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Impact of substitutional metallic dopants on the physical and electronic properties of germanene nanoribbons: A first principles study

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ABSTRACT

Density functional theory (DFT) has been used to investigate doped armchair germanene nanoribbons (AGeNRs) doped by low-concentration metallic atoms (Pt, Ag, Au, In and Sn). The structural stability and electronic properties of these doped nano-structures have been analyzed. The formation energy of the examined ribbons shows that they are thermodynamically stable. Examination of E-k band structures and density of state (DOS) has shown that depending on the type of metal atom, different energy bands can be seen around the Fermi level. Doping of the nano-ribbon by Pt and Sn in N = 7 only reduces the band gap compared to the pristine structure and the nano-ribbon stays semiconducting. However replacing the In, Ag, and Au atoms in AGeNR leads to the semiconducting-metal transition. Moreover, metallic doping of the ribbon in N = 8, yields an increase of the band gap and a transfer is observed from metal to semiconductor.

Introduction

Because of the benefits obtained from scaling of electronics devices based on Moore's law in CMOS technologies which has led to improvement of their performance, researchers and large semiconductor companies pay particular attention to this issue. Due to the problems and constraints of common current technology in the electronics industry, much research has been carried out to identify and use alternative materials in this industry. In recent years, much attention has been paid to 2D materials, especially graphene which is a planar structure with one atomic layer of thickness and has a Dirac cone band structure [1–7]. The graphene due to its unique characteristics such as high mobility of carriers [8,9], quantum Hall effect [9,10], near ballistic transport at room temperature [10,11] and massless Dirac fermions [12–14], is considered as one of the most desirable material for the development of high performance and low power electronic devices [10,13,15,16]. However, graphene has no band gap. To use this material in electronic devices a band gap must be opened. One of the important strategies for opening the band gap is to convert the graphene sheet into a one-dimensional (1D) nanostructure. [15,17–24]. Like graphene sheets, 1D graphene nanoribbons (GNRs) have unique properties depending on size, geometry, external electric field and pattern of passive edge [25–28]. Experimental and theoretical studies on graphene have led to considerable interest in Group IV elements of honeycomb lattice, particularly germanene due to the similarity of the synthesis and fabrication process with current CMOS technology. Germanene due to the combination of sp^2–sp^3 hybridization is a buckled crystal structure compared with planar graphene [29–32]. Germanene nanoribbons include zigzag or armchair edges which are similar to graphene with significant electronic and magnetic properties [6,33]. It has been shown that one way to improve the properties of graphene and to expand its applications in many fields is by adsorption and substitution of metallic atoms. In recent years, doping of graphene with transition metal (TM) atoms has been the focus some researches [34–42]. It has been shown that the presence of TM atoms at low concentrations induces scattering, magnetization, and superconductivity and strongly modifies the electronic structure at high concentrations. Studies have reported the stability of graphene doped with metals. TM doping is an effective way to modify the electronic and quantum transport properties of graphene and GNR. Not only the nature of doping, but also the concentration of dopant and the position of doping atoms in the structure are main factors controlling the properties of doped GNRs [32,34–42].

Due to the importance of doping and the results reported for graphene, we decided to investigate the effects of metallic dopings on the germanene nanoribbon (GeNR). Hence, in this work, we investigate the structural and electronic properties of armchair germanene nanoribbons (AGeNRs) doped with Pt, Ag, Au, In and Sn atoms using DFT

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based first-principles calculations.

Calculation method

Optimization of geometry, structural stability, and electronic properties of AGeNR doped with different metallic atoms have been performed using density functional theory (DFT). The calculations and results are obtained by the Atomistix Tool Kit Virtual NanoLab (ATK-VNL) simulation package [43]. In this computational package for solving the Kohn–Sham equation, the exchange-correlation functional utilized is the generalized gradient approximation(GGA) in the Perdew-Burke-Ernzerhof parameterization (PBE) [6]. The cutoff energy of the plane wave and a k-point grid are 150 Ry and 1 × 1 × 100, respectively, to obtain more accurate results. In discussed models, the ribbon grows along the z-axis but is limited in two other directions. In addition, in the x- and y-directions vacuum layers of approximately 25 Å is selected to prevent undesired interaction between image-image. All atomic positions in the ribbon were relaxed to obtain the optimal structure so that the maximum force smaller than 0.02 eV/Å is achieved. The edges of GeNR are highly reactive because of the dangling bonds, so the edges on both sides were passivated with hydrogen atoms.

