Armchair and Zigzag Nanoribbons of Gold and Silver: A DFT Study

Pooja Kapoor[1,a)], Munish Sharma[1], Ashok Kumar[2] and P.K. Ahluwalia[1]

[1]Department. of Physics, Himachal Pradesh University, Shimla, H. P., India, 171005
[2]Centre for Physical Sciences, School of Basic and Applied Sciences, Central University of Punjab, Bathinda, India, 151001

[a]Corresponding author: pupooja16@gmail.com

Abstract. This paper presents the results from a DFT-based computational study of structural and electronic properties of zigzag and armchair edge shaped nanoribbons of gold and silver in hexagonal phase. The cohesive energy of the considered nanoribbons are found to be more than the corresponding 2D counterpart, thereby, suggesting Au and Ag nanoribbons to be more stable in 1D as compared to 2D. All nanoribbons are found to be metallic with a modulation in quantum ballistic conductance with length and edge type of the nanoribbon. Au nanoribbons are found to have higher conductance than Ag nanoribbon. There is increase in conductance with increase in length of nanoribbon.

INTRODUCTION

With the advancement of nanotechnology in past decades, Au nanostructures have gained huge attention due to their fascinating properties and wide applications in various fields like electronics, photonics, sensing and biomedicine [1, 2]. The properties of Au nanostructures vary with their size, shape, dimensionality and crystal phase [3]. Nanoribbon is one amongst the most studied 1D Au nanostructures. A number of methods have been developed for synthesis of gold and silver nanoribbons [4-7]. Recently, synthesis of Au nanoribbon in 4H hexagonal phase has been reported with a different optical response as compared to FCC phase [8]. Ag in 4H and 2H phase has also been reported to be synthesized [9]. It represents an important landmark in development of novel noble-metal nanostructures and opens up new possibilities for functionalized nanomaterials with enhanced properties and wider applications.

Motivated by these developments and in search of new novel nanomaterials, we present a DFT based computational study of armchair nanoribbons (ACNRs) and zigzag nanoribbons (ZZNRs) of different sizes in hexagonal phase where we wish to look at the variation in structural and electronic properties of nanoribbons with edge shape, size and phase (Figure 1).

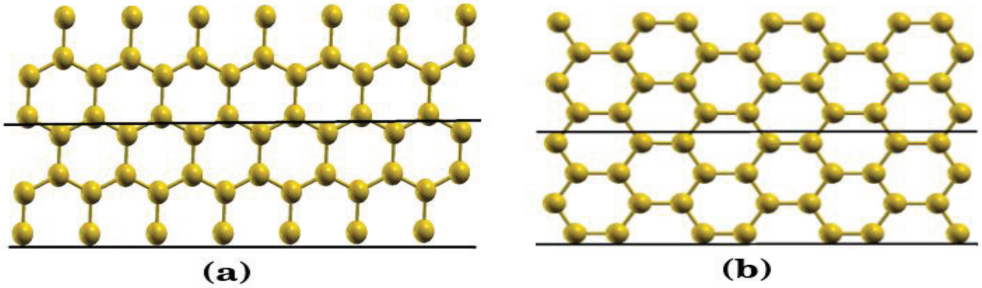

FIGURE 1. The top view of (a) ACNR2 (b) ZZNR2 where their edge directions have been highlighted respectively.

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COMPUTATIONAL DETAILS

All the calculations have been performed using the SIESTA (*Spanish Initiative for Electronic Simulation with Thousand of Atoms*) code [10] and method which uses an ab initio pseudopotential based density functional theory (DFT). We have used well tested [11] Troullier Martin, norm conserving relativistic pseudopotential in fully separable Kleinman and Bylander form. The exchange and correlation energies are treated within the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) parameterization [12]. Numerical atomic orbitals (NAOs) with double zeta polarization (DZP) basis set with confinement energy of 0.01 Ry have been used for geometry optimization. A 1x1x40 Monkhorst-Pack of k points have been used for sampling the Brillion zone. The mesh cutoff energy has been taken equal to 250 Ry. Minimization of energy has been carried out using standard conjugate-gradients (CG) technique until the force on each atom was less than 0.04 *eV/Å*. We have taken nanoribbons of two different lengths 16 atom (NR1) and 28 atom (NR2) long 1D nanoribbons of silver and gold both in armchair and zigzag directions with a vacuum of more than 20Å in x and y directions.

