Evaluating graphene nanoribbons for miniaturization of field effect transistors: A density functional theory study

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Abstract. For the past 60 years, the number of silicon transistors — the building blocks of integrated circuits — that can be packed onto a microchip has doubled every two years. This phenomenon, famously termed Moore's Law, has driven technological progress. However, this trajectory is approaching a barrier known as the "Silicon limit." At sizes below a certain threshold, the efficiency of silicon diminishes, posing a challenge to continued miniaturization. Thus, the development of novel transistor materials has become a critical step towards realizing 'beyond-silicon nano-electronics'. Graphene, a two-dimensional material composed of carbon atoms arranged in a hexagonal lattice, has risen to prominence as a potential way forward in the field of nano-electronic devices due to its numerous advantages, including high electron and hole mobilities, an atom-thin structure, and the ease of doping to enhance conductivity. However, the lack of a band gap in graphene poses a significant challenge in designing efficient nano-electronic devices. While cutting graphene into nanoribbons can open a band gap, further scaling down graphene nanoribbons will be difficult and costly. Therefore, alternative approaches to further enlarging the band gap based on the current size scale are essential. In this study, we propose a novel method to successfully increase the band gap of 7-armchair nanoribbons by introducing the pre-designed shape of cutting. Additionally, by further manipulating the cutting shape, we also propose a method to increase carrier's mobility while retaining the band gap. These findings represent a significant advancement in optimizing the electrical performance of future carbon-based transistors. The utilization of pre-designed cutting shapes offers a flexible approach to tailor device performance according to specific requirements, thereby enhancing the versatility and functionality of carbon-based electronic devices.

Keywords: Graphene, Nanoscale, DFT, ab initio, nanoribbons, gFET

1. Introduction

The development of the transistor, and corresponding exponential growth of low-cost computing have created a new information age. In recent years, to further the development of digital information systems and ultimately achieve more powerful computers, technology companies have devoted billions of dollars into the research and development of smaller, faster transistors – the building blocks of modern electronics. One such company, Apple, recently unveiled their latest microchip, the M3 Max, consisting of feature sizes as small as 3 nanometers for implementation in their desktops [1]. At the same time, rival companies like Huawei and IBM have developed 7 nanometer and 2 nanometer technology,

respectively, for implementation in their own chips [2,3]. This evolution of information devices has facilitated an international race for the smallest and most efficient computer chips.

Gordon Moore, one of the founders of Intel, predicted in 1968 that the density of transistors on a computer chip would double every two years; Moore's Law, which has remained true for over fifty years, has improved our lives in countless ways [4]. At the same time, this rapid growth of computer integrated circuits focused advancement on lithography – printing smaller feature sizes on silicon single crystal wafers [5]. During the last decade, progress towards a higher density of transistors and faster clock speeds have slowed significantly due to physical limitations, and this has led to an intense effort to find alternative materials that can unblock the continued advancement of computer technology [6-8].

Two-dimensional materials are considered a promising way to overcome the current limitations on continued miniaturization due to their single atom thin structures, and their physical properties. One such material, graphene, is a planar sheet of carbon in a hexagonal arrangement; its applications in electronic devices are currently an active field of research for the development of the future's information devices [9-13]. In fact, graphene has been identified by the semiconductor industry as one of a small number of viable materials with advantageous properties [14]. Namely, in comparison to silicon, graphene's cost of energy is significantly lower; graphene's carrier mobility – a measure of the velocity of carriers (i.e. electrons or holes) – is considerably greater than that of silicon. In other words, an increased velocity of electrons in graphene makes for easier and more efficient conduction of electricity [9,11-12]. Furthermore, graphene can very easily be doped with carriers to improve its conductivity; for graphene, manipulating and controlling the type of doping as well as the doping levels can simply be achieved by applying voltage [12].

However, there is a noteworthy drawback to implementing graphene in electronics: graphene is neither a semiconductor material nor a typical metal. Instead, graphene is a semimetal – the valence band maximum (VBM) and the conduction band minimum (CBM) are in contact at the Dirac point, leaving no band gap [9,15]. In other words, pristine graphene is unable to serve as a semiconductor due to the absence of a band gap.

This study addresses two major challenges in semiconductor technology: miniaturizing semiconductor devices and introducing a band gap in graphene. Quasi one dimensional strips of graphene, called nanoribbons (GNRs), with their atom-scale width, offer a promising solution for the miniaturization of transistors. Additionally, by altering the structure of these nanoribbons, we can achieve semiconducting properties. The focus of our research is thus twofold: firstly, to open a band gap in graphene, and secondly, to manipulate the band structure by precisely cutting the edges of the graphene nanoribbons. These approaches are key to advancing the performance and scalability of semiconductor devices.

