HYDROGEN REACTIVITY ON AU SINGLE-ATOM CHAINS AND THE FRACTIONAL CONDUCTANCE QUANTUM

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One of the most exciting prospects of nanotechnology is the possibility to exploit the relation between chemical reactivity and system size. Small particles are known to enhance the reactivity of molecules with metals and/or oxides. Metallic nanowires, and, in particular, atomic chains as those formed in stretched Au nanocontacts, are expected to offer the ultimate limit for the increase in reactivity.

Conductance histograms, where the information from a large number of individual conductance traces are collected, have proven to be an extremely useful tool for investigating the structural, mechanical and transport properties of nanocontacts. Peaks in the histograms are related to statistically more probable atomic configurations emerging in the process of breaking. The number, position, shape and amplitude of the peaks are not significantly modified by the presence of defects, and by changes in the bias voltage conditions, and thus provide a unique characterization for a given metal.

However, these conductance histograms do change with the introduction of certain molecules in the UHV chamber. Csonka et al [1] have recently analyzed how the presence of H_2 modifies the mechanical properties and conductance of Au nanowires. In particular, they have clearly shown the presence of two additional peaks with maxima located at ~0.55 G_0 and ~1.45 G_0 . They have attributed the origin of these fractional peaks to dimerization within the atomic wire accompanied by H_2–assisted stabilization of gold dimers.

The aim of our work is twofold: (i) to analyze the Au nanowire reactivity to the H_2 adsorption, focusing on the energetics of the possible dissociation of the molecule, and (ii) to discuss the changes of the Au nanowire conductance induced by the molecular or dissociative adsorption of H_2.

These issues have been addressed with first-principles total-energy simulations combined with the non-equilibrium Keldysh Green's function approach for the electronic transport. Our starting point is a Au nanocontact, that includes a monoatomic gold chain with up to 4 atoms, that has been naturally formed along the stretching process of a thin (111)-oriented Au nanowire. Details on the initial configuration and the stretching process are similar to those considered in our recent work on Al nanowires, where for the first time, we were able to reproduce the characteristic increase in the conductance with the strain in the last plateau observed in the experiments [2,3]. The energetics of adsorption and dissociation of H_2 are then studied on three different configurations obtained during the stretching process, namely those corresponding to a dimer, a 3-atom and a 4-atom chain.

Our results show that H_2 tend to dissociate on the long Au chains formed in the final stages of the nanowire stretching process. On the other hand, H chemisorbed on the chain reduces significantly the conductance to values around ~0.6 G_0 . Thus, the enhanced reactivity of the single-atom chains, that are formed only in Au nanocontacts upon stretching, provides an explanation for the appearance of fractional peaks in Au and its absence in other metals [4].

References:

[1] Sz. Csonka et al, Phys. Rev. Lett. 90, 116803 (2003).
[2] P. Jelinek et al, Phys. Rev. B 68, 085403 (2003); Surf. Sci. 566-568, 13 (2004).
[3] P. Jelinek et al, Nanotechnology, in press (2005).
[4] P. Jelinek et al, submitted (2005).

