Sensitivity of gold nano conductors to voids, substitutions and electric field: *ab initio* results

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

MSED, Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8553, Gaithersburg, MD 20899, USA

Abstract

Gold nanowires are good candidates for nanoelectronics devices. A previous study has shown that the beryllium terminated BeO (0001) surface may be a useful platform for supporting nano gold conductors, since it preserves the nano-wire configuration and does not restrict its conductivity. Here, we used *ab initio* simulations to determine the sensitivity of potential gold nano-conductors to the presence of point defects, O_2 substitutions and to an applied perpendicular electric field, as in field effect transistors. We found that the presence of the point defects cause only small changes in the atomic bond lengths of the NW, does not alter the NW configuration, but may affect the overall conductivity. The conductive ability of the conductor depends on the available conductive channels. Single or double voids on the same channel reduce the conductance by 28 % at most, but when the voids arrange in a way that only one channel remains for conductance, it reduces by factor of two to $\approx 1\ G_0$ ($G_0 = 2e^2/h$). The presence of a single O_2 molecule as a substitution reduces the electron availability in the neighboring Au atoms, in most cases reducing the conductance. The perpendicular electric field, which is typical for field effect transistors, affects the electron density distribution, shifts and changes the conductance spectra profile, but does not decrease the conductivity.

Keywords: Conductance, gold nanowire, nano electronic, point defects, *ab-initio*

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1. Introduction

Transistors have been a key component of the technological development that characterized the twentieth century. Since its introduction, the transistor has continuously been reduced in size, to the point that modern devices are orders of magnitude smaller than the original ones. This drastic size reduction has led to both tremendous performance gains and per unit cost decreases, but existing device designs are approaching their theoretical limits [1, 2, 3]. Only the development of new near-atomic size nano-electronics components may provide a viable path to continue this miniaturization process.

Gold nanowires (NWs) are good conductor candidates for nano-electronics applications because they are extremely ductile, comparatively non-reactive and exhibit both good conductance and appreciable band gaps [4,5], depending on the atomic arrangement. Such a structural dependence in the conductance opens up the possibility of more versatile all-Au nano-electronic devices.

While many experimental [6,7,8,9,10,11,12,13,14,15] and theoretical [5,16,17,18,19,20,21,22,23,24,25,26,27,28] works have investigated electronic properties in freestanding nanowires, only few of the earlier studies [29,30, 31,32] have focused on determining the conductance of Au NWs placed on top of a suitable substrate. Such a layered configuration is required for manufacturing devices. These earlier studies investigated the transport properties of gold chains on a metallic NiAl (110) substrate. Such a system is useful for conductive, straight, single atom chains, but may prove to be inadequate for more complicated chain configurations, such as two dimensional (2D) hexagonal structures, because of its surface symmetry. It may also not be ideal for making nano-scale circuits, which include resistors and semiconductors made from these NWs, due to its high conductivity.

Because insulating substrates are the ideal choices for nano-scale circuitry, an excellent candidate to support nano-scale gold chains is α-wurtzite BeO (0001). This compound has a large band gap (10.6 eV [33]), high thermal conductivity [34], sixfold symmetry on the basal plane and bond lengths which are similar to the Au-Au bond length in low-energy nano-scale configurations. Moreover, BeO has good corrosion and thermal-shock resistance, and it is already used in semiconductor applications. In addition, previous studies have already determined that gold atoms are attracted to the BeO (0001) surface [35] and that various gold nanowire structures remain stable if deposited on the Be-terminated surface of this compound [36]. In general, it was found that the presence of the slab maintains the high conductivity of the NW; in some cases it even enhances it. A previous study has shown that gold NWs with the "Hexa-1" structure are stable over the BeO slab, and have the highest conductivity among the several, tested NW configurations [36]. Moreover, it was found that the adsorption of O_2 or H_2O molecules does not alter the superior conductivity [37].

In this study, we used gold NWs with a Hexa1 atomic configuration on a BeO (0001) substrate as a model for this class of conductors, and we probed the effects of point defects and electric field on its conductivity. These effects have to be investigated for this potential nano conductor because they will be present in any real device: the conductor will be exposed to electric field that control gates in field effect transistors and very likely there will be point defects due to the manufacturing process. Our results suggest that the presence of isolated, or two adjacent, point defects does not affect the NW atomic configuration. The absence of one or two gold atoms in the same channel reduces the conductivity in such a channel, but the overall conductivity decreases only by 28 % at most and the NW still retains its ballistic ability. The electric field has a

small effect on the conductance of this nano-conductor. A low bias of ± 1 V does not change the conductance, and higher biases increase it by a relatively small amount.

