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S. Barzilai, F. Tavazza, and L. E. Levine

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Disparate effects of an O₂ internal impurity on the elongation and quantum transport of gold and silver nanowires

S. Barzilai, F. Tavazza, and L. E. Levine
MSED, Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8553, Gaithersburg, Maryland 20899, USA

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In this work, we investigated the effects of an internal O₂ impurity on the conductance of elongated gold and silver nanowires (NWs) using density functional theory calculations. We found that the O₂ interacts with these metallic NWs very differently. In the case of gold NWs, the presence of an internal oxygen molecule locally strengthens the wire, therefore, forcing the phase transformations connected to the thinning process (3D to 2D and 2D to single atom chain) to occur far from the oxygen. As a consequence, towards the end of the elongation, the internal O₂ is located far from the main conductance channel and therefore has little influence on the conductance of the NW. In contrast, in silver NWs, the presence of an internal oxygen molecule involves a larger charge transfer from the metallic atoms to the oxygen, therefore, weakening the Ag-Ag binding. During the initial stages of the elongation, several metallic bonds adjacent to the impurity break, so that in most simulations the NW thinning takes place near the O₂. This thinning mechanism places the O₂ near the main conductance channel, therefore, significantly reducing the conductivity of the elongated silver NWs. For both metals, our findings agree well with the published experimental results. © 2013 AIP Publishing LLC.

I. INTRODUCTION

The demand for decreasing chip dimensions creates the need to scale down the size of both integrated circuits and interconnect wires. Gold and silver nanowires (NWs) can be thinned down to single atom chains (SACs) during tensile deformation. This ability makes them good candidates for applications such as nanoelectronics, as well as very attractive from a fundamental science point of view. This is exemplified by the many experimental1–15 and theoretical16–53 studies that have been carried out to characterize their electronic properties and to understand the influence of atomic configuration and impurities on their conductance.

The influence of molecular oxygen on the conductance of gold and silver NWs during elongation has been experimentally examined by Thijsse4 et al.14,15 Significant changes were found in the conductance histogram of Ag NWs at 4.2 K after exposure to O₂: a dominant conductance peak around 0.1 G₀ appeared, together with a large background below 1 G₀ (where G₀ = 2e²/h, with e as the electron charge and h as Planck’s constant). In contrast, the conductance of Au NWs at the same temperature was hardly changed with the introduction of O₂ into the experimental chamber. In this case, the effect of the contaminant only started to be noticeable at higher temperatures: at 40 K, an additional conductance peak did appear at 0.1 G₀. Several theoretical attempts were made to understand the effect of oxygen on the conductance of Au or Ag48–53 NWs. It was found that when atomic oxygen is incorporated into a SAC of gold or silver, it increases the electron scattering and decreases the conductance. However, most of the studies considered atomic oxygen species which are already on a SAC. This consideration neglects the effect of the O₂ original position prior to the elongation and its ability to dissociate and to reach the SAC zone. The only exceptions were the work of Jelínek50 and the work of Qi et al.52 Jelínek et al. neglect the dissociation stage but do show that atomic oxygen can reach the SAC during elongation of three-dimensional (3D) gold NWs. Qi et al. found that when the O₂ is on the silver SAC, it can incorporate into it during the elongation process, but did not address the ability of O₂ molecule to reach the SAC during elongation. Moreover, in an experimental system, a sample is created by “crashing” the tip of a metallic wire onto a flat metallic plate to form a contact junction. A nanowire is then formed by drawing the wire away from the plate. When a contaminant is a priori absorbed on the tip or on the plate surface, it can be trapped in the contact junction and form an internal contaminant which can affect the measurements.

To study the effect of an internal O₂ molecule contamination on gold and silver NWs, and its ability to reach the SAC region during elongation, we simulated tensile deformation of 3D gold and silver NWs contaminated with an internal O₂ impurity. Different behavior was found for the two metals. In the case of gold NWs, the O₂ remained confined inside the NWs and never reached the SAC zone, while for the silver NWs, in most of the simulations, the O₂ was pushed from its internal site to the NW surface, and ended in or nearby the SAC. This difference results in dissimilar structural changes during the elongation of the two metals, and different conduction states for the NWs.

II. METHODOLOGY

Pure gold and silver NWs containing 115 atoms were built with (110) planes perpendicular to the NW axis.
The conductance calculations were performed at zero bias using a non-equilibrium Green’s function technique based on the Landauer formalism,63 as implemented in the ATK package.22,64,65 The system was divided into three regions: a left and a right electrode (made from Au for the gold NWs and Ag for the silver NWs), and a central scattering region between them. For the latter, we used the atomic configurations obtained by the DFT elongation. The attachment of the electrodes to the scattering zone was completely seamless since the grip atoms in the deformation simulations had been kept fixed into ideal FCC positions. Huckel tight binding66 was utilized for all of the cluster-based configurations, using the Cerda parameterization67 for Au and Ag, while the Hoffmann parameterization68 was used for O and H atoms.