Armchair germanene nano-ribbons are expressed as N-AGeNRs, depending on the number of germanium (Ge) atoms along the ribbon width. It is noteworthy that armchair germanene nanoribbon is divided into three groups based on the number of atoms along the width (N). It is comprised of three categories denoted by 3p, 3p + 1 and 3p + 2 (p is a positive integer). Among these three categories, 3p + 2 and 3p + 1 have the lowest and highest band gaps, while N = 3p possesses a band gap between these two widths [6]. In this work, N = 7 and N = 8 are selected to investigate the effects of doping impurities. In the structure discussed, a low-concentration doping was considered to maintain the integrity of the ribbon structure and to prevent any notable deformation. This means that the selection of a supercells consist of 2 primary unit cells, as shown in Fig. 1. According to Fig. 1, the corresponding structures of N = 7 and N = 8 both consist of 8 Hydogen atoms. The former structure has 28 Ge atoms while the latter possess 32 Ge atoms. The dopants are introduced into AGeNR by replacing existing germanium atoms. In this work, five metallic atoms including Pt, Ag, Au, In and Sn are considered, which three elements belong to transition metals (TMs), and others (Sn and In) are metals. Also, these elements are completely representative samples due to the presence of different groups in the periodic table. To maintain the symmetry of the structure, S4 position for width of 7 and S5 position for width of 8 are considered as the place of substitutional doping, as illustrated in Fig. 1.

Results and discussions

This section analyzes the results obtained from the DFT simulations. In particular we have emphasized on the geometrical stability and electronic properties of AGeNRs subjected to substitutional metallic dopants.

Geometrical stability

In order to evaluate the stability of AGeNRs, their formation energy is calculated based on the following formula:

$$E_f = (E_{AGeNR-M} - n_M E_M - n_{Ge} E_{Ge} - n_H E_H)/(n_{Ge} + n_M + n_H) \quad (1)$$

where E AGNR-M is the total energy of the system after metal doping, E_i (i = Ge, Metal, H) is the total isolated energy of the Ge atom, and n represents the number of Ge, metal, and H atoms in one supercell [44]. All formation energies related to metal substitution at the specified position in Fig. 1 are summarized in Table 1. According to this table, it can be seen that all the formation energies are negative, meaning that the formation is an exothermic reaction. Also, compared with the pristine structure, doped crystalline structures are more stable. Therefore, the stability can be increased by doping of AGeNR with the metallic dopants. Note that the lower the formation energy, the easier the substitution will be.

Tables 2 and 3 also represents the length of the bonds between adjacent germanium atoms and metal atoms located at the determined position in N = 7 and N = 8 cases, respectively. According to the results, length of the bonds which indicates different interactions between the metal atom and the host AGeNR depends on the type of metal atom. This is because of the different atomic radius of each metallic dopant. Except for Ag, in other metals under study, it is observed that in the periodic table as the atomic number of the metal increases, the bond lengths will be increased (for example, bond lengths associated with Sn doping is more than corresponding bond lengths due to introduction of In doping).