2. Methodology

In the present study, we used density functional theory (DFT) to relax Hexa1 Au NWs, with various point or extended defects, on BeO substrates, and a non-equilibrium Green's function technique based on the Landauer formalism to characterize their transport properties.

To build the substrate, six alternating Be- and O- layers were used; each layer contains thirty atoms. A previous investigation [35] found this thickness (5.2 Å the substrate alone, 8.4 Å the substrate and gold nanowire together) adequate for representing the gold-surface interaction. The width of the substrate is 10.2 Å. When relaxing the system we used a 100 Å x 100 Å x 16 Å super-cell with periodic boundary conditions. These conditions provide continuity along the NW axis and large separation distances along the two other axes.

The structural relaxation calculations were carried out in the framework of DFT, using the DMol^3 code [38,39,40]. We used a real-space cutoff of 4 Å, a double-zeta, atom-centered basis set (dnd), and one k-point sampling. The exchange-correlation potential was treated within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) approach [41]. The ion core electrons of the Au were described by a hardness conserving semilocal pseudopotential (dspp) [42]; only the outer electrons ($5s^2\ 5p^6\ 5d^{10}\ 6s^1$) were treated as valence electrons. To ensure that the results of the calculations are directly comparable, identical conditions were employed for all systems. The geometry optimization was performed using a conjugate gradient

approach based on a delocalized internal coordinate scheme [43,44]. The system was considered converged when the change in total energy dropped below 10^{-3} eV (5×10^{-5} Ha) and the maximum displacement dropped below 10^{-4} Å. To save computer resources, we removed individual gold atoms from several representative sites of the already relaxed Hexa1 (retrieved from a previous study [36]), and applied further relaxation to bring each system to its equilibrium state. To study the effect of oxygen substitution, we placed the O_2 in these vacancies and applied further relaxation. Fig. 1a shows the atoms that were removed to simulate vacancies and adsorption sites.

The conductance calculations were performed at zero bias using a non-equilibrium Green's function technique based on the Landauer formalism [45] and a local density approximation (LDA) [46] with a double-zeta polarized (DZP) numerical basis set [47] as implemented in the ATK package [24,48,49]. The system was divided into three regions: a left Au electrode, a right Au electrode, and a central scattering region. For the latter, we used the DFT-relaxed atomic configurations previously obtained for the NW on BeO. The electrodes were one atom thick and had the same structure as a (111) Au surface; they attached to the gold NW without limiting the conductance. To evaluate the effect of electrical field on the NW, an electrostatic gate attached to dielectric material with dielectric constant $\varepsilon=4\varepsilon_0$, corresponding to SiO_2, was placed above the Hexa1 NW. In this work, we used six different gate potentials (± 1 V, ± 2 V, ± 5 V). Results obtained with these potentials were compared to those obtained at zero gate potential. We applied Dirichlet boundary conditions for the electrode direction and Neumann boundary conditions for the two other directions.

3. Results and discussion

Previous studies have shown that gold NWs with the Hexa1 configuration on a BeO (0001) substrate may be a good candidate for future nano-conductor designs [36]. However, the effect of real-life imperfections must be probed to assess the applicability of such devices. Therefore, we investigated the stability of this structure to point defects, and its conductance sensitivity to the presence of vacancies (sec. 3.1) or to O_2 substitutional defects (sec. 3.2) inside the NW. To study the effect of electric field on the NW conductivity, we applied an external field perpendicular to the Hexa1 structure and compared the resulting structure and conductance to what was obtained without the field (sec. 3.3).

