

Possible mechanisms of atom transfer in scanning tunneling microscopy

by Robert Gomer

Various mechanisms for the sudden transfer of an atom from or to the tip of a scanning tunneling microscope are considered. It is concluded that thermal desorption could be responsible and also that quasi-contact in which the adsorbed atom is in effect "touching" both surfaces, which would still be separated from each other by 2–4 Å, can lead to unactivated transfer via tunneling. For barrier widths as small as 0.5 Å, however, tunneling becomes negligible.

Introduction

It is reported by various investigators [1] that there are occasional abrupt, usually irreversible, changes in the tips of scanning tunneling microscopes, and it has been speculated that these result from the transfer of an atom or group of atoms from substrate to tip or vice versa. This communication examines various possibilities for such transfers. The mechanisms examined are atom tunneling, thermally activated desorption, and field ionization.

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Atom tunneling

When two surfaces are brought into close proximity, there is the possibility that a weakly bound atom on one surface may tunnel to the other. For simplicity we assume a parabolic barrier of height V_0 and half-width x_0 . If we take the rate constant for tunneling to be

$$k_t = \nu \exp -2(2m/\hbar^2)^{1/2} \int_{-x_0}^{x_0} \sqrt{V(x) - E} dx, \quad (1)$$

with

$$V(x) = V_0[1 - (x/x_0)^2], \quad (2)$$

we find easily that

$$\begin{aligned} k_t &= \nu \exp -(2m/\hbar^2)^{1/2} \pi V_0^{1/2} x_0 \\ &= \nu \exp -69(MV_0)^{1/2} x_0, \end{aligned} \quad (3)$$

where M is the mass in a.m.u., V_0 the barrier height in eV, and x_0 its half-width in Å. Let us assume that a jumping event occurs on average once a day, so that $k_t = 24 \times 3600)^{-1} = 10^{-5} \text{ s}^{-1}$. We then find, assuming $\nu = 10^{12} \text{ s}^{-1}$, that $MV_0 = (0.57/x_0)^2 \text{ (a.m.u.) eV/Å}^2$. If $M = 28 \text{ a.m.u.}$ corresponding to Si and $x_0 = 0.5$, so that the actual barrier base width is 1 Å, $V_0 = 0.5 \text{ eV}$. For such a small barrier, thermally activated transfer would totally dominate and lead to a lifetime of 10^{-10} s . The situation changes dramatically, however, when $x_0 = 0.1 \text{ Å}$. For such a distance and again for $M = 28 \text{ a.m.u.}$, $V_0 = 1.1 \text{ eV}$. It should be noted that at such

small separations, i.e., with the potential curves of the adsorbate on the two surfaces intersecting, the barrier height can be much less than the heat of binding H_a (Figure 1).

Other assumed barrier shapes, for instance rectangular or triangular, do not alter the above conclusions materially.

This calculation suggests that tunneling across gaps as small as 1 Å between the equilibrium atom positions corresponding to adsorption on the two substrates is prohibitively slow, but becomes quite probable when this distance is reduced to ~0.1 Å. Since the equilibrium separation of an adsorbed atom from its substrate is 1–2 Å, the virtual overlap of positions corresponding to adsorption on the two substrates does not mean that the surfaces themselves are "touching," merely that they are both "in contact" with an adsorbed or otherwise protruding atom. Such situations could arise, for instance, if the tip were moved over a local asperity. If the effective barrier width should become <0.1 Å in this process, atom transfer by tunneling could become much more probable than once a day.

Thermally activated desorption

We assume that the appropriate rate constant k_d is given by

$$k_d = \nu \exp -Q/kT, \quad (4)$$

where ν is an attempt frequency and Q , the activation energy of desorption, is equal in this case to the binding energy H_a . Again we assume $k_d = 10^{-5} \text{ s}^{-1}$ and find $H_a = 1 \text{ eV}$ if $T = 300 \text{ K}$ and $\nu = 10^{12} \text{ s}^{-1}$. This makes thermal desorption at least a good possibility.

