Mechanochemistry in Cu nanowires: N and N_2 enhancing the atomic chain formation

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We show using *ab initio* total-energy calculations based on density-functional theory how H, B, C, N, O, S, and N_2 impurities incorporated to thin copper nanowires could affect their mechanical properties and electronic structure. An interesting mechanochemical effect arises from the insertion of N and N_2 in the linear atomic chain. These impurities form not only stable but also very strong *p-d* bonds, in such a way that they can extract atoms from a stable tip enhancing the atomic chain suggesting the possibility to pull a string of copper atoms through the production of copper nanowires in nitrogen atmospheres.

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Metallic nanowires (NWs) have been the subject of intense research in the past years, motivated by the possibility of their use as nanocontacts. Experiments using a mechanically controlled break junction (MCBJ) (Refs. 1–6) technique or driving a scanning tunneling microscopy (STM) tip into a metallic sample and then pulling it out[7–9] exhibited clear plateaus in the conductance. The lowest value of the quantized conductance ($1G_0=2e^2/h$) observed for a long periods of time[1–9] is now considered an evidence of the formation of point contact and one-atom-thick NWs for many metals.

Copper NWs, in particular, have attracted a lot of interest. Experiments of high-resolution transmission electron microscopy (HRTEM) observed the formation of NWs. In such experiments it was possible to follow the structural changes in these NWs stretched along the [100], [110], and [111] crystallographic directions that evolved to form linear atomic chains (LACs), until their rupture.[6] Our theoretical work showed details of the dynamical evolution, formation and break of copper linear atomic chains using tight-binding molecular dynamics[10] and some aspects of the electronic structure using *ab initio* techniques.[11] Other interesting works studied deposited copper NWs on a Cu (111) surface using a STM tip, evidencing the possibility to use them as one-dimensional conductors for larger distances,[12–14] copper corral structures exhibited well-defined resonances in their electronic structure[15,16] and cobalt-copper atomic chains revealed an electronic coupling between these metals, opening possibilities of their use in spintronic devices.[17] These are examples of exciting possibilities concerning the use of copper as nanoconductor.

HRTEM images of gold NWs showed the formation of LACs that evolved up to rupture.[18] In such images, the interatomic distances between gold atoms were larger than the bulk distances and also larger than simulations results from tight-binding[19] and *ab initio*[20] calculations in gold NWs. This difference was attributed to the effect of light impurities which could not be observed in the HRTEM images. Since then, a lot of theoretical efforts were made to find the best candidates compatible with the observed distances[21–23] evidencing new and interesting phenomena. Examples are the insertion of oxygen in the gold LAC produced strong bonds, so strong that under stress the LAC increased its size with the oxygen behaving as a clamp rearranging the tips and consequently, inserting more atoms into the LAC (Refs. 24 and 25) or the spectacular effect that thiolate molecules presented in drawing out gold one-atom-thick chains from gold surfaces.[26] These are interesting mechanochemical effects in gold nanowires.

Since copper NWs became a promising possibility as nanocontacts and motivated by the recent works about the interaction between thiolates with copper clusters or surfaces[27,28] or by the interesting results obtained from gold NWs doped with light impurities, one investigation about the mechanochemistry of light impurities in copper NWs is demanded. In this work, we study theoretically the behavior of copper NWs doped with H, B, C, N, O, S, and N_2 impurities under stretching conditions until their rupture, observing their mechanical and electronic structure properties. Our main result shows a strong tendency of N and N_2 to make strong bonds in copper NWs, causing the formation of longer copper LACs. Before the rupture, we obtained the LAC distances, density of electronic states and charge to characterize and understand the behavior of these strong bonds.

We performed calculations based in *ab initio* total-energy density-functional theory[29,30] using the SIESTA code.[31] In order to make the calculations more realistic we used a pure [111] copper NW constructed as a stack of three layers with 7, 6, and 7 atoms repeated four times (80 atoms) relaxed previously by molecular-dynamics[10] and *ab initio* calculations.[11] Norm-conserving Troullier-Martins pseudopotentials[32] with nonlocal partial-core corrections[33] were used to describe the interaction between Cu valence ($3d^{10}$ $4s^1$) and core electrons. The exchange-correlation energy was calculated using the local-density approximation (LDA) (Ref. 34) and generalized gradient approximation (GGA).[35] The basis sets were described with a split valence double-zeta basis (spin-polarized) and localized numerical orbitals were used with a confining energy of 0.08 eV and 0.18 eV for LDA and GGA, respectively.[11] The grid integration to represent the charge density was defined with a cutoff of 200 and 300 Ry (LDA and GGA) to perform the relaxation and increased to 400 Ry to study the electronic structure. Supercell dimensions are $(30,30,38<L<46)$ Å, where L is the NW length. These periodic boundary conditions were chosen to define chain geometry. Brillouin zone sampling used eight Monkhorst-Pack k points[36] along the NW axis. The stretching of the copper NWs were achieved by pulling them quasistatically using conjugated gradient (CG) in steps of 0.1 Å, until all force components were

