Impact of geometry on transport properties of armchair graphene nanoribbon heterojunction

Weixiang Zhang\textsuperscript{a}, Cemal Basaran\textsuperscript{a,}\textsuperscript{*}, Tarek Ragab\textsuperscript{b}

\textsuperscript{a} Electronic Packaging Laboratory, University at Buffalo, NY 14260, USA
\textsuperscript{b} Arkansas State University, State University, AR 72467, USA

\textbf{Abstract}
Electron transport properties of undoped armchair Graphene Nanoribbon Heterojunction (GNRHJ) has been studied using semi-empirical extended Hückel method (EH). A two-probe configuration device utilizing armchair GNRHJ has been proposed. It is shown that a potential barrier was formed at the heterojunction interface between semiconductor and semi-metal, which resemble the conventional Schottky barrier at the interface of semiconductor/metal. Transmission spectrum was analyzed at finite bias; and current-bias voltage characteristic relations were established. Results show that the I–V characteristics of the heterojunction have rectifying nature, with its rectification ratio affected by the geometric asymmetry of the heterojunction.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction
Graphene has attracted considerable attention because of its extraordinary mechanical, thermal and electrical properties\textsuperscript{[1–20]}. Graphene has a monolayer two-dimensional structure with hexagonal lattice, and electrons in graphene behave like massless quasi-particles\textsuperscript{[21]}. As a result graphene has unique properties of semi-ballistic transport and very high charge carrier mobility. It is believed that graphene is a very promising candidate in nanoelectronics applications in the post-silicon age. Most electronic applications rely on the presence of a gap between valence bands and conduction bands\textsuperscript{[22]}. However, graphene sheet has no band gap, therefore direct applications of graphene as a semiconductor are very difficult. Fortunately, there are a few methods that can effectively open a band gap in graphene, including substrate induced band gap opening\textsuperscript{[23,24]}; chemical substrate doping\textsuperscript{[25–27]}; graphene nano-mesh\textsuperscript{[28–31]}; and quantum confinement, i.e., graphene nanoribbon (GNR)\textsuperscript{[32–34]}. Among them graphene nanoribbon is the most direct and convenient method that can modulate the band gap, which make GNR a desirable form for electronics application.

Using first principle study\textsuperscript{[35]}, it is known that armchair GNR (aGNR) has band gap depending on its width, where as the width increases, band gap decreases. For aGNR with dimer number equal to 3p and 3p+1, where p is a positive integer, band gap ranges from 0.4eV to 2.5eV. So 3p and sp+1 aGNR are semiconductor. For aGNR with 3p+2 dimer, band gap has values ranging from 0 to 0.3eV and it reaches below 0.036eV when p is greater than 6, which is small enough and close to the thermal fluctuation energy at room temperature. Thus 3p+2 type of aGNR can be regarded as semi-metallic with dimer number greater than 20.

Inspired by the idea that the band gap of armchair GNR can be tuned by controlling its geometry, we propose a heterojunction structure by connecting aGNRs of different widths. The right side of the HJ belongs to 3p+1 genre and is a semiconductor; the left side of the HJ belongs to 3p+2 genre with p greater than 6 to make it metallic.

In the literature, graphene heterojunction structures have been studied extensively and has been widely examined in the development of graphene based nano-devices. Lam et al.\textsuperscript{[36]} has studied the application of graphene heterojunction as the channel of graphene Tunneling Field Effect Transistors (TFET). They reported a large band gap region created in the middle of the channel due to the existence of heterojunction, and an increase of I\textsubscript{ON}/I\textsubscript{OFF} ratio of the TFET. Li et al.\textsuperscript{[37]} has studied the graphene nanoribbon heterojunction formed by connecting armchair GNR and zigzag GNR. They reported rectification effect and asymmetric IV characteristics of their aGNR|zGNR heterojunction. Cai et al.\textsuperscript{[38]} reported bottom-up fabrication method of heterojunction of pristine and Nitrogen-doped graphene. They showed that band shift of 0.5eV occurred at the interface region of the HJ which is similar to traditional p-n junction. A.R.Cadore et al.\textsuperscript{[39]} investigate the graphene/metal...
heterojunction contact interface. They reported asymmetrical resistance in electronic transport for electrons and holes due to electrostatic interaction. They showed that the contact resistance can be tuned in a reversible manner by exposing graphene device to H2. Yamaguchi [40] demonstrated the tunnel barrier characteristics of graphene/transition metal dichalcogenide (TMD)/metal vertical stacked heterojunction. They showed that the tunnel resistance in graphene/WS2/metal hetero-structure increase exponentially with the number of WS2 layers. Zhu et al. [41] studied the graphene/blue phosphorus van der waals heterojunction using density functional method (EH). In order to get a clear understanding of the electron transport properties, Density of States (DOS) and Projected Local Density of States (PLDOS) are calculated. Meanwhile I transport properties, Density of States (DOS) and Projected Local

1.1. Geometry and methodology

The aGNR-HJ device consists of three regions: a finite central scattering region where carriers are transported through, and two semi-infinite electrodes of which their unit cells are confined within the rectangles as shown in Fig. 1. The length of the central scattering region is 13.35 nm, which is long enough to avoid edge effect influence on the transport properties [43].

