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Investigation of gas sensing properties of armchair graphene nanoribbons

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Abstract

A theoretical approach based on a tight-binding model is developed for studying the effects of finite concentration gas adsorption (for what are known as diatomic, triatomic and quadratomic gas molecules in the general forms denoted by XY, XY₂ and XY₃, respectively) on electronic properties of armchair graphene nanoribbons (AGNRs). To consider the edge effects on electronic properties of pure AGNRs for the first time, two hopping parameters, for hydrogen–carbon and carbon–carbon nearest neighbor hopping, are considered. We found, for some specified values of hopping integrals and random on-site energies, that adsorbed molecule AGNRs act as donors or acceptors, which is consistent with reported experimental results for CO, NO₂, O₂, N₂, CO₂ and NH₃ adsorption on graphene. Then by using these parameters and the coherent potential approximation, we investigated the effect of finite concentration gas molecule adsorption on the average density of states. Our results could be used to make p-type or n-type semiconductors by means of finite concentration adsorption of gas molecules or a gas sensor.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Graphene is a single atomic layer of graphite with a honeycomb crystal structure and has prompted a great number of research activities [1], such as structural property, electrical conductance and quantum Hall effect investigations directed towards making novel nanoelectronic devices [2–4]. Another type of two-dimensional system known as the nanoribbon has finite width but large length. For the graphene system, such systems are known as graphene nanoribbons (GNRs). GNRs have been studied extensively [5–11]. It is now possible to make GNRs by various experimental methods, such as tailoring via a scanning tunneling microscopy tip [12], exfoliating from highly oriented pyrolytic graphite [3, 4, 13], and graphitizing SiC wafers [14]. GNRs are classified into two types, according to their edge configurations: either armchair or zigzag. The electronic properties of hydrogen-passivated and F-passivated AGNRs have been investigated on the basis of a tight-binding model and first-principles

calculations [5, 6, 10, 15]. These earlier works have shown that AGNRs are semiconductors and their energy gap scales inversely with the ribbon width, and established that these band gaps originate from quantum confinement. These results agree well with calculated energy band gaps of graphene nanoribbons [16]. In this experiment, temperature dependent conductance measurements show that different graphene nanoribbons with various widths are semiconductors and that the energy gap depends strongly on the width of the GNRs. Recently, a new generation of gas sensors have been demonstrated, using graphene [17]. The sensing property is based on changing resistivity due to molecules being adsorbed on the graphene sheet that act as donors or acceptors; for example NH₃ and CO act as donors while H₂O and NO₂ act as acceptors. In order to consider the feasibility of using AGNRs as gas sensors, we investigated the effect of gas adsorption on electronic properties of armchair graphene nanoribbons (AGNRs). Since the gas molecules are adsorbed randomly by the AGNR atoms, the Green function in the equation of

motion is random and the local behavior could be different from the whole system behavior; hence we should calculate configurationally averaged properties. We approached this using the coherent potential approximation formalism to take the average over all possible adsorbed molecule configurations where their probabilities are large enough (we can ignore those configurations where the probabilities are very small, such as configurations with probabilities less than $c(1 - c)^{15}$ where c is the concentration of adsorbed gas), and investigated the effect of adsorption of some gas molecules (what are known as diatomic, triatomic and quadratomic gas molecules in the general forms denoted by XY, XY₂ and XY₃ respectively) on the electronic properties of H-passivated AGNRs using a tight-binding approach and the coherent potential approximation. To find exact values of hopping integral deviations and random on-site energies in the finite concentration gas adsorption calculations, for the case of one-molecule adsorption, we varied the hopping integral deviations and random on-site energies to obtain local densities of states that are consistent with recent experimental results for the graphene [17]. Then by using these parameters and the coherent potential approximation formalism, we investigated the effects for finite concentration gas adsorbed semiconductor AGNRs.

The paper is organized as follows. Section 2 contains the model and method of calculations. In section 3, firstly the edge effects on the energy gaps of chemically modified armchair graphene nanoribbons are investigated; then calculations are done for one-molecule adsorption to obtain appropriate hopping integral deviations and random on-site energies for use in the finite concentration gas adsorption calculations. At the end of this section, the local density of states is calculated for different configurations for one-gas-molecule adsorption. In section 4, we introduce the application of the coherent potential approximation (CPA) formalism for our system, to find finite gas adsorption configuration effects on AGNRs. Finally, the last section contains the conclusions.

2. Model and formalism

We introduce our model for hydrogen edge terminated armchair GNRs, as illustrated in figure 1. In the tight-binding model the total wavefunction of the system is a linear combination of the s orbitals of hydrogen atoms and p_z orbitals of carbon atoms, so the total wavefunction of the system can be written as

$$|\psi\rangle_p = C_A \sqrt{\frac{2}{N_x(N+1)}} \sum_{x_{A_i}} \sum_{i=1}^N e^{ik_x x_{A_i}} \sin\left(\frac{p\pi}{N+1}i\right) |A_i\rangle + C_B \sqrt{\frac{2}{N_x(N+1)}} \sum_{x_{B_i}} \sum_{i=1}^N e^{ik_x x_{B_i}} \sin\left(\frac{p\pi}{N+1}i\right) |B_i\rangle \quad (1)$$

where $p = 1, 2, \dots, N$ and $|A_i\rangle$ and $|B_i\rangle$ are the wavefunctions of the s orbitals of a hydrogen atom located in the A and B sublattices, respectively, if i is equal to 1 or N , while they are the wavefunctions of the p_z orbitals of a carbon

atom located in the A and B sublattices if $i = 2, \dots, N - 1$. A simple case of this model without hydrogen termination is used [10].

On the basis of the general random tight-binding model, the Hamiltonian is [18]

$$H = - \sum_{ij\alpha\beta} t_{ij}^{\alpha\beta} c_i^{\alpha\dagger} c_j^\beta + \sum_{i\alpha} (\epsilon_i^\alpha - \mu) \hat{n}_i^\alpha \quad (2)$$

