Electronic properties of armchair graphene nanoribbons doped with Cobalt atoms

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Abstract. We have investigated the electronic properties of Co doped armchair graphene nanoribbons (AGNR) within the framework of density functional theory. We have considered Co as an adsorbed atom as well as substitutional dopant in AGNR. Adsorption is found energetically favorable over substitutional doping. The calculated formation energy suggests edge as the most energetically favorable site for Co atoms in AGNR. It is observed that for all the considered sites, Co atoms effectively modify the electronic band structures of AGNR and introduce metallicity. Moreover, substitutional Co-doping induces a large number of conducting channels crossing the Fermi energy and thereby enhancing the metallicity in AGNR as compared to Co-adsorption. The observed highly metallic nanoribbons are crucial for nano interconnects and other technological applications.

1. Introduction
Graphene is the one atom thick 2-D sheet of C atoms exhibiting extraordinary electronic, physical and chemical properties. Initially it was assumed that 2-D materials do not exists in real physical world. The successful synthesis of graphene by K. S. Novoselov and A. K. Geim in 2004 [1] worked as the formal invitation for the research community to work with graphene. Research on graphene was further accelerated by the development of various experimental (synthesis and characterization) techniques which made it possible to produce graphene in controlled number of layers [2], large area synthesis of monolayer graphene [3] and production of graphene nanoribbons (GNR) with sharp edges [4]. GNR are quasi 1-D strips of graphene presenting promising properties for various applications such as field effect transistors [5, 6], spin filters [7], p-n junction diodes [8] and negative differential resistance devices [9]. Depending up on the shape of edges, GNR are known as either zigzag graphene nanoribbons (ZGNR) or armchair graphene nanoribbons (AGNR) [10]. The most striking application of GNR has been shown in electrical, chemical and bio-sensors [11-13]. Recently, Wang et al demonstrated single atom substitutional doping of monolayer graphene [14]. They used metal atoms to deposit in the mono and di-vacancies of single layer graphene. Efforts have been made to alter the band gap of GNR with metallic impurities [15, 16]. It is reported in previous theoretical investigations that transition metal (TM) impurities can induce a magnetic moment in GNR [17, 18]. Further, TM impurity can exist in graphene/GNR either as a substitutional dopant or in the form of adsorbed adatoms. Efforts have been done to study both types of TM impurities in GNR [21-23]. However, both types of TM impurities have been investigated individually but still, there is lack of research comparing the adsorption of TM impurities with that of substitutional doping in nanoribbons. Therefore, we study the adsorption of Co atoms in AGNR and compared the results with substitutional Co impurities in AGNR.
2. Computational Method
In the present work, we perform first principles calculations within the density functional theory (DFT) framework. We use supercell model to probe the stability and electronic properties of adsorbed as well as substitutionally doped Co atoms in AGNR. Vacuum space of 10 Å was used to eliminate the Coulomb interaction of ribbons with their periodic images. All the considered structures under consideration were optimized by using local density approximation (LDA) for the exchange correlation functional as proposed by Perdew and Zunger [19]. For structure relaxation and obtaining the ground state of the system, we used DFT based ATK-VNL simulation package as provided by quantumwise [20]. The convergence process was continued in a self consistent manner until the maximum force on every atom (including the impurity atoms) reaches to less than 0.05eV/Å. The k-point sampling of 1x1x100 k-points was selected with an energy cutoff value of 100 Rydberg.

3. Results and discussions
We select AGNR having width=7 as the representative ribbon and considered four configurations to compare the adsorption and substitutional doping of Co atoms. These configurations are edge adsorption (EA), centre adsorption (CA), edge substitutional doping (ES) and centre substitutional doping (CS). The considered doping sites and the rule adopted to define the ribbon width are presented in Figure 1.

