Modeling of low-dimensional pristine and vacancy incorporated graphene nanoribbons using tight binding model and their electronic structures

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Abstract. Graphene, with impressive electronic properties, have high potential in the microelectronic field. However, graphene itself is a zero bandgap material which is not suitable for digital logic gates and its application. Thus, much focus is on graphene nanoribbons (GNRs) that are narrow strips of graphene. During GNRs fabrication process, the occurrence of defects that ultimately change electronic properties of graphene is difficult to avoid. The modelling of GNRs with defects is crucial to study the non-idealities effects. In this work, nearest-neighbor tight-binding (TB) model for GNRs is presented with three main simplifying assumptions. They are utilization of basis function, Hamiltonian operator discretization and plane wave approximation. Two major edges of GNRs, armchair-edged GNRs (AGNRs) and zigzag-edged GNRs (ZGNRs) are explored. With single vacancy (SV) defects, the components within the Hamiltonian operator are transformed due to the disappearance of tight-binding energies around the missing carbon atoms in GNRs. The size of the lattices namely width and length are varied and studied. Non-equilibrium Green's function (NEGF) formalism is employed to obtain the electronics structure namely band structure and density of states (DOS) and all simulation is implemented in MATLAB. The band structure and DOS plot are then compared between pristine and defected GNRs under varying length and width of GNRs. It is revealed that there are clear distinctions between band structure, numerical DOS and Green's function DOS of pristine and defective GNRs.

Keywords: graphene nanoribbons (GNRs); non-equilibrium Green's function (NEGF); single vacancy (SV); tight binding; electronic structure

1. Introduction

Two-dimensional graphene which has hexagonal lattice structure (Wang and Chan 2015, Zenkour 2016) has attracted much attention of researchers in the semiconductor field due to its striking properties (Geim and Novoselov 2007, Bouadi *et al.* 2018, Rodriguez-Perez *et al.* 2017). GNRs are made up of finite size graphene crystals (Gracia-Espino *et al.* 2013) which can be categorized into AGNRs and ZGNRs, depending on their edge structure (Wakabayashi *et al.* 1999). They are 30° apart of each other in orientation, as shown in Fig. 1.



Fig. 1 Zigzag – edged and armchair – edged GNR (Wakabayashi *et al.* 1999)

*Corresponding author, Ph.D., E-mail: michael@utm.my According to Nakada (Nakada *et al.* 1996), electronic properties of GNRs are highly dependent on their width and length. Considering N-AGNR and N-ZGNR, (letting N be the number of dimer lines or zigzag lines along the ribbon side), N-AGNR varies with width, alternating between 2 semiconducting states and then followed by a metallic state. Unlike AGNR, ZGNR has no significant bandgap, and thus it is metallic at any given width.

Schrödinger's equation (Schrödinger 1926) is used in the study of the electronic properties of carbon-based nanostructures by obtaining the energy values from quantum transport models. Solving Schrödinger's equation involves the solution of integrals for each energy state existing in the whole system. As a system enlarges, the mathematical analysis will be more advanced and complex. Schrödinger's equation can be solved by using NEGF formalism (Datta 2002). The Hamiltonian operator, H, of Eq. (1) holds the complete information containing the position of particles in the content and their interaction with each other of a particular system. With the defined operator, the wave function, ψ paired with H can be used to deduce the available energy spectrum, and then the electronic properties of the system. With the complete information embedded within the Hamiltonian operator, SV defect, where there is one atom is missing from the lattices can be incorporated in the system. This phenomenon indicates the loss of the interactions of that particular atom with neighbouring atoms.

$$E\{\Psi\} = [H]\{\Psi\}$$
(1)

The crystallographic defects should be taken into consideration as it is not uncommon due to the constraints in present technique for synthesis of carbon-based nanostructures, including GNRs (Guseinov et al. 2016). Those quantum transport models with ideal physical conditions cannot effectively describe the quantum mechanical behaviour of defective GNR, due to the defects having a significant impact on the electronic characteristics of the nanostructures, including their band structure and density of states (Chang et al. 2013). In this work, tight binding model of GNRs with SV defects based on the NEGF formalism (Datta 2002) is presented. The model considers the simplifying assumptions proposed by Datta (1997) in his work. Our computational work includes the automatic generation of the Hamiltonian matrix GNR model allows users to define the specifications, for educational and research purposes.