III. RESULTS

The effect of oxygen contamination on the conductance of gold and silver NWs during their elongation is shown in Fig. 1. The computational results are well correlated with the experimental results mentioned previously.14,15 At the late stages of elongation, the conductance of both pure NWs is around 1 G0, while the conductance of the contaminated NWs varies. In most of the gold NW simulations, the oxygen has only a small effect on the conductance; whereas for most of the silver NW simulations, the conductance decreases well below 1 G0. This difference is related to the location of the oxygen at this (late) stage of the elongation. Fig. 2 presents atomic configuration snapshots from tensile simulations of the impure gold and silver NWs. For the gold NW, during the entire elongation the impurity is surrounded by gold atoms and the phase transformations from 3D to 2D, and afterward to a SAC, occur far from the impurity location. This result was found in all of the gold + O2 simulations, and explains the small effect the oxygen has on the computed conductance values (Fig. 1). The small decrease below 1 G0 is a well-known phenomenon and is related to the atomic configuration of the gold atoms.29,30,36 For the silver case, the oxygen interacts with the Ag atoms in a different manner; in most simulations, the O2 was pushed out from its internal site to the surface of the NW. In only one simulation, where the oxygen was initially located in the shoulder, it did remain inside. These results demonstrate that, in the early stages of elongation, the Ag-Ag bonds in the vicinity of the oxygen are weakened, allowing the impurity to move towards the thinned out part of the wire (the main conductance channel) and therefore decreasing the conductance. At the latter stages of elongation, when the oxygen is already on the surface, the NW continues to thin down to a SAC. When this thinning occurs in the vicinity of the oxygen, the conductance decrease below 1 G0, but, when the thinning takes place away from the oxygen, a conductance level of 1 G0 was obtained.

Mulliken population analysis shows that 0.7 electrons are transferring from the silver atoms to the oxygen, while the gold atoms only transfer 0.1 electrons. Thus, even before causing structural changes in the NWs, the oxygen has a higher impact on the conductance of silver NWs than of gold ones. This can be seen in Fig. 1, observing the beginning of the elongation (where both NWs length are ≈15 Å). At this stage, the conductance of both pure wires is ≈6.5 G0, but replacing one internal metallic atom with an O2 molecule
decreases it to $5.5 \, \text{G}_0$ in the case of gold and to $\approx 5 \, \text{G}_0$ in the case of silver.

To further clarify the effect of the impurities on the conductance, the electronic properties and transmission pathways were computed for a variety of cases for pure and contaminated gold and silver NWs. Representative results are displayed in Fig. 3. Electron depletion was found for all of the gold and silver atoms in the vicinity of the O$_2$ impurity. For the gold NWs, during the entire elongation, the O$_2$ was surrounded by many gold atoms, and therefore, by several conductance channels. Each channel utilized only a fraction of the available electrons to feed the main transmission pathway, and therefore, the electron depletion hardly affected such a pathway (Fig. 3(a)). For the silver NWs, in most of the cases, the O$_2$ moved away from its initial internal site toward the surface and then became incorporated in or near the bottleneck of the transmission pathway. In such a position, only one conductance channel exists so that the electron depletion around the O$_2$ (Fig. 3(b)) significantly decreases the availability of conducting electrons and increases the probability that such electrons are scattered. In the remaining cases, where the O$_2$ remained far from the main transmission pathway, the electron depletion hardly influenced the conductance, similar to what was found for the gold NWs.

To better understand the differences in the oxygen’s behavior in the studied NWs, further calculations were made to estimate the stability of oxygen inside the NWs. Fig. 4

![FIG. 1. The computed conductance of pure and contaminated NWs during elongation. The hollow and solid symbols represent a tensile direction of 6° and 48° off the Z axis, respectively. The triangular symbols refer to the NWs where the O$_2$ was placed in the shoulder, while the circles and the stars refer to the NWs that initially had O$_2$ in the center, oriented 45° and 90° from the Z axis, respectively.](image1)

![FIG. 2. Atomic configurations of gold and silver NWs obtained after relaxation for representative tensile strains. For both NWs, the O$_2$ was located initially in the shoulder.](image2)
shows the energy increase of the $\Delta E(O_2)$ for both NWs calculated at the five initial steps of elongation. This energy increase is related to the interaction with the metallic atoms and was calculated according to Eq. (1). As can be seen in Fig. 4, the oxygen (O$_2$) inside the silver NWs is less stable than the oxygen inside the gold NW; in silver, its energy increased by $\approx 0.8$ eV, while in gold its energy only increased by $\approx 0.1$ eV with respect to the energy of an isolated relaxed oxygen molecule

$$\Delta E(O_2) = E_{O_2}^{\text{non-relax}} - E_{O_2}^{\text{relax}}.$$  

Here, $E_{O_2}^{\text{non-relax}}$ is the energy of the two oxygen atoms with the same bond length as inside the NWs and $E_{O_2}^{\text{relax}}$ is the energy of the isolated oxygen molecule after relaxation.

