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Sørensen, Mads Reinholdt; Jacobsen, Karsten Wedel; Jonsson, Hannes

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Thermal Diffusion Processes in Metal-Tip-Surface Interactions: Contact Formation and Adatom Mobility

Mads R. Sørensen,[1] Karsten W. Jacobsen,[1,2] and Hannes Jónsson[1,3]

[1]*Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark*
[2]*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853*
[3]*Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195*

We have carried out computer simulations to identify and characterize various thermally activated atomic scale processes that can play an important role in room temperature experiments where a metal tip is brought close to a metal surface. We find that contact formation between the tip and the surface can occur by a sequence of atomic hop and exchange processes which become active on a millisecond time scale when the tip is about 3–5 Å from the surface. Adatoms on the surface are stabilized by the presence of the tip and energy barriers for diffusion processes in the region under the tip are reduced. This can cause adatoms to follow the tip as it is moved over the surface.   [S0031-9007(96)01810-8]

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The scanning tunneling microscope (STM) has become one of the most important experimental techniques for surface science studies. The STM has mainly been used for *imaging* of surface structure and topography, but dynamic surface phenomena such as diffusion have also been studied. In other experiments, one has made constructive use of tip-surface interactions by using a STM as a tool for *manipulating* atoms or molecules on the surface [1]. Recently, electronic and mechanical properties of atom-sized metallic contacts have been investigated during indentation and subsequent retraction of a STM tip on a metal substrate [2–4].

It is well known from STM experiments that when a metal tip is brought close enough to a metal surface, the tip and surface rapidly form a contact [2,3,5]. Similar observations have been made using mechanically controllable break junctions [6,7] and other techniques [8]. In experiments at a temperature of 4 K, or below, it has been observed that the contact consisted of a single atom [2,6,8]. At room temperature, this has been reported in some experiments [5], whereas in others [3,7] a contact of 10–100 atoms formed right away.

On the theoretical side, a mechanism involving a sudden jump-to-contact due to a mechanical instability at close proximity of the tip and surface was originally proposed by Pethica and Sutton [9] and has been studied by several workers [10]. The picture that has emerged from continuum modeling, static atomistic calculations, and molecular dynamics (MD) is the following: When two surfaces are brought close to each other, the system becomes unstable at a certain critical distance of a few angstroms, and the surfaces suddenly jump into contact. This so-called "adhesive avalanche" involves collective motion of many atoms and occurs within approximately 1 ps in a MD simulation.

In this Letter, we suggest another mechanism for contact formation. At higher temperatures, e.g., room temperature, and on the time scale of a typical experiment, thermally activated processes can play a role in the process of contact formation. The contact can be formed by a sequence of individual hops of atoms from the tip towards the surface. We refer to this scenario as "diffusion-to-contact."

We have carried out calculations of the interaction of a Au tip and a Au surface. The surface is modeled by a Au(100) slab consisting of six layers of atoms [11]. The tip has a crystalline structure of stacked Au(100) layers. Two layers at the top of the tip and at the bottom of the substrate are static. The energies and forces of the atoms are calculated using potentials derived from the effective medium theory [12]. These potentials provide an approximate and computationally efficient description of the interatomic interactions in metallic systems, and they have been applied successfully in studies of surface science phenomena such as diffusion, surface relaxations and reconstructions, and surface premelting.

There is a very large difference between the time scale of a typical tip-surface experiment (10^{-3} s) and the time scale of a MD simulation (10^{-10} s). Processes which can occur readily in an experiment will likely not be seen in a direct, dynamical simulation. In order to identify and characterize processes which could take place in an experiment, we have carried out the following computational procedure: First, we have performed MD simulations at an elevated temperature of 520 K, where diffusion events can take place and a tip-surface contact can form. From the MD simulation trajectories we have extracted atomic configurations and quenched them in order to clearly identify the atomic migration processes that have taken place and to determine the stable initial and final configuration for each process. Second, for each migration process, we have used the nudged elastic band method [13] to determine a minimum energy path (MEP) [14] for the transition from the

