Role of atomic force in tunneling-barrier measurements

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Experimental measurements of the apparent barrier height as a function of tip-sample separation using a scanning tunneling microscope (with clean *W* tips and clean Si surfaces in ultra high-vacuum) show that the barrier height starts at 3.5 eV at large separations, increases to 4.8 eV at about 1.5 Å before the mechanical contact, and then drops to below 0.3 eV within a fraction of an ångström. At the distances encountered in scanning tunneling microscopy, forces between sample and tip can be significant. Using a simple model of this system including tip-sample forces leads to a calculated apparent barrier height which quantitatively reproduces the observed variation in apparent barrier height over the entire range of tip-sample separations.

An understanding of the tunneling barrier is important to the interpretation and understanding of scanning tunneling microscopy experiments.[1] Although only infrequently measured, a knowledge of the tunneling barrier height can be used to enhance analysis of tunneling spectroscopy measurements,[2] to reveal effects of charging and band-bending on semiconductor surfaces,[3] and to definitively establish whether sample and tip are in strong mechanical contact.[4,5] Yet, the tunneling barrier height remains one of the least understood properties of the scanning tunneling microscope (STM). Due to the strong electric field and the geometric asymmetry of the STM tunnel junction, the barrier height is no longer independent of tip-sample separation.

One contribution to the variation in barrier height at STM distances was made by Lang[6] who showed that the exchange–correlation part of the potential varies as the cube root of the electron density, and as a result the apparent barrier height is predicted to show a slow decrease over 3–5 Å as the sample and tip approach one another. However, experimental measurements (discussed below) show that the measured barrier height exhibits a slight *increase* as the sample and tip approach one another, up to a point on contact; beyond this point the apparent barrier height drops by an order of magnitude within only 1 Å. We assert that the explanation of this behavior lies in the existence of significant *forces* between sample and tip,[7–9] which have been neglected in previous treatments. In this paper, we show that at small tip-sample separations these forces significantly affect the experimental measurement and that by including realistic forces between sample and tip, it is possible to accurately model the variation in the measured apparent barrier height over the entire range of tip-sample separations.

The experimental barrier height measurements were performed using an ac modulation method, by applying a small 0.05 Å modulation to the *z*-piezo at a frequency ω_{mod} (here, 2 kHz) which is above the closed-loop bandwidth of the feedback control system but well below the lowest mechanical resonance frequency of the STM, and measuring the induced modulation of the tunneling current (dI) using a lock-in amplifier. We believe that this method is more accurate than the dc method used in the earlier barrier-height measurements.[10] In our experiments, the sample was a clean Si(111) sample (*n*-type, Sb-doped, 5 mΩ-cm) which was cleaned by high-temperature annealing to reveal well-ordered regions of Si(111)-(7×7) in the STM. The barrier height as a function of tip-sample separation was made by centering the tip above a well-ordered (7×7) region, then withdrawing the tip from the sample, and finally slowly pushing the tip toward the sample (by adjusting the average current demanded by the feedback controller) while simultaneously measuring the average tunneling current, the modulated tunneling current component at frequency ω_{mod}, and the output of the feedback loop controller. Each experiment was stopped when, as described below at a sufficiently close separation a marked decrease in the modulation dI was observed; this is attributed to mechanical contact between tip and sample. Subsequent imaging of the same area usually revealed a marked amount of tip-induced disorder, which necessitated moving the tip to a new region of the sample between experiments. In all cases, there barrier height measurements were performed with tips that provided atomic resolution.

From the output of the feedback controller and the known calibration of the *z*-piezoelectric scanner, we obtain the (apparent) displacement δz and also obtain a measure of the tip-sample separation z (to within an unknown additive constant). The absolute calibration of the piezoelectric scanners represents the larger uncertainty in the measurements and is estimated to be accurate to within 15%. Dividing the output of the lock-in (dI) by the known *z*-piezo modulation (dz) and the average tunneling current (I) gives $d\ln I/dz \equiv (1/I)(dI/dz)$.

