from the difference in tip and sample work functions $\Delta\Phi=\Phi-(\chi+\phi_n)$. Under the influence of this field, and any external bias voltage V applied to the sample, the surface potential V_d is obtained from a straightforward integration of Poisson's equation in the depletion approximation. Assuming no significant surface-state charge density, this yields

$$V_d(s,V)=\Delta\Phi\{[1+(s/s_0)^2+V/\Delta\Phi]^{1/2}-s/s_0\}^2 . \quad (1)$$

$\Delta\Phi$ serves as a natural voltage scale for the surface potential while $s_0=\epsilon_0/\epsilon_s W(\Delta\Phi)$ provides a natural length scale for the vacuum gap width. Here, ϵ_s/ϵ_0 is the dielectric constant of the semiconductor relative to vacuum and $W(\Delta\Phi)$ is the zero-bias, zero-separation depletion width which varies inversely as the square root of the doping. At fixed tip-sample separation the surface potential increases with positive sample voltage (reverse bias), decreases with negative sample voltage (forward bias), and vanishes (flat-band condition) when the external potential exactly compensates for the difference in work functions ($V=-\Delta\Phi$). For fixed tip-sample bias on the other hand, the surface potential decreases with increasing vacuum gap width. As s/s_0 approaches zero, which is the regime of negligible tip-sample separation, or of very light doping, all of the voltage drop occurs in the semiconductor (ideal Schottky barrier limit). Alternatively, when s/s_0 becomes infinite, which occurs either for very large gap spacings, or at very high doping, the entire voltage drop occurs across the insulating gap (metallic sample limit).

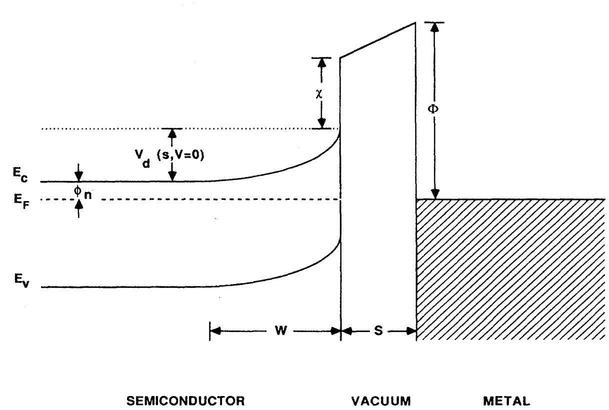

FIG. 1. Band bending at an ideal semiconductor-vacuum interface in the absence of an external bias voltage . Note that the drawing is not to scale since, typically, $W\gg s$.

Current conduction in a nondegenerate MIS structure is conventionally thought to be governed by the thermionic emission equation[7]

$$I = I_s e^{-q[V_d(s,V)-V]/kT}\{e^{-qV/kT}-1\}\,, \quad (2)$$

which describes a two-step conduction process. Free majority carriers of charge q in the semiconductor must possess enough kinetic energy normal to the interface to surmount the potential barrier presented by V_d and access the semiconductor surface. Having reached the surface, they then tunnel through the vacuum barrier into the metal. This picture ignores any contribution from tunneling through the semiconductor space-charge region, of length $W \gg s$. The vacuum tunneling term is given in the Wentzel-Kramers-Brillouin (WKB) approximation by[8]

$$I_s = A^* T^2 e^{-\phi_n/kT} e^{-A\langle\Phi\rangle^{1/2}s}\,, \quad (3)$$

where $\langle\Phi\rangle$ refers to the mean barrier height experienced by tunneling electrons, $A = 1.025$ eV$^{-1/2}$ Å^{-1}, and A^* is an effective Richardson constant.