initial to the final configuration. In this method, a discretized path consisting of 20–40 replicas of the system is constructed by linear interpolation between the given initial and final states, and then optimized iteratively. Assuming that diffusion can be well described within harmonic transition-state theory, the diffusion rate, $1/\tau$, at a temperature T can be written as $1/\tau = \nu \exp(-E_a/k_B T)$, where E_a is the activation energy barrier and the prefactor, ν, is an effective vibrational frequency. For each migration process, the energy barrier E_a is obtained as the maximum energy along the MEP, E_t, minus the potential energy at the initial state, E_i, i.e., $E_a = E_t - E_i$. For self-diffusion on metal surfaces, prefactors are typically on the order of 10^{12} s^{-1}, which implies that a process with an energy barrier lower than 0.50 eV occurs within less than 1 ms at room temperature.

The first set of simulations is performed with a tip that has a single apex atom at the bottom and then 9, 16, 25, 36, 49, and 64 atoms in the six subsequent layers [Fig. 1(a)]. The vertical (core) distance between the apex atom and the surface atoms just below is 3.3 Å, when the atomic positions are relaxed. At this distance, a contact between the tip and surface does not form spontaneously at 0 K. When the tip is moved 0.3 Å closer to the surface, the separation becomes unstable, and the tip and surface get connected by a one-atom point contact.
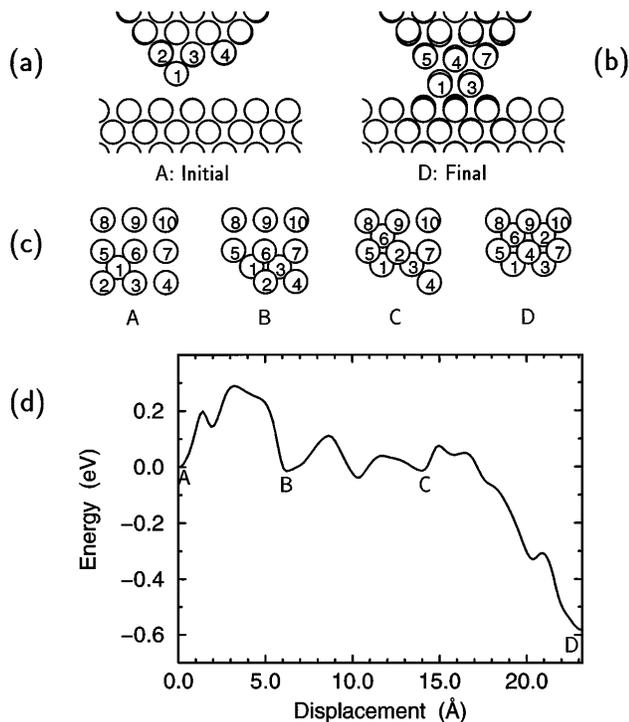

FIG. 1. Formation of a contact between a Au tip and a Au(100) surface. (a) Side view of initial configuration. (b) Final configuration. (c) Top view of four stable configurations, A–D, showing three two-atom exchange processes leading to contact formation. (d) Potential energy along minimum energy path. Labels, A–D, indicate points corresponding to configurations in (c).

In the high temperature simulations, atoms from the second tip layer migrate down to the bottom layer. In this way, a contact with a cross section of four or five atoms is formed. The processes involved are typically one-atom hops or two-atom exchange processes, but some of the processes are quite complicated in the sense that several atoms may be displaced significantly.

We have picked out one of the transitions for a more detailed discussion. Snapshots of the system in stable, intermediate configurations along the MEP are shown in Fig. 1(c). The corresponding variation in the potential energy is shown in Fig. 1(d). A compact contact is formed with four atoms in the bottom tip layer and six atoms in the second layer. The energy of the system is 0.58 eV lower in the final state compared to the initial state. The potential energy change can be understood as a competition between a lowering of the surface energy and an increase in elastic strain. The slowest migration process is the initial two-atom exchange process by which a contact with a cross section of essentially two atoms is formed [A → B in Fig. 1(c)]. The activation energy is 0.29 eV, which implies the process would occur on a time scale of approximately 0.1 μs at room temperature. The subsequent migration processes can also be described as two-atom exchange processes, but they have significantly lower energy barriers and thus have much higher rates. This implies that in a typical laboratory experiment, the contact formation could appear as an instantaneous cascade rather than a sequence of individual events.