3.1. Stability analysis
To examine the energetic favourability and stability of various considered AGNR structures, we have calculated formation energy (FE) and binding energy (BE) and summarized the findings in Table 1. It is noticed that adsorption of Co on AGNR is energetically more favorable than its substitutional doping as indicated by large negative FE [Table 1]. Moreover, edge is the most preferred site for adsorption of Co atoms in AGNR. The difference between FE of ES and CS is much appreciable than the FE difference of EA and CA configurations. Previously, Cocchi et al., also found edge as the most preferred site for Co impurities in GNR [21]. Analysis of BE suggests that substitutional Co atoms have stronger binding with AGNR whereas adsorbed Co impurities exhibit a rather loose binding which is also supported by the positive BE. We observed that Co is most strongly bound with AGNR when present as a substitutional dopant at the centre of the ribbon which is similar to the behavior of Ni substitutional impurity in AGNR [22]. From the optimized bond lengths (d_{C-Co}) [Table 1], we can infer that substitutional Co possesses the shorter bond length which also points towards the maximum stability. The larger bond lengths of adsorbed Co atom are according to the weaker binding of these configurations as compared to substitutionally doped Co atoms.

![Figure 1](image_url)  
**Figure 1.** The schematic diagram of supercells depicting the considered adsorption and substitutional sites. Pink sphere represent the position of Co atom in (a) edge Co-adsorption (EA) and (b) centre Co-adsorption (CA), (c) The ellipses at the edge and the centre of supercell respectively represent the position of Co atoms for edge substitutional (ES) and centre substitutional (CS) doping.
Table 1. The calculated formation energy (FE), binding energy (BE) and the optimized bond length between C-Co

| Configuration | FE (eV) | BE (eV) | d_{C-Co} (Å) |
|---------------|---------|---------|--------------|
| EA            | -20.43  | 1.42    | 1.98         |
| CA            | -19.89  | 1.96    | 1.98         |
| ES            | -5.52   | -2.85   | 1.80         |
| CS            | -3.18   | -3.30   | 1.81         |

3.2 Electronic Structures

The band structures of considered configurations are depicted in Figure 2 (a)-(c). Only the band structures of EA and CS configurations have been shown since these are the most stable sites for adsorption and substitution of Co atoms respectively. The band structure of pristine AGNR has been presented for the comparison. The behavior of CA (ES) was also metallic similar to EA (CS). It is observed that band structure of pristine ribbon is significantly disturbed due to the presence of Co impurity. For EA, there exists a flat dispersive band at the Fermi level which is due to localized 3d electrons of Co [Figure 2(b)]. For CS, we noticed maximum perturbation in the band structure [Figure 2 (c)]. Strong hybridization between C-2p and Co-3d orbital causes the origin of a number of additional bands across the Fermi level which makes this configuration highly metallic.

![Figure 2](image)

Figure 2. The band structure of (a) Pristine (b) edge Co-adsorbed and (c) centre Co doped AGNR. The Fermi energy is set at 0 eV.

Similar additional bands across the Fermi level were also observed for ES configuration (to be concise, that band structure is not shown here). Therefore, we can conclude from the above observations that both types of Co impurities (adsorption and substitutional) cause metallicity in AGNR which were otherwise semiconducting. This induced metallicity sustains irrespective of the doping site. We also noticed that metallicity is much enhanced when Co is present as the substitutional dopant rather than the adsorbed atom.

4. Conclusion

We probed the stability and electronic properties of AGNR with adsorbed/substitutional Co impurities by means of DFT using LDA. It is revealed that the adsorption of Co impurity on AGNR is energetically more favorable over the substitutional doping. However, the substitutional doping of Co results in stronger binding than that of adsorption. The electronic band structure of the ribbons was significantly altered and a semiconductor to metallic transition was observed in all the considered
structures. An enhanced metallicity is obtained in AGNR irrespective of the doping site. The observed high metallicity is crucial for making metallic contacts, interconnects in nanoelectronic and various other technological applications.

Acknowledgments
We thank the Computational Nanoscience and Technology Laboratory (CNTL), ABV- Indian Institute of Information Technology and Management, Gwalior for providing the computational resources and infrastructural facilities.

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