The local tunneling barrier height measured in STM experiments is extracted from a modulation of the tip-sample separation and following Lang[5] we define the apparent barrier Φ_A as

$$\Phi_A = [(-1/A)d\ln I/ds]^2\,. \quad (4)$$

For an unpinned semiconductor surface, the fraction of applied bias voltage which drops in the semiconductor is a sensitive function of the gap spacing. Modulating the tip-sample separation therefore inevitably modulates the surface potential as well. For the thermionic emission formulation of Eq. (2), one finds that[9]

$$d\ln I/ds = -A\langle\Phi\rangle^{1/2} - q/kT[dV_d(s,V)/ds]\,. \quad (5)$$

Since the surface potential decreases with increasing tip-sample separation, the new term in (5) is the opposite sign of the familiar tunneling contribution. Thus, one predicts that STM measurements of Φ_A at unpinned semiconductor surfaces will yield low values. This situation arises because of a competition between the two physically different steps governing the flow of current: widening the gap exponentially suppresses tunneling through the vacuum barrier, while at the same time it exponentially enhances the number of free carriers capable of reaching the semiconductor surface.

The implications of (4) and (5) for the specific case of a planar, passivated, nondegenerate, n-type Si(111)/Au junction are shown in Fig. 2, where we have plotted Φ_A versus tip-sample separation for a small forward bias and several different sample dopings. The prediction of (5) in the absence of any band-bending effects ($dV_d/ds = 0$) is also shown for comparison. The differences are dramatic, and persist to large values of s, especially at low doping (this is a direct consequence of the scaling with s_0 mentioned above).

To test the quantitative reliability of these phenomenological predictions we have also formulated a more complete quantum-mechanical treatment. The calculational approach involves numerical solution of a one-dimensional (1D) Schrödinger equation in the effective-mass approximation. The method avoids use of the WKB technique while it also permits an explicit assessment of the significance of tunneling through the semiconductor space charge in parallel with thermionic emission.

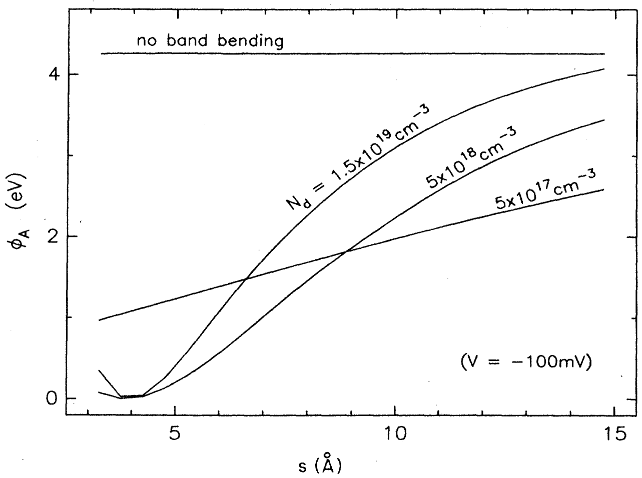

FIG. 2. Apparent tunnel barrier height vs tip-sample separation, as a function of semiconductor doping, for thermionic emission in the Au/n-type Si(111) system. $T = 300$ K, $\Phi = 5.1$ eV, and $\chi = 4.3$ eV (Ref. 21).

The space-charge potential computed in the depletion approximation is parabolic in x, the direction normal to the vacuum interface, decaying from V_d at the semiconductor surface to zero at $x = -W$ in the bulk. The vacuum barrier is taken as trapezoidal, and the metal is treated as a free-electron Fermi gas. Image potential effects are ignored.[10]

The semiconductor is modeled in a one-band, many-valley, effective-mass approximation including anisotropy. The indirect conduction band minima in silicon lie along the six equivalent $\langle 100\rangle$ directions in the Brillouin zone, and the constant-energy surfaces are ellipsoidal.[11] Following Stratton and Padovani,[12] the anisotropic effective mass equation is reduced to an equivalent 1D Schrödinger equation for motion through the semiconductor in the (111) direction.[13] We assume the single-band effective mass computed for allowed conduction-band states also properly describes tunneling through the space-charge region. This equation is then solved by discretizing the position-dependent electron potential energy into a series of piecewise linear segments[14] and employing matrix methods to calculate the overall transmission probability, with appropriate wave function derivative matching at discontinuities in electron effective mass.[15]