The HJ structure was formed by connecting two aGNRs of different width followed by geometric optimization of central scattering region using Brenner potential in the ATK quantum mechanics software package [44-47] with a convergence tolerance of 0.001 eV/Å. In order to ensure a balance of accuracy and efficiency, the electronic transport properties of the aGNR HJ were calculated using semi-empirical extended Hückel method (EH) combined with Non-Equilibrium Green’s Function (NEGF) formalism.

To calculate the transport properties of the HJ, first we need to obtain the self-consistent density matrix of the central region, which is shown below:

\[
\hat{D}(V_b) = \int_{-\infty}^{\infty} \left[ \hat{\rho}^L (\epsilon, V_b) f(\epsilon - \mu_L) + \hat{\rho}^R (\epsilon, V_b) f(\epsilon - \mu_R) \right] d\epsilon
\]

where \( \hat{\rho}^L (\epsilon, V_b) \) is the contribution to the spectral density of states from left (right) scattering state. \( V_b \) is the bias voltage; \( \epsilon \) is the Fermi level, \( \mu \) is the chemical potential, \( f \) is the Fermi function.

From the density matrix, the real-space density in the central region can be calculated using the following equation for spatial distribution of the induced electron density:

\[
\delta n(\vec{r}) = \sum_{\mu} \delta m_{\mu} \sqrt{\frac{\alpha_{\mu}}{\pi}} |\vec{F}^c - \vec{F}^s|^2
\]

where \( \delta m_{\mu} \) is the excess charge of atom \( \mu \) as obtained from the Mulliken population \( m_{\mu} \) and the ion valence charge \( Z_{\mu}, \alpha_{\mu} \) is the width of the Gaussian orbital.

From the real-space density, we can further obtain the Hartree potential and define Hamiltonian as following:

\[
H_I = \begin{cases} E_i + \delta V_H(\vec{R}_i) & \text{if } i = j \\ \frac{1}{4} (\vec{\beta}_i \cdot \vec{\beta}_j) (E_i + E_j) S_{ij} + \frac{1}{2} (\vec{\delta}V_H(\vec{R}_i) + \vec{\delta}V_H(\vec{R}_j)) S_{ij} & \text{if } i \neq j \end{cases}
\]

where \( E_i \) is an orbital energy and \( \beta_i \) is an adjustable parameter (often chosen to be 1.75). \( \delta V_H(\vec{R}_i) \) is the Hartree potential. \( S_{ij} \) is the overlap matrix.

Finally, with the Hamiltonian, we can calculate the transmission spectrum and obtain the transport current using Landauer-Butiker equation:

\[
I = \frac{e}{h} \int T(\epsilon) [f(\epsilon - \mu_+) - f(\epsilon - \mu_-)] d\epsilon
\]

where \( e \) is electron charge; \( h \) is Planck’s constant; \( f \) is the Fermi function; \( T(\epsilon) \) is the transmission coefficient which is given by

\[
T(\epsilon, \vec{k}) = \sum_{m} \sum_{n} t_{mn}(E, \vec{k}) t_{nm}^*(E, \vec{k})
\]

where \( t_{mn}(E, \vec{k}) \) is the transmission amplitude from Bloch state \( \psi_m(\vec{k}) \) in the left electrode to Bloch state \( \psi_n(\vec{k}) \).

To ensure numerical accuracy of the EH calculation, Pauz-Mixer algorithm was used for iteration control with a damping factor of 0.1. 20 Â of vacuum was added in the transverse directions to decouple from periodic boundary condition. 100 k-points (points in k-space) were sampled in the transport direction. Two-dimensional fast Fourier transform (FFT2D) was used for Poisson solver. Density mesh cut-off was set as 100 Ha (1Ha = 27.1 eV).