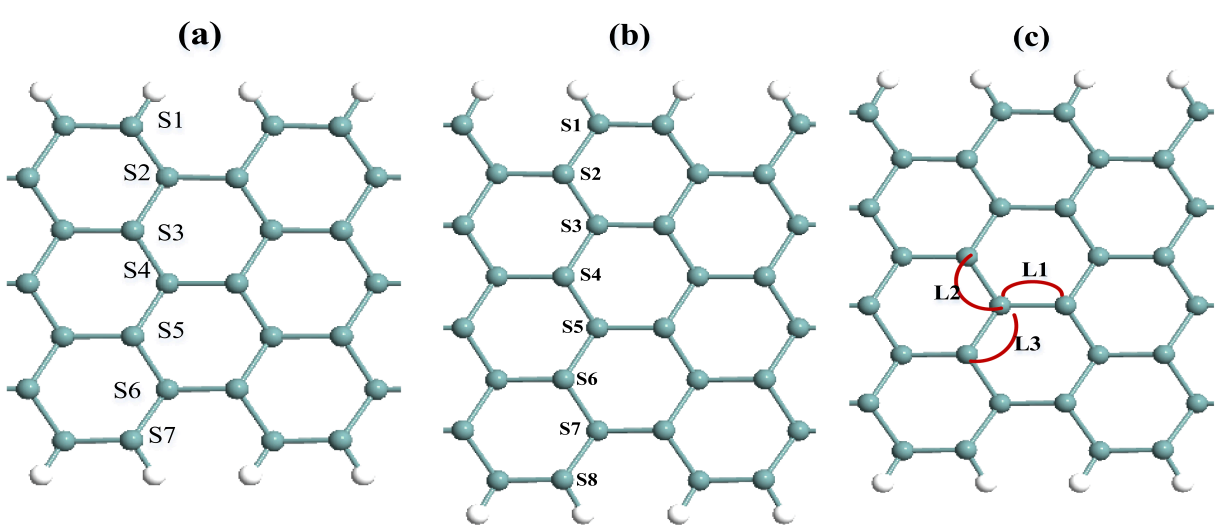

Fig. 1. Optimized geometry for armchair germanene nanoribbon. Supercells for (a) N = 7; and (b) N = 8 Ge atoms along the width are shown. (c) Position of the bond length around a metallic doping in the super cell.

Table 1
The metal substitution formation energies at of pristine and doped 7 and 8-AGeNRs.

Sites	AGeNR	Pt-AGeNR	Ag-AGeNR	Au-AGeNR	Sn-AGeNR	In-AGeNR
7	−3.1	−3.18	−3.20	−3.17	−3.33	−3.30
8	−3.08	−3.17	−3.20	−3.17	−3.3	−3.3

Table 2
Bond lengths, band gap and density of states (DOS) for the optimised geometry of pristine and doped 7-AGeNRs.

S. No	Material	Bond length L1 (Å)	Bond length L2 (Å)	Bond length L3 (Å)	Band gap (eV)	Density of States (eV^{-1}) at Fermi level
1	7-AGeNR	2.457	2.456	2.456	0.48	0
2	Pt-AGeNR	2.453	2.418	2.418	0.42	0
3	Ag-AGeNR	2.589	2.562	2.562	0.34	13
4	Au-AGeNR	2.484	2.484	2.484	0.35	12
5	In-AGeNR	2.541	2.529	2.529	0.41	11
6	Sn-AGeNR	2.574	2.588	2.588	0.47	0

Table 3
Bond lengths, band gap and density of states (DOS) for the optimised geometry of pristine and doped 8-AGeNRs.

S.No	Material	Bond Length L1 (Å)	Bond Length L2 (Å)	Bond Length L3 (Å)	Band Gap (eV)	Density of States (eV^{-1}) at Fermi level
1	8-AGeNR	2.455	2.450	2.444	0.02	22.5
2	Pt-AGeNR	2.448	2.410	2.431	0.22	0
3	Ag-AGeNR	2.55	2.53	2.562	0.3	0
4	Au-AGeNR	2.482	2.481	2.513	0.23	0
5	In-AGeNR	2.535	2.529	2.533	0.42	0
6	Sn-AGeNR	2.588	2.588	2.583	0.04	21

Electronic properties

To study changes in the electronic structure of the doped nanoribbon, the energy band structures along with the density of states (DOS) were analyzed in the most stable S4 substitution position, as shown in Fig. 1. To compare the findings, the band structure of the pristine AGeNR is provided (Fig. 2). First, two widths are examined in pristine case with no doping. As shown in Fig. 2, the band gaps associated with N = 7 is 0.48 eV, indicating that this ribbon is semiconductor. However, the band gap for N = 8 is 0.02 eV, which is semimetallic. Obtained band gaps are in agreement with the previous results reported elsewhere [6]. The energy bands near the Fermi level are mainly composed of p orbital and contribution of s orbital is very small compared to p orbital.

Fig. 3 shows that when ribbons are doped by Sn and Pt atoms, N = 7 maintains their semiconducting features and but in N = 8 the ribbon becomes semiconductor or semi-metal. However, they have different band gaps depending on the type of doped atom. This is due to the fact that with the doping of the ribbon by the metal, both the transfer of electrons between Ge and metals atoms and the effects of orbital hybridization occur. This results in the flexibility of tuning the AGNR electronic structure with metal doping. The main orbitals of the conduction and valance band of the doped ribbons with these metals are still the p orbital. However for Pt in both bands, the orbital hybridization of d orbital for Pt and p orbital for Ge is observed. From the band structure given in Fig. 3, it can be seen that the Pt band gaps are 0.42 eV and 0.22 eV, for N = 7 and 8, respectively. In addition, when Sn is introduced as a doping, the band gap for N = 7 and 8 are 0.47 eV and 0.04 eV, respectively. As a result the presence of impurities in these two widths has led to a change in the value of the band gap compared to the pristine case.