2. Related research

Previous simulation work has been done by Goh et al. (2018) primarily focuses on pristine GNR. An ideal GNR model is introduced using the numeric computational approach on MATLAB. The electronic properties of ZGNR and AGNR have been well discussed in their work, demonstrated by the plots of band structure, DOS and the transmission properties. In this work, an additional SV defects condition is implemented in the tight-binding model and simulated under NEGF formalism, with assumptions introduced by Datta (1997, 2005). Datta (1997) suggests three simplifying assumptions for device modelling. Firstly, the use of basis function adapted from Hartree's assumption (Tsuneda 2014), which states that the number of single electron wave function equals to the number of electrons in the respective system, that allows one to define the system by a single-particle electron approach. They represent the wave functions of electrons of the molecules that are only involved in their respective transport. Considering a onedimensional (1D) system that consists of three hydrogen atoms as shown in Fig. 2, a free hydrogen atom has a valence electron and thus, the wave function of the hydrogen 1s electron orbital serves as the basis function. Extending this into a multi-level orbital system, for example, a two-dimensional (2D) GNR, only the π -electron of the 2pz orbital serve as the basis function of the system, despite having 2 shells.

Secondly, these wave functions are only affected by their nearest neighbours. In Fig. 2, the overlapping of wave



Fig. 2 A 1D system with three hydrogen atoms with 1s orbital wave function

functions of *1s* only occurs among the atoms which are directly next to each other. This is known as the singleneighbour tight binding model (Reich 2008) that puts limitations on the applied forces. Lastly, the discretization of the Hamiltonian operator and its basis functions into matrix equations. The structure of the lattice itself consists of discrete atoms at an atomic level. Considering the assumptions, the Hamiltonian matrix of three hydrogen atoms illustrated in Fig. 2 can be constructed as Eq. (2), where u_1 , u_2 and u_3 represent the *1s* orbital wave function. The term u_{11} , u_{22} and u_{33} are the self-interacting energies, whereas u_{12} , u_{21} , u_{23} and u_{32} are the interacting energies between respective nearest neighbour atoms.

$$E \begin{cases} \Psi_{1} \\ \Psi_{2} \\ \Psi_{3} \end{cases} = \begin{bmatrix} u_{11} & u_{12} & 0 \\ u_{21} & u_{22} & u_{23} \\ 0 & u_{32} & u_{33} \end{bmatrix} \begin{cases} \Psi_{1} \\ \Psi_{2} \\ \Psi_{3} \end{cases}$$
(2)

In Eq. (2), the wave function of the Schrödinger equation acts as the eigenfunction, and the accompanying Hamiltonian operator contains the eigenvalues that correspond to the allowable quantum energy states (Oxtoby *et al.* 2015). Applying this concept, the defect properties can be well exhibited in the Hamiltonian operator. The structural defect applied on GNR causes the changes in the interactions among the carbon atoms in GNR, which directly affect the components in that particular Hamiltonian operator.

Han et al. (2007) observed that narrower graphene nanoribbons have larger band gap during temperature dependent conductance measurement. They have also conducted an investigation into the electronic transport namely on GNR conductance as a function of gate voltage measured at different temperatures (Han et al. 2007) which we will incorporate in future work. Tight-binding approach by Tong (2013) has been carried on deformed GNRs where stress was applied on ideal GNRs. However, the work by Tong (2013) and Han et al. (2007) focus on structurally well-defined graphene rather than single vacancy. de Brito Mota et al. (2015) uses Density Functional Theory (DFT) method to study and compare the electronic properties of perfect and defective nanoribbons by Boron Nitride (BN) (de Brito Mota et al. 2015). DFT unable to take into account the full interaction between atoms for a large system. As such, tight-binding approach is more suited to be used in enormous calculations. It is also demonstrated that defects play an important role in graphene physicochemical properties (Terrones et al. 2012). In the review by Terrones et al., exploration is carried out on structure with different types of defects. In addition, most first-principles simulations were on the ferromagnetism and antiferromagnetism. It is found that minimal work focusses on the effects of single vacancy defect and doping on the band structure and density of states of carbon-based material. As such, these non-idealities in GNR are addressed in our study.

