Simulating cyclic loading of atomic-sized gold tips on gold surfaces via classical molecular dynamics and density functional theory transport calculations

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Abstract. The ability to probe atomic-level interactions via scanning tunneling microscopy and other techniques has led to great interest in contact formation between atomic-sized metal electrodes. In the present work, it is demonstrated by atomistic simulations that atomic-sized gold surfaces can be mechanically annealed, or work hardened, until they are sharp and stable. We study the effect of the initial geometrical configuration of the tip on the process of formation of a stable structure between a tip and a flat gold surface, by using two different initial shapes of the tip in classical molecular dynamics simulations. Density functional theory transport calculations are performed to obtain the conductance of the simulated structures and compared directly with experimental measurements. Our results show that both configurations lead to stable structures after repeated cyclic loading and that the number of cycles required to reach stability depends on the initial configuration. The calculated conductance values at first contact between the tips and surface are consistent with the best available experimental data.

1. Introduction

The desire to manufacture smaller electronic devices and overcome constraints on the size and number of transistors that can be packed onto an integrated circuit [1], has perpetuated active research into various alternatives to well-established silicon technology[2–4]. One such avenue of research deals with atomic-sized conductors [5], in which fundamental processes such as bonding and the manifestation of friction at the atomic level become important. The scanning tunneling microscope (STM) or mechanically controllable break junction (MCBJ) [5, 6] are typically used for studying these systems. Both can be used to realize atomic-sized contacts between two surfaces experimentally. The accuracy of both techniques is made possible through the use of piezoelectric ceramics with the ability to displace, with subnanometer precision, one surface relative to the other [5]. A bias voltage is routinely applied across the two surfaces in order to measure the current as a function of the relative displacement between the surfaces. Small bias

voltages are used to ensure that the surfaces are in equilibrium at all times and consequently, that the electron transport across the atomic-sized contact region between the surfaces is adiabatic [5]. Under such conditions the conductance G ($= 1/R$, the inverse of resistance) across the electrodes can be obtained directly from the measured current, by dividing it by the bias voltage. The conductance instead of the resistance is measured because it exhibits quantization under certain circumstances in metallic nano-contacts, among other atomic-sized systems of various geometries and made from different materials [7, 8]. Conductance is usually expressed in units of $G_0 = 2e^2/h$, the quantum of conductance, with 2 being the multiplicity of the electron's spin, e its charge and h Planck's constant.

Nanocontacts have been studied extensively both experimentally and theoretically. (See Ref. [5] and the references therein.) Such systems exhibit many interesting phenomena. On the one hand, some metals such as Au, can form long monoatomic chains during stretching and before breaking of a nanojunction [9, 10]. This behaviour was first identified through observation of long plateaus in the conductance traces immediately before breaking [11]. Long monoatomic gold chains have also been observed directly in transmission electron microscopy measurements [12]. On the other hand, the conductance through the nanocontact during breaking or contact formation can exhibit very unique behaviours that depend on the type of metal as well as the geometry of the contacts [13, 14]. Interestingly, the geometries of the tips immediately before and after contact can be inferred from the conductance values obtained [15] by means of classical molecular dynamics (CMD) simulations [16, 17] and density functional theory (DFT) transport calculations [18, 19]. In this work we focus on how the geometry of the electrodes will influence the values of measured conductance in the particular case of gold contacts.

2. Computational methods

In previous works [20, 21] we showed that it was possible to model, via CMD simulations and DFT transport calculations, the repeated reforming and breaking of contact between two atomic-sized gold tips obtained from a ruptured gold nanojunction, which gave rise to very stable configurations of the tips in a process known as mechanical annealing (or work hardening). The results exhibited good agreement with the best available experimental data [15]. Here the same approach is taken to model the interaction between a sharp tip and a flat surface (mimicking the STM setup). This configuration is very different from the one we used previously: a narrow neck (mimicking the MCBJ setup). Thus, we aim to explore the influence of electrode geometries on the structures formed after contact formation. Moreover, experimental measurements of conductance between sharp tips and various surface geometries have been performed by the group of Kröger and others (see Ref. [14] and references therein).

We employ the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [22, 23] to run our CMD simulations. The empirically and computationally fitted embedded-atom-model (EAM) potential [24] serves to describe the forces between the atoms in our CMD simulations. Furthermore, in order to simulate work hardening of atomic-sized gold surfaces, we employ a simple but widely used type of EAM potential that has been fitted to various basic material properties of gold [25].