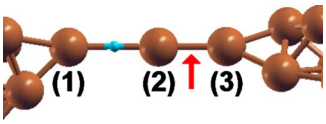

FIG. 1. (Color online) Configuration of a copper NW before the rupture with one light impurity (the small atom) representing the H, B, C, O, and S impurities. The red (gray) arrow shows the breaking bond.

smaller than 0.01 eV/Å, repeating this procedure until the rupture. The evolution was performed first using LDA. The GGA calculation was done from the LDA configuration before rupture, evolving similarly with the CG procedure as in the LDA, until rupture.

The effect of light impurities was studied and the new NWs included the formation of a Cu-*X*-Cu (*X* denotes the impurity) structure in the LACs. The contamination of the NWs with H, B, C, O, and S impurities did not change structurally the previous NWs. Figure 1 shows the typical final configuration before the rupture for these impurities. In all cases, the impurities were incorporated into the LAC making stronger bonds than the ones between copper atoms, with LACs always breaking in a Cu-Cu bond, but not sufficiently strong to alter the tips structure and enhance the atomic chain size. The calculated LAC distances and forces for these impurities are presented in Table I using both exchange-correlation functionals. Results regarding the electronic structure of these impurities gave the following results: Hydrogen formed a delocalized sd_{z^2} bond, boron made a sd_{z^2} bond more localized than the hydrogen one and also a σ-type pd_{yz} bond. Carbon, oxygen, and sulfur, on the other hand, have a sd_{z^2} bond, a strong σ-type pd_{z^2} bond and also π-type pd_{yz} bond. These last three impurities all have a similar behavior and the reason for this is that carbon has two p electrons with the same spin direction, oxygen and sulfur are isoelectronic with three electrons with the same spin direction and one more in the opposite direction. While carbon has two open shell electrons the other two impurities have two electrons in a closed shell and also two open shell electrons similarly as carbon, therefore the overall behavior of these three impurities is expected to be similar which is indeed what we found. Small spin anisotropy was observed for carbon, oxygen, nitrogen, and sulfur impurities.

In the process of studying the effect of impurities a few surprises emerged in the cases of doping with N and N_2, therefore we discuss these cases in more detail. Figure 2

TABLE I. LAC distances (Å) and forces (nN) before the rupture using LDA/GGA calculations. Labels (1), (2), and (3) denote the atoms from Fig. 1.

	(1)-(2)	(2)-(3)	Forces
H	3.47/3.54	2.62/2.63	1.9/2.2
B	3.91/3.90	2.62/2.64	1.7/1.6
C	3.66/3.68	2.63/2.65	2.0/1.9
O	3.60/3.62	2.61/2.58	2.4/2.1
S	4.32/4.33	2.61/2.69	2.1/2.3

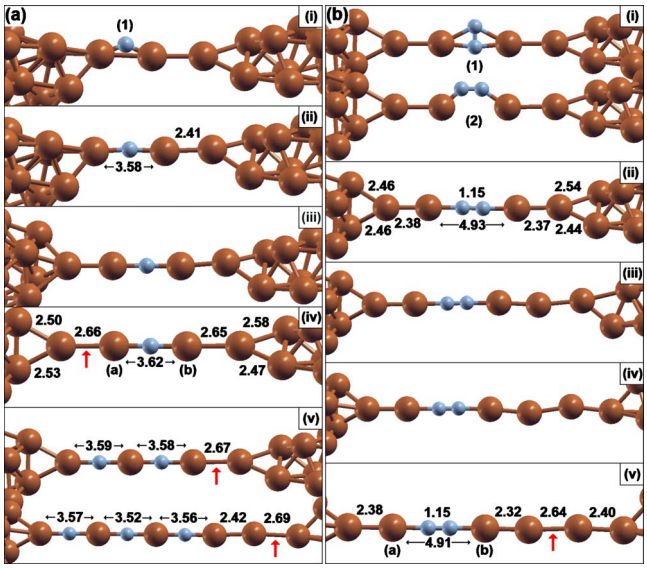

FIG. 2. (Color online) Quasistatic LDA evolution of copper [111] NW with (a) N and (b) N_2 impurities. The red (gray) arrows show the breaking bonds.