While graphene is semimetal, GNRs with a particular edge geometry, called armchair, have been shown to have a bandgap and to act as a semiconductor [16-18]. The armchair edge pattern results from cutting a graphene sheet at an angle of 30 degrees to the primary crystal axis [16]. On the other hand, if a graphene nanoribbon is cut along the primary axis, the resulting edge geometry is called a zigzag pattern. A ribbon with zigzag edges, however, is not a semiconductor; instead, it is a good conductor [16,19].

To generate ideal semiconducting properties for applications in modern electronics, GNRs can be cut and manipulated so they contain both armchair and zigzag edges – thereby achieving band structure engineering. For that reason, the objective of this research is to evaluate and parameterize electronic properties presented in a range of shapes of GNRs, using density functional theory (DFT). This study can enable future research and pave a path for the next generation of engineering nanoscale devices.

Armchair edges can result in band gap opening in the band structure, at the same time, zigzag edges can lead to metallic electronic properties. As cutting the edges can change the configuration of edges along GNRs, we could achieve further band structure engineering by modifying the edges' topography. In this way, we propose a new way to control the band structure of 2D materials for applications in electronics.

In this study we first compare the results of the band structure of graphene and GNRs by using CASTEP with those of previous published studies. After evaluating the properties of a range of widths of armchair and zigzag GNRs the topology of the edges of the nanoribbons is modified to measure the changes this produces in the properties of the bandgap.

2. Methods

In this study, Cambridge Sequential Total Energy Package (CASTEP), a software package which is based on density functional theory (DFT), was used to analyze the properties of structures. First, GNRs with armchair or zigzag edges will be built by cutting graphene [20,22]. Then, geometry optimization of the GNR models is performed to gain the most stable structures. After that, the total energy and the electronic properties, such as the band gap and band structure, are calculated. The same procedure is applied to GNR models with mixed armchair and zigzag edges. The band structure and band gap results of GNRs with armchair edge, zigzag edge, and mixed edge are then compared and analyzed.

DFT is a computational quantum mechanical modeling method for investigating the electronic structure of systems such as atoms and molecules. In practice, DFT involves solving the Kohn-Sham equations, a set of single-particle equations, to achieve the ground state energy. The process of a DFT calculation can be represented as a schematic flow-chart, which involves the following steps: an initial guess for the electron density; solving the Kohn-Sham equations using the initial electron density; calculating a new electron density using electron wavefunctions from Kohn-Sham equations; a self-consistency check between the initial guess and new electron density; and the output. During the self-consistent calculations (SCF), if the difference between the electron density in the current iteration and the density in the previous iteration differ by a tolerance level deemed acceptable, then the calculation is complete; if not, the process is repeated [22].

A band gap, in the context of solid-state physics and chemistry, refers to the energy difference between the top of the valence band and the bottom of the conduction band in a material. This gap represents an energy range where no electron states can exist. In a graph of the electronic band structure of a material, the band gap can be identified as the region between the valence and conduction bands where no energy states are present. Furthermore, the band gap is a crucial property of semiconductors, influencing their electrical and optical properties. For instance, in graphene, the conduction and valence bands meet at the Dirac points, resulting in a zero-band gap.

Altering the band structure, a process known as band structure engineering, is essential for optimizing electronic devices. In the case of graphene, creating a sizable band gap can transform it from a semimetal into a semiconductor, expanding its potential applications in electronics.