It is first necessary to select a particular tip configuration before we can run simulations. We take two different approaches. In the first approach a cone of near perfect symmetry, generated directly by means of LAMMPS and oriented along the (001) crystallographic direction, has been used (see figure 1). In figure 1(a), the apex atom on the cone-shaped tip approaches an absorbed atom (adatom) on a (111)-oriented surface from directly above (these two atoms will be the first to make contact and so have been colored brown for clarity). This mixed crystal orientation has been chosen based on the fact that (111)-oriented surfaces are the most stable energetically, and thus a tip with a (001) crystallographic orientation remains relatively stable during cyclic loading since (111)-oriented crystal planes form on its oblique faces. In addition, we placed an

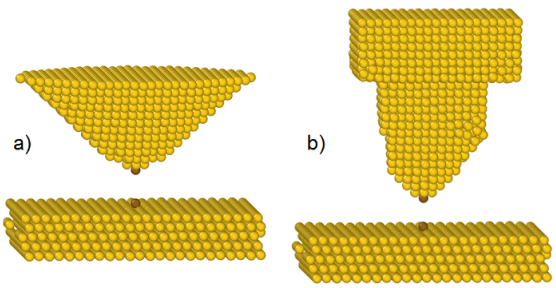

Figure 1. (Colour online) The initial configurations used in the simulations: a) a nearly perfectly shaped conical tip above an adatom on a clean surface, and b) a tip that was obtained by repeated rupture and contact formation of a notched nanowire, above the same surface with the adatom. Both tips are oriented along the (001) crystallographic direction, while the surface has a (111) orientation.

adatom on the surface directly beneath the lowest atom on the tip because this geometrical arrangement has been of particular interest in a number of works (see Ref. [14] and references therein).

Experimentally, however, in order to make a very stable tip and before performing the intended measurements, the tip is prepared by repeated contact formation [26]. To mimic this process, we have generated a second type of geometry of the tip (see figure 1(b)) using simulations similar to those performed previously in our group [15, 20, 21]. We started with a notched (001)-oriented nanowire and performed repeated rupture and contact formation on it to a maximum number of 6 atoms in the minimum cross-section of the constriction. (see Ref. [21] for details).

During the simulations performed in this work, the internal motion of the atoms in the first two top and bottom layers of the initial structures in figure 1 are frozen. The atoms in the top two layers of the tip are then displaced towards (during contact formation) or away (during rupture) from the surface at 0.004Å every picosecond, the remaining atoms responding dynamically to the rigid motion of the top layers. The velocity (equivalent to 0.4m/s) is about four orders of magnitude below the speed of sound in gold (3000m/s) [27], and combined with the low simulation temperature of 4.2K ensures that longer time-scale diffusive processes are negligible. The temperature is kept constant during the simulations by a Nose-Hoover thermostat [28, 29].

To demonstrate that mechanical annealing occurs upon repeated cyclic loading of the tips on the surface, the vertical distance between the first two atoms on the tip and surface to come into contact during approach, is plotted as a function of the bulk tip displacement. Contact is judged to occur when these two atoms come within a distance halfway between first and second nearest neighbours in a perfect gold FCC lattice (about 3.48Å). When the resulting minimum distance traces begin to overlap reproducibly, the surfaces are deemed to be stable and sharp, and the process of work hardening complete. Since experimental conductance traces only exhibit reproducibility up to contact conductances of around $5G_0$ during cyclic loading [20], the contact formation phases of cyclic loading in our simulations only continue until there are 6 atoms in the minimum cross-section. (See Ref. [21] for details on how the number of atoms in the minimum cross-section of the contact structures are determined). This follows from the observation that a monovalent gold atom contributes exactly one eigenchannel to transmission across atomic-sized gold junctions [5, 18, 19].

By definition, there are no electrons in CMD simulations: their effects are contained in the interatomic potentials described above. Thus, complementary methods, such as DFT transport calculations [18, 19] are required to make the analogy with experiments complete. So, to permit a comparison with experimental conductance values at first contact between the tips and surface, the DFT-based transport code ANT.G [30, 31] was employed. Such calculations are very computationally expensive. Therefore, to save time we have selected only 500 of the 5000 atoms from our CMD configurations, since the few atoms in the minimum cross-section

determine the transmission coefficient that is obtained from quantum transport calculations [18, 19]. On the other hand, to make the calculation more exact, an eleven electron basis set has been assigned to between 20 and 40 atoms in the minimum cross-section of the structures employed.

3. Results and discussion

Figure 2 plots minimum distance versus bulk tip displacement after 20 cycles of work hardening of the two initial configurations shown in figure 1. In figure 2(a) we see that it takes only three cycles before the traces overlap in a highly reproducible manner, demonstrating that a sharp and stable tip has formed. In figure 2(b), one additional cycle of contact formation is needed to achieve overlapping traces. These results are consistent with the cyclic loading performed on the wide (001)-oriented notched wire in Ref. [21]. The insets in figure 2 show the first-contact structures for two contact formation cycles (cycle 10 and 20 in both cases), once the tips and surfaces are sharp and stable. In figure 2(a), the first-contact structure resembles a monomer with 4 atoms in the layers immediately above and below it. In figure 2(b), however, the situation is more complicated with more than one atom in the minimum cross-section in both insets. The initial shape of the tip clearly plays a role in the arrangements of atoms in the minimum cross-section at first contact between tips and surfaces.