where α and β refer to $A_{1,0}, A_{1,1}, A_{1,2}, \dots, A_{N,1}$ and $A_{N,2}$ or $B_{1,0}, B_{1,1}, B_{1,2}, \dots, B_{N,1}$ and $B_{N,2}$ subsites inside the unit cell for diatomic gas (figure 1), $A_{1,0}, A_{1,1}, A_{1,2}, A_{1,3}, \dots, A_{N,2}$ and $A_{N,3}$ or $B_{1,0}, B_{1,1}, B_{1,2}, B_{1,3}, \dots, B_{N,2}$ and $B_{N,3}$ subsites inside the unit cell for triatomic gas, and $A_{1,0}, A_{1,1}, A_{1,2}, A_{1,3}, A_{1,4}, \dots, A_{N,3}$ and $A_{N,4}$ or $B_{1,0}, B_{1,1}, B_{1,2}, B_{1,3}, B_{1,4}, \dots, B_{N,3}$ and $B_{N,4}$ subsites inside the unit cell for quadratomic gas. $A_{i,0}$ and $B_{i,0}$ for $i = 2, 3, \dots, N - 1$ refer to carbons inside the unit cell and $A_{1,0}, B_{1,0}, A_{N,0}$ and $B_{N,0}$ refer to H or F. $N - 2$ is the number of dimer lines across the ribbon width, as shown in figure 1. We refer to an AGNR with N dimer lines as an N -AGNR. $c_i^{\alpha\dagger}$ (c_i^α) is the creation (annihilation) operator for an electron on site α in the unit cell i , and $\hat{n}_i^\alpha = c_i^{\alpha\dagger} c_i^\alpha$ is the number operator. $t_{ij}^{\alpha\beta}$ are the hopping integrals for hopping between the subsites α and β in the Bravais lattice unit cells i and j , μ is the chemical potential and ϵ_i^α is the random on-site energy for subsite α in the Bravais lattice unit cell i . The equation of motion for electrons with the above Hamiltonian, equation (1), is

$$\sum_l ((E\mathbf{I} - \epsilon_l \mathbf{I} + \mu \mathbf{I}) \delta_{il} + \mathbf{t}_{il}) \mathbf{G}(l, j, E) = \mathbf{I} \delta_{ij} \quad (3)$$

where the random Green function matrix $\mathbf{G}(i, j, E)$ for a diatomic gas adsorbed armchair GNR is

$$\mathbf{G}(i, j, E) = \begin{pmatrix} G^{A_{1,0}A_{1,0}} & G^{A_{1,0}A_{1,1}} & G^{A_{1,0}A_{1,2}} & G^{A_{1,0}B_{1,0}} & G^{A_{1,0}B_{1,1}} \\ G^{A_{1,1}A_{1,0}} & G^{A_{1,1}A_{1,1}} & G^{A_{1,1}A_{1,2}} & G^{A_{1,1}B_{1,0}} & G^{A_{1,1}B_{1,1}} \\ G^{A_{1,2}A_{1,0}} & G^{A_{1,2}A_{1,1}} & G^{A_{1,2}A_{1,2}} & G^{A_{1,2}B_{1,0}} & G^{A_{1,2}B_{1,1}} \\ G^{B_{1,0}A_{1,0}} & G^{B_{1,0}A_{1,1}} & G^{B_{1,0}A_{1,2}} & G^{B_{1,0}B_{1,0}} & G^{B_{1,0}B_{1,1}} \\ G^{B_{1,1}A_{1,0}} & G^{B_{1,1}A_{1,1}} & G^{B_{1,1}A_{1,2}} & G^{B_{1,1}B_{1,0}} & G^{B_{1,1}B_{1,1}} \\ G^{B_{1,2}A_{1,0}} & G^{B_{1,2}A_{1,1}} & G^{B_{1,2}A_{1,2}} & G^{B_{1,2}B_{1,0}} & G^{B_{1,2}B_{1,1}} \\ G^{B_{2,0}A_{1,0}} & G^{B_{2,0}A_{1,1}} & G^{B_{2,0}A_{1,2}} & G^{B_{2,0}B_{1,0}} & G^{B_{2,0}B_{1,1}} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ G^{A_{1,0}B_{1,2}} & G^{A_{1,0}B_{2,0}} & \dots & \dots & \dots \\ G^{A_{1,1}B_{1,2}} & G^{A_{1,1}B_{2,0}} & \dots & \dots & \dots \\ G^{A_{1,2}B_{1,2}} & G^{A_{1,2}B_{2,0}} & \dots & \dots & \dots \\ G^{B_{1,0}B_{1,2}} & G^{B_{1,0}B_{2,0}} & \dots & \dots & \dots \\ G^{B_{1,1}B_{1,2}} & G^{B_{1,1}B_{2,0}} & \dots & \dots & \dots \\ G^{B_{1,2}B_{1,2}} & G^{B_{1,2}B_{2,0}} & \dots & \dots & \dots \\ G^{B_{2,0}B_{1,2}} & G^{B_{2,0}B_{2,0}} & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (4)$$

where, in the case of diatomic gas adsorbed 8-AGNRs, the Green function matrix, $\mathbf{G}(i, j, E)$, and other matrices are 60×60 matrices. The full random Green function matrix, $\mathbf{G}(i, j, E)$, can be expanded in terms of the clean system Green function matrix, $\mathbf{G}^0(i, j, E)$, and a random potential [18–20]:

$$\mathbf{G}(i, j, E) = \mathbf{G}^0(i, j, E) + \sum_{l'} \mathbf{G}^0(i, l, E) \mathbf{V}_{ll'} \mathbf{G}(l', j, E) \quad (5)$$

where the random potential matrix, $\mathbf{V}_{ll'}$, is defined by

$$\mathbf{V}_{ll'} = \varepsilon \delta_{ll'} - \delta \mathbf{t}_{ll'} \quad (6)$$

where $\delta \mathbf{t}_{ll'} = \mathbf{t}_{ll'} - \mathbf{t}_{ll'}^0$ are hopping integral deviations. The mn component of the clean system Green function matrix, $\mathbf{G}^0(i, j, E)$, is given by

$$[\mathbf{G}^0(i, j, E)]_{mn} = \frac{2}{N_x(N+1)} \times \sum_{k_x p} e^{+ik_x x_{ij}} \sin\left(\frac{p\pi}{N+1}M\right) \sin\left(\frac{p\pi}{N+1}N\right) \times [E\mathbf{I} - \epsilon_{k_x p} + \mu\mathbf{I}]_{mn}^{-1} \quad (7)$$

where the mn component of the band structure matrix, $[\epsilon(k_x p)]_{mn}$, is

$$[\epsilon(k_x p)]_{mn} = -\frac{2}{N_x(N+1)} \sum_{ij} e^{-ik_x x_{ij}} \sin\left(\frac{p\pi}{N+1}M\right) \times \sin\left(\frac{p\pi}{N+1}N\right) [\mathbf{t}_{ij}^0]_{mn}. \quad (8)$$