shows the evolution until rupture of a copper NWs doped with (a) N and (b) N_2. Considering the case of N, Fig. 2(a) shows (i) the starting configuration of N positioned close to the first Cu-Cu bond. The relaxed structure was reached (ii) trough the insertion of the N impurity into the LAC between two copper atoms, pushing the tips and the neighbor LAC bond to form new Cu-N-Cu bonds. Structure (iii) exhibits the rearrangement of the left tip with the incorporation of one atom into the LAC, (iv) shows the distances of the NW before the rupture. Since N helped the inclusion of Cu atoms into the LAC, we also investigated the doping with more N atoms and (v) displays the LAC doped with two and three N atoms. The LAC doped with two N atoms evolved to rupture with the same number of atoms, on the other hand the LAC saturated with three N atoms increased its length adding two more atoms extracted from the right tip. Figure 2(b) presents (i) two starting positions for N_2 molecule. In (1) the N_2 is perpendicular and (2) it is parallel to the LAC. The evolution of both possibilities evolved to (ii) the NW showing N_2 going into the LAC on the horizontal position pushing the tips apart. As the stretching evolved in (iii) one and in (iv) another atom was added to the LAC from the right tip with (v) showing LAC distances before the rupture. The forces before rupture were 1.9 and 2.0 nN for N and 1.7 and 1.8 nN for N_2 impurities (LDA and GGA, respectively) as encountered in the cases of the other impurities.

The electronic structure of the copper NWs with N and N_2 impurities is discussed in Fig. 3 through the projected density of states (PDOS) of the copper NW with N (left panel) and N_2 (right panel) for structures before rupture. The panels show the s and d orbitals for copper (1), which has a similar PDOS to atom (2), also the s and p orbitals of the N and N_2 impurities, respectively. There are minor differences in the density of states and charge density calculated with LDA and GGA. Therefore we only present the electronic structure in the GGA approximation. In the case of the N impurity (left

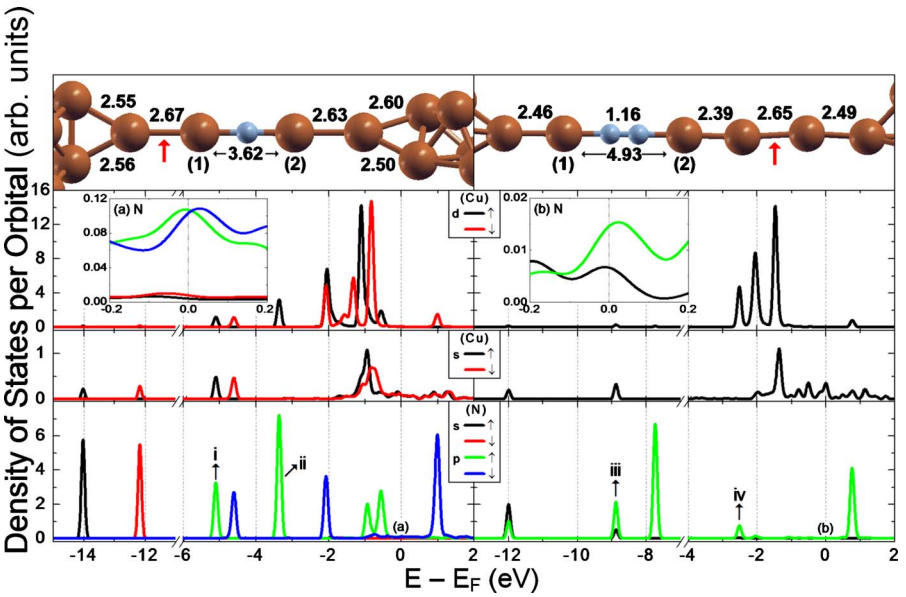

FIG. 3. (Color online) LAC distances and density of states projected per orbital for copper NWs with N (left) and N_2 (right) impurities using GGA. The relevant peaks associated to the strong bond, labeled (i)–(iv) have their local DOS plotted and discussed in the Fig. 4. The insets show details around the Fermi level.

lower panel), the PDOS exhibits nine peaks with five peaks associated to electrons with spin up (black line) and four other peaks of spin down (red/gray line) up to the Fermi level. The peaks (i) and (ii) with energies around −5.1 eV and −3.3 eV, respectively, have the major concentration of charge with contributions from N_p and Cu_d orbitals, besides a small contribution from Cu_s orbital in (i). The right lower panel of Fig. 3 depicts the effect of N_2 impurity showing four PDOS peaks. The strong-bonding effect comes from states with energies around (iii) −8.9 eV evidencing N_s and N_p states bonded to Cu_s and Cu_d states as well as states around (iv) −2.50 eV with a N_p states bonded to Cu_d states. The (a) and (b) insets show p states around the Fermi level in both cases, however, with a minor intensity in the N_2 suggesting that the copper NW doped with N should be a better conductor than the one with N_2.