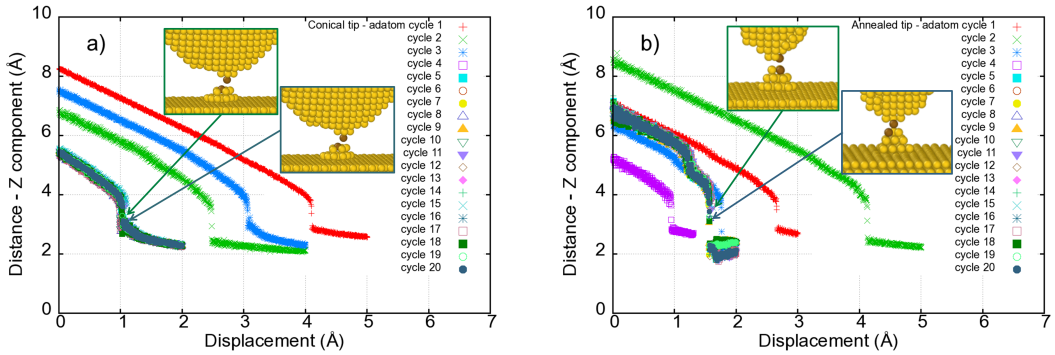

Figure 2. (Colour on-line) Minimum distance between the tips and surface versus bulk tip displacement for: (a) a cone-shaped tip oriented along the (001) direction, with its lowest atom positioned directly above an adatom in a three-atom hollow on the (111) surface, and (b), a (001)-oriented tip obtained by (simulated) cyclic loading of a notched nanowire, with its lowest atom positioned directly above the same surface and adatom as in (a).

It bears mentioning that the CMD simulations of a tip on a surface do not result in indentation through the surface, since in general the STM tip has to be harder than the substrate for this to occur [5, 32, 33]. Instead, after contact a tip is formed on top of the surface as shown in the insets in figure 2. The formation of a small mound on a gold surface after cyclic loading of a STM tip on a clean gold surface has actually been observed experimentally (see figure 3). Figure 3(a) shows the surface before contact with the STM tip and figure 3(b) after cyclic loading (the crystallographic orientations of the tip and surface are unknown in this case) [34]. Although the temporal and spatial resolutions of the experiments and our simulations differ greatly, the overall phenomenon is the same.

Previously in our conductance calculations, we used a valence basis set of only one electron per gold atom (6s atomic orbital). However, this led to an anomalously high value of around $1.60G_0$ for the monomeric gold contact obtained in Ref. [21]. In the present work, an eleven

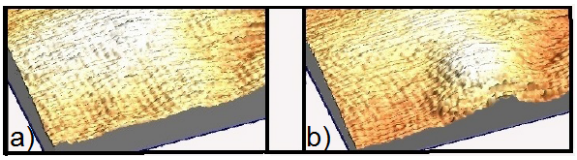

Figure 3. (Colour online) The formation of a mound on a gold surface (20nm x 10nm in dimension) before (a) and after (b) repeated contact formation at $4.2K$ between a STM tip and a clean surface, both made of 99.995 percent gold (of unknown crystallographic orientation) [34].

electron basis set (5d sub shell + 6s sub shell) was assigned to 10 atoms, including the monomer, in the contact region. An improved conductance of $1.18G_0$ was obtained in this way, which is within the range expected for this type of single-atom junction [15]. Applying the 11 electron basis to an even larger number of atoms in the constriction did not affect the outcome of the calculation appreciably. Hence, the eleven electron basis set has been assigned to between 20 and 40 atoms in the minimum cross-section of the structures employed in conductance calculations. As a result, we obtained a value between $1.0-1.20G_0$ for the monomers in the insets in figure 2(a) and around $1.70G_0$ in the case of the structures in the insets in figure 2(b).

4. Conclusion

It is demonstrated that repeated contact formation between gold surfaces mimicking the STM geometry also lead to stable and sharpened tips. In particular, the tips deposit atoms on the surface as cyclic loading proceeds, forming gold mounds resembling sharp tips. This confirms the equivalence between the STM and MCBJ experimental techniques for pure gold nanojunctions.

In the case of the symmetrical tip in figure 1(a), the stable configuration that is obtained after cyclic loading resembles a monomer, and conductance calculations on two first-contact simulation snapshots from two different contact formation cycles yield values within the range expected for monomeric contacts ($0.76 - 1.20G_0$) [15]. The less symmetrical tip in figure 1(b), however, does not produce a simple first-contact geometry. Various atoms overlap directly at the moment of first contact. Nevertheless, the conductance at first contact is consistent with less probable conductance values seen in histograms constructed from hundreds of thousands of conductance traces [13].

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