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A comparable study of structural and electrical transport properties of Al and Cu nanowires using first-principle calculations

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The structural and quantum transport properties of Al and Cu nanowires with diameters up to 3.6 nm are studied using density functional theory combined with Landauer formalism. Contrary to the classical electronic behavior, the conductance of Al wires is larger than that of Cu. This is mainly attributed to the larger contribution of conductance channels from Al-3p, which is determined by the chemical nature. Meanwhile, the stronger axial contraction of Al wires plays a minor role to conductance. This makes Al wires possible candidate interconnects in integrated circuits. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4858408]

In keeping with Moore’s law, the miniaturization of chip dimensions also creates the need to downscale interconnects, making the improvement of interconnects essential in ultra-large scaled integration. The bulk conductivity of presently used Cu is superior to nearly all conventional metals (except Ag), while the electrical conductivity is one of essential requirements for interconnects. However, as the size approaches the electron mean free path (λ), the electrical conductivity deviates downward from their bulk value seriously induced by surface and grain boundary scatterings. It is reported that the size-dependent electrical conductivity is anisotropic; thus, the electrical transport properties for structures with small size need to be investigated since alternative materials may possess superior conductance to Cu.

It is known that the electrical conductance is from both Ohm’s and quantum mechanisms. For macroscopic conductors, to calculate conductance Ohm’s law is considered only. However, as the size reduces, the role of quantum mechanism cannot be ignored any more, which even becomes dominant, as being observed in experiments. Then, the point like electron motion would be replaced by the spread out quantum waves. It would lead to different behaviors, which have been proved in theoretical results. The study reported that the quantum conductance (G) values of Cu nanowires (NWs) were slightly larger than those of Ag. Nowadays, Intel has begun high volume production with 22 nm process technology, which has been smaller than λ of bulk Cu (39 nm at 298 K). Thus, the quantum mechanism of electronic transports is an exciting field of both fundamental and applied relevance.

In the quantum area, G is determined by the valence state of the respective atom. Building off of this reasoning, Hasmy et al. reported that the conductance for Al nanocontacts converged to a value between 1–1.5 G0 (the unit G0 = e2/h, where e is the electronic charge and h is the Planck’s constant), thus they concluded that Al nanocontacts are better conductors than any monovalent metal. The better conduction behavior of Al was also confirmed in single atomic wires. However, the theoretical models predicted that it was difficult for both Al and Cu to form the monatomic chains. Thus, in this study, the structural and quantum transport properties of Al and Cu wires with diameter (D) up to 3.6 nm are investigated. Density functional theory (DFT) is performed to calculate the band structures and the Landauer formalism is used to determine G. It is found that G values of Al NWs are larger than those of Cu.

The sufficiently thin NWs could turn helical, thus magic configurations were investigated. However, for Al wires with D larger than 1 nm, the regular fcc stacking prevails. And nonhelical crystalline configuration is always more stable for Cu wires. Herein, we investigate the size-dependent transport properties, thus the regular fcc configurations are considered. The NWs are modeled with one-dimensional periodic boundary conditions along the [001] direction. Figure 1(a) is the rectangular cross section configuration, which contains two (100) and (010) surfaces. The D value for this pattern is defined as the diameter of circular structure with the same cross-sectional area. In order to investigate the effect of cross-sectional shape to transport, circular cross-sectional configuration is also constructed in Figure 1(b). Each wire is named in terms of the number of atoms (n) per unit cell. The structures in Figures 1(a) and 1(b) are marked with Al225 and Alc241 NWs, respectively, where “c” represents circular cross section. The configurations and the corresponding D values are listed in Table I of supplementary material.

The calculations are carried out by DFT, which is provided in DMol3 model. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) method is used as the exchange-correlation interaction. DFT semicore pseudopotentials (DSPP) are employed to replace the core electron potentials by a single effective potential, which also account for some degree of relativistic effects. In addition, Double Numerical plus polarization is chosen as the basis set. The k-point is set to 1 × 1 × 4 with orbital cutoff of 4.6 A. We use smearing techniques with a smearing value of 0.01 Ha (1 Ha = 27.2114 eV). The stable structures are obtained by relaxing both axial lattice constants and atomic positions. The starting lattice constants are...
obtained from the relaxation of bulk. The axial lattice constants are regarded as the lengths of the repeating unit along the [001] direction, and the percentage changes before and after optimization (Δ) are also shown in Table I of supplementary material. The relaxation along the NWs is important since the transport is along this direction. The structures are relaxed using the delocalized internal coordinate optimization scheme. The convergence tolerance of energy is 1.0 × 10⁻⁵ Ha, the maximum force is 0.002 Ha Å⁻¹, and the maximum displacement is 0.005 Å in the geometry optimization. An interwire distance of at least 5 Å on each side is established to ensure negligible interaction between the wires.