Note that M and N are integers that for the case of a diatomic gas adsorbed 8-armchair GNR are $M = \frac{m-1}{6} + 1$ and $N = \frac{n-1}{6} + 1$. It is reported that the bonding distances between carbon atoms at the edge sites (a_2 and a_{N-1}) are shorter than others in the middle of GNRs [6, 21]. Such effects have been observed in large aromatic molecules such as ovalene ($C_{32}H_{14}$) [22]. An analytic expression for the TB matrix elements connecting carbon atoms [23] shows that a decrease in the inter-atomic distance could induce increasing in the hopping integral between π orbitals. Using this, we consider the hopping integral deviation as $t_{(ij)}^{A_{1,0}B_{1,0}} = t_{(ij)}^{A_{N,0}B_{N,0}} = 0$ while $t_{(ij)}^{A_{1,0}B_{2,0}} = t_{(ij)}^{B_{1,0}A_{2,0}} = t_{(ij)}^{A_{N-1,0}B_{N,0}} = t_{(ij)}^{B_{N-1,0}A_{N,0}} = t(1 + \delta')$, $t_{(ij)}^{A_{2,0}B_{2,0}} = t_{(ij)}^{A_{N-1,0}B_{N-1,0}} = t(1 + \delta)$ and $t_{(ij)}^{A_{n,0}B_{n',0}} = t_{(ij)}^{B_{n,0}A_{n',0}} = t$ for n and $n' = 3, \dots, N - 2$. Also we allowed hopping integrals for hopping to the nearest neighbors, with the others neglected, so

$$t_{(ij)\langle nn' \rangle}^{A_{n,0}B_{n',0}} = t_{(ij)\langle nn' \rangle}^{B_{n,0}A_{n',0}} = t \quad (9)$$

for n and $n' = 3, \dots, N - 2$ where $t = 2.7$ eV is the clean system nearest neighbor hopping integral in the middle of AGNRs. In our calculation, we take $\mu = 0$ which corresponds to one electron per carbon atom. Hence the hopping integral matrix is

$$\mathbf{t}_{(ij)\langle nn' \rangle} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & (1 + \delta') & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ (1 + \delta') & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & (1 + \delta') & 0 & 0 & (1 + \delta) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & (1) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ (1 + \delta') & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ (1 + \delta) & 0 & 0 & (1) & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & (1) & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ (1) & 0 & 0 & (1) & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \quad (10)$$

So, the dispersion relation is given by

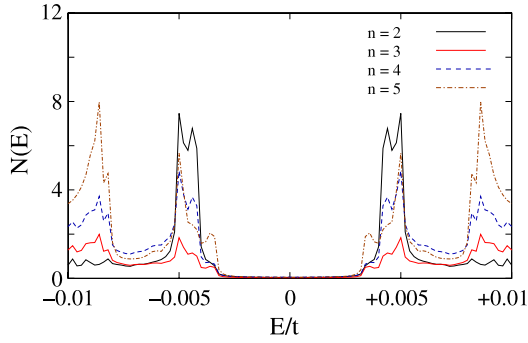


Figure 3. The local densities of states for different subsites $A_{2,0}$, $A_{3,0}$, $A_{4,0}$, $A_{5,0}$ across the ribbon width for $\delta = +0.15t$ and $\delta' = -0.25t$. It is clear that the energy gaps are equal across the ribbon width.

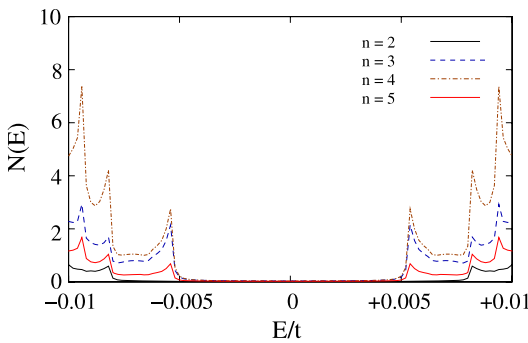


Figure 4. Comparison of the local densities of states for different subsites $A_{2,0}$, $A_{3,0}$, $A_{4,0}$, $A_{5,0}$ across the ribbon width for $\delta = +0.15t$ and $\delta' = +0.25t$.

We introduce the effect of geometric deformation in our theoretical calculations via two parameters, δ and δ' . In recently reported calculational work it is shown that the C–C bond length at the edges of the ribbon decreases [6, 21] and this decrease in inter-atomic distance induces a increase in the hopping integral for hopping between π orbitals [23]. Now by examining the different values of δ' we show that we can control the energy gap of the 8-AGNR, which corresponds to controlling the energy gap of the 8-AGNR by using different edge addends (H, F etc). Figure 2 shows the local density of states of the $B_{2,0}$ subsite for different values of δ' : (a) $\delta' = +0.25t$, (b) $\delta' = +0.0t$, (c) $\delta' = -0.15t$ and (d) $\delta' = -0.25t$. We see that on decreasing δ' , the energy gap decreases. Also we investigated the effects of the $\delta' = -0.25t$ and $\delta' = +0.25t$ values of δ' on the energy gaps of different dimers across the ribbon width. Figure 3 shows for the $\delta' = -0.25t$ value of δ' the energy gaps in the different dimers to be equal, but the effects of zero and $\delta' = +0.25t$ values of δ' on the energy gaps in the different dimers across the ribbon width are not same. This result has been shown in figure 4. We found the negative values of δ' decreasing the energy gap while the positive values of δ' were slightly increasing the semiconducting energy gap.

Then we tuned the hopping integral deviations and also on-site energies of the adsorbed gas molecules such that the adsorbed molecule bound states locate inside the semiconductor AGNR energy gap to produce an n-type or a p-

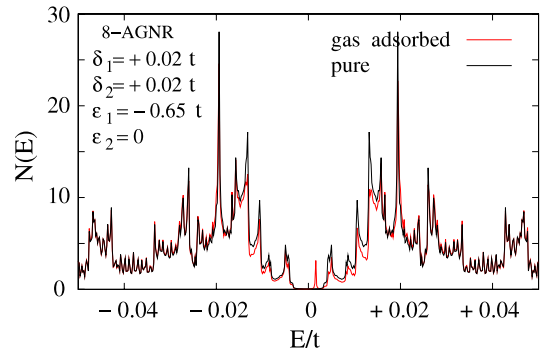


Figure 5. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states of the $A_{3,0}$ subsite of site 0, where a diatomic gas molecule is adsorbed and $\delta' = -0.25t$. The hopping deviations and on-site energy are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ respectively. In this case an n-type semiconductor 8-AGNR has been produced.

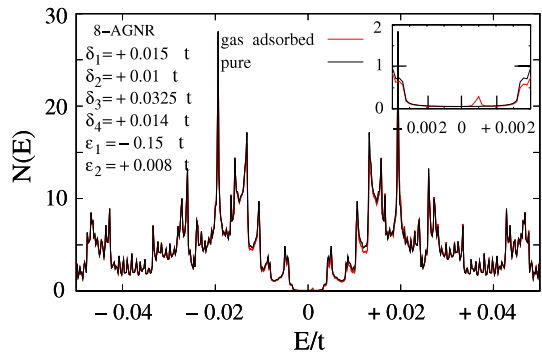


Figure 6. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states for the $A_{3,0}$ subsite of site 0, where a quadratomic gas molecule is adsorbed and $\delta' = -0.25t$. The hopping deviations and on-site energy are chosen to be $\delta_1 = +0.015t$, $\delta_2 = +0.010t$, $\delta_3 = +0.0325t$, $\delta_4 = +0.014t$, $\epsilon_1 = -0.15t$ and $\epsilon_2 = +0.008t$ respectively. In this case an n-type semiconductor 8-AGNR has been produced.

type semiconductor AGNR. Figure 5 illustrates the comparison of the local density of states of pure 8-AGNR at the $A_{3,0}$ subsite with respect to the local density of states at the $A_{3,0}$ subsite of the site 0, where $A_{3,0}$ at the site 0 has adsorbed a diatomic gas molecule. The hopping integral deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ respectively.