It can be seen from Fig. 1(d), that several metastable configurations are found along the MEP. In some of these configurations [not shown in Figs. 1(a)–1(c)], atoms occupy positions that do not correspond to ideal lattice sites. Because of the strain on the system, the potential energy landscape is qualitatively different from that of the crystal.

With the limited set of simulations we have carried out, we have not found all possible transition paths for contact formation. However, we have investigated in detail the first migration process by which an atom from the second tip layer migrates down and forms a contact with a cross section of two atoms. We have calculated energy barriers for all such processes that are either one-atom hops or two-atom exchange processes, and we find that the two lowest activation energies belong to two exchange processes; one is the process A → B in Fig. 1(c), and the other can be described as atom 2 moving down and atom 1 moving one site to the right, with an energy barrier of 0.27 eV. Another low-barrier process is a one-atom hop with a barrier of 0.36 eV [atom 4 moving down]. The main point is that several processes have energy barriers significantly lower than 0.5 eV, and they therefore occur at room temperature on the time scale of a typical experiment.

In the following, we study the effect of the tip-surface distance. Here we have chosen a flat tip (analogous to

several previous simulations [10]) with 5×5 atoms in the bottom layer. Again, there are six layers in the tip and in the substrate. We have calculated the barriers for all one-atom hops or two-atom exchange processes by which an atom moves down from the lowest tip layer and ends up as an apex atom at the bottom of the tip. If the tip and surface are close enough, a one-atom point contact will form.

One of the migration processes is shown schematically in Fig. 2(a). It is a one-atom hop of an atom initially positioned at the corner of the bottom layer of the tip. The variation in the potential energy along the MEP is shown in Fig. 2(b) for three different tip-surface separations.
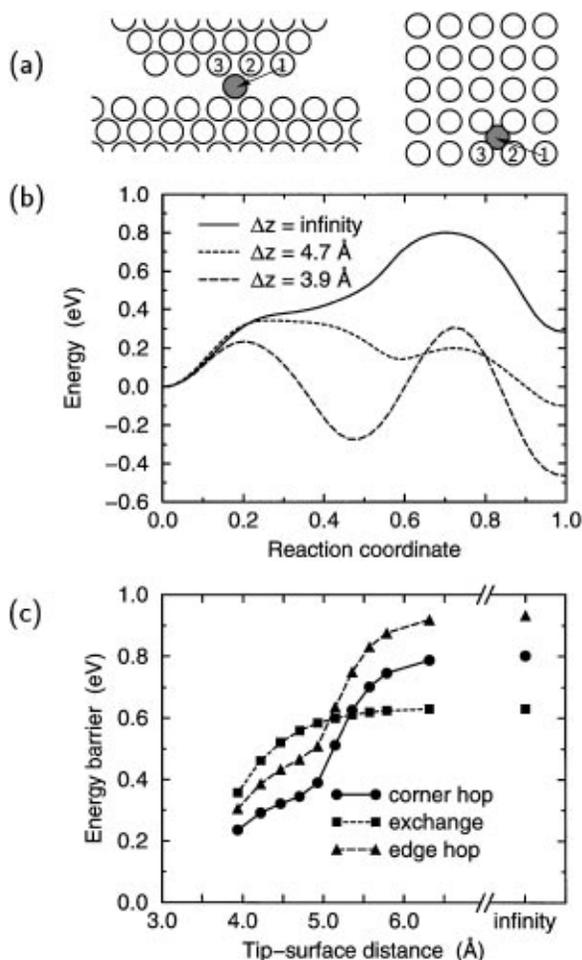

FIG. 2. (a) Schematic illustrations of a migration process where atom 1 at the corner of the bottom layer of the tip hops down and becomes an apex atom (shown gray) at the bottom of the tip. (b) Variation in potential energy along the minimum energy path for the process shown in (a) at three different tip-surface separations. Δz is the difference between the average (relaxed) height of the atoms at the bottom of the tip and the average (relaxed) height of the surface atoms underneath the tip. (c) The energy barrier as a function of tip-surface separation. Circles: the process shown in (a). Squares: a two-atom exchange process where atom 2 moves down and is replaced by atom 1. Triangles: a single-atom hop where atom 3 moves down.