Equilibrium distribution functions at finite temperature are used for electrons in both metal and semiconductor. The phase-space summation, conserving energy and transverse momentum, reduces to a single, unrestricted integral provided the transmission coefficient T depends only on E_x, the energy component normal to the barrier.[16] The net current density is then given by the expression

$$j = \frac{qm_t}{\gamma^{1/2}m_0}\int_0^\infty dE_x T(E_x)[N_0(E_x) - N_0(E_x - qV)]\,, \quad (6)$$

where N_0 is the one-dimensional supply function[17] for electrons in semiconductor and metal, respectively, while γ is the anisotropy factor for Si⟨100⟩ ellipsoidal pockets projected along the ⟨111⟩ direction.

Computations based on (6) reveal that thermally activated tunneling through the semiconductor space charge is responsible for the majority of the observed current at moderate doping levels. This effect is illustrated in Fig. 3 for $N_d = 5\times10^{18}$ cm^{-3}.[18] The current distribution as a function of normal energy peaks well below the top of the surface potential barrier for all of the distances of interest. The inset shows how the fraction of total current arising from thermionic emission always remains small. There are two reasons for this. First, the effective mass for tunneling in the ⟨111⟩ direction is small, $m_x = 0.26m_0$. Second, and more important, V_d is enormous on the scale of kT (e.g., several hundred meV) so that despite relatively long depletion widths, tunneling through the space charge is favored.

Nevertheless, there is still a very substantial lowering of Φ_A due to band bending. This is illustrated in Fig. 4, where we display our predictions from (6) versus tip-sample separation, at the same bias and sample dopings considered in Fig. 2. At the lowest doping shown, the results differ little from the expectations based on MIS phenomenology, whereas the other curves are shifted upward relative to where they were before. The distinction arises because the logarithmic ratio of $j_{\text{thermionic}}$ to j_{total} is a more quickly increasing function of distance at higher doping.[19]

Lang[5] has predicted that at short distances, where tip and sample approach single-atom contact, there is a dramatic lowering of Φ_A in metal-vacuum-metal systems.[20] Approximately 5 Å from tip-sample contact, however, Φ_A approaches its asymptotic limit, given by the work function determined from photoemission. This may be contrasted with our theory, which takes no account of short distance phenomena, but predicts results of much longer range. For example, with an unpinned Si sample

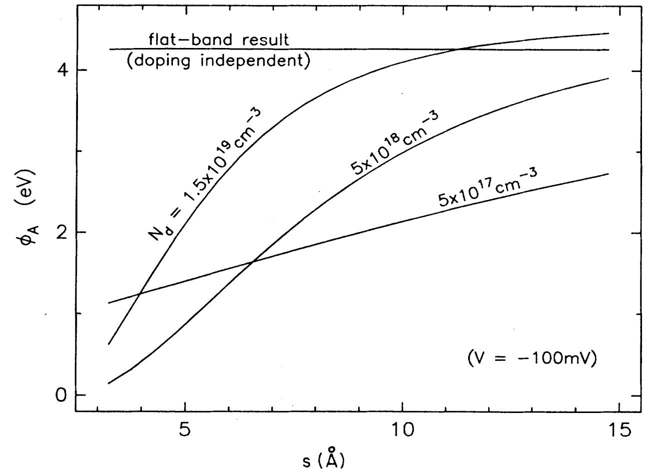

FIG. 4. Apparent barrier height vs tip-sample separation as a function of sample doping, with tunneling through the semiconductor space-charge region included.

doped at 5×10^{17} cm^{-3}, an STM measurement of Φ_A will show a low value at any distance, provided sufficient current can be drawn to stabilize the position of the probe tip.