Defects such as vacancy defects (Kim *et al.* 2011), Stone-Wales (S-W) defects and impurity defects (Zhang *et al.* 2011) occur in GNRs. Among the defects, SV defects are prevalent, and likely to trigger other defects like



Fig. 3 (a) SV defect; (b) DV defect in a AGNR lattice, with red dotes represent missing atoms

divacancies (DV) (Vicarelli *et al.* 2015). The changes in the geometrical structure after defects are applied is a critical issue as it directly affects the periodic configuration of carbon atoms, as well as ways of interacting among each other. The determination of the actual shape of a defect is done through a relaxation procedure (Meyer *et al.* 2008, Zaminpayma *et al.* 2017) where the lattice length and position will re-adjust themselves due to the interaction among atoms. This research, however, does not consider the bond length, but only the interaction among atoms. Due to the interaction among atoms around the defect location, a variety of relaxed geometric configuration of carbon atoms is formed as shown in Fig. 3.

SV defect occurs when one carbon atom is missing in GNR, resulting in a total of three bonds being lost which are between the missing atom and atom A, B and C respectively. DV defect occurs when two carbon atoms are missing in GNR, that results in a total of five bonds being lost which are between the missing atom and atom A, B, C, D and E. This configuration of the SV defect is taken for modelling framework. The missing bonds is due to the vanishing of respective tight-binding energies.

3. Research design and implementation

An ideal GNR model is constructed using the computational framework by Indra *et al.* (2018), for ZGNR and AGNR. Based on the Hamiltonian operator of ideal GNR, the framework script for defected GNR is developed respectively that allows a user to define the SV defect location on the GNR plane. The modelling algorithm simulation scheme is written in MATLAB scripts. The input for the scripts are the length of GNR, l, width of GNR, n, tight-binding energy, t, and the SV defect location, and the output are graphical plots such as subband structure, bandgap value, DOS and comparison between pristine and defective GNR. In this context, the development of an algorithm is carried out to remove the tight-binding energies from the Hamiltonian operator due to the missing carbon atoms.

3.1 Generation of Hamiltonian Operator

Referring to the simplifying assumptions for device modelling discussed in the previous section, the basis function used in this work is the wave function of 2pz electron. The graphene layer is stable because of the strong σ bond formed by sp2 (2s, 2px, 2py) orbitals, however, the electronic properties of planar graphene are dominantly decided by the 2pz orbitals (Tran et al. 2017). This 2pz orbital is not involved in the formation of an σ bond among carbon atoms, but involving in a free-moving delocalized π orbital, which is responsible in the charge transport. This is the only electron band of interest for modelling in this research. Generally, there are interactions of each π orbital with three of its nearest neighbour π orbitals in a graphene layer. However, this may or may not be the case when it comes to GNR with finite dimension unlike graphene. In this research, the dangling bonds at the edge carbon atoms in GNR are assumed to be passivated with hydrogen atoms, and they do not contribute the electronic states near the Fermi level of the whole system, thus reducing the complexity of the problem of the Hamiltonian device. In this context, the Hamiltonian device is generated with an open boundary condition. The width and length of GNR, ZGNR and AGNR are defined in unit cells accordingly, as shown in Figs. 4 and 5 respectively.

The decomposition of a quasi-2D GNR structure into a 1D structure is done by collapsing in the width direction into a single matrix form. They are defined as alpha matrix, α , and beta matrix, β that describe the interaction between all the alpha matrixes. The number of rows in alpha and beta matrices equals to the number of carbon atoms present in a GNR unit cell. The numbering sequence of these α and β during computational calculations are strictly followed throughout the research.

Once both the alpha matrices and beta matrices are defined, they are combined to generate a final Hamiltonian matrix. The GNR Hamiltonian will have the same general structure for the same widths nanoribbon, but with different alpha and beta matrices content. For 4-ZGNR and 4-AGNR with lengths of 3, the Hamiltonian is shown in Eq. (3). The Hamiltonian matrix of 4-ZGNR in Fig. 4 is written as Eq. (4) and the formalism is based on the numbering sequence as proposed by Indra *et al.* (2018).

$$H_{4-ZGNR/AGNR, L=} = \begin{vmatrix} \alpha_{11} & \beta_{12} & 0\\ \beta_{21}^{\prime} & \alpha_{22} & \beta_{23}\\ 0 & \beta_{21}^{\prime} & \alpha_{23} \end{vmatrix}$$
(3)



