Current-Induced Embrittlement of Atomic Wires

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Recent experiments suggest that gold single-atom contacts and atomic chains break at applied voltages of 1 to 2 V. In order to understand why current flow affects these defect-free conductors, we have calculated the current-induced forces on atoms in a Au chain between two Au electrodes. These forces are not by themselves sufficient to rupture the chain. However, the current reduces the work to break the chain, which results in a dramatic increase in the probability of thermally activated spontaneous fracture of the chain. This current-induced embrittlement poses a fundamental limit to the current-carrying capacity of atomic wires.

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Recently it has been possible to make single chains of Au atoms [1–3]. These chains are the thinnest possible metallic wires. Experimentally, it is seen that Au single-atom contacts and chains break at applied voltages of 1 to 2 V [2,4–6]. Failure of conventional interconnects in integrated circuits is often due to electromigration, which is caused by electron scattering at defects in the metal. The Au chains, however, are defect-free, ballistic conductors. So, why are they affected by the passage of a current?

In this Letter we calculate the current-induced forces on atoms in a Au chain suspended between two Au electrodes. We then calculate, both with and without a current, the work to fracture each bond in the chain, and the ultimate tensile strength (UTS) of the chain. We estimate the current-induced change in the time required for thermally activated fracture. We find that the current-induced forces create a weak bond in the chain, they lower the UTS of the chain, and they dramatically increase the probability of thermally activated fracture, setting a fundamental limit to the current-carrying capacity of the wire.

The atomic chain in our calculations is shown in Fig. 1. The chain consists of four Au atoms. Each end of the chain is bonded to a contact consisting of three Au atoms arranged in a triangle. The plane of this triangle is perpendicular to the axis of the chain. Each contact is bonded to the surface of a semi-infinite Au electrode. The electrodes have a face-centered cubic (fcc) crystal structure. Their surfaces are (111) atomic planes.

The electronic structure of the system is described by a single-orbital tight-binding model, fitted to the cohesive energy and lattice parameter of bulk Au [7]. The model gives an excellent description of the elastic properties of bulk Au [7]. For an infinite perfect linear Au chain, the model predicts an equilibrium bond length of 2.52 Å and a cohesive energy of 2.78 eV per atom, within the range of different density functional calculations [8,9].

To calculate the forces on atoms in the presence of current, we employ a self-consistent tight-binding formalism, described earlier [10]. A voltage V is applied by rigidly shifting the two electrodes relative to each other in energy by an amount eV, where e is the electron charge. This results in a flow of electrons from left to right. Self-consistency is maintained by adjusting the on-site energies on all chain atoms, on all contact atoms, and on all electrode atoms bonded to contact atoms, until all these atoms are charge neutral. The self-consistent one-electron tight-binding density matrix $\rho(V)$ is calculated. The bond force between atoms n and m is given by

$$\mathbf{F}_{nm}(V) = -4(\nabla_n H_{mn}) Re[\rho_{nm}(V)] - \nabla_n \phi_{nm} . \quad (1)$$

The total force on atom n is given by $\mathbf{F}_n(V) = \sum_{m \neq n} \mathbf{F}_{nm}(V)$. Here H_{nm} is the Hamiltonian matrix element between atoms n and m and ϕ_{nm} is a repulsive pair potential. If R_{nm} is the distance between the atoms, then $\phi_{nm} = \epsilon (a_f/R_{nm})^p$ and $H_{nm} = -(\epsilon c/2)(a_f/R_{nm})^q$, where a_f is the fcc lattice parameter. ϕ_{nm} and H_{nm}