3. Results

The DFT computer-based methods used in this study were able to replicate the previously published band structure of an infinite sheet of graphene as shown in Figure 1. In this figure, the y-axis is the energy level, with the valence band below zero eV, and the conduction band above zero eV. The valence band maximum and conduction band minimum meet at the Dirac point that is shown in the middle of the figure - at the K symmetry point in the first Brillouin zone. The x-axis is the band structure along a path from the Γ high symmetry point to the K high symmetry point to the M high symmetry point, back to the Γ high symmetry point in the first Brillouin zone.
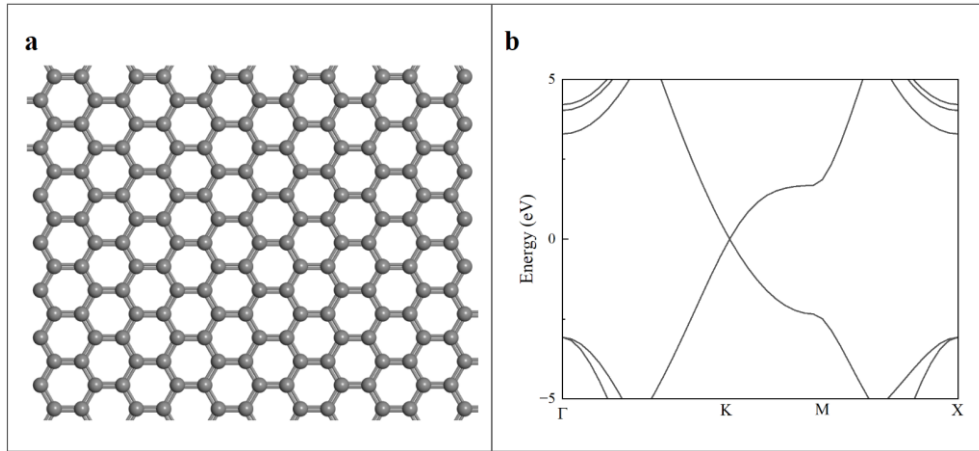
Figure 1. (a) Two dimensional graphene crystal structure. (b) Band structure of graphene.

The mobility of carriers (electrons and holes) can be determined from these band structure diagrams by measuring the curvature of the valence band (holes) and conduction band (electrons) at the point where the bands are closest (K point in Figure 1). Equation 1 below shows the relationship between the effective mass of a carrier, and the second derivative of the energy (E) with respect to the wave number (k). Since the mobility is inversely proportional to the effective mass, a greater curvature ($\frac{d^2E}{dk^2}$) corresponds with a lower effective mass and a higher mobility of carriers.

$$m^* = \hbar\left(\frac{d^2E}{dk^2}\right)^{-1} \tag{1}$$

where $\hbar$ is the reduced Planck's constant, and m^* is the effective mass. (Eq. 1)

The unit cell atomic structures and the band structures of armchair graphene nanoribbons (AGNRs) with various widths are shown in Figures 2-4. The carbon atoms in the ribbons are represented by the solid circles in gray while the hydrogen atoms are indicated by the white circles. These nanoribbons are one-dimensional. A direct band gap can be observed at the Γ high symmetry point.
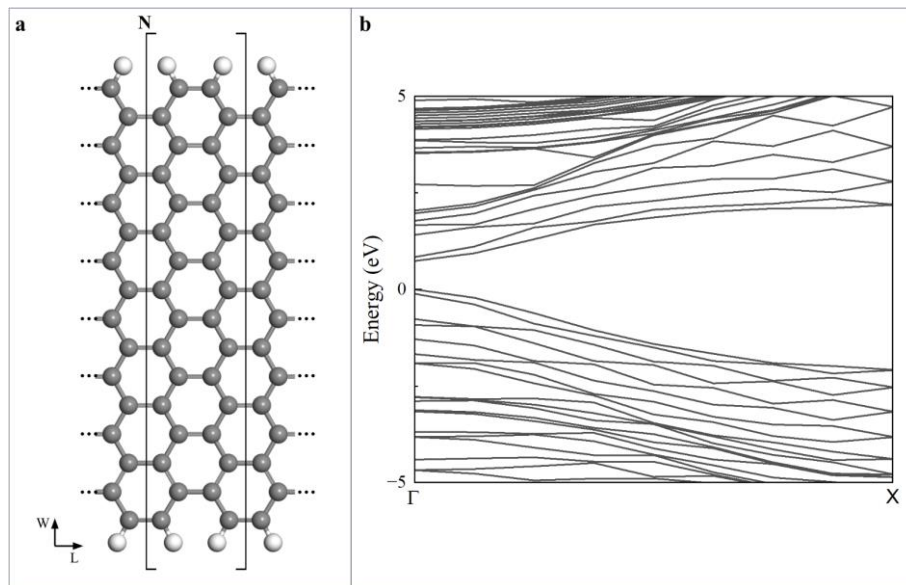