3.2 Generation of defective device Hamiltonian

In this section, methods and algorithm used in this computational work to remove the t term automatically from the pristine Hamiltonian devices are discussed. Various numbers of loops are used in the MATLAB script to fulfil the purpose of developing the defective Hamiltonian matrix from a pristine one. They are not a single MATLAB command, but rather a series of conditions and limitations set in algorithms to extend the way of configuration of the defect location as discussed previously. The main concepts are discussed for a better understanding of the big frame of the script. The defect location is annotated as Eq. (5)

$$Defect \ location = (x, y)n \tag{5}$$

where x represents the x-coordinate of the defect point; y is the y-coordinate of the defect point; and lastly, n is the direction of the defect point in the particular unit cell. The xterm follows the unit cell sequence of the structure (extending horizontally), where the y term depends on the length of the GNR structure (extending vertically). Both x and y must be integers within the dimension of GNR structure, where *n* is in a string format, that can be either A, B or N, depending on the configuration of a desired SV defect location. Users must firstly have a good understanding of these configurations to define the desired defective Hamiltonian operator for the simulation. Figs. 4 and 5, which are 4-AGNR and 4-ZGNR, respectively, well illustrate the definition of a defect point location. Fig. 4 shows a 4-AGNR structure with numbered carbon atoms in the second unit cell. A red dot is noticeable at the position of 2A in the second unit cell. If a SV defect is to be at the location represented by the red dot as shown in Fig. 4, the annotation shall be (2,3)A. If one wants the other opposite carbon atom in the same unit cell to be the defect point as represented by the green dot in Fig. 4, then the defect location is annotated as (2,3)B.

A similar method is applied to the ZGNR structure as well, except for the definition of n term. Fig. 5 shows a 4-ZGNR structure with numbered carbon atoms in the second unit cell as well. For instance, the defect location at the location represented by the red dot in Fig. 5 is annotated as (2,3)N. In the case of ZGNR, the n value is consistently written as N because the ZGNR unit cell does not have a mirrored component like the AGNR unit cell. One can note that the numbering for ZGNR is in a vertically extending manner.



Fig. 4 4-AGNR with defect locations at (2,3)A (red dot), and (2,3)B (green dot)



Fig. 5 4-ZGNR with defect locations at (2,3)N (red dot)

3.2.1 Defective alpha

Alpha matrix shows how the carbon atoms interact among each other in the defined unit cell. As carbon atoms are arranged in a honeycomb configuration periodically in the GNR structure, the interactions among carbon atoms are periodically traceable. In the Hamiltonian matrix, the loss of the bonds will cause the neighbouring t terms to be removed, as long as they are within the boundary of the defined unit cell. As such, *find()* function is used to scan the surrounding t terms at the defect point. The defect location shown by the red dot in Fig. 5 is (2,3)N. In the matric form, it is expressed by Eq. (6) where the defect points appear to be at the third column of the second unit cell. Here, the tcomponent that are likely to be removed are highlighted. In comparison to Eq. (4), one can easily find the affected t components that are removed due to the loss of bonds. The *find()* function is used to find those relevant *t* components in unit cells, and substitute them with zeroes.



Similar approach applies to AGNR, except in a few cases due to the uniqueness configuration of their unit cell. Unlike ZGNR where each carbon atom interacts with two neighbours at most in one unit cell, the carbon atoms in AGNR interact with three carbon atoms within one unit

cell, most of the time. Knowing that the red dot point defect location in Fig. 4 is (2,3)A, losing a carbon atom at the 3A position will cause the bonding of 2A-3A, 3A-4A and 3A-3B to be removed, as illustrated as in Eq. (7), where *t* terms are removed and replaced with highlighted '0'. In such cases, *find*() function cannot be implemented. Therefore, a manual loop of condition checking is written in the script to overcome the shortcoming.



3.2.2 Defective beta

The construction of defective beta matrix in AGNR is more easily achieved than in the alpha matrix. In Fig. 4, the first carbon atom starts at the 2A position and the numbering continues clockwise (Indra et al. 2018). From the fourth atom onwards, bonding to other unit cells occur, that contributes to t terms in the beta matrix, and this is repeated at every 2-atom interval. Following this pattern, a combination of looping script is written to scan whether the checking condition meets the defect point given by users, where the values of y and n take important roles. When the condition meets, the particular t term will be removed and replaced with the value of zero in the pristine Hamiltonian matrix. However, there are some cases that the t term in beta matrix are not removed because the defect point does not occur at the situation aforementioned. In Eq. (7), the defect location of (2,3)A does not impact the respective beta matrix, as they do not interact with any other neighbouring unit cells.