This energy difference, and therefore, the oxygen stability inside the NW, is related to the differences in O-O bond length inside the metallic NWs. Relatively large bond lengths (1.39 Å to 1.44 Å) were found for the oxygen inside the silver NWs, while smaller bond lengths (1.26 Å to 1.29 Å) were determined for oxygen inside the gold NWs. For the relaxed molecule, the bond length was computed to be 1.23 Å, which is in good agreement with the experimental value of 1.21 Å. The binding energy of the oxygen inside the metallic NWs was also considered. This energy was computed for the initial steps of the elongation according to Eq. (2). It was found that the oxygen inside the silver is more strongly coupled to the NWs, and its binding energy is $\approx 1.2$ eV higher than the binding energy inside the gold NWs

$$E_b(O_2) = E_{NW+O_2}^{\text{relax}} - (E_{NW}^{\text{non-relax}} + E_{O_2}^{\text{non-relax}}).$$  

Here, $E_b(O_2)$ is the binding energy of the oxygen inside the metallic NWs, $E_{NW+O_2}^{\text{relax}}$ is the energy of the relaxed NW with oxygen, after a specific elongation step, $E_{O_2}^{\text{non-relax}}$ is the energy of the oxygen after removing the metallic atoms, and $E_{NW}^{\text{non-relax}}$ is the energy of the metallic NW atoms of the relaxed contaminated NWs but after removing the oxygen atoms.

The DOS of the contaminated gold and silver NWs are quite similar. For both kinds of NWs, the 2p electrons of the oxygen mainly interact with the d electrons of the metallic atoms near it. This interaction changes the DOS of the d electrons, and new bands adjacent to the Fermi energy and at $\approx 7$ eV appear beneath it. Fig. 5 displays representative DOS of oxygen inside the NW and metallic atoms which are near the oxygen and far from it. The main difference between the Au and the Ag cases is related to the charge transfer between the metallic atom and the O$_2$. Mulliken population analysis indicates that the charge transfer to the oxygen molecule in the Ag NW is more than three times higher than the charge transfer to the oxygen molecule in the Au NW. It was found
that ≈0.7 electrons, mostly from the nearest Ag atoms, were transferred to the 2p states of the O₂.

IV. SUMMARY AND CONCLUSIONS

Tensile simulations of pure and oxygen contaminated NWs were performed to study the effect of an internal O₂ impurity on the structure and conductance evolution of gold and silver NWs during elongation. As a comparison, similar simulations were run for the pure NWs as well. At the late elongation steps, the pure NW structures transform to a SAC and the conductance of both converges to ≈G₀. However, as was observed in conductance measurements, the contaminated NWs behave differently. At the late steps of the elongation, the presence of oxygen hardly affects the conductance of the gold NWs, but significantly decreases it for the silver NWs.

For both NWs, the electronic characterization shows that the 2p electrons of the oxygen interact mainly with the d electrons of the metallic atoms adjacent to the oxygen. However, for the silver NWs, this interaction evokes a higher charge transfer from the NW to the oxygen and therefore it may have greater impact on the conductance. Moreover, for the gold NWs, it was found that the presence of oxygen reinforces the Au-Au binding of the NW adjacent to the oxygen, and therefore, during the elongation, in all of the simulations, the oxygen stays inside the NWs, surrounded by gold atoms. In these simulations, the thinning area of the NW down to SAC occurs far from the O₂. Therefore, the electron depletion of the Au atoms around the oxygen does not affect the conductance at the late steps of the elongation. For the silver NWs, it was found that the presence of oxygen weakens the silver NW in its vicinity. For five out of six different tensile simulations, the Ag-Ag bonds adjacent to the oxygen were broken. In most of these cases, the NW thinning and phase transformations occurred in the vicinity of the oxygen. In addition, the strong binding energy calculated for the internal O₂ with the silver atoms helps the oxygen to be attached to the Ag atoms and to incorporate into the main transmission pathway. At this location, the electron density decrease due to the Ag-O₂ interaction reduces the availability of electrons needed for the conductance.

This study suggests that the different behavior between gold and silver NWs can be related to differences in the charge transfer from the metallic atoms of the NW to the oxygen molecule, and to the ability of the oxygen to incorporate near the main conductance channel at the late steps of the elongation. When the oxygen stays inside the NW (as was the case for the Au NW) it does not affect the conductance, but when it pops out and reaches the thin part on the NW, the charge transfer becomes crucial and decreases the conductance.
54 Commercial software is identified to specify procedures. Such identification does not imply recommendation by the National Institute of Standards and Technology.
64 Atomistix ToolKit version 11.08, QuantumWise A/S.