In the following, the band structure of Ag, Au and In-doped AGeNR is examined, as illustrated in Fig. 4. As can be seen the band structures are formed by passing a half-filled band from the Fermi level and placing it in a pristine AGeNR band gap. For N = 7 case, it can be stated that the presence of half-filled band leads to the semiconducting-metal transition. But in the case of N = 8, it is observed that Fermi level shifts upwards or downwards depending on the type of used impurities. Therefore, the semi-metal in pristine AGeNR becomes a semiconductor when subjected to these impurities. It can be said that the transfer from metal to semiconductor occurs. For N = 7, in In-doped AGeNR, due to close proximity of the half-filled band to the valence band, an additional hole is injected into the structure which indicates we have a p-type semiconductor. However in Ag/Au-doped AGeNR, close proximity of the half-filled band to the conduction band leads to the injection of

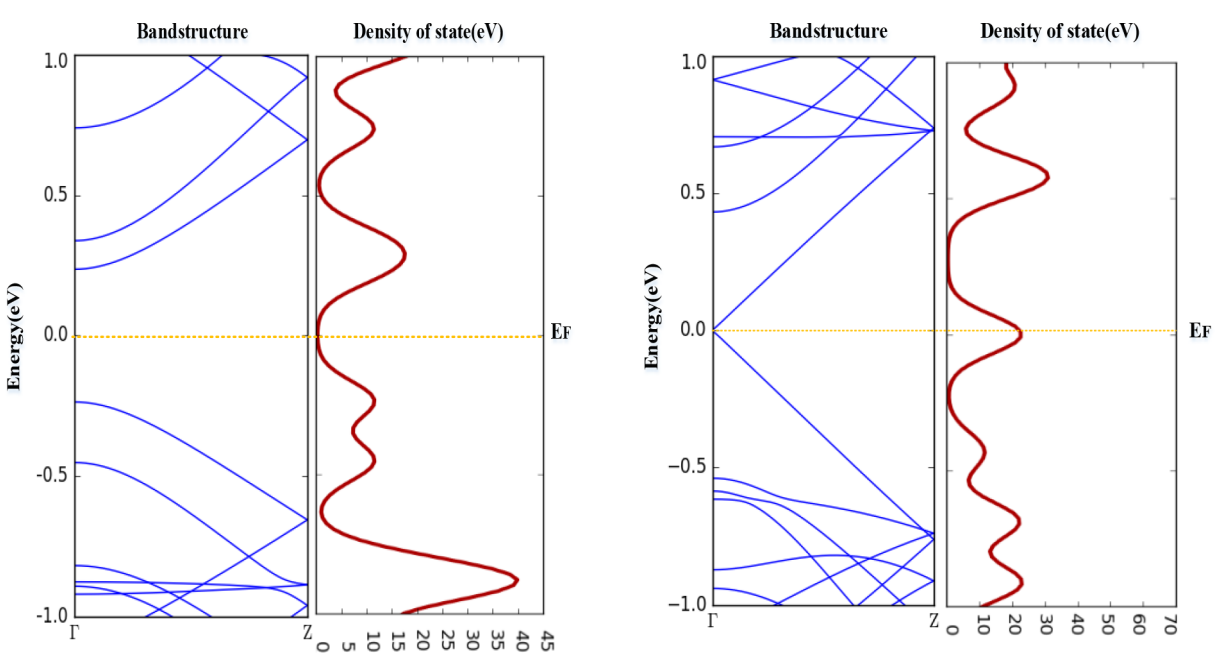

Fig. 2. The band structure and DOS for the pristine AGeNR of 7 and 8.