On the other hand, there is an alternate construction of the defective beta matrix in ZGNR where the interaction between unit cells occurs in a special way, as shown in Table 1.

Table 1 Bonding pairs of unit cell o and p in 4-ZGNR

	Unit cell o	Unit cell p
Bonding pairs	<i>o</i> 1	<i>p</i> 2
	<i>o</i> 4	<i>p</i> 3
	<i>o</i> 5	<i>p</i> 6
	08	<i>p</i> 7

The table is constructed based on the interaction between first and second unit cell of 4-ZGNR from Fig. 5, namely o and p, respectively. The carbon atoms are bonded to each other in ascending order, but jumping alternatively in between two unit cells. o1 will be paired with p2; p3 will be paired with o4, and this pattern will continue till the end of the width of the ZGNR structure. Thus, a script is written to find the bonding sequence of ZGNR between unit cells. Whenever a condition where the defect point location meets any of the bonding sequences, the particular t terms will be removed. For the 4-ZGNR defect location of (2,3)N in Fig. 5, the affected bonding pair will be between the third atom from second unit cell and fourth atom from the first unit cell. The resulting Hamiltonian is the same as in Eq. (6), where one can see the single highlighted '0' at β_{12} and β_{21} areas, respectively.

3.2.3 Defective Hamiltonian

With the well-defined method of defective alpha and beta matrices generation, the defective Hamiltonian matrix is formed by simply substituting it with a zero value at the particular coordinates given by defective alpha and beta matrices in the previous section. In the script, *H* is the pristine Hamiltonian operator, and $H_defected$ is a clone of *H*, which is modified to obtain the defective Hamiltonian operator. The coordinates that are specified by the preceding defective alpha and beta matrices generation are then replaced with zeroes, by using the command $H_defected(m,n) = 0$ in the script, where *m* represents x coordinate in Hamiltonian matrix, and *n* is the *y* coordinate. The complete defective Hamiltonian matrix of 4-AGNR with a defect location at (2,3)A and 4-ZGNR with defect location at (2,3)N are shown in Eqs. (6)-(7), respectively.

3.3 Plotting of sub-band structure

By applying basis functions as the constraint, the dispersion relation is the relationship between band energies, E, and the wave-number, k. Dispersion relation of a system describes the effect of dispersion in the system over the travel of waves within the system. It simply relates the electron energy to the respective wave vector (Datta 1997). When the basis functions are considered as the constraint, the dispersion relation describes the relationship between band energies, E and the wavenumber, k. When one sums up all the allowed energy levels at k-points for a given momentum, the band structure of a system can be obtained. From the visualization of the band structure, one can induce the intrinsic characteristics of the system (either metallic, semiconducting or insulating) from the minimum band-gap between the minimum conduction band (CB) and maximum valence band (VB). The range of k values is usually taken from the first Brillouin Zone (BZ) which is from π to π .



Fig. 6 1D N - atom chain

Thus, corresponding to this, the Hamiltonian matrix can be refined with the derivation of dispersion relation in a general form of Eq. (8), with the visual aids as shown in Fig. 6.

$$E \begin{cases} \Psi_{1} \\ \Psi_{2} \\ \vdots \\ \Psi_{N-1} \\ \Psi_{N} \end{cases} = \begin{vmatrix} \varepsilon & t & 0 & \cdots & t \\ t & \varepsilon & t & 0 & \cdots \\ 0 & t & \varepsilon & t & 0 & \cdots \\ \vdots & \ddots & \ddots & \ddots & \ddots \\ \vdots & \ddots & \ddots & \ddots & \ddots \\ t & \cdots & 0 & t & \varepsilon \end{vmatrix} \begin{pmatrix} \Psi_{1} \\ \Psi_{2} \\ \vdots \\ \Psi_{N-1} \\ \Psi_{N} \end{pmatrix}$$
(8)