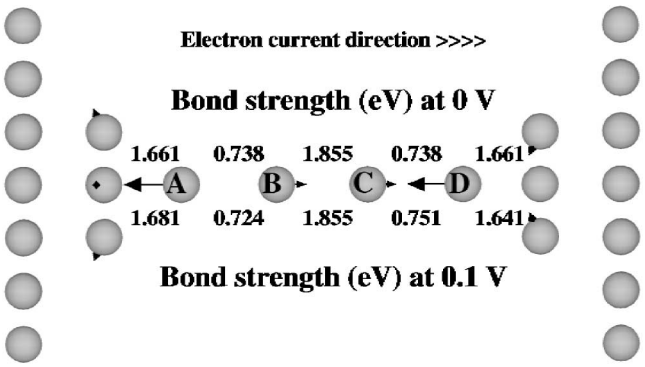

FIG. 1. The geometry used for the calculations. The length of bonds AB and CD is 2.58 Å, and that of BC is 2.47 Å. The arrows show current-induced forces on atoms at voltage $V = 0.1$ V. The two largest arrows, on atoms A and D, correspond to a force of 0.021 eV Å^{-1} against the electron current. The numbers above and below each bond give the work to fracture, in eV, for that bond at $V = 0$ and at $V = 0.1$ V, respectively. The extreme left and right numbers give the energies to fracture simultaneously the three backbonds of atoms A and D, respectively.

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are truncated just beyond the second nearest-neighbor distance in fcc. The band is filled until there are 0.727 22 electrons per atom, and $a_f = 4.08$ Å, $p = 11$, $q = 4$, $\epsilon = 0.007\,868\,0$ eV, $c = 139.07$. The fitting procedure for the model is described elsewhere [7]. At $V = 0$, Eq. (1) enables us to calculate all interatomic forces in the absence of current flow. At finite V, this equation gives the interatomic forces in the presence of current.

In Fig. 1, the electrode separation and the atomic positions within the chain and contacts have been adjusted at $V = 0$ until the tension in the system is zero. The zero-voltage conductance of the system is $0.82G_0$, where $G_0 = 2e^2/h$. This is a typical ballistic conductance for a one-dimensional wire. The slight suppression below G_0 is due to electron backscattering at the contacts and to the small atomic displacements resulting from the relaxation of the chain. The presence of a single conduction channel in the chain agrees with experiment [2], and with self-consistent *s-p-d* tight-binding calculations, which show that the current in Au chains is carried by a single channel up to voltages of at least 1.5 V [11].

A voltage of 0.1 V is now applied. The resultant current-induced force, $\mathbf{F}_n(V) - \mathbf{F}_n(0)$, on each atom in the chain and contacts is shown by an arrow in Fig. 1. We have performed calculations at similar voltages on Cu chains [10] and on other Au chains. In all these calculations, the largest current-induced force appears on the first or the second atom from each chain end. This dominant force is typically of the order of 0.01 eV Å^{-1} for an applied voltage of 0.1 V and points against the electron current. The forces in the chains generally form an alternating pattern, as in Fig. 1.

Let us consider qualitatively the physical origin of these forces. The symmetry of the current-induced forces is discussed below. It shows that we are in the linear regime where these forces are proportional to the current. Linear forces arise as a result of electron scattering. Most of the scattering in our metallic junction may be expected to occur in the regions of the chain-electrode connections. This is the reason why the dominant forces in the chain occur at atoms near the chain ends.

The sign of these dominant forces may be understood notionally as follows [10]. A point defect in a current-carrying bulk jellium metal may be expected to experience an electron-wind force, pushing the defect along with the electron current. By contrast with a defect, however, the metallic atomic chain in our case enables and facilitates current flow between the electrodes. It appears natural that current-induced forces on this current facilitator should be the reverse to those acting on a current obstructor. Thus, the dominant forces within the chain may be expected to point against the electron current, as we have found both in Cu and Au chains [12]. However, this notional argument may not always be applicable, because, in individual structures, an unambiguous separation of atoms into current facilitators and current obstructors may not be possible.

The symmetry of the forces in Fig. 1 may be expected in any system with inversion symmetry, in the linear regime [10]. In the linear regime, where the current-induced force on an atom is proportional to the applied voltage, this force changes only in sign under reversal of the voltage. In any system with inversion symmetry, furthermore, equivalent atoms exchange their roles under reversal of the voltage. Therefore, with a given voltage, the current-induced forces on equivalent atoms, such as atoms A and D in Fig. 1, must be identical [10].

The current-induced force patterns we have found in Cu and Au chains always result in weakening either the first or the last bond within the chain. In Fig. 1, it is the first chain bond, AB, that is weakened by the current. However, even at V of the order of a volt, the current-induced forces will still be a small fraction of a nanonewton and will be insufficient to rupture the chain outright.