In order to further understand the formation of these bonds, Fig. 4 shows charge-density isolines[37] and isosurfaces. We believe that these are the strong bonds responsible for the mechanochemical effect of insertion of copper atoms extracted from the NWs tip, making longer LACs. In the case of N, from Fig. 4 (i) and (ii), they show clearly (i) a strong σ-type pd_{z^2} bond and also (ii) a π-type pd_{xz} bond. The effect of N_2 is displayed in Fig. 4 (iii) that shows a σ-type pd_{z^2} bond and in (iv) a π-type pd_{xz} bond as well the case above, but in this case (iv) the pd_{xz} bond has a larger concentration of charge than the (ii) bond, evidencing that the N_2 forms a stronger bond than the N case, as can be seen through the evolution depicted in Fig. 2. Figure 4(a) shows the up (black) and down (red/gray) total charge density which displays the spin anisotropy localized in the vicinity of the nitrogen. This anisotropy comes from the states in the energy interval from −0.7 eV up to the Fermi level displayed in the PDOS of Fig. 3 (left). Figure 4(b) depicts only the up charge density due to the absence of spin anisotropy in this case. The lowest energy p state in both cases is associated to the pd_{z^2} bond, the followed state is a pd_{xz} bond in N and associated to the dimer bond in N_2 and the highest energy state is related to the anisotropy for N and to the pd_{xz} bond for N_2. Note that the first p bond of N_2 occurs at lower energy than to the case of N, providing a much greater strength responsible for the extraction of atoms from the tips.

Concluding, we used state of the art computer simulations to study the effect of light impurities to the mechanical and electronic properties of realistic copper NWs, from their insertion up to the NWs break. We showed that most of the impurities did not modify the structure of the NWs and presented LAC distances and forces just before rupture. The knowledge of these distances could be useful to explain larger bond distances that could be obtained in HRTEM images. Among these impurities, N and N_2 stood out as very

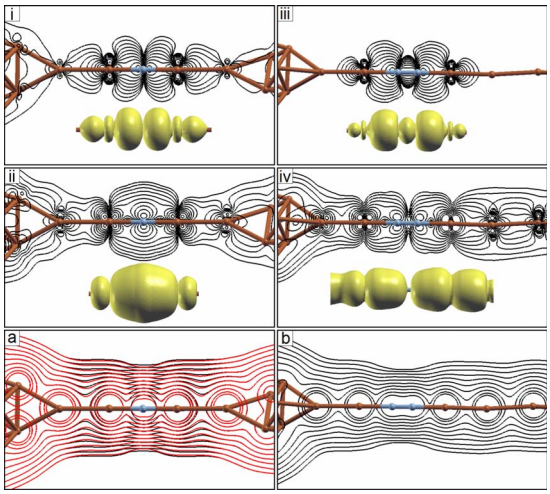

FIG. 4. (Color online) All panels show the charge-density isolines varying from 0.0001 to 0.1 electrons/(Bohr)^3 (ten lines in logarithmic scale) for a narrow energy windows of (i) (-5.10 ± 0.20) eV and (ii) (-3.35 ± 0.20) eV for N on the left, also (iii) (-8.88 ± 0.20) eV and (iv) (-2.50 ± 0.20) eV for N_2 on the right. The isosurfaces were plotted for a value of 0.001 electrons/(Bohr)^3. The bottom panels (a) and (b) show the total charge density considering spins up (black) and down (red/gray).

interesting cases showing an interesting mechanochemical effect. In particular, we have investigated how N and N_2 can affect the structure and rupture of the NW. We established that N and N_2 can form not only stable but also very strong bonds with the copper atoms, in such a way that they can extract atoms from a stable tip producing longer LACs. These strong bonds have a pd_{z^2} and pd_{xz} character and details about their DOS and the electronic charge density and states around these impurities were given. This work opens up possibilities of further studies: (i) the validity of the local bond-strength interpretation, (ii) how stable the tips could be, (iii) the general stability properties, and (iv) the effect of these impurities to the transport properties of copper NWs. Finally, the current study suggests that N and N_2 may be used as controllable handles to draw and manipulate monoatomic copper NWs with the possibility to enhance their atomic chain formation in nitrogen atmospheres. Therefore we believe that this work could be fruitful to motivate further investigation of copper NW from an experimental point of view.

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