Similar results were found for quadratomic gas molecule adsorbed 8-AGNR (in the form denoted by XY_3); in this case the appropriate hopping integral deviations and on-site energies are chosen to be $\delta_1 = +0.015t$, $\delta_2 = +0.010t$, $\delta_3 = +0.0325t$, $\delta_4 = +0.014t$, $\epsilon_1 = -0.15t$ and $\epsilon_2 = +0.008t$ respectively. This result is similar to the reported results based on first-principles calculations for NH_3 adsorption by AGNRs, where gas molecule adsorbed AGNR behavior is that of an n-type semiconductor. This result has been shown in figure 6.

Also we found that by choosing some other values of hopping integral deviations and on-site energies an p-type AGNR semiconductor could be produced. Figure 7 shows the

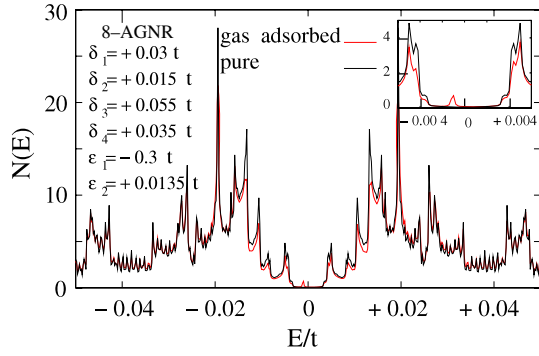


Figure 7. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states for the $A_{3,0}$ subsite of site 0, where a diatomic gas molecule is adsorbed and $\delta' = -0.25t$. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.03t$, $\delta_2 = +0.015t$, $\delta_3 = +0.055t$, $\delta_4 = +0.035t$, $\epsilon_1 = -0.3t$ and $\epsilon_2 = +0.0135t$, respectively. In this case, a p-type semiconductor 8-AGNR has been produced.

comparison of the local density of states of pure 8-AGNR at the $A_{3,0}$ subsite with respect to the local density of states at the $A_{3,0}$ subsite in the site 0 where $A_{3,0}$ in the site 0 adsorbed a triatomic gas molecule. The hopping integral deviations and on-site energies are chosen to be $\delta_1 = +0.03t$, $\delta_2 = +0.015t$, $\delta_3 = +0.055t$, $\delta_4 = +0.035t$, $\epsilon_1 = -0.3t$ and $\epsilon_2 = +0.0135t$ respectively.

Now by using the hopping integral deviations and on-site energies of the diatomic gas obtained, we show that the change of δ' has no effect on the behavior of the AGNR (as n-type or p-type semiconductor). For this purpose we consider the effect of adsorption of a diatomic gas on the local density of states of the 8-AGNR for two different values of δ' : $\delta' = -0.25t$ and $\delta' = +0.25t$. Figure 8 illustrates the comparison of the local density of states of pure 8-AGNR at the $A_{3,0}$ subsite with respect to the local density of states at the $A_{3,0}$ subsite of the site 0 where $A_{3,0}$ at the site 0 adsorbed a diatomic gas molecule, for (a) $\delta' = -0.25t$ and (b) $\delta' = +0.25t$. The hopping integral deviations and on-site energy are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ respectively.

To see that the local density of states depends on the adsorbed molecule situation (configurational dependence), we investigate the effect of gas adsorption on the local density of states for the $A_{n,n}$ subsite and its nearest neighbors when the $A_{n,n}$ subsite has adsorbed a diatomic gas molecule and repeat this work in the cases where different $A_{n,n}$ subsites across the ribbon width of the 8-AGNR have adsorbed a diatomic gas molecule. Figure 9 shows the comparison of the local density of states of $A_{2,0}$ and its nearest neighbors with respect to their pure local density of states when the $A_{2,0}$ subsite in the 0 site has adsorbed a diatomic gas molecule. Results for the cases where one of the $A_{3,0}$, $A_{4,0}$ or $A_{5,0}$ subsites has adsorbed a diatomic gas molecule have been shown in figures 10, 11 and 12 respectively. Comparing figures 9, 10, 11 and 12, we conclude that the local density of states of a gas adsorbed 8-AGNR is strongly configurational dependent. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ respectively.

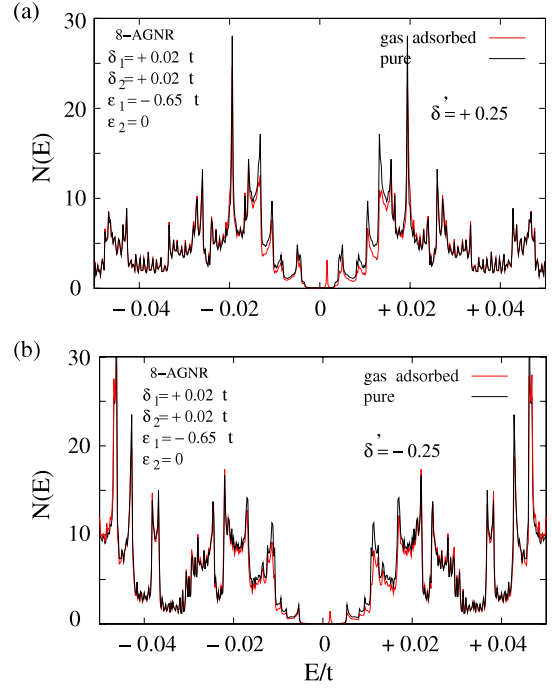


Figure 8. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states for the $A_{3,0}$ subsite of site 0, where a diatomic gas molecule is adsorbed, for two different values of δ' : (a) $\delta' = -0.25t$ and (b) $\delta' = +0.25t$. The hopping deviations and on-site energy are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$, respectively. In this case an n-type semiconductor 8-AGNR has been produced.