$G$ is given by the Landauer formalism, which is reasonably valid in evaluating quantum transport for metallic wires. Based on the formalism, at zero Kelvin, $G$ is given by

$$G = G_0 \sum_{i=1}^{N} T_i,$$

where $T_i$ is the transmission probability of the $i$th channel and $N$ is the number of propagating modes crossing Fermi energy ($E_F$). In case of perfect transmission in ballistic transport, no scattering is considered, namely, $T_i$ is always unity.

The stress induced by surface under-coordinated atoms makes the structural reconstruction. Take Al25 and Cu25 wires as examples, the cross-sectional displacements are schematically shown in Figure S1 of supplementary material. The relaxation mainly occurs at the surface, while atoms in the interior maintain the bulk configuration. For Al NWs with rectangle cross section, the relaxation direction changes from inward for the atoms on the diagonals to outward for the atoms on the symmetrical medians, meanwhile the atomic movements in diagonals of $-0.465\% -- -2.637\%$ are slightly smaller than those in medians of $1.842\% -- 3.692\%$. While for Cu wires, all the atoms move outward the center with the slightly smaller atomic displacements on the vertexes of $0.599\% -- 1.686\%$ compared with $1.156\% -- 3.121\%$ on the medians. The round corners appeared in NWs are similar to previous results in Cu nanorods. For NWs with circular cross section, the relaxed structures are more close to cylindrical.

Meanwhile, the axial lattices of all Al and Cu wires contract, $\Delta$ values are $-3.372\% -- -5.119\%$ and $-0.028\% -- -2.611\%$, respectively. Thus, both atomic displacements in radial and axial directions of Al NWs are larger than those of Cu. The axial contraction of Al single atomic wire was reported to arrive at 17%. The more notable lattice contraction of Al nanocrystals compared with other fcc metals was also been found.

Figure 2 shows $G$ values of Al and Cu NWs as a function of $D$. $G$ value of Al and Cu NWs increases as $D$ increases due to the enhancement in the number of conduction channels crossing $E_F$. Moreover, there is no evidently fluctuation of $G$ values between the structures with different cross-sectional shapes. It is concluded that $G$ value is only dependent on the cross section, which gives the area for transport. Thus, in the following, we only consider the NWs with rectangular cross section. In addition, $G$ values of Al NWs are generally larger than those of Cu, and the difference between them increases as $D$ increases.

It was reported that the $G$ values of Ag and Cu NWs with the same $n$ are almost equal, where Ag and Cu are in the same group. Herein, we first consider the role of chemical nature, which plays an essential role in ballistic transports. According to the theory of one-atom contact, $d$ orbitals of Cu are generally considered not contributing to transport, thus the number of relevant open conducting channels is only one. While for Al one-atom contact, both Al-3$s$ and Al-3$p$ orbitals contribute to transport, which gives rise to three conducting channels. However, as shown in Table I of supplementary material, it is found that $G$ values of Al NWs are about two times larger than those of Cu with the same $n$, which is smaller than three as expected.

To understand the corresponding electronic changes, we present the band structures and partial density of states (PDOS) of Al25 and Cu25 NWs as examples in Figure 3. The band structures in the left panel of Figure 3 reveal metallic characteristics with 14 and 8 bands crossing $E_F$ for Al25 and Cu25 wires, respectively (note that three Al bands are two-fold degenerate). Based on Eq. (1), $G$ value of Al25 wire is larger than that of Cu25.
have similar states distribution near $E_F$. For a detailed insight into the conductance, we proceeded with a careful analysis of PDOS in the right panel of Figure 3. Due to the partial covalent nature of Al bonding, some electrons in Al-3$s$ and Al-3$p$ overlap, confirming the $sp$ hybridization. Moreover, all the Al-3$s$, Al-3$p$, and Al-3$d$ states cross $E_F$, demonstrating all of them contribute to conductance. The largest state crossing $E_F$ is Al-3$p$, which is much larger than that of Al-3$s$ and Al-3$d$. It suggests that the Al-3$p$ orbitals have significant contribution in conduction with Al-3$s$ and Al-3$d$ playing a minor role. Other Al NWs have similar states distribution near $E_F$ as shown in Figure S2 of supplementary material.