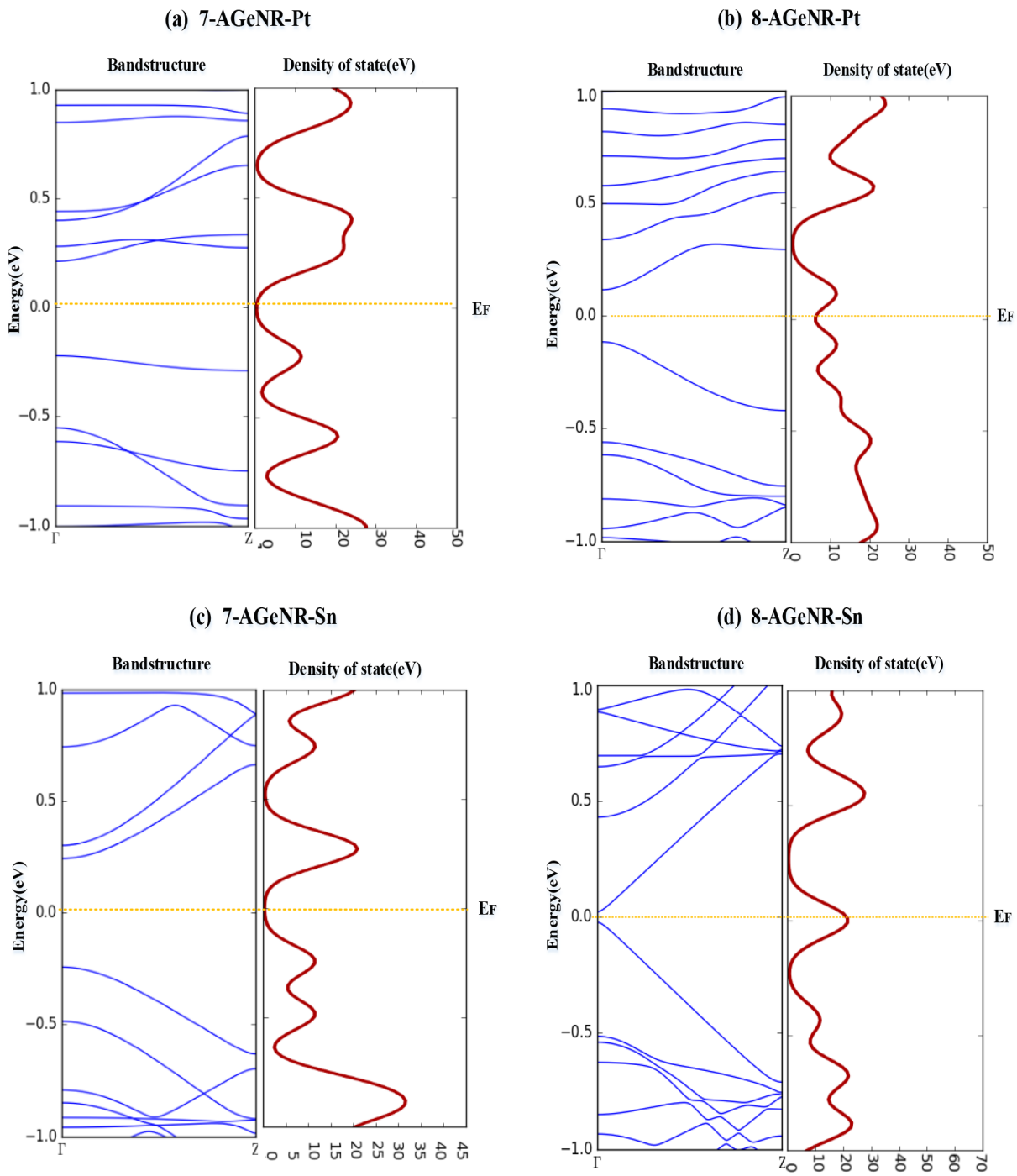

Fig. 3. The band structure and density of states (DOS) for all doping ribbons for: (a) 7-AGeNR-Pt, (b) 8-AGNR-Pt, (c) 7-AGNR-Sn (d) 8-AGeNR-Sn.

additional electrons into the system, indicating n-type semiconductor. The band gap of In-doped AGeNR and Ag/Au-doped AGeNR are 0.41, 0.34 and 0.35 eV, respectively, which reveals a decrease in the band gap compared to the pristine band gap. In addition, due to the shift of the Fermi level towards the conduction band or the valence band in Ag/Au-doped and In-doped AGeNR, the proper value of DOS in zero volt energy is provided (Tables 2 and 3). For N = 8, it can be seen that with the presence of these dopants, the band gap increases. The obtained band gap value is 0.42, 0.3 and 0.23 for In, Ag and Au doped AGeNR respectively. Overall, the presence of dopents in the structure leads to a significant change in the electronic properties, which can be beneficial for use in electronic applications.