2. Result and discussion

In order to study the size effect of heterojunction on transport properties, five geometric configurations were examined, namely, a20_a19, a20_a16, a20_a13, a20_a10, and a20_a7, which are illustrated in Fig. 2. Here aM_aN notation denotes the aGNR heterojunction structure with left side having dimer number M and right side having dimer number N. As an initial point of study, the a20_a19 structure was studied, which has a modest geometric difference at the HJ interface. a20_a19 is formed by combining a20 and a19 GNRS, which, according to EH calculation results, have a band gap value of \( E_g = 0.036 \) eV and \( E_g = 0.533 \) eV, respectively. In order to examine the potential barrier created at the interface, the Projected Local Density of States (PLDOS) was calculated and are resolved across the HJ device using color contour, as shown in Fig. 3b. The Density of States (DOS) of a20 and a19 GNR are shown
Calculations show that the DOS results for a20 and a19 are consistent with the PLDOS contour, with zero density range corresponding to the black region and pink lines represent density peaks. The good agreement between DOS and the PLDOS contour indicates that the electronic structure of the two ends of the HJ is undisturbed by the interface. The band offset curvature of the conduction/valence band is characterized by the green/red curves, respectively. In Fig. 3b, it is shown the green curve and red curve is nearly symmetric about the Fermi level, indicating the similarity of offset of conduction band valence band at the HJ’s interface, which is located in the middle of PLDOS and is of ~15 Å long (65 Å–80 Å).

In order to examine the influence of band offset at the interface region, the bias dependent transmission spectrum and the I–V characteristics were plotted in Fig. 4. Fig. 4a shows that the I–V curve is nonlinear and rectifying with I = 0 in bias range of ~ [-0.4, 0.4] V, which is in good accordance with the band gap range of a19 GNR. It is also observed that I–V curve is almost symmetric where the current at ± Vb have very similar magnitudes. The nearly-symmetric feature of the I–V characteristic for a20_a19 is due to the very modest conduction/valence band offset difference at the HJ interface.

In Fig. 4b it is observed that the transmission spectrum responds differently to positive and negative bias Voltage. In the positive bias range, the right end of the zero transmission range or the Lowest Unoccupied Molecular Orbitals (LUMOs) shift to the right as the bias becomes more positive, while the left end of the zero transmission range or Highest Occupied Molecular Orbitals (HOMOs) are rather insensitive to positive bias change, leading to larger current for higher positive bias voltage.

In the negative bias range, the HOMOs shifts to the left as bias become more negative, while the LUMOs are insensitive to negative bias change, leading to larger current for higher negative bias voltage. The mirror-image response of transmission spectrum to positive and negative bias explains the symmetric nature of the I–V curve.

In order to further examine the effect of width difference on the transport properties of aGNR heterojunction, parametric study was carried out for the geometries a20_a16, a20_a13, a20_10, and a20_a7. Same as a20_a19, these four heterojunction geometries all have a length of 13.35 nm and they all consist of two semi-infinite electrodes on the two sides and one finite central scattering region in the middle. The left side of these heterojunction is semi-metallic and remains 20 atoms wide, while the right sides are semi-conducting with their band gap value increasing as width decreases. The band gap value for a16, a13, a10 and a7 GNR are
characterized in their density of states (DOS) distribution, which is shown in Fig. 5. In Fig. 5 the DOS are established within energy range of \([-1\text{eV}, 1\text{eV}]\) for a16, a13, a10 and a7 GNR, respectively. The band gap of GNRs are represented by the zero density regions in the DOS distributions. It is clearly shown that the band gap increases as the armchair GNR dimmer number decreases from 16 to 7. It is also noted that the energy state distribution above the conduction band and below the valence band resemble each other and are nearly symmetric about 0eV. While as the GNR dimmer number in width direction decrease from 16 to 7, the difference becomes more and more appreciable, as the distance between peaks is wider for under-valence-band region and narrower for above-conduction-band region. The lowest peak shown in other DOS is missing in a7 case, and it lies outside the \([-1\text{eV}, 1\text{eV}]\) range.

In order to characterize the interface region where band gap offset occurs, the Projected Local Density of States (PLDOS) were plotted and resolved across the transport direction as shown in Fig. 6. Projected Local density of states (PLDOS) resolved in transport direction of a. a20_a16, b. a20_a13, c. a20_a10, d. a20_a7. Green and red curves characterize the valence band and conduction band, respectively. (A colour version of this figure can be viewed online.)
Fig. 6. It is shown that the forbidden band (represented by the black region) becomes wider as the width of the semiconductor side of aGNR decreases, which is consistent with the result in Fig. 5. The offset of conduction bands and valence bands are characterized by the green curves and red curves, respectively. In Fig. 6a the interface region is about 15 Å over which both the conduction band and the valence band were offset in a stepped-manner. While in Fig. 6b and c, as the geometric difference of the semi-metallic/semiconductor regions become larger, the offset of conduction band and valence band become different. The former one are steeper and shorter while the latter one exhibits a gentle slope, creating a significantly long interface region of 40–50 Å. In Fig. 6d the red curve which represents valence band offset has a convex shape. The different behavior of conduction band and valence band offset indicates different electron transport behavior at positive and negative bias.