4. Finite concentration of gas molecule adsorption on AGNRs

Since the gas molecules are randomly adsorbed by AGNR atoms, the system is a disordered system. The exact solution of the equation of motion of such a system is impossible, so here we use the coherent potential approximation (CPA) to solve the equation of motion, equation (3), to obtain the average Green function matrix $\overline{\mathbf{G}}(i, j, E)$. So, by using the relation between the average Green function $\overline{\mathbf{G}}(i, j, E)$ and average density of states, we can investigate the effect of finite concentration of diatomic, triatomic and quadratomic gas molecule adsorption on the average density of states of an 8-AGNR. First we introduce the CPA formalism for this system and then we present our results. The Dyson equation for the averaged Green function matrix, $\overline{\mathbf{G}}(i, j, E)$, corresponding to equation (3) is

$$\overline{\mathbf{G}}(i, j, E) = \mathbf{G}^0(i, j, E) + \sum_{l'} \mathbf{G}^0(i, l, E) \Sigma(l, l', E) \overline{\mathbf{G}}(l', j, E) \quad (20)$$

where the self-energy $\Sigma(l, l', E)$ is defined by

$$\sum_{l'} \langle \mathbf{V}_{ll'} \mathbf{G}^{\text{imp}}(l', j, E) \rangle = \sum_{l'} \Sigma(l, l', E) \overline{\mathbf{G}}(l', j, E). \quad (21)$$

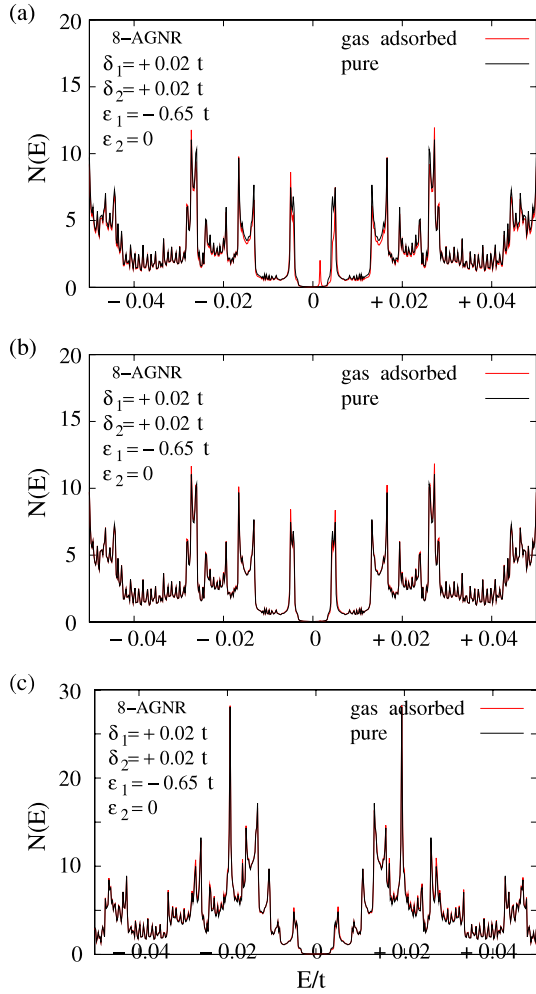


Figure 9. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states of (a) $A_{2,0}$, (b) $B_{2,0}$, (c) $B_{3,0}$ subsites of site 0, where a diatomic gas molecule is adsorbed by the $A_{2,0}$ subsite of site 0 and $\delta' = -0.25t$. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$, respectively.

The Fourier transformation of $\overline{\mathbf{G}}(i, j, E)$ in equation (20) is given by

$$\begin{aligned} [\overline{\mathbf{G}}(i, j, E)]_{mn} &= \frac{2}{N_x(N+1)} \\ &\times \sum_{k_x p} e^{+ik_x x_{ij}} \sin\left(\frac{p\pi}{N+1}M\right) \sin\left(\frac{p\pi}{N+1}N\right) \\ &\times [\mathbf{E}\mathbf{I} - \epsilon_{k_x p} - \Sigma(k_x, p, E)]_{mn}^{-1} \end{aligned} \quad (22)$$

where

$$\begin{aligned} [\Sigma(i, j, E)]_{mn} &= \frac{2}{N_x(N+1)} \\ &\times \sum_{k_x p} e^{+ik_x x_{ij}} \sin\left(\frac{p\pi}{N+1}M\right) \sin\left(\frac{p\pi}{N+1}N\right) \\ &\times [\Sigma(k_x, p, E)]_{mn} \end{aligned} \quad (23)$$

is the self-energy Fourier transform. Since equations (5), (20) and (22) could not be solved exactly, here we solve these equations in the CPA formalism. In the CPA method, multiple scattering is neglected and all sites are replaced by effective

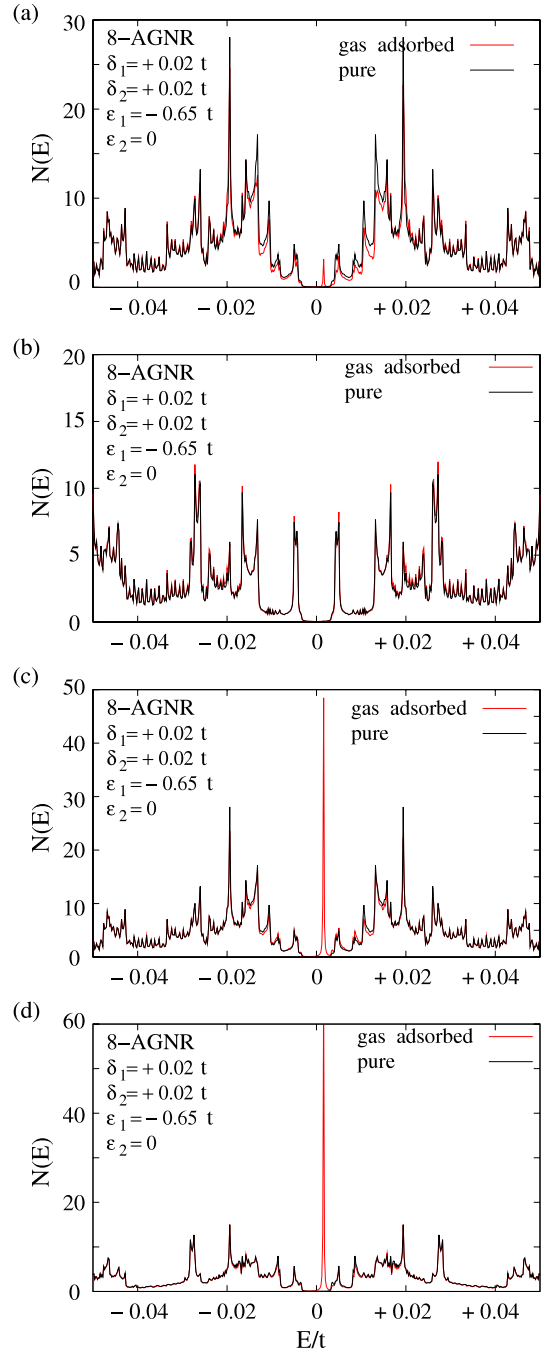


Figure 10. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states of (a) $A_{3,0}$, (b) $B_{2,0}$, (d) $B_{4,0}$ subsites of site 0 and (c) the $B_{3,0}$ subsite of site 1, where a diatomic gas molecule is adsorbed by the $A_{2,0}$ subsite of site 0 and $\delta' = -0.25t$. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$, respectively.