By definition, ε represents the self-interacting energies of the atoms, represented by a black cross, whereas *t* represents the interaction energies of atoms amongst each other. A periodic boundary condition is added in the chain as the bolded *t* that shows that the first atom and N-th are adjacent to each other. The added condition allows the expression of the overall matrix equation into a single linear equation form as shown in Eq. (9)

$$E_{\Psi n} = t_{\Psi n-1} + \mathcal{E}_{\Psi n} + t_{\Psi n+1} \tag{9}$$

Due to the fact that the linear matrix equation is timeindependent, the approximation of a wave function can be done with a plane wave Eq. (10) (Datta 1997), simplifying it into a function of wave number, k, as shown in Eq. (11).

$$\Psi_n = \Psi_0 e^{+ inka} \tag{10}$$

$$\frac{\Psi_{n-1}}{\Psi_n} = \frac{e^{+i(n-1)ka}}{e^{+inka}} = e^{-ika}$$
(11)

Thus, the final dispersion relation is formed as Eq. (12), and it is ready to be used for the energy spectra calculation throughout this research.

$$E = te^{-ika} + \varepsilon + te^{+ika} \equiv \varepsilon + 2t\cos ka \tag{12}$$

3.4 Plotting of Density-of-States (DOS)

DOS describes the number of states available to be occupied at each energy level. For a zero DOS, it simply means that none of the states at that particular energy level is available to be occupied. In semi-classical physics, DOS of a semiconductor represents the energy of the number of solutions to Schrödinger's equation. There are various ways for the DOS calculation, one being done mathematically with the delta δ function (Datta 2005). Eq. (13) represents the total DOS of a particular system with N bands. The value of N is twice the number of electrons that are involved in the transport due to conduction-valence subband pair by each electron.

$$DOS(E) = \sum_{i=1}^{N} \frac{1}{2\pi} \int \delta \left[E_i \left(k \right) - E \right] dk$$
(13)

Solving the delta function gives Eq. (14), which is used to compute one of the DOS.

$$DOS(E) = \sum_{i=1}^{N} \frac{1}{2\pi} \sum_{all \, k} \frac{\eta_{G}}{\left[E_{i}\left(k\right) - E\right]^{2} + \eta_{G}^{2}}$$
(14)

Another equation to compute DOS is by the methods of Green's function (Datta 1997, Li and Lu 2008). The relation between Green's function and DOS is described by Eq. (15).

$$DOS(E) = \frac{1}{\pi} \operatorname{Im} \left[Trace \left[G_{F} \right] \right]$$
(15)

where G_F is the retarded Green's function expressed by

$$G^{\text{retarded}} = \left[\left(E + i\eta \right) * I - H \right]^{-1}$$
(16)

Note that η is a very small imaginary value preventing the inverse matrix from diverging, *I* is an identity matrix, and *H* is the Hamiltonian operator matrix.



Fig. 7 Simulated sub-band structure for AGNR with widths 6, 7 and 8 respectively



Fig. 8 Sub-band structures benchmark (Tong 2013)

One should note that the calculation of DOS via band structure will not contain any lengthy information of the system unlike Green's function method, due to the existence of the Hamiltonian operator. Both methods are used in this work for comparison purposes.

4. Results, analysis and discussion

4.1 Simulated sub-band structure

AGNR electronic properties depend on width, alternating between 2 semiconducting states, followed by a metallic state, as shown in the sub-band structure in Fig. 7. The simulated result has a close agreement with other works (Tong 2013), as shown in Fig. 8. AGNR is semiconducting for widths n = 3p and n = 3p + 1, whereas it is metallic when having widths of n = 3p + 2. These are consistent with the simulated result for 6-AGNR, 7-AGNR and 8-AGNR, respectively.

For ZGNR, the sub-band structure is degenerated at points k = 2/3. This goes for all widths of ZGNR, where the increasing widths increase the number of bands, as shown in Fig. 9. When SV defect is introduced inside the atomic structure of AGNRs, the shape of the sub-band structure and bandgap will change. Figs. 10, 11 and 12 show the simulated defective sub-band structure for 6-AGNR, 7-AGNR and 8-AGNR at length of 3, 10 and 20. The SV defect is fixed at the intersection of 2^{nd} row and 5^{th} column. The blue lines represent the pristine AGNR subband structures, and the red lines represent the defective AGNR sub-band structures. For the annotations on the top of sub-band structures, '*Bandgap*' represents the band gap of defective AGNRs and the '*Bandgap2*' represents the