Bonding of transitional metals is mainly because of the overlap among $d$ shells accompanied with a little hybridization of $s$-$p$-$d$ electrons. Thus, Cu-3$d$, Cu-4$s$, and Cu-4$p$ states are drawn in PDOS of Figure 3(b). Consistent with previous studies, the energies between $-5.0$ to $-1.0$ eV are almost exclusively contributed by Cu-3$d$ orbitals, which are displayed as the dense and nearly flat bands in band structure. Moreover, the inset of PDOS suggests that the conductance channels are not purely Cu-4$s$ and have comparable size from the Cu-4$p$ to Cu-3$d$ levels. The similar states are also found in PDOS for other Cu wires in Figure S2 of supplementary material. Compared with the PDOS of Al25 and Cu25 NWs, the more states of Al25 wire at $E_F$ is mainly derived from Al-3$p$ orbitals, which is caused by the more Al-3$p$ electrons. Thus, the larger $G$ values for Al NWs are mainly caused by the conductance channels from Al-3$p$. Valence charge polarization and the locally entrenched core electron by the local strain could be a possible mechanism for the ballistic transport variations in NWs.

Thus, in the following, the contribution of axial and radial strains for transports is investigated. Figure 4 shows $G$ values of Al and Cu wires with axial and radial atomic relaxed or unrelaxed. It is found that $G$ values of both axial and radial atomic relaxed Al wires are evidently larger than others. Moreover, compared with Al wires with radially atomic relaxed and unrelaxed, $G$ value of the former is slightly larger than the latter for wires at small sizes, while $G$ values of Al225 and Al289 wires are not affected by the radial relaxation. For Cu wires, the values before and after relaxation are almost equal. It is noteworthy that the axial contraction increases jump between the neighboring layers due to the nature of the ballistic transport and thus increases $G$, while the effect of radial strain is little. Thus, the chemical nature plays a critical role in ballistic conductance, meanwhile the effect of axial contraction is minor.

Finally, the knowledge of $G$, allowed us to evaluate total electrical conductance $G_T$

$$G_T = G \left(1 + \frac{L}{Z} \right)^{-1}$$

in the diffusive regime, where $L \gg \lambda$ ($L$ is the length of interconnects). The two parts in Eq. (2) are the quantum and Ohm’s conductance, respectively. At lower temperature and $D$ is smaller than $\lambda$ of bulk, the $\lambda$ in one-dimensional nanostructures is approximately equal to $D$. Then, Eq. (2) reads

![Figure 3. Band structures and PDOS for (a) Al25 and (b) Cu25 NWs. Both band structures show metallic characteristics with 14 and 8 modes crossing $E_F$ for Al25 and Cu25 wires, respectively (three Al bands are two-fold degenerate). The Fermi level is set at zero. The inset of right panel in (b) is a magnified plot near $E_F$, and the scales in the horizontal axis are the same as that in (a).](image1)

![Figure 4. $G$ values as a function of $n$ for both axial and radial relaxed (filled symbols), only radial relaxed (hollow symbols), and both axial and radial unrelaxed (dotted symbols) wires. The light and dark symbols denote the data of Al and Cu wires, respectively.](image2)
Thus, for wires with the same size, $G_T$ is only dependent on $G$. $G$ values of Al wires are larger than those of Cu as shown in Figure 2, thus $G_T$ values of Al wires are larger than those of Cu.

Al, as the interconnects, had been used for almost 40 years before 180 nm technology due to its advantage in lithographic processing. Moreover, a coherent interface between the self-formed Al$_2$O$_3$ layer in surface and Al interconnects would reduce the surface scattering effects. According to our previous model, as the size reduces, the impact of grain boundary scattering for Al becomes less important than Cu. Besides, the possibility of the formation of Al single crystal on a groove was proved, which could weaken the grain boundary scattering. Combined with the results in this study, thus Al wires are potential candidates for interconnects.

In summary, using DFT and Laudauer formula, we comparatively calculate the structural and electrical transport properties of Al and Cu NWs with $D$ up to 3.6 nm. It is found that $G$ value is only dependent on the cross-sectional area.

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17See supplementary material at http://dx.doi.org/10.1063/1.4858408 for structural parameters of Al and Cu NWs, the cross-sectional relaxation of Al25 and Cu25 wires, PDOS of Al and Cu NWs.
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\[ G_T = G \left(1 + \frac{L}{D}\right)^{-1}. \]