At any finite temperature, however, a local thermal fluctuation may provide sufficient energy to break a bond in the chain, allowing the two chain segments to collapse onto their respective substrates. We must therefore consider the energy required to break bonds in the chain and the change in this energy due to the current. To estimate this energy, we choose a bond and break it by rigidly pulling the system apart. The bond force in Eq. (1) is integrated to give the work to fracture for the bond, W. Figure 1 gives W for each bond, at $V = 0$ and at $V = 0.1$ V. In the case with the current, the atoms in the two 3-atom contacts and the four chain atoms were re-relaxed, before applying the rigid pull to each bond.

The values of W show that even at $V = 0$ the first bond, AB, and the last bond, CD, within the chain are much weaker than the rest. This reflects a general property of metallic bonding: as the coordination number increases the bond strength decreases. Atoms B and C each have two neighbors. But atoms A and D each have four neighbors, and their bonds will be weaker than bond BC. The equilibrium bond length BC is consequently less than other bonds, which increases further the relative strength of the BC bond.

By symmetry, the current-induced changes in W for the two intrinsically weak bonds are equal in magnitude and opposite in sign. The bond for which W is reduced by the current—in this case the first bond, AB, along the chain—is where fracture is most likely to occur [13]. If $W_{AB}(V)$ designates the value of W for bond AB at a general voltage V, then, at temperature T, that bond will undergo thermally activated fracture after a mean time of

$$t = (1/f)\exp[W_{AB}(V)/k_BT], \tag{2}$$

where for the attempt frequency f we use the Einstein frequency for an infinite linear chain, which can be calculated analytically as 7×10^{12} Hz. With $W_{AB}(0) = 0.738$ eV, at $T = 200$ K and $V = 0$, Eq. (2) gives $t \approx 6$ days. Therefore, at zero voltage, spontaneous fracture is very unlikely

over normal laboratory time scales. If we assume that $W_{AB}(V)$ decreases linearly with V, and write $W_{AB}(V) = W_{AB}(0) - 0.14eV$, then at $T = 200$ K and $V = 1.5$ V, t is reduced to 3 s.

We have found that the variation of the current-induced forces for the geometry in Fig. 1 with voltage begins to show deviations from linearity at around $V = 1$ V. The promotion of electrons under current flow from states below the Fermi level to states above the Fermi level of more antibonding character results in a reduction, quadratic in the current, in the strength of all bonds in a defect-free conductor [10,14]. In the nonlinear region, this second-order bond weakening will cause a further decrease in the stability of the AB bond, accompanied by a decrease in stability of all other bonds in the chain.

The inelastic electron mean free path in a ballistic junction like ours exceeds greatly the length of the junction, and, therefore, individual electrons dissipate a small fraction of their energy, while crossing the junction. Under the high current densities, attainable in such junctions, however, the total power delivered to each atom in the junction by the current-carrying electrons can still be significant, resulting in substantial local heating [15]. As a consequence, the temperature T in Eq. (2) will itself be a function of voltage. An estimate of the temperature in the center of a general ballistic nanoscale junction of length L is given by [15,16]

$$T = (\theta_0^4 + \theta_V^4)^{1/4}, \tag{3}$$

where θ_0 is the ambient temperature and $\theta_V = \gamma\sqrt{LV}$. For a typical metal, $\gamma = 60\ \mathrm{K\,V^{-1/2}\,nm^{-1/2}}$. With $L \approx 2$ nm and $V = 1.5$ V, $\theta_V \approx 100$ K.

Equation (3) is based on crude approximations and its quantitative accuracy in the case of an atomic chain is uncertain. Qualitatively, however, it establishes two points. First, at voltages of the order of a volt, it places a lower limit of the order of 100 K on T. Second, it predicts the existence of two regimes, depending on the ambient temperature. If $\theta_0 < \theta_V$, then $T \approx \theta_V$, and therefore T is set by the voltage. If $\theta_0 > \theta_V$, then $T \approx \theta_0$, and therefore T is set by the ambient temperature.