There is also, in theory, the possibility of tunneling through a much reduced barrier combined with thermal activation. The considerations of the previous section indicate that this effect must be extremely small for massive adsorbates and can be neglected.

Field desorption

In a scanning tunneling microscope it may happen that the work functions of tip and substrate differ by 1–2 eV, particularly if the tip is dirty tungsten with $\phi = 5\text{--}6.5 \text{ eV}$ while the substrate is a clean semiconductor with $\phi = 4.5 \text{ eV}$. If tip and substrate are electrically connected, a contact potential is thus created; and if the separation is 1–2 Å, fields of the order of 1 V/Å can exist at or just in front of the surfaces. It has been shown previously [2] that the intersection of the field-deformed ionic and undeformed neutral potential curves for a system $M + A$, where M is a conducting substrate and A an adsorbed atom, is given by

$$Fex_c = I - \phi + H_a - Q - e^2/4x_c, \quad (5)$$

where F is the applied field, I the ionization potential of A , ϕ the work function of M , H_a the heat of adsorption, and Q the activation energy of field-assisted but thermally activated desorption, and $e^2/4x_c = 3.6/x_c$ in electron volt-angstrom units is an image correction (Figure 2). Equation 5 holds for

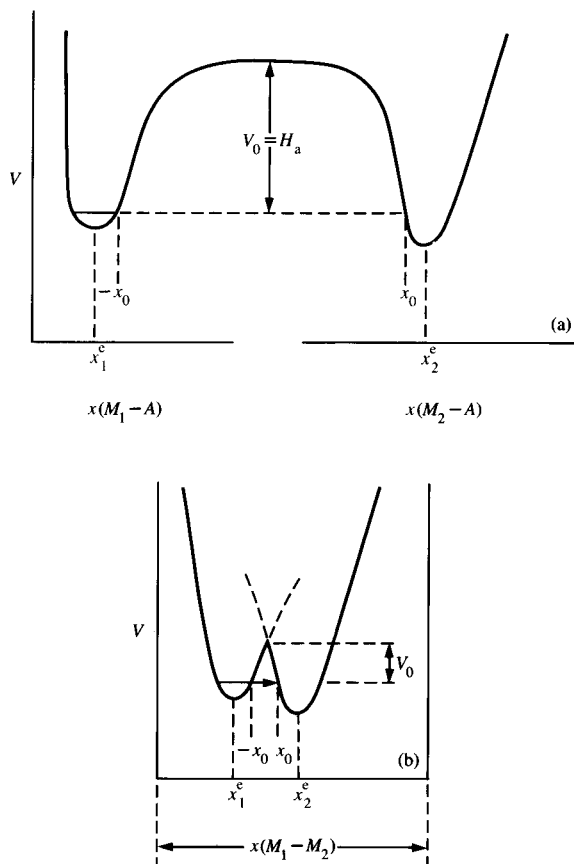


Figure 1

Potential energy diagram for an atom A adsorbed on either of two substrates M_1 and M_2 which are (a) moderately close, (b) so close that the potential curves overlap substantially. $x(M_1 - A)$: Separation of atom adsorbed on M_1 surface from that surface; $x(M_2 - A)$: Separation of same atom when adsorbed on M_2 surface from that surface; $x(M_1 - M_2)$: Separation of M_1 surface from M_2 surface; $-x_0, x_0$: End points of tunneling barrier, measured from position of barrier maximum, so that barrier width is $2x_0$; x_1^e, x_2^e : Equilibrium positions of A relative to M_1 and M_2 surfaces.

singly charged ions and can of course be modified trivially for higher charges. Let us see if a field of 1 V/Å can decrease the activation energy of thermal desorption appreciably. We assume that $I - \phi = 4 \text{ eV}$ and $F = 1 \text{ V/Å}$ and then find that for $H_a - Q = 0.5 \text{ eV}$, $x_c \approx 3.5 \text{ Å}$. If we pick $x_c = 3 \text{ Å}$, we find that $H_a - Q = 0.2 \text{ eV}$.