Fig. 9 Simulated sub-band structure for 4-ZGNR, 5-ZGNR and 30-ZGNR



Fig. 10 Defective sub-band structure for 6-AGNR at length of 3, 10 and 20



Fig. 11 Defective sub-band structure for 7-AGNR at length of 3, 10 and 20



Fig. 12 Defective sub-band structure for 8-AGNR at length of 3, 10 and 20



Fig. 13 Defective sub-band structure for 4-AGNR at length of 15, 20 and 30



Fig. 14 Defective sub-band structure for 5-AGNR at length of 15, 20 and 30

band gap of pristine AGNRs. One can notice that red lines and blue lines do not coincide with each other at most of the energy level, indicating that SV defect does cause changes in sub-band structure. This is because SV defect will cause removing of -2.7eV tight-binding energy at certain position inside the Hamiltonian matrix.

When we observe the sub-band structure of defective 6-AGNR at length of 3, 10 and 20, we found that red lines deviate significantly when compared with blue lines for the defected sub-band structures of 6-AGNR at the length of 3. However, for the defected sub-band structures of 6-AGNR at the length of 20, red lines almost coincide with blue lines. For pristine 6-AGNR at length of 3, there is 36 carbon atoms inside the atomic structure. With SV defect, defective percentage is calculated to be 2.78% whereas the defective percentage for the 6-AGNR at length of 20 is only 0.42% as there are 240 carbon atoms inside a pristine atomic

structure. Higher defective percentage will cause larger deviation inside the atomic structure. The same patterns also can be observed at the sub-band structure of defective 7-AGNR and 8-AGNR. In addition, it is found that defective AGNR has narrower bandgap compared with pristine AGNR. This is in agreement with the result of Chang *et al.* (2013).

Similar to AGNR, the shape of the sub-band structure of ZGNR will change when SV defect is introduced inside the atomic structure. Figs. 13 and 14 show the simulated defective sub-band structure for 4-ZGNR and 5-ZGNR at length of 15, 20 and 30. The SV defect is fixed at the intersection of 2^{nd} row and 5^{th} column. The blue lines represent the pristine ZGNR sub-band structures, whereas the red lines represent the defective ZGNR sub-band structures. For the annotations on the top of sub-band structures, '*Bandgap*' depicts the band gap value of

defective ZGNRs whereas '*Bandgap2*' shows the band gap value of pristine ZGNRs. One can notice that red lines and blue lines do not coincide with each other at every energy level, indicating that SV defect prompted changes in subband structure of ZGNR. This is due to the fact that tightbinding energy of -2.7eV are removed at affected position inside the Hamiltonian matrix. As ZGNR is metallic, pristine ZGNR has zero band gap and remains the same when SV defect is introduced inside the atomic structure.

Nevertheless, when the sub-band structure of defective 4-ZGNR at length of 15, 20 and 30 is observed, the red lines diverge from blue lines for the defective sub-band structures of 4-ZGNR at the length of 15. The defective sub-band structure of ZGNR is not as smooth as pristine ZGNR or defective AGNR. There are many Van Hove singularities peaks at the defective ZGNR sub-band structure. However, for the defected sub-band structures of 4-ZGNR at the length of 30, the deviation is much smaller. For pristine 4-ZGNR at length of 15, there is 120 carbon atoms inside the atomic structure. As such, SV defective percentage is at 0.83% whereas defective percentage for the 4-ZGNR at length of 30 is lower at 0.42% since it contains 240 carbon atoms inside the pristine atomic structure. Thus, a higher defective percentage will cause larger deviation inside the atomic structure. Similar patterns can also be observed at the sub-band structure of defective 5-ZGNR.

4.2 Numerical computation of DOS

The computation of DOS for both AGNR and ZGNR is done using the delta equation substituted with distribution function from Eq. (14). Numerical DOS does not contain information regarding length of GNR. Numerical DOS varies with widths, converging to approximately the same



Fig. 15 Numerical DOS plots for 6-AGNR, 7-AGNR and 30-AGNR respectively at length of 10