sites, except one which is denoted as the impurity; hence, the self-energy is diagonal, $\Sigma(l, l', E) = \Sigma(E)\delta_{ll'}$. So equations (5), (20), (22) and (21) at the impurity site are reduced to

$$\begin{aligned} \mathbf{G}^{\text{imp}}(i, i, E) &= \overline{\mathbf{G}}(i, i, E) + \overline{\mathbf{G}}(i, i, E)[\mathbf{V}_{ii} - \Sigma(E)] \\ &\times \mathbf{G}^{\text{imp}}(i, i, E), \end{aligned} \quad (24)$$

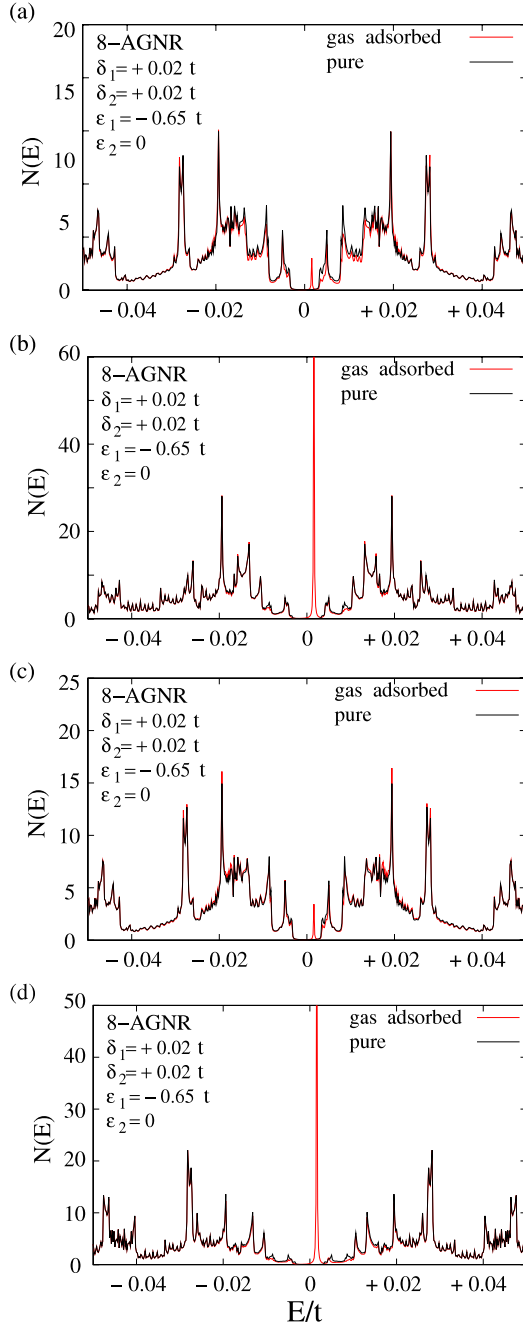


Figure 11. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states of (a) $A_{4,0}$, (b) $B_{3,0}$, (c) $B_{4,0}$, (d) $B_{5,0}$ subsites of site 0, where a diatomic gas molecule is adsorbed by the $A_{2,0}$ subsite of site 0 and $\delta' = -0.25t$. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$, respectively.

$$\begin{aligned} \overline{\mathbf{G}}(i, i, E)_{mn} &= \frac{2}{N_x(N+1)} \\ &\times \sum_{k_x p} \sin\left(\frac{p\pi}{N+1}M\right) \sin\left(\frac{p\pi}{N+1}N\right) \\ &\times [\mathbf{E}\mathbf{I} - \epsilon_{k_x p} - \Sigma(k_x, p, E)]_{mn}^{-1} \end{aligned} \quad (25)$$

and

$$\langle \mathbf{V}_{ll} \mathbf{G}^{\text{imp}}(l, j, E) \rangle = \Sigma(l, l, E) \overline{\mathbf{G}}(l, j, E) \quad (26)$$

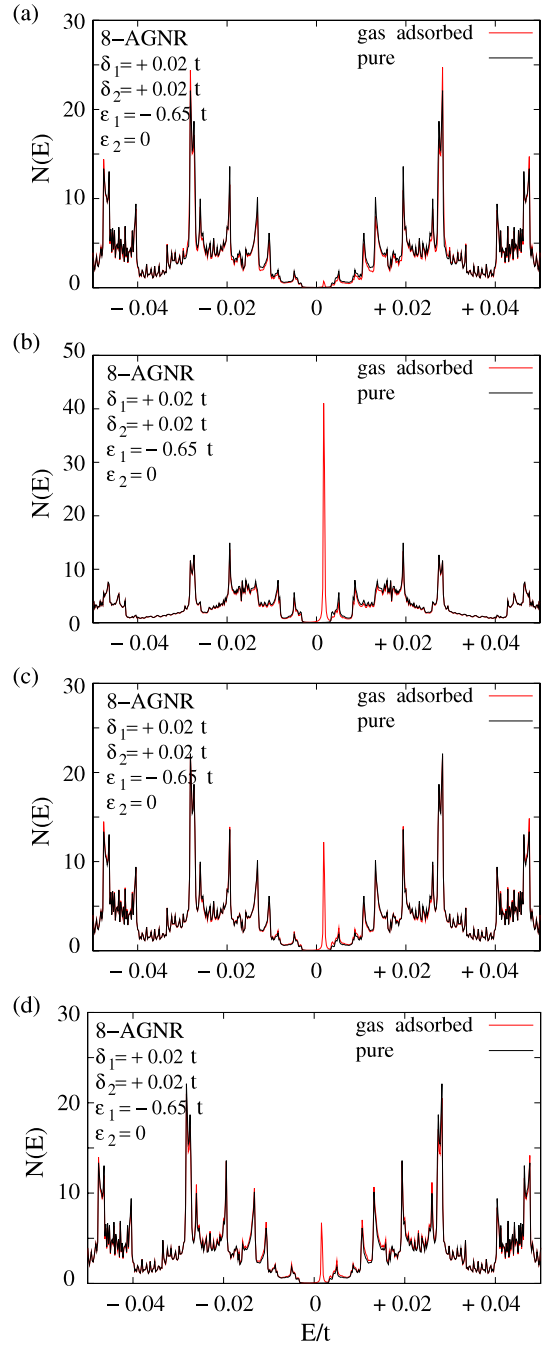


Figure 12. Comparison of the local density of states of a pure 8-AGNR with respect to the local density of states of (a) $A_{5,0}$, (b) $B_{4,0}$, (d) $B_{6,0}$ subsites of site 0 and (c) the $B_{5,0}$ subsite of site 1, where a diatomic gas molecule is adsorbed by the $A_{2,0}$ subsite of site 0 and $\delta' = -0.25t$. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$, respectively.