RESULTS AND DISCUSSIONS

We have already reported the DFT based computational study of pristine 2D monolayer of gold and silver in hexagonal graphene like structure [11]. The binding energies for these monolayers have been found to be 1.76 eV for silver and 2.24 eV for gold, respectively [13]. Similar to the case of graphene, nanoribbons of gold and silver can be obtained by cutting their pristine monolayer along armchair (AC) or zigzag (ZZ) directions. The lattice constant and bond-length of considered AC and ZZ nanoribbons for two different lengths NR1 (16 atoms long) and NR2 (28 atoms long) are almost similar therefore values reported in table 1 are only for NR1. The lattice constant is higher for ZZ nanoribbons as compared to AC nanoribbons. The values of lattice constant and bond length are higher for Ag nanoribbons as compared to their Au nanoribbons. The value of bond length is similar for both edge types, however, some deformations along the edges of nanoribbons leads to the variation in bond lengths. In order to investigate the relative stability of Au and Ag NRs, we have computed the cohesive energy of both AuNRs and AgNRs in AC and ZZ directions and are given in table 1.

TABLE 1. The value of lattice constant (a) in Å, bondlength (d) in Å and cohesive energy (ΔE_c) in eV for the armchair (AC) and zigzag (ZZ) nanoribbons (NRs) of Ag and Au.

System	*Ag ACNR*	*Ag ZZNR*	*Au ACNR*	*Au ZZNR*
a (Å)	7.65	9.13	7.62	9.04
d (Å)	2.75	2.74	2.67	2.66
ΔE_c *(eV)*	1.87	1.91	2.35	2.39

Note that the cohesive energy (ΔE_c) of a nanoribbon is calculated as

$$\Delta E_c = \left[\left| E_{total} - nE_A \right| \right] / n$$

where E_{total} is the total energy of the nanoribbon and E_A is the energy of a single isolated atom and n is the total number of atoms present in the nanoribbon. The negative value of cohesive energy indicates the stability of the given system. The value of cohesive energy of nanoribbons is more than the binding energy of their respective 2D monolayers. It further indicates that the one-dimensional (1D) nanoribbons are energetically more favourable than their 2D counterparts. The cohesive energy is higher for Au nanoribbon suggesting them to be more stable than Ag nanoribbons. The cohesive energy is higher for larger sized nanoribbons in all the cases; however the change is small of the order of 0.04-0.05 eV.

Electronic Properties

Next we study the electronic band structure and density of states for the studied nanoribbons. All the nanoribbons have been found to be metallic, similar to the behavior of their 2D counterparts [11, 13]. However, there is change in the number of bands crossing the Fermi-level. Note that for a system if n number of bands are crossing the Fermi-level, the quantum ballistic conductance of the system is found to be nG_0. Ag ACNR1 has least conductance and Au ZZNR2 has the highest conductance (table 2). The zigzag nanoribbons have a higher conductance as compared to armchair nanoribbons. There is increase in conductance with increase in length of nanoribbon (from going to 16 atom long nanoribbon to 28 atoms long nanoribbon) except in case of Ag ZZNR (i.e. conductance increases from $4G_0$ to $6G_0$ as we go from Au ACNR1 (16 atom long) to Au ACNR2 (28 atom long).

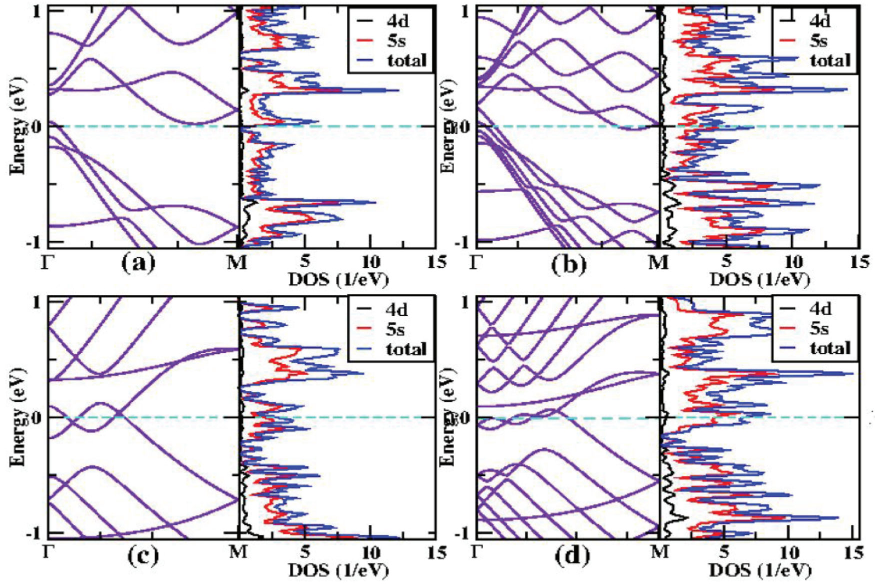

FIGURE 2. Electronic band structure and density of states for (a) AgACNR1 (b) AgACNR2 (c) AgZZNR1 and (d) AgZZNR2. The Fermi-level is at 0 eV and brillion zone path is along Γ-M- Γ.