The apparent barrier height, from experimental point of view, is defined as:

$$\phi = (\hbar^2/8m_e)(d\ln I/dz)^2 \simeq 0.952(d\ln I/dz)^2. \qquad (1)$$

Figure 1 shows experimental measurements of the apparent barrier height as a function of tip-sample separation obtained in this manner on a clean Si(111)-(7×7) sample with a sample bias of −1 volt with respect to the tip. As a function of tip-sample separation, the barrier height versus distance can be separated into four distinct regimes: 1) At

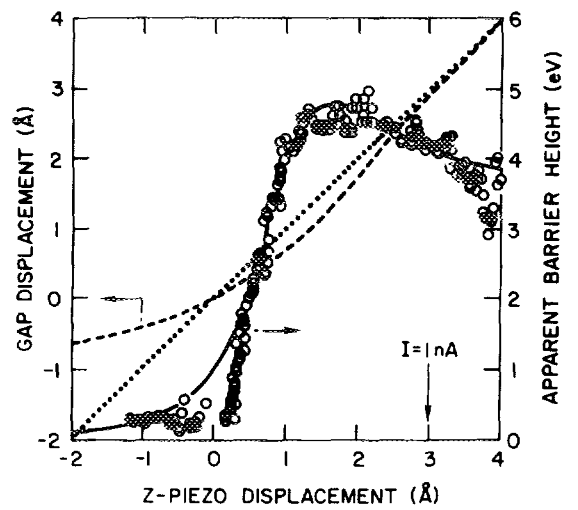

FIG. 1. Variation of the measured apparent barrier height with z-piezo displacement and its interpretation. Circles are data points, see text. Solid curve is derived from Eq. (8), by assuming that the "apparent barrier height by definition" is 3.5 eV over the entire range of operation, but the tip deforms due to the force between the tip and the sample. Dashed curve is the actual gap displacement as a function of the measured z-piezo displacement. Dotted curve, the fictitious gap displacement in the absence of force, is included for comparison. The equilibrium distance, where the net force is zero, is taken as the origin of z. Because the attractive force has a longer range than the repulsive force, the absolute equilibrium distance, that is, the distance between the nucleus of the apex atom of the tip and the top-layer nuclei of the sample at which the net force is zero, is slightly less than the sum of the atomic radii of both atoms. It is estimated to be $\simeq 2$ Å. The normal topographic images are usually taken at $I = 1$ nA, corresponding to a distance of $\simeq 3$ Å from the equilibrium point, or $\simeq 5$ Å from nucleus to nucleus.

large separations the barrier height is approximately 3.5 eV, which (within the estimated 15% calibration uncertainty) is roughly equal to the average work functions of tungsten and silicon. 2) As the tip-sample separation is decreased, the barrier height first exhibits a small *increase* to about 4.8 eV. 3) Further decreasing the tip-sample separation causes the barrier height to plummet by more than a factor of ten with only a 1 Å change in tip-sample separation. 4) Pushing the tip toward the sample even further produces only a small modulation of the current dI/dz, leading to an apparent barrier height of near zero. We note that the observed behavior of the apparent barrier height is *continuous* and *reversible* if the tip is not pushed too deep, which is consistent with the observations of Dürig *et al.* on metal surfaces,[4] as well as the first-principle calculations of Ciraci *et al.*[8,9]

Clearly, the fourth regime corresponds to a tip-sample contact. Here, the gap displacement δs is much smaller than the z-piezo displacement δz, and the observed barrier height is much smaller than its actual value. This is similar to the case of imaging graphite in air.[5] Although silicon is much more rigid than graphite, as pointed out by Pethica *et al.*,[7] and Ciraci *et al.*,[8,9] tip and sample deformation under atomic forces during STM operation is a universal phenomenon.

Here, we propose that the often-neglected forces between sample and tip[7-9] play crucial roles in determining the apparent barrier height in STM measurements. The observed variation of apparent barrier height with z-piezo displacement can be understood in terms of this force, which causes a deformation of the tip and the sample near the contact region. The deformation makes the z-piezo displacement δz (as measured through the voltage applied on the z-piezo) *different from the gap displacement* δs (see Fig. 1). Although in some experiments, a hysteresis near the contact point was observed,[10] first-principle calculation of a clean tip-sample system shows that the process of going back and forth up to a mechanical contact can be completely reversible, with no instability.[8,9] Our experiments confirm this prediction. In the strong repulsive-force region, the tip-sample separation is virtually constant regardless of the z-piezo displacement. Therefore, in this region, the apparent barrier height measured through the z-piezo displacement $[d \ln I/dz]^2$, is much lower than the actual value of the "apparent barrier height by definition", $[d \ln I/ds]^2$. A similar idea has been used to interpret STM images of graphite, where the force between the sample and the tip lead to large deformation of the soft graphite and low apparent barrier heights.[5] However, even for rigid and highly conductive tips and samples, an apparent barrier-height lowering will be observed when there are repulsive interactions between sample and tip. In the attractive-force regime, the actual gap displacement δs may be greater than the measured z-piezo displacement δz because of the positive force gradient (see Fig. 1).