Figure 2. (a) Atomic structure and (b) band structure of 2.04 nm AGNR. Hydrogens (in white) are passivated along the edges of the carbon (in gray) nanoribbon. The bandgap in this GNR is 0.74 eV.
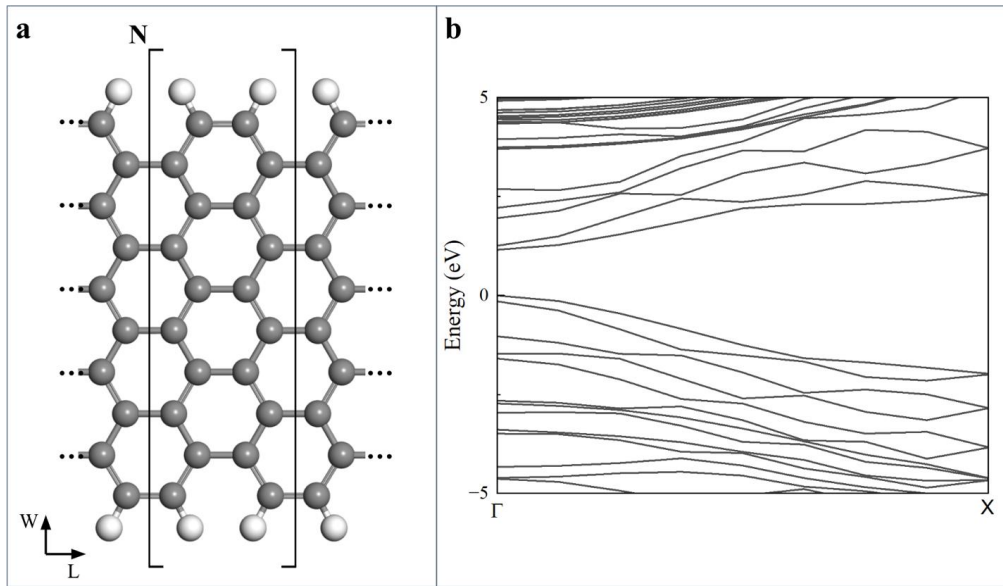
Figure 3. (a) Atomic structure and (b) band structure of 1.30 nm AGNR. The size of the bandgap is 0.90 eV.
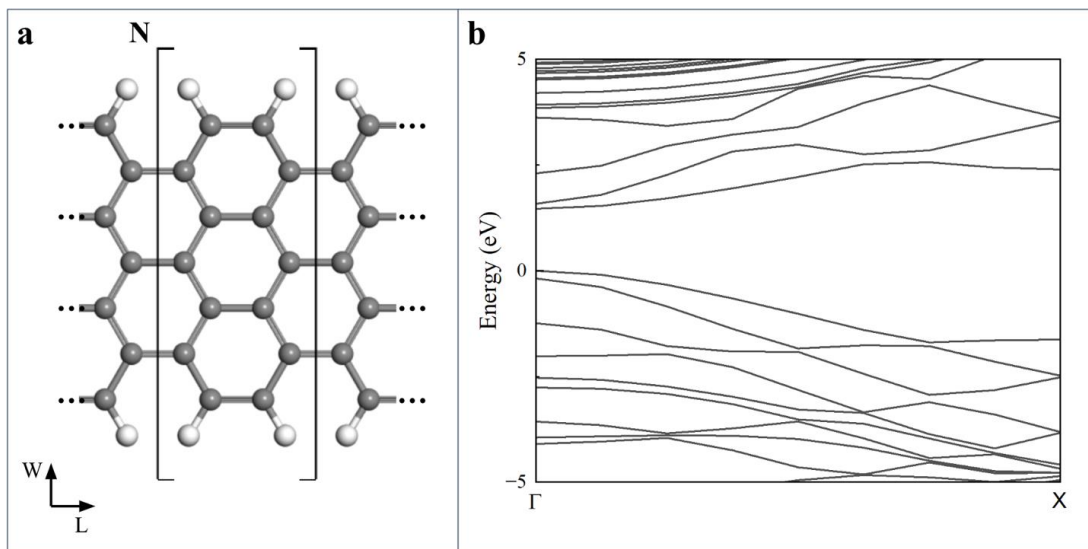