3.1 The effect of vacancies on the structure and conductance

We investigated the effects of vacancies by removing, one at a time, an individual or a pair of gold atoms from various locations along the relaxed Hexa1 configuration, then relaxing the new structure. We computed the energy cost of creating each point defect (E_{void}) using Eq. 1, where $E_{tot}^{Hexa1+pointdefect}$ is the total energy of the relaxed Hexa1/BeO system after removing one or pair of Au atoms, E_{tot}^{Hexa1} is the total energy of the relaxed system before removing the atoms, and E^{Au} refers to the total energy of one or two isolated Au atoms.

$$E_{void} = E_{tot}^{Hexa1+pointdefect} + E^{Au} - E_{tot}^{Hexa1} , \quad (1)$$

We found that the energy needed to create a single point defect in the Hexa1/BeO system is between 3.1 eV and 3.7 eV, while the formation of a two-atom vacancy

requires energies between 5.8 eV and 6.8 eV (Table 1). These energy ranges are caused by differences in the coordination number of each site, and by variations in the distance between the gold atoms and the substrate surface. Fig. 1a shows the Hexa1 NW configuration and the atoms that were artificially removed. The differences in E_{void} for vacancy "a" and vacancy "c" are governed by the NW-substrate equilibrium distance. The Hexa1 NW is not parallel to the substrate surface, so that the Be-Au bond lengths at the "a" side are shorter by 0.9 Å from these at the "c" side.

From a structural point of view, we found that the NW preserved its original configuration in all of the studied cases. The presence of the void only gave rise to small deformations, mostly in the vicinity of the void. More specifically, most of the Au-Au bond lengths changed by no more than 0.1 Å, getting closer to a length of 2.775 Å, which is the optimal bond length for a free standing Hexa1 NW [5]. Fig 1b shows representative NWs after removing various Au atoms and relaxing it on the substrate. To make the illustration clearer, the substrate was removed from the figures.

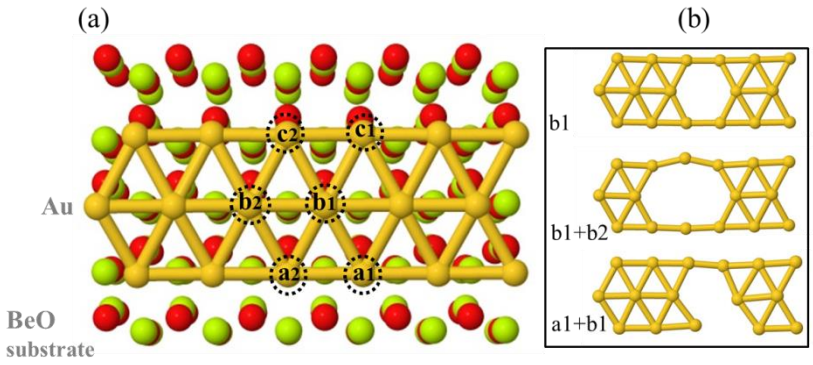

Fig. 1. Top view of the relaxed configuration of Hexa1 system: (a) The Hexa1 conductor without point defects. The letters on the NW indicate the Au atoms that were removed individually (a1, b1, c1) or removed in pairs (a1+a2, b1+b2, c1+c2, a1+b1, a1+c1, b1+c1) to form vacancies, and are then used in Table 1 and Table 2. (b) Representative relaxed conductors with the vacancy defects. To make the illustration clearer, the BeO substrate was removed.

The electronic analysis shows a small increase in the electron density for the Au atoms near the vacancy (see Fig 2a). The same tendency was also observed using the Mulliken population analysis. An additional negative charge between 0.1 and 0.2 electrons, especially for the s state, was computed for the Au atoms around the vacancy.

The transport analysis shows that the presence of the vacancies decreases the conductance. For single vacancies or coupled vacancies that are on the same channel (a1+a2 or b1+b2 or c1+c2), the conductance decreased from 2.1 G_0 to (1.5 to 1.9) G_0, where $G_0 = 2e^2/h$. In all of these cases, the main conductance path was through the two undisturbed channels. Larger conductance decreases were observed when the two vacancies sit on separate conductance channels. In these cases, the conductivity was mainly through the remaining uninterrupted channel, and the conductance decreased to (0.9 to 1.5) G_0. Representative conductance paths and spectra are shown in Fig. 2b and 2c, respectively. The conductivities of the entire configurations are presented in Table 1.