On reaching the other electrode, the positive ion A^+ formed at x_c is then neutralized, so that the entire process is equivalent to transferring A from M_1 to M_2 via a thermally activated process with an activation energy $Q < H_a$. If A has a high electron affinity and M_1 a low work function, field desorption of a negative ion from M_1 could also occur if F had the opposite sign from that assumed here, i.e., if M_1 were negative with respect to M_2 . In that case $I - \phi$ in

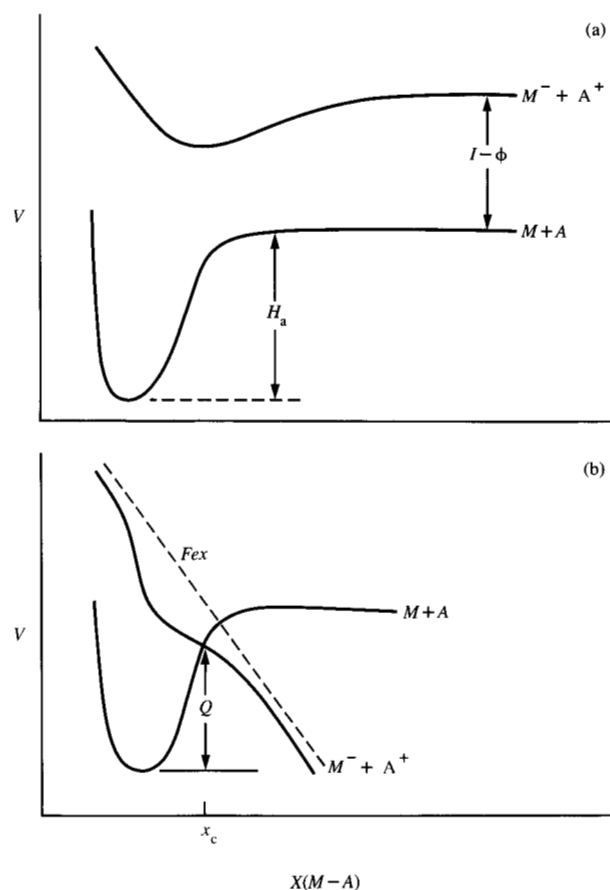


Figure 2

Schematic diagram illustrating the mechanism of field desorption of an adsorbed atom A. I : Ionization potential of A; ϕ : Work function of substrate M; H_a : Heat of adsorption; Q : Activation energy of desorption when a field is applied. Shown in part (a) are neutral ($M + A$) and ionic ($M^- + A^+$) curves for $F = 0$. Part (b) shows the curves in the presence of an applied field, which deforms the ionic curve but leaves the neutral curve unchanged, except for polarization effects which have been ignored here. For desorption of negative ions, the sign of the field must be reversed and $I - \phi$ replaced by $\phi - Af$, where Af is the electron affinity of A. x_c is the transition point where A becomes ionized, and is given by the solution of Equation (5). For simplicity, curve splitting at x_c is not shown.

Equation 5 would have to be replaced by $\phi - Af$, where Af is the electron affinity of A, i.e., the energy gained in forming A^- , and the upper curves in Figure 2 would have to be relabeled $M^+ + A^-$.

Conclusion

The foregoing suggests that tunneling of atoms across distances ≤ 0.1 Å can occur with reasonably high probability. This can happen for adsorbed or protruding atoms when the bulk of the tip and the substrate surfaces are still separated by 2–4 Å, depending on the details of the relevant atom-

substrate potential curves. Tunneling across gaps larger than 0.1–0.2 Å, however, seems prohibitively slow. In addition, thermal desorption, possibly field-assisted, could also occur. The latter should show a strong temperature dependence, as indicated by Equation (4), and it might therefore be possible to look for the frequency of atom transfer as a function of temperature.

Acknowledgments

This work was supported in part by Contract N00014-77-0018 from the Office of Naval Research. I have also profited from the Materials Research Laboratory of the National Science Foundation at the University of Chicago. This work was stimulated by the Workshop on Scanning Tunneling Microscopy, organized by H. Rohrer and G. Binnig and supported by IBM Europe. It is a pleasure to thank them for the opportunity to attend.

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Received August 5, 1985; accepted for publication September 12, 1985

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