The distinct curvature of conduction band and valence band offset can be explained by the dissimilar energy state distribution in the under-valence-band and above-conduction-band region in Fig. 5. Furthermore, the difference of chemical potential/Fermi level of aGNRs on the left and right side of the HJ also contribute to the conduction/valence band offset difference as shown in Table 1. The conduction/valence band offset difference since the Fermi level of two aGNR must be aligned when an interface is formed between them.

In order to examine the influence of different offset on con-duction band and valence band at the interface region, the I–V characteristics and the corresponding bias-dependent transmission spectrum were calculated as illustrated in Figs. 7 and 8.

In Fig. 7, it is clear that all the heterojunction structures have nonlinear and rectifying I–V characteristics which has very small current near 0 V and much larger current at higher bias. It is noted that the maximum current $I_{\text{max}}$ on the I–V curve decreases by 4 order of magnitude from a20-a16 to a20-a7. Such a huge difference arises from the exponential relation of band gap value with respect to the conductivity. [48]. The decrease in maximum current is also illustrated in the bias dependent transmission spectrum. In Fig. 6a–d, as the band gap of the semiconducting region increases from a19 (0.53eV) to a7 (1.35eV), the zero-transmission part of spectrum become wider, making the conduction of electron more

### Table 1

<table>
<thead>
<tr>
<th>a20</th>
<th>a19</th>
<th>a16</th>
<th>a13</th>
<th>a10</th>
<th>a7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-6.13923\text{eV}$</td>
<td>$-6.19025\text{eV}$</td>
<td>$-6.22081\text{eV}$</td>
<td>$-6.28949\text{eV}$</td>
<td>$-6.35282\text{eV}$</td>
<td>$-6.37929\text{eV}$</td>
</tr>
</tbody>
</table>

Fig. 7. Current-Bias voltage (I–V) characteristics of a. a20-a16, b. a20-a13, c. a20-a10, d. a20-a7. Current was calculated from -1 V to 1 V in a step of 0.2 V. (A colour version of this figure can be viewed online.)

Fig. 8. Bias dependent transmission spectrum. a. a20-a16, b. a20-a13, c. a20-a10, d. a20-a7. Blue and red curves represent transmission at positive and negative bias, respectively, green curve represents non-biased transmission. For clarity each trans-mission curve is shifted by 0.3 unit. (A colour version of this figure can be viewed online.)
difficult for the same bias voltage. Therefore, to better compare the transport properties of different geometries, semi-log plots of I–V curves were developed as illustrated in Fig. 9a, in which current is expressed in absolute value. It is observed in Fig. 9a that I–V curves are in V-shape, and as the width of semiconductor region of the heterojunction decrease, the magnitude of current also decrease at each bias point.

It is noted in Fig. 7 that as the geometric difference between the metallic and semiconducting regions become more significant, the I–V curve becomes more asymmetric. Typically, the magnitude of current at −V is larger than the current in +V. In order to describe the asymmetric feature of the I–V curve behavior, the rectification ratio is defined as the magnitude of I(−Vb)/I(+Vb) as plotted in Fig. 9b. It is observed in Fig. 9b that the rectification ratio is always greater than 1, which is a result of the geometric difference between the metallic and semiconducting region of the heterojunction. Remarkably, the rectification ratio increases as the geometric difference increase and for a20_a7, the current difference at −V can be as high as 7 times.

3. Conclusions

We propose a two-probe potential barrier device based on undoped armchair GNRHJ with left and right side having different width. We have applied semi-empirical extended Huckel method to study the transport properties of the heterojunction structure. We shown that a potential barrier was formed at the heterojunction interface, which resemble the conventional Schottky barrier formed at the interface of metal/doped-semiconductor. Our calculation results show that the I–V characteristics of the HJ have rectifying nature, with its rectification ratio affected by the geometric asymmetry of the HJ. The asymmetric rectifying behavior of proposed GNRHJ would shed light on developing graphene based geometric diode and switches.

Acknowledgments

This project is sponsored by US Navy, Office of Naval Research, Advanced Naval Research Platform Power and Energy Program (Award Number N00014-15-1-2216) under the direction of Program Director Capt. Lynn Petersen.

References

[29] Vukmirovic Nesad, Vladimir M. Stojanovic, Mihajlo Vanevic, Electron-phonon coupling in graphene antidot lattices: an indication of polaronic behavior,


Atomistix ToolKit version 2016.4, QuantumWise A/S.


Amrozia Shaheen, Wasif Zia, Muhammad Sabieh Anwar, Band Structure and Electrical Conductivity in Semiconductors, LUMS School of Science and Engineering, Lahore, Pakistan, 2011.