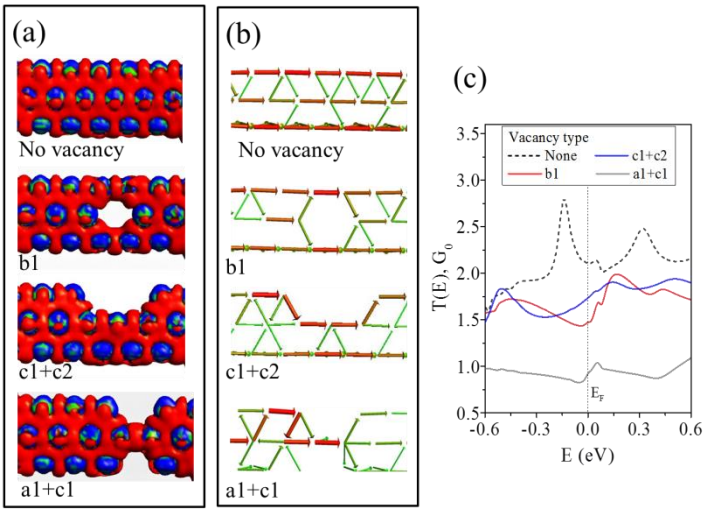

Fig. 2. Representative electronic analysis of the relaxed Hexa1 system with and without vacancies: (a) differential electron density iso-surface, where the dark (blue) and the light (red) shades represent an increase and decrease, respectively, of the differential electron density by 0.02 e/Å^3. (b) Transmission pathway: the thickness of the arrows is related to values of the local conductance between each pair of atoms and is normalized to the maximal value in the figure. The thicker arrows are also distinguished from the

thinner ones by thier color. To make the picture clearer, only arrows correponding to conductance values of at least 50 % of the maximum are shown. (c) Transmission spectra for the same configurations.

Table 1: Main results obtained from the point defect simulations.

Vacancy type	E_{void} [eV]	Conductance [G_0]
a1	3.70	1.68
b1	3.36	1.48
c1	3.13	1.52
a1+a2	6.82	1.96
b1+b2	6.55	1.81
c1+c2	5.84	1.73
a1+b1	6.65	1.47
a1+c1	6.76	0.93
b1+c1	6.47	1.13
None	---	2.10

3.2 The effect of substitutional oxygen on structure and conductance

Point defects on a surface can act as attractive sites for contaminants. Contamination of a freestanding NW affects the wire ability to conduct and, in certain circumstances, decreases the conductance significantly [26 50]. Thus, the combination of vacancies and contamination may be critical factors for the NW conductance. A previous study [37] showed that the conductance of a Hexa1 system is minimally affected by the absorption of a H_2O molecule but it is strongly affected (≈ 30 %) by the absorption of a single O_2 molecule. To study the synergistic effect of contamination and point defects on the conductance of Hexa1, we decided to investigate substitutional impurities. To do so, we simulated eight individual O_2 substitutional sites by replacing one or two gold atoms in the Hexa1 configuration with a single O_2 molecule, and then relaxing the new structure. In general, during the relaxation, the NWs preserved their atomic configuration and only small changes in the gold atom positions were observed. In

seven out of the eight cases, the bond length of the Au-Au in the vicinity of the O_2 molecule increased by at most 2 % to 3 %, while the length of the next Au-Au bond changed less. In the eighth case (Fig 3c), the O_2 dissociated and caused larger changes to the bond length in the local vicinity of the substitution. In this case, the maximum bond length change was 6 %, but still most Au atoms on the wire preserved their relative positions in the configuration. Fig. 3 presents representative configurations of the relaxed NW. To make the picture clearer, we removed the substrate from the illustration.

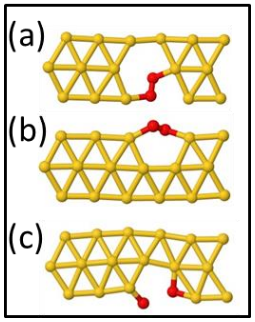

Fig. 3. Representative top views of the relaxed configurations of the Hexa1 system with O_2 substitution. In these figures, the O_2 replaced the gold atoms in positions (a) a1+b1, (b) c1 and (c) a1, with "a1" and "b1" defined as in figure 1. To make the illustration clearer, the BeO substrate was removed.