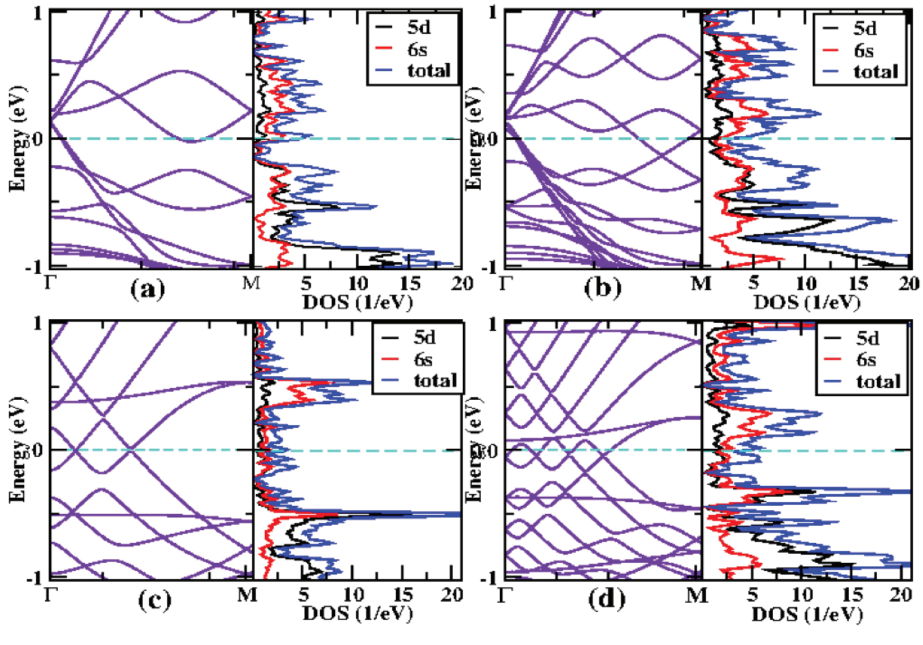

FIGURE 3. Electronic band structure and density of states for (a) AuACNR1 (b) AuACNR2 (c) AuZZNR1 and (d) AuZZNR2. The Fermi-level is at 0 eV and brillion zone path is along Γ-M- Γ.

Au nanoribbons are found to have higher conductance than Ag nanoribbon except in case of Au ZZNR1.

To have a deeper understanding of orbitals contributing to the bands near Fermi-level, we analysed the density of states plots. Surprisingly, in case of Ag NRs, the major contribution is of 5s orbitals while 4d orbital has minimal contribution. In case of Au NRs, in valance band region 5d orbital has a major contribution and 6s orbital also has significant contribution and in conduction band region 6s orbital has a major contribution while 5d orbital also has some contributions. To investigate the magnetic properties of these systems, we further did spin polarized calculation however these systems came out to be non-magnetic with zero magnetic moment.

TABLE 2. The value of quantum ballistic conductance for the armchair (AC) and zigzag (ZZ) nanoribbons (NRs) of Ag and Au.

System	***Ag ACNR1***	***Ag ZZNR1***	***Ag ACNR2***	***Ag ZZNR2***	***Au ACNR1***	***Au ZZNR1***	***Au ACNR2***	***Au ZZNR2***
Conductance (G_0)	1	4	4	3	4	2	6	7

CONCLUSIONS

In conclusion, we have carried out a DFT based computational study of armchair and zigzag nanoribbons of different lengths (16 atoms and 28 atoms) of gold and silver. We studied here the structural and electronic properties of theses nanoribbons and the effect of change in edge shape and length on the properties of these nanoribbons. The zigzag edged nanoribbon has higher lattice constant than armchair edged nanoribbon. We calculated the cohesive energy of these nanoribbons which is found to be more than their corresponding 2D counterpart which suggests the more stability of these ribbons as compared to 2D monolayers. All the nanoribbons are found to be metallic with a variation in quantum ballistic conductance with change in size and edge type of the ribbon. Au nanoribbons are found to have higher conductance than Ag nanoribbon.

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