When the tip and surface are separated by a large distance, the activation energy is 0.8 eV, and the energy at the final state is 0.3 eV larger than the energy at the initial state. As the tip moves closer to the surface and the distance becomes shorter than approximately 5 Å, the activation energy is reduced significantly, and furthermore the process becomes energetically favorable. The energy barrier is only 0.35 eV at a separation of 4.7 Å. The potential energy landscape also changes qualitatively with the tip-surface separation.

The activation energy for three different processes is given as a function of the tip-surface distance in Fig. 2(c). One is the process shown in Fig. 2(a). The others are a hop of an edge atom and a two-atom exchange process. In all three cases the activation energy is reduced significantly when the tip is close to the surface, but there is a crossover from two-atom exchange to one-atom hop.

The results presented in Fig. 2 indicate that for the geometry in Fig. 2(a), tip atoms can diffuse down and form a contact on a millisecond time scale at room temperature when the tip-surface distance is less than approximately 5 Å. Moreover, the simulation results in Fig. 1 suggest that once the contact formation is initiated, subsequent migration of atoms can make a one-atom contact evolve quickly into a contact of several atoms. This has been confirmed by MD simulations of the system in Fig. 2(a) at a temperature of 520 K. In these simulations we observe that approximately one half of the atoms in the bottom layer of the tip migrate towards the surface, thereby forming a contact of 10–15 atoms. When comparing the diffusion-to-contact to the "avalanche," we find that the former mechanism occurs in simulations where the tip-surface distance is too large for the latter mechanism to operate. More generally, the competition between diffusion and avalanche depends on a number of parameters besides time scales and temperature; the most important being tip shape and surface structure and materials. Indeed, a perfect pyramidal tip without adatoms is very stable and preferably forms contact by the avalanche mechanism.

We now address a different effect in tip-surface interactions. Instead of focusing on how the surface affects the barriers for migration of atoms on the tip, we now discuss the influence which the tip may have on diffusion of adatoms on the surface. We have chosen the geometry shown in the inset in Fig. 3 for the calculations. It is the same as in Fig. 1(a) except that the tip apex atom has been removed, and instead an adatom is initially placed on the surface outside the interaction range of the tip (position 1). In Fig. 3, the potential energy is shown as the adatom hops into the region underneath the tip (reaction coordinate $1 \rightarrow 5$) and is then transferred from the surface to the tip (reaction coordinate $5 \rightarrow 6$).

There are two important observations to be made from Fig. 3. First, energies at stable sites on the surface close to the tip are lower than energies at stable sites far from
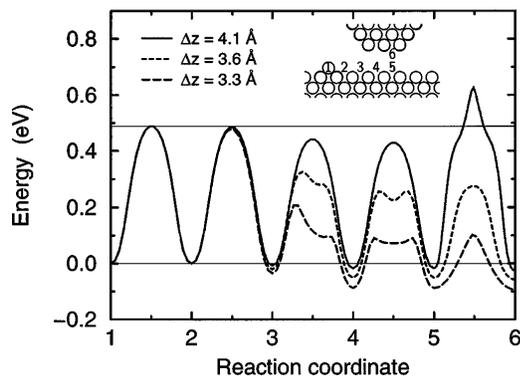
FIG. 3. Variation of potential energy when an adatom diffuses on a surface underneath a tip. The three curves correspond to three different tip-adatom separations, Δz. [Δz is the relaxed height difference when the adatom is in position 5 underneath the tip.] Inset: Side view of a part of the system.

the tip. This implies that the density of adatoms will be higher in the tip region compared to other regions on the surface. Second, the local energy maxima are reduced more than the local energy minima. Thus, the energy barriers for diffusion are lowered by the influence of the tip. At small tip-surface distances, the energy barrier for atom transfer between tip and surface becomes small and ultimately vanishes, as found in previous *ab initio* calculations for an Al atom between two Al(100) slabs [15]. However, one can find tip-surface distances for which the energy barrier for transfer is large and still the energy barrier for surface diffusion is significantly lowered by the tip.