The adsorption energy of each O_2 (E_{ads}) molecule was computed according to Eq. 2.

$$E_{ads} = E^{Hexa1^*+O_2} - E^{O_2} - E^{Hexa1^*} , \qquad (2)$$

where $E^{Hexa1^*+O_2}$ is the total energy of the relaxed Hexa1 NW on BeO after removing one or a pair of Au atoms and adding an O_2 molecule, E^{Hexa1^*} is the total energy of the relaxed system that contains the point defect only, and E^{O_2} refers to the total energy of an isolated O_2 molecule. As a general result, we found that the O_2 molecules are attracted to the point defect of the Hexa1 system, with adsorption energies between 0.4

eV and 3.4 eV (Table 2). The lower adsorption energy values correspond to molecules that settled in the middle cannel of the NW, while the higher values were observed for molecules located at the edges of the NW. In one particular case, the molecule dissociated and the net energy was computed as 4.2 eV. According to a Mulliken population's analysis, a transfer of ≈ 0.2 electrons from the nearest gold atoms to the O_2 is involved for most of the simulations. This electron transfer decreases the conductance of the nano-conductor by (0.43 ± 0.27) G_0 with respect to the same geometry of the NW without the O_2 (see conductance values in table 1 and table 2). For one particular case (where the O_2 replaces the Au atoms at b1+c1 places) the O_2 bridges the disconnected channel and the conductance increases by 0.3 G_0.

Table 2: Main results obtained from the O_2 substitutional simulations.

Substitution location	E_{ads} [eV]	Conductance [G_0]
a1	-4.24*	1.05
b1	-0.38	1.46
c1	-1.37	1.19
a1+a2	-3.42	1.85
b1+b2	-0.65	0.94
c1+c2	-1.43	1.18
a1+b1	-2.70	1.01
b1+c1	-0.92	1.43
None	---	2.10

*In this case the O_2 molecule dissociates into two O atoms.

3.2 Electric field on Hexa1

Good nano-conductors should be structurally stable, have high conductivity and be sufficiently robust that the presence of point defects or adsorbed impurities wouldn't cause a noticeable decrease in the conductance. Moreover, to be utilized in a transistor device, the conductor should also preserve its conductivity under the electric field that

is applied in the transistor gate. To test that, in this section we investigate the conductivity of the studied nano-conductor in the presence of various electric fields from +5 V to -5 V. The fields were applied perpendicular to the conductance directions as displayed in Fig. 4.

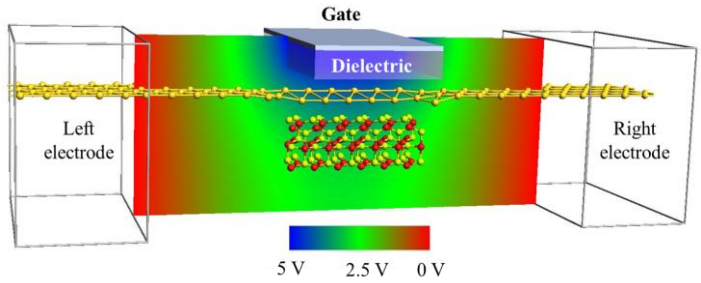

Fig. 4. Schematic illustration of the Hexa1 system exposed to a representative external gate potential of 5 V.

We found that the electric field affects the electron distribution and therefore the capacity of each conductance path. A positive gate potential attracts the electrons, therefore increasing their density between the dielectric material and the NW. In contrast, a negative gate potential repels the electrons and decreases their density in that region. Fig. 5 shows the differential electron density for the positive, negative and zero potential gates. The redistribution of the electron density is mainly due to movement of electrons with energies near the Fermi energy. These are the electrons responsible for the conductivity and for the bonding. To better understand the effect of the potential gate on the conductance, we computed the conductance spectra for various gate potentials using a Green's function technique based on the Landauer formalism [45].

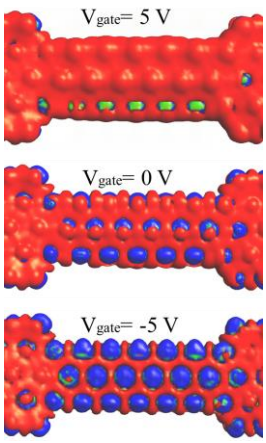

Fig. 5. Top view of representative differential electron density iso-surfaces for the Hexa1 system with gate potentials of 5 V, 0 V and –5 V. The dark (blue) and the light (red) shades represent a decrease and increase of the electron density by 0.02 e/Å^3 relative to isolated atoms, respectively. To make the illustration clearer, the BeO substrate was removed.