Because of the exponential dependence in Eq. (2), the fracture time is very sensitive to $W(V)$. At $T = 200$ K, a change in $W(V)$ of only 0.2 eV will change t by 5 orders of magnitude. The precise value of $W(V)$ is geometry specific. For the reasons given earlier, it may be expected to be particularly sensitive to the bonding between the ends of the chain and the contacts. Therefore, small adjustments in geometry may result in dramatic changes in stability.

Equation (2) overestimates t, since we have ignored the activation entropy for fracture, which is positive and facilitates fracture. The experimental observations of large bond lengths in Au chains [1–3] suggest that the chains may be under tension. This would also reduce the work to fracture for the bonds and would decrease t.

Some density functional calculations suggest that the chains may have a spinning zigzag geometry [9], and that this may cause an electron microscope [1,3] to resolve only alternate atoms in the chain, producing an apparently larger bond length than exists in reality. Our tight-binding model does not include directional bonding and cannot distinguish between a straight and a zigzag geometry. However, we do not expect the embrittling effect of current flow to be affected qualitatively by the bond angles in the chain.

In addition to assisting thermally activated fracture, the embrittling effect of the current manifests itself as a reduction in the UTS of the chain. To calculate this effect, the electrodes are pulled apart, while all chain atoms are allowed to relax at each step. As the system is stretched, the tension reaches a maximum. At this point the chain becomes unstable and snaps. Figure 2 shows this maximum tension as a function of voltage. The UTS at $V = 0$ agrees well with the force needed to break a single-atom contact in experiment [17]. At $V = 1$ V the UTS of the system has been reduced by over 15%. This current-induced reduction in UTS should be a measurable effect.

In conclusion, we consider the generality of the above arguments. The end atoms in an atomic chain between two electrodes (atoms A and D in Fig. 1) have a higher coordination number than atoms inside the chain (atoms B and C in Fig. 1). As a consequence of the relation between coordination number and bond strength in metallic bonding, this causes the first and the last bonds within the chain (bonds AB and CD, respectively, in Fig. 1) to be intrinsically weaker than the other bonds within the chain (bond BC in Fig. 1). Electron scattering at the chain-electrode junctions results in current-induced forces, linear in the current, on atoms near the chain ends. By general symmetry properties, these forces weaken further one of the two intrinsically weak bonds, and strengthen the other one. The one that is weakened by the current (in this case, bond

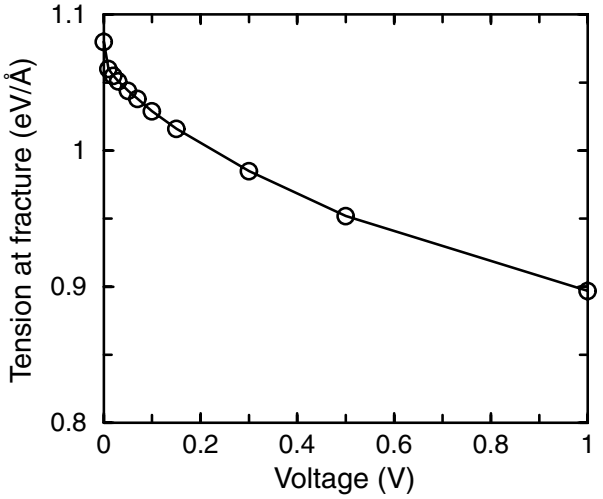

FIG. 2. The ultimate tensile strength of the chain, as a function of voltage.

AB in Fig. 1) becomes vulnerable to fracture. Our simple tight-binding model shows that the effect is large enough to make thermally activated fracture observable over laboratory time scales under voltages in the range of 1 to 2 V. Second-order bond-weakening forces may be expected to cause a further reduction in the time to fracture. We also stress that the precise values of the bond strengths and the time to fracture may be expected to depend sensitively on system-specific factors, such as the chain-electrode contacts and the tension in the chain. The reduction in UTS under current flow is another manifestation of the weakening of chemical bonds under current flow. This weakening poses a fundamental limitation to the mechanical stability not only of atomic chains but of any atomic-scale conductor.

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