Conclusion

In summary, the calculations of first-principles have been used to examine the geometrical and electronic (band gap and density of states) properties of pristine and metallic doped armchair germanene nanoribbon (AGeNR). The pristine structure showed a semiconducting or semi-metallic behavior depending on the width of NR with a direct band gap. It was observed that using Pt, Au, Ag, In and Sn impurities, made the structure more stable while its band structure varied. Addition of In dopants produced close proximity of the half-filled band to the valence band and thus, P-type semiconducting behavior was observed while addition of Ag/Au dopants caused close proximity of the half-filled band to the conduction band and as a result, N-type

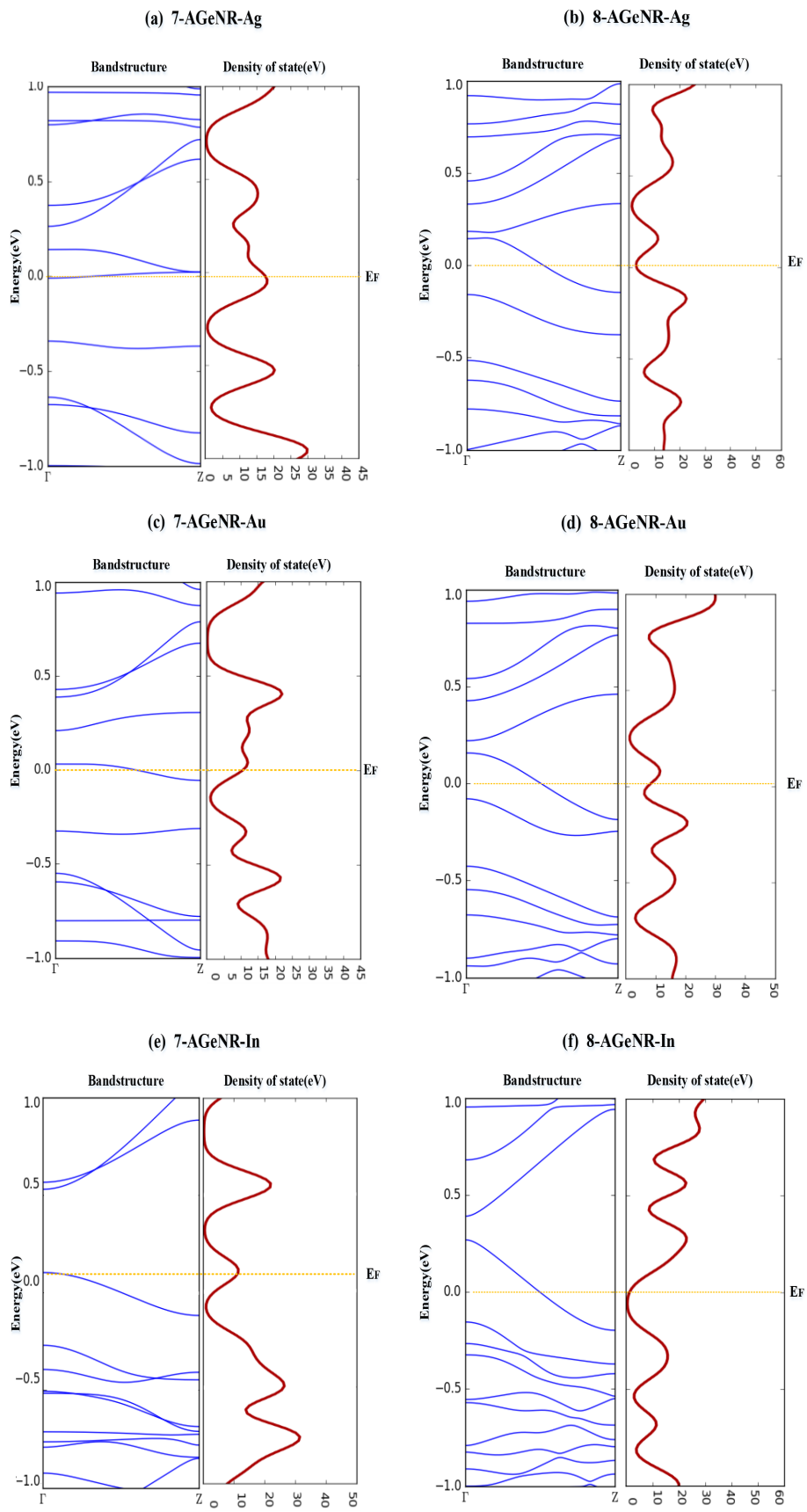

Fig. 4. The band structure and density of states (DOS) for all doping ribbons for : (a) 7-AGeNR-Ag (b) 8-AGNR-Ag, (c) 7-AGNR-Au (d) 8-AGeNR-Au (e) 7-AGeNR-In (f) 8-AGNR-In.

semiconductor was obtained. Utilizing metallic dopants as well as changes in the width of the ribbon considered as effective ways of changing or tuning electronic properties of germanene nanoribbons in nanoelectronic applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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