Fig. 6 presents the conductance spectra of a Hexa1 NW lying on a BeO (0001) substrate for gate potentials between 5 V and -5 V. The results show that the negative potential shifts the conductance spectra with respect to the Fermi level. This shift does not change the conductance at the Fermi level for low values of the gate potential: for gate potentials of both -1 V and for -2 V, the conductance remains about what it was without the field (≈ 1.9 G_0). However, at higher potentials, this shift increases the conductance up to 2.6 G_0. For -5 V, the conductance was ≈ 2.25 G_0. A slightly different behavior is observed for positive potentials. In this case, no significant shift is found, while an increase in the size of the main features of the spectrum is observed as the potential increases. For zero gate potential, as well as for +1 V, the conductance is ≈ 1.9 G_0 while for +2 V and +5 V it increases to just ≈ 2 G_0 and ≈ 2.5 G_0 respectively.

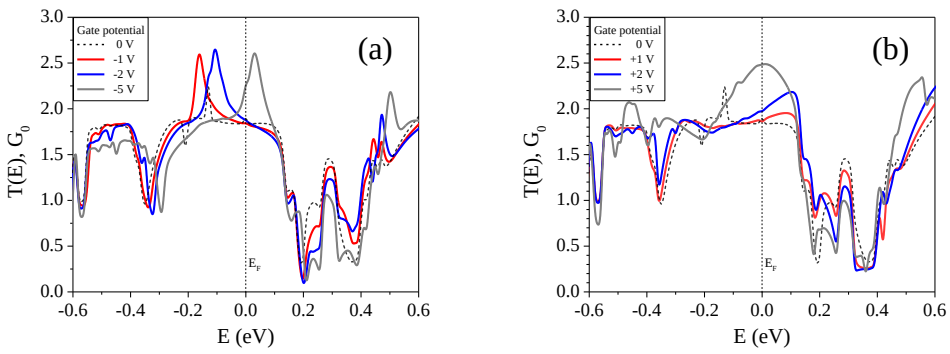

Fig. 6. The conductance spectra for negative (a) and positive (b) gate potentials. The dashed line represents a zero gate potential.

4. Summary and conclusion

In a previous study [36], we showed that gold nano structures with a Hexa1 configuration over a Be-terminated surface of BeO (0001) may be an appropriate

design for nano-conductors because it has a robust structure and remarkable ballistic conductance. Further investigation [37] showed that the electronic transport of this structure is not sensitive to common contaminations. More specifically, we found that adsorption of H_2O does not decrease its conductance while adsorption of single O_2 only decreases the conductance from 2.1 G_0 to ≈ 1.5 G_0, at most. In this study, we extended this sensitivity investigation and computed the conductance of this system in the presence of several kinds of point defects and for substitutional O_2 molecules in various positions. We also investigated the system conductance sensitivity to an applied electric field perpendicular to the NW surface.

We found that the nano-conductor under investigation preserves its atomic configuration in all cases, and that the gold NW remains stable over the BeO substrate even after removing one or two gold atoms from the NW itself. The same level of stability was found after replacing these point defects with O_2 contaminants. The conductance obviously depends on the number of available channels in the NW. For the Hexa1/BeO system, there are three main open channels, and the conductance is 2.10 G_0. The presence of point defects decreases the number of available channels, and therefore the conductance is lowered to (1.47 to 1.97) G_0, when two channels remain open, and is reduced to ≈ 1 G_0 with just one open channel. In general, having O_2 as a substitutional contaminant reduced the conductance. The magnitude of the reduction depends on the location of the impurity. The average reduction was ≈ 0.4 G_0. The only exception was the case where two gold atoms were removed and the oxygen was relaxed between two channels, creating a conductance bridge. In this case, the conductivity actually increased instead of decreasing, going from 1.12 G_0 to 1.43 G_0. The sensitivity of our system's conductivity to electrical fields was found to be small. The gate potential (positive and negative) controls the electron distribution around the

nuclei of the gold atoms but does not reduce the conductivity. In fact, the conductivity increases slightly, especially for gate voltages higher than 2 V.

In conclusion, our results show that the suggested nano-conductor has a robust configuration and the presence of point defects or substitutional oxygen molecules does not change its atomic configuration. Moreover, it is not sensitive to electrical fields applied for transistor gates. The conductance properties of the conductor with point defects are depends on the availability channels of the NW. Single or double voids on the same channel reduce the conductance by at most 28 %, but when the voids are arranged in a way that only one conductance channel remains open, the conductivity may reduce by factor of two to $\approx 1\ G_0$. In most cases, the presence of a single O_2 molecule as a substitution reduces the number of electrons available for transport in the Au atoms in the vicinity of the impurity and reduces the conductance.

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