respectively. Equations (24)–(26) constitute a complete set of equations that should be solved self-consistently to obtain $\overline{\mathbf{G}}(i, j, E)$ and $\Sigma(E)$. So, we can obtain the average density of states $\overline{N}(E)$ in terms of the average Green function as $\overline{N}^{A_{n,n}A_{n,n}}(E) = -\frac{1}{\pi} \text{Im} \overline{\mathbf{G}}^{A_{n,n}A_{n,n}}(i, i, E)$. Figure 13 shows the effect of the diatomic adsorbed gas molecule concentration c on the average density of states of the $A_{3,0}$ subsite for

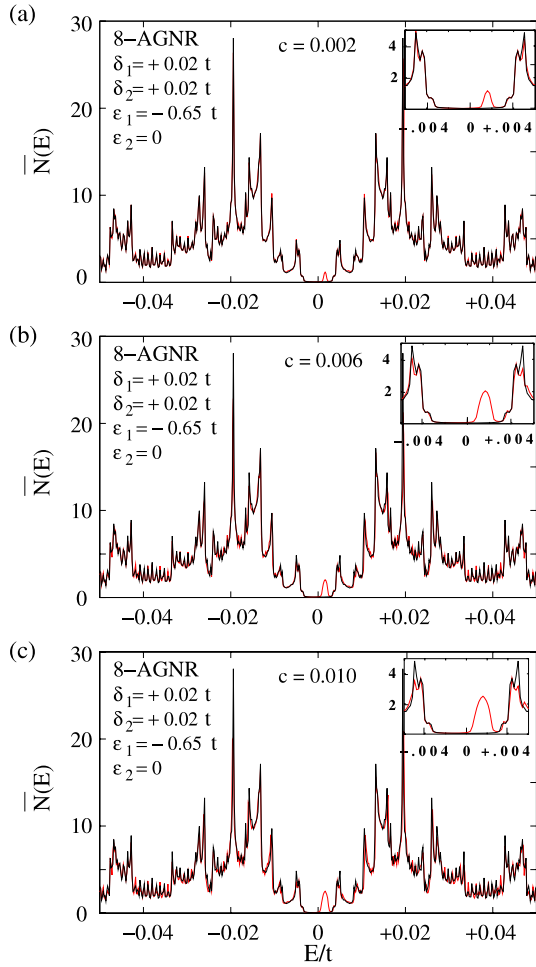


Figure 13. The density of states of gas adsorbed 8-AGNR for diatomic gas molecule concentrations of 0.002, 0.006 and 0.010. The hopping integral deviations and on-site energies are $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ respectively and $\delta' = -0.25t$. The average density of states indicates an n-type semiconductor, where the height and width of the donor band increase on increasing the adsorbed gas concentration.

$c = 0.002, 0.006$ and 0.010 . We use the hopping integral deviations and on-site energies $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ obtained in the previous section. The average density of states indicates an n-type semiconductor behavior, where the width and height of the donor band increase on increasing the adsorption gas molecule concentration. The other interesting results are the differences between the effects of gas adsorption on the average densities of states at different subsites across the ribbon width; in particular, gas adsorption has no effect on the average density of states for subsites at the edges of the ribbon. These results have been shown in figure 14.

Figure 15 shows the effect of the triatomic adsorbed gas molecule concentration, c , on the average density of states for the $A_{3,0}$ subsite for $c = 0.002, 0.006$ and 0.010 . We use the hopping integral deviations and on-site energies $\delta_1 = +0.030t$, $\delta_2 = +0.015t$, $\delta_3 = +0.055t$, $\delta_4 = +0.035t$, $\epsilon_1 = -0.30t$ and $\epsilon_2 = +0.0135t$ obtained in the previous section. The average density of states indicates an n-type

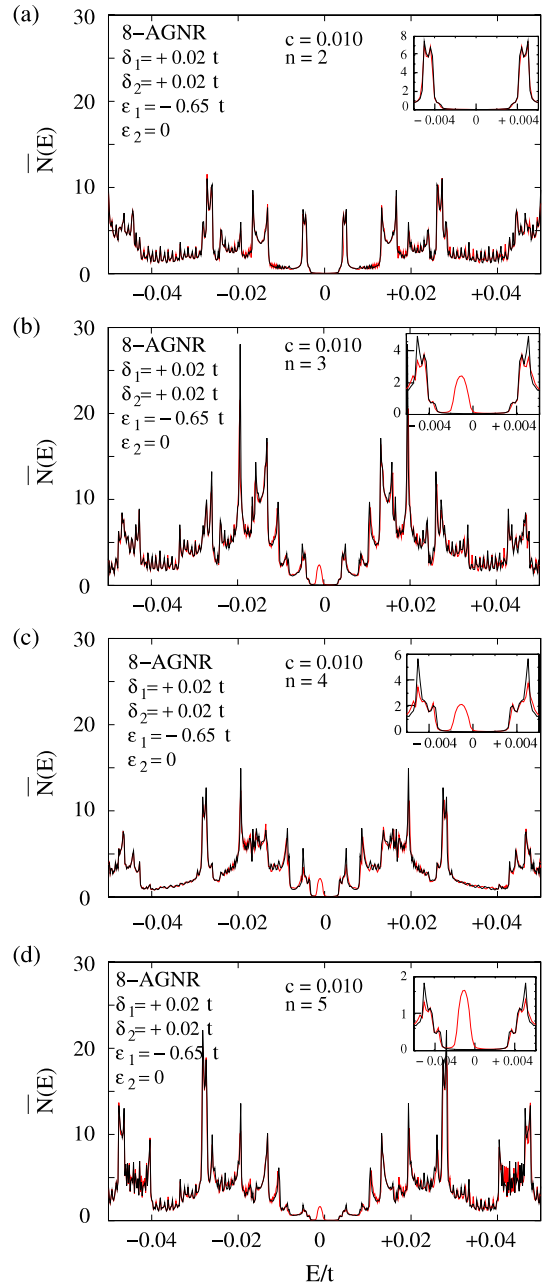


Figure 14. The differences between the effects of gas adsorption on the average density of states at different subsites across the ribbon width; (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, (d) $n = 5$. The hopping deviations and on-site energies are chosen to be $\delta_1 = +0.02t$, $\delta_2 = +0.035t$, $\epsilon_1 = -0.655t$ and $\epsilon_2 = +0.0$ respectively and $\delta' = -0.25t$.

semiconductor behavior, where the width and height of the donor band increase on increasing the adsorption gas molecule concentration.