Band-bending effects may also be distinguished through their unique voltage signature. Figure 5 displays the apparent tunnel barrier height versus distance for several different bias voltages applied to the same sample. At a given tip-sample separation, Φ_A depends critically in this bias due to the sensitivity of V_d to the field between tip and sample.[2]

In summary, a simple classical theory of thermionic emission in planar MIS junctions suggests that, at ideal semiconductor surfaces, the strong distance dependence of the tip-induced surface potential in an unpinned sample

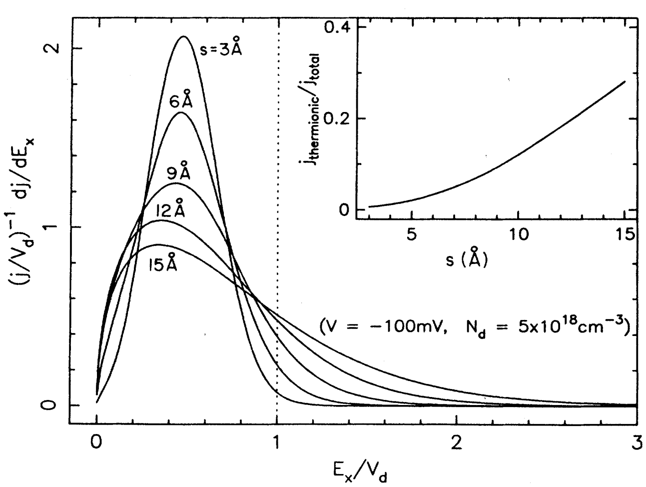

FIG. 3. Differential current density distribution vs normal energy (relative to the semiconductor surface potential) as a function of tip-sample separation. Inset: Thermionic contribution as a fraction of total current density.

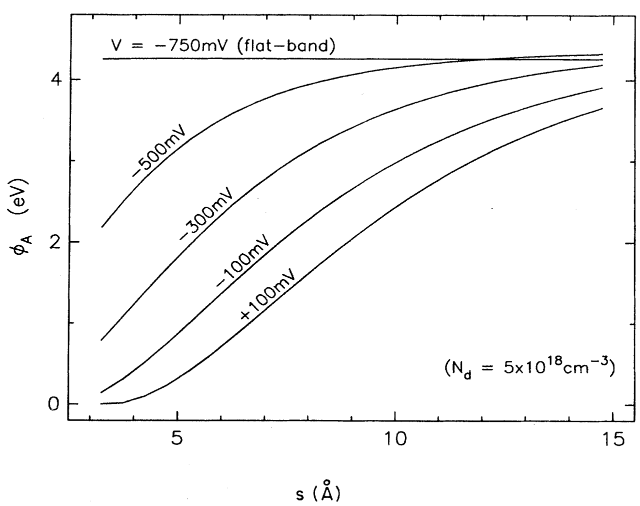

FIG. 5. Apparent barrier height vs tip-sample separation as a function of sample bias for fixed doping, with tunneling through the semiconductor space-charge region included.

has a profound influence on the apparent tunneling barrier, Φ_A, measured in STM experiments. A more complete quantum mechanical treatment for the nondegenerate, passivated, n-type Si(111)/Au system, which includes tunneling through the semiconductor space charge, confirms the qualitative lowering of Φ_A due to band bending predicted classically. The effects are substantial and of easily detectable magnitude. This phenomenon may be distinguished from other barrier lowering mechanisms by virtue of its range, and through a unique voltage signature which derives from the sensitivity of the surface potential to the electric field between tip and sample.

The authors are grateful to W. J. Kaiser for stimulating their interest in the Schottky barrier problem, as well as for many fruitful discussions. One of us (M.W.) also wishes to acknowledge the helpful comments of J. Stroscio. This work was supported by the Office of Naval Research under Contract No. N00014-86-K-0214, and by the Shell Company Foundation.

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[19]The results in Fig. 2 were also computed via Eq. (6), restricting the energy integration to $E_x > V_d$, so that the comparison reflects only the differences due to space-charge tunneling.

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