These results have implications for the ability to manipulate atoms on a surface by the presence of a tip in a STM experiment. To move a metal adatom at a very low temperature, one has to move the position of the potential energy minimum at which the adatom is trapped. This requires a very short tip-adatom separation, most likely it requires actual contact between tip and adatom. Eigler and co-workers have moved adsorbed atoms or molecules on metal surfaces at 4 K in a controlled way using a STM [1]. At higher temperatures, an adatom can hop by thermal activation if the energy barrier is low enough. If the barrier is reduced by the presence of a tip close to the surface, the adatom may be able to hop underneath the tip but unable to hop away from the tip region, thereby making the adatom follow the motion of the tip along the surface. This kind of mechanism might be operating in recent STM experiments on Ag(110) where at a temperature of 50 K, Ag adatoms could be moved along the close packed rows as the tip scanned the surface [16]. At 295 K, monoatomic steps could be displaced by hundreds of angstroms.

[1] J. A. Stroscio and D. M. Eigler, Science **254**, 1320 (1991); M. F. Crommie, C. P. Lutz, and D. M. Eigler, Science **262**, 218 (1993).

[2] N. Agraït, J. G. Rodrigo, and S. Vieira, Phys. Rev. B **47**, 12 345 (1993).

[3] L. Olesen *et al.,* Phys. Rev. Lett. **72**, 2251 (1994); M. Brandbyge *et al.,* Phys. Rev. B **52**, 8499 (1995).

[4] J. I. Pascual *et al.,* Science **267**, 1793 (1995); L. Kuipers, M. S. Hoogeman, and J. W. M. Frenken, Surf. Sci. **340**, 231 (1995); A. Stalder and U. Dürig, J. Vac. Sci. Technol. B **14**, 1259 (1996); G. Rubio, N. Agraït, and S. Vieira, Phys. Rev. Lett. **76**, 2302 (1996).

[5] J. K. Gimzewski and R. Möller, Phys. Rev. B **36**, 1284 (1987); U. Dürig, O. Züger, and D. W. Pohl, Phys. Rev. Lett. **65**, 349 (1990).

[6] J. M. Krans *et al.,* Phys. Rev. B **48**, 14 721 (1993); J. Voets *et al.,* Phys. Rev. B **53**, 1072 (1996).

[7] C. J. Muller *et al.,* Phys. Rev. B **53**, 1022 (1996).

[8] D. P. E. Smith, Science **269**, 371 (1995).

[9] J. B. Pethica and A. P. Sutton, J. Vac. Sci. Technol. A **6**, 2490 (1988).

[10] J. R. Smith *et al.,* Phys. Rev. Lett. **63**, 1269 (1989); U. Landman *et al.,* Science **248**, 454 (1990); P. A. Taylor, J. S. Nelson, and B. W. Dodson, Phys. Rev. B **44**, 5834 (1991).

[11] The unreconstructed Au(100) surface is known experimentally to be metastable. When heated above 100 °C the surface reconstructs into a quasihexagonal structure. [See, e.g., J. F. Wendelken and D. M. Zehner, Surf. Sci. **71**, 178 (1978)]. For simplicity, we treat an unreconstructed surface in this study.

[12] K. W. Jacobsen, J. K. Nørskov, and M. J. Puska, Phys. Rev. B **35**, 7423 (1987); K. W. Jacobsen, Comments Condens. Matter Phys. **14**, 129 (1988); K. W. Jacobsen, P. Stoltze, and J. K. Nørskov, Surf. Sci. **366**, 394 (1996); P. Stoltze, J. Phys. Condens. Matter **6**, 9495 (1994), and references therein.

[13] G. Mills, H. Jónsson, and G. K. Schenter, Surf. Sci. **324**, 305 (1995).

[14] The MEP is such that at any point along the path, the potential energy increases for displacements perpendicular to the path. Being the path of largest statistical weight, the MEP is often used to define the reaction coordinate.

[15] S. Ciraci *et al.,* Phys. Rev. B **46**, 10 411 (1992).

[16] J. Li, R. Berndt, and W.-D. Schneider, Phys. Rev. Lett. **76**, 1888 (1996).