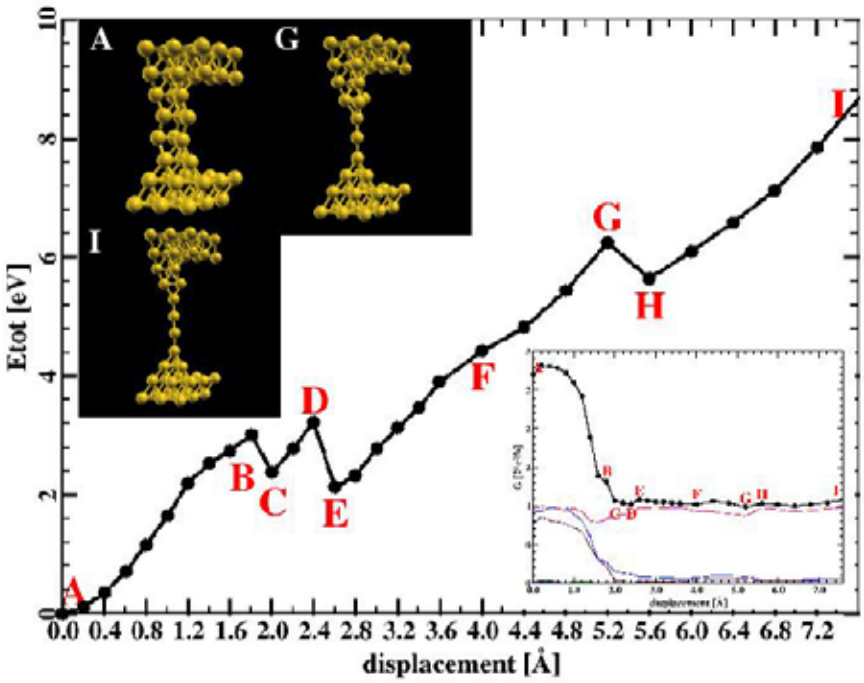
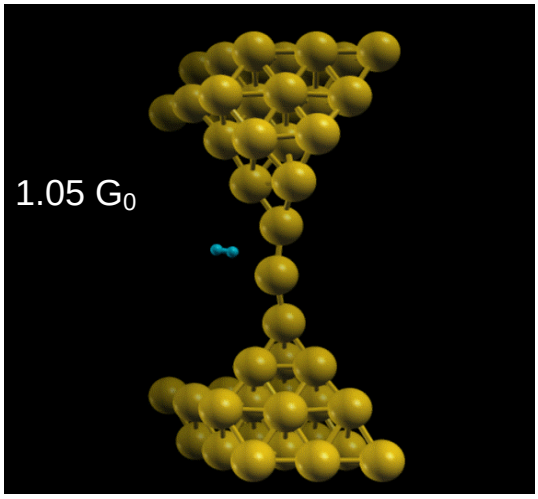
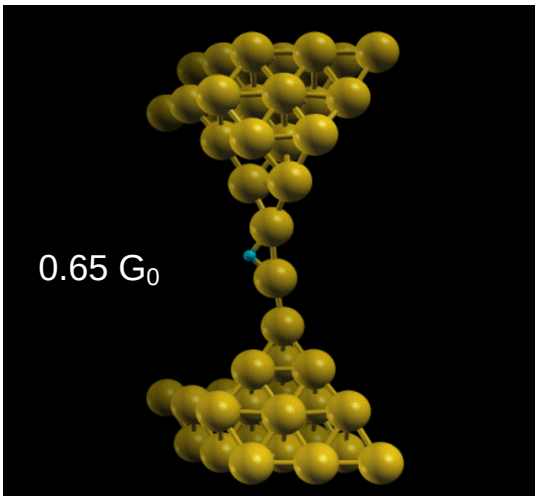


Figure 1: Total energy, total differential conductance (in units of the $2e^2/h$) and channel contribution (inset) for the clean Au nanowire as a function of the stretching displacement.





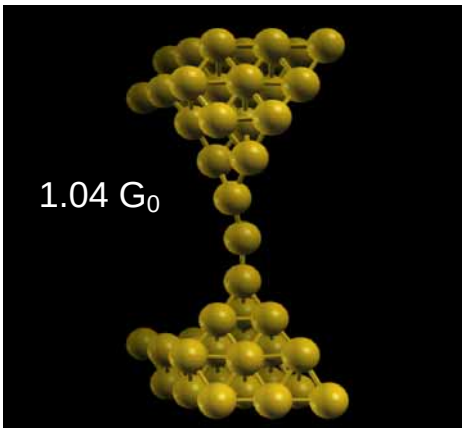


Figure 2: Ball-and-stick model of the structure and total differential conductance for the Au nanowire upon adsorption of a H_2 molecule or an H atom in the 3-atom chain configuration ontained during the stretching process. H chemisorbed on the chain reduces significantly the conductance to values ~ 0.6 G_0 .