Fig. 16 Numerical DOS plots for 4 – ZGNR, 5 – ZGNR and 30 – ZGNR respectively at length of 10

shape, by increasing the structure widths. These applied to both AGNR and ZGNR structures, which are illustrated in Figs. 15 and 16, respectively. Fig. 15 shows the numerical DOS plots for 6-AGNR, 7-AGNR and 30-AGNR respectively at length of 10 for pristine and defective structure where the defective location is at the intersection of 2nd row and 5th column. Fig. 16 shows the numerical DOS plots for 4 – ZGNR, 5 – ZGNR and 30 – ZGNR respectively at length of 10 for pristine and defective structure where the defective location is at the intersection of 2nd row and 5th column. At large enough widths, the plot takes the form similar to that of a 2D graphene sheet. Note that the energy peaks of numerical DOS for either AGNR or ZGNR correspond to the value of 2.7 eV, the tight-binding energy for the 2pz π -orbital.

The blue and red lines represent the characterizes of

pristine and defective AGNR and ZGNR numerical computation DOS respectively. The removal of tight binding energies affects the numerical DOS as well as subband structures. From the red lines in Figs. 15 and 16, it is observed that the value of defective numerical computation DOS is lower than the value of pristine numerical computation DOS.

4.3 Green's function approach

The DOS plotting in this section is simulated using the retarded Green's function from Eq. (16) which is a subcomponent of the DOS equation in Eq. (15). The DOS equation directly involves the Hamiltonian operator. Thus, any changes in the content of the Hamiltonian matrix will affect the Green's function DOS plot, including the removal



Fig. 17 Green's function DOS for 6 – ZGNR, 6 – AGNR, 7 – AGNR and 8 – AGNR of lengths of 3, respectively. Blue lines represent the pristine GNR plots; red lines represent the defective GNR plots



Fig. 18 Green's function DOS for 20 – ZGNR, 20 – AGNR, 50 – ZGNR and 50 – AGNR of lengths of 3, respectively. Blue lines represent the pristine GNR plots; red lines represent the defective GNR plots

of tight-binding energies due to the SV defect. Fig. 17 depicts the resulting Green's function DOS plot, where 6-ZGNR, 6-AGNR, 7-AGNR and 8-AGNR at length of 3 with defect location at row of 2 and column of 5 are illustrated. The blue and red lines represent the pristine and defective GNR Green's function DOS respectively. One can notice that both lines do not coincide with each other at most of the energy level, indicating that SV defect does cause an energy peak shift in DOS. Electron confinement occurs at different specific energy levels when SV defect is applied.

However, the effect of the SV defect is significant for GNRs below a width of 10. At fixed length of 3 with width larger 20, Green's function DOS for pristine and defective GNR begin to coincide with each other. Both 20-AGNR and 20-ZGNR in Fig. 18 has moderate agreement with one another. The agreement improves dramatically when the widths are increased to 50. Both lines are overlapping with each other, showing that the effects of SV defect becomes lesser in a large-scale GNR due to the lower percentage of defect. For a smaller width GNRs, the percentage of SV defect is higher and vice versa.

5. Conclusions

A computational nanoelectronics algorithm based on tight-binding model for GNR with point defect is implemented in MATLAB. The GNR model is simulated under NEGF formalism, with three main simplifying assumption that are the utilization of basis function, Hamiltonian operator discretization and plane wave approximation. The tight-binding model is generated by collapsing a quasi-2D structure of GNR into an equivalent 1D matrix system by using alpha and beta matrices, which represent the interactions in the unit cell and between unit cells, respectively. With SV defects, the components within these matrices change due to the disappearance of tight binding energies of carbon atoms in graphene. Our findings show that there are differences between band structures and numerical computation DOS of pristine and defective GNR as the Hamiltonian operator is changed due to disappearance of tight binding energies of carbon atoms in GNRs. These defects decrease the value of numerical DOS and band structure. Green Function's DOS shows that the defects shift the energy confinement on GNR, making different energy peak at specific energy levels. However, the effect of defects is not significant in GNR with widths beyond 20 units of carbon atoms. The model could be further improved by including other common vacancy defects such as divacancy and S-W defect (Chang et al. 2013). In addition, our future work will also include by the addition of substitutional impurities atoms in GNR. In this context, it can be implemented by substituting the bonding energy, t term. The possible atoms to be bonded with carbon atoms in GNR are boron and nitrogen (Ashrafi et al. 2013). A simple GNR simulator known as GNRSIM has been developed using graphical user interface (GUI) that can be utilized as educational and development kits in the learning and teaching processes (Wong et al. 2018).

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