The observed variation of apparent barrier height in our experiments can be understood quantitatively based upon the following three assumptions:

(1) Over the entire range of STM operation, the tunneling conductance G depends exponentially on the true tip-sample distance s

$$G \propto \exp(-2\kappa s), \tag{2}$$

where κ is the decay constant of the sample wave function, $\kappa = \sqrt{2m_e\phi}/\hbar$. In fact, up to a firm contact, almost all the reported measurements are consistent with this assumption.[11] Theoretical calculations show that if the barrier lowering follows a $1/s$ law, as in the case of image force, the value of $[(d \ln I)/ds]^2$ should be approximately a constant over the entire distance range of STM operation.[11]

(2) The force on the entire range of tip-sample distance can be described by the Morse curve[12]

$$F = -2\kappa U_e\{\exp[-\kappa(s-s_e)] - \exp[-2\kappa(s-s_e)]\}, \tag{3}$$

where U_e is the binding energy of chemisorption, and s_e is the equilibrium distance, i.e., the distance at which the net force is zero. In the following, we will argue that the constant κ in the expression of the Morse curve is equal to that of the sample wave function based both on experimental evidence and theoretical arguments. The experimental evidence comes from the direct measurement of the attractive force as a function of tip-sample distance. Dürig *et al.* have shown that in the attractive-force regime, the value of force exhibits an exponential dependence on tip-sample separation with a rate of one order of magnitude per two ångströms, i.e. a factor of two slower than the tunneling conductance, one order of magnitude per ångström.[4] Theoretically, it is based on the fundamental equality[13] between Bardeen's tunneling matrix element[14] M and the Heisenberg–Pauling resonance energy[15] U, i.e. the energy lowering between two atomic systems approaching each other due to wave-function overlap. Since the tunneling conductance is proportional to the square of Bardeen's tunneling matrix element,[14] the energy lowering U is proportional to the square root of tunneling conductance G

$$U \propto -\sqrt{G}. \qquad (4)$$

From Eq. (2) and the definition of force, $f = -\partial U/\partial s$, we find

$$F \propto \exp(-\kappa s). \qquad (5)$$

(3) The mechanical loop of STM responses to the force and exhibits an elastic deformation. By formally introducing an elastic constant, the deformation is

$$\delta z = \alpha F. \qquad (6)$$

For a well-designed STM or AFM, the deformation takes place predominately near the end of the tip. This deformation has been studied extensively by Pethica *et al.*[7] They show that the elastic constant α is on the order of

$$\alpha = (E^* a_0)^{-1} \cong E_T^{-1} + E_S^{-1}) a_0^{-1}, \qquad (7)$$

where E^* is the effective Young's module, which is determined by the Young's module of the tipe, E_T, and that of the sample, E_S; a_0 is a characteristic radius of the tip end.

The observed z-piezo displacement is then the sum of $\delta z = \alpha F$ and the true tip-sample displacement δs. Using Eqs. (3) and (6), we find

$$dz/ds = 1 - \beta\{\exp[-\kappa(s - s_e)] - 2\exp[-2\kappa(s - s_e)]\}. \qquad (8)$$

The dimensionless quantity $\beta = 2\alpha\kappa^2 U_e$ is a measure of the relative stiffness of the STM and the tunneling gap. An excellent fit to the measured data is found using $\beta = 0.95$ and assuming the actual apparent barrier height $0.952(d \ln I/ds)^2 = \text{const.} = 3.5$ eV throughout the entire distance range, as shown in Fig. 1.

Using Eq. (7), we can estimate the characteristic radius of the end of the tip. Assuming $U_e = 1.5$ eV, with the Young's module of tungsten, $E_T = 34 \times 10^{11}$ dyn/cm^2 and that of silicon, $E_S = 12 \times 10^{11}$ dyn/cm^2,[16] we find $a_0 \simeq 6$ Å. This is a reasonable value for tips which exhibit atomic resolution, such as these used in our experiments.

In conclusion, we provide evidence that the atomic force between the tip and the sample can induce deformation to the tip and the sample in the vicinity of the tunneling gap even with clean samples and tips, and tunneling currents on the order of nanoamperes. As a result, the measured z-displacement (through the reading of the voltage applied on the z-piezo) may be not equal to the true displacement of the gap. Using a simple model, we find a quantitative explanation of the variation of the measured apparent barrier height with measured z-displacement.

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