Same calculations were done for the quadratomic gas molecule adsorption with finite concentrations of 0.002, 0.006 and 0.010. Figure 16 shows the adsorbed quadratomic molecule AGNR average density of states for the $A_{3,0}$ subsite. The hopping integral deviations and on-site energies used are $\delta_1 = 0.015t$, $\delta_2 = 0.010t$, $\delta_3 = 0.0325t$, $\delta_4 = 0.014t$, $\epsilon_1 = -0.15t$ and $\epsilon_2 = 0.008t$, provided in the previous section.

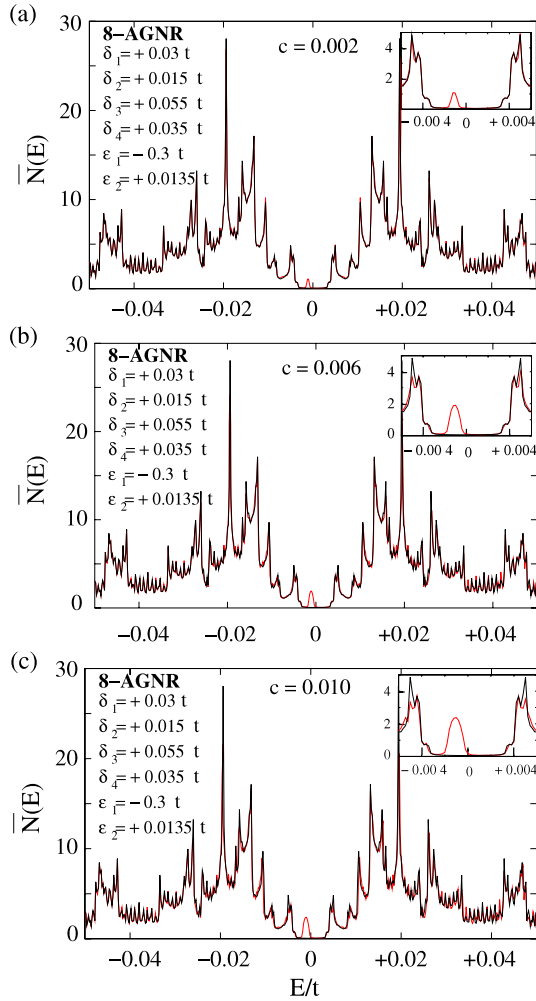


Figure 15. The density of states of a gas adsorbed 8-AGNR for triatomic gas molecule concentrations of 0.002, 0.006 and 0.010. The hopping integral deviations and on-site energies are $\delta_1 = +0.030t$, $\delta_2 = +0.015t$, $\delta_3 = +0.055t$, $\delta_4 = +0.035t$, $\epsilon_1 = -0.30t$ and $\epsilon_2 = +0.0135t$ respectively and $\delta' = -0.25t$. The average density of states indicates a p-type semiconductor.

We found that adsorbed molecules with finite concentrations create a band near the AGNR conduction band; the height and width are increased on increasing the adsorbed molecule concentration. The average density of states indicates an n-type semiconductor.

5. Conclusion

First, by consideration of the local density of states of pure 8-AGNR in the tight-binding model, the effects of chemical edge modifications on electronic properties of an 8-AGNR are studied. We did this by introducing two parameters, δ and δ' , for the hopping integral deviations, and saw that we can control the energy gap of the AGNR by changing the δ' ; this could be corresponding to the different edge addend atoms (H, F etc). Then by calculation of the local density of states in the tight-binding model, the effects of finite diatomic, triatomic and quadratomic gas molecule adsorption on the electronic properties of an 8-AGNR were studied. To find appropriate

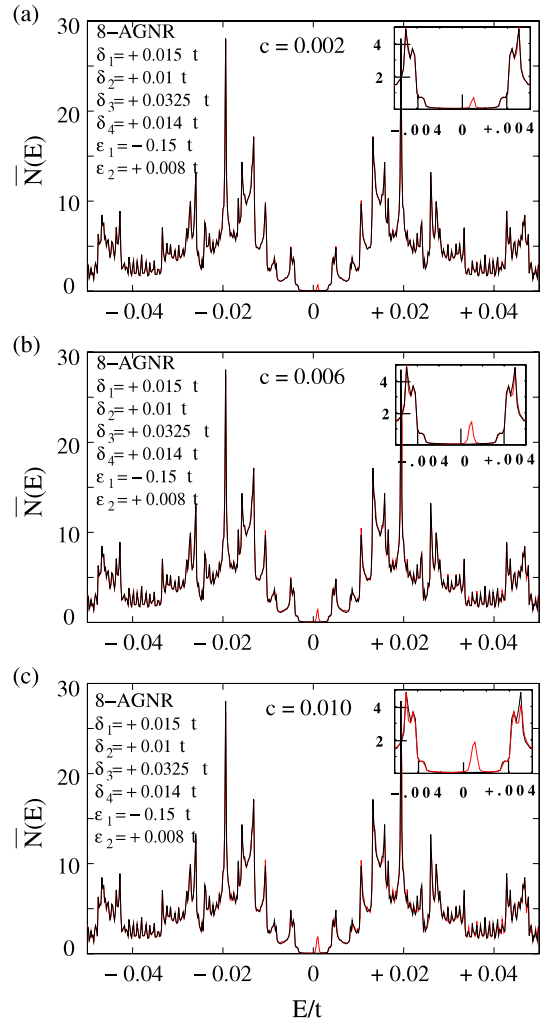


Figure 16. The density of states of a gas adsorbed 8-AGNR for quadratomic gas molecule concentrations of 0.002, 0.006 and 0.010, respectively. The hopping integral deviations and on-site energies are $\delta_1 = 0.015t$, $\delta_2 = 0.010t$, $\delta_3 = 0.0325t$, $\delta_4 = 0.014t$, $\epsilon_1 = -0.15t$ and $\epsilon_2 = 0.008t$ respectively and $\delta' = -0.25t$. The average density of states indicates an n-type semiconductor, where the height and width of the donor band increase on increasing the adsorbed gas concentration.

hopping integral deviations and on-site energies, first, one-molecule adsorption is investigated. The hopping integral deviations and on-site energies were varied until the results obtained were the same as the experimental results. These hopping integral deviations and on-site energies were used for calculation of the effects of finite concentration adsorption on 8-AGNR. Since the gas molecules are adsorbed randomly by the 8-AGNR atoms, the Green function in the equation of motion is random and the local behavior could be different from the whole system behavior; hence we should calculate configurationally averaged properties. We approached this using the coherent potential approximation formalism to take the average over all possible adsorbed molecule configurations where their probabilities are large enough. We found that the adsorbed gas molecule could produce states inside the semiconducting energy gap of the 8-AGNR. When these states are near the 8-AGNR conduction band, an n-type

semiconductor is obtained, while when these states are located near the valence band, a p-type semiconductor is obtained. Our results show that it is possible to produce p-type and n-type semiconductors by means of finite concentration adsorption of gas molecules. These could be used as gas sensors.

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