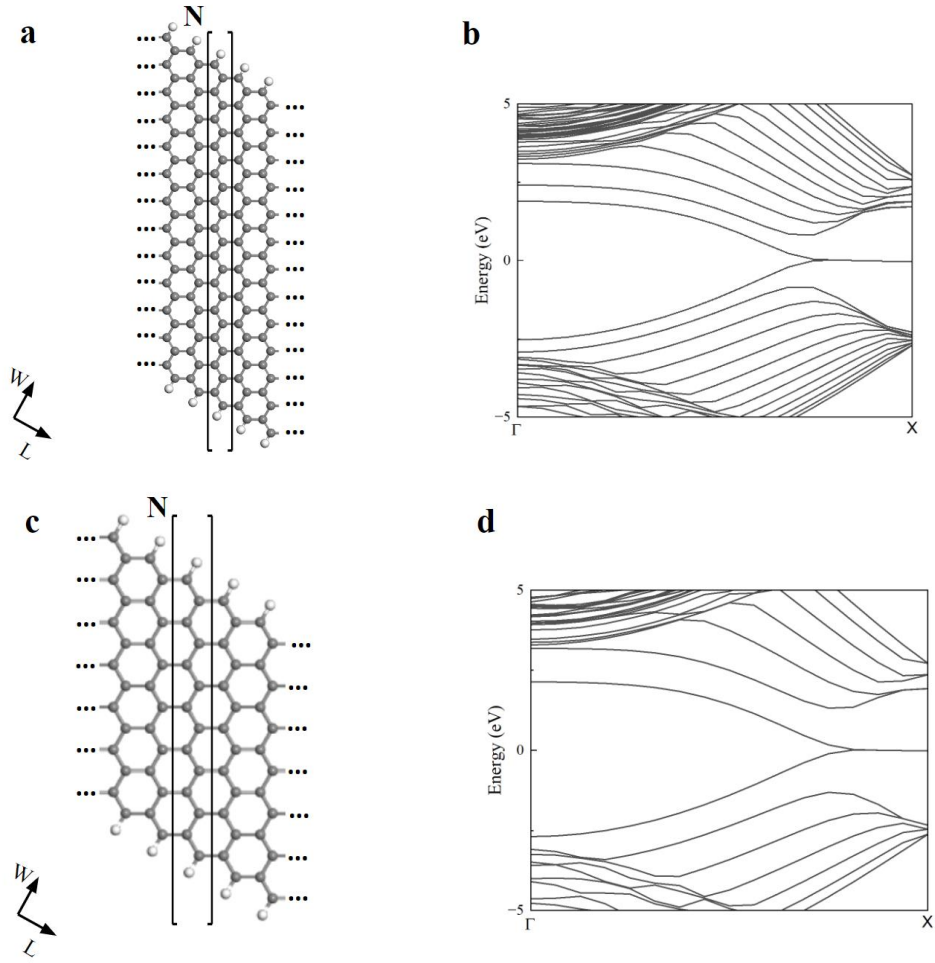**Figure 4.** (a) Atomic structure and (b) band structure of 0.935 nm AGNR.

Figure 5. (a) Atomic structure and (b) band structure of 3.28 nm ZGNR. (c) Atomic structure and (d) band structure of 1.80 nm ZGNR.
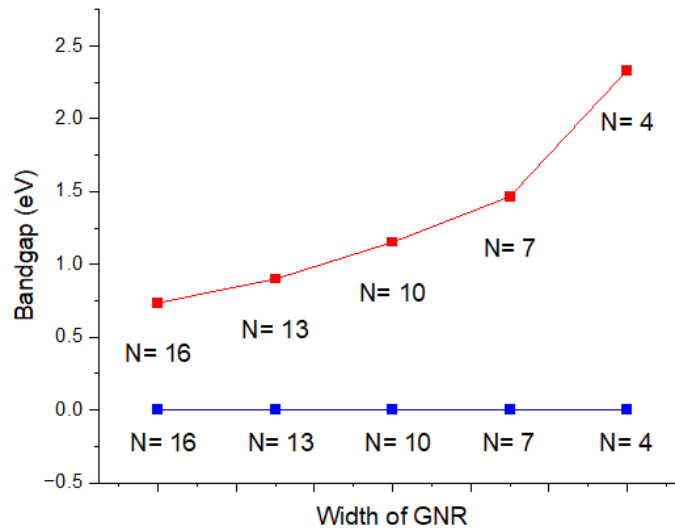

Figure 6. Bandgap comparison of armchair (red) and zigzag (blue) GNRs with different widths.

In Figure 6, comparing the AGNRs with various widths, we note that the size of the band gap decreases as the width of the nanoribbon is increased.

In order to reduce the band gap without increasing the width of the nanoribbon, a range of types of concave cuts were made to the unit cell of the AGNR. Figure 7 shows a depth cut of either 3 or 6 is made into the GNR where a significant change in the shape of the band gap in the first Brillouin zone path is observed. The result of this experiment clearly shows a significant decrease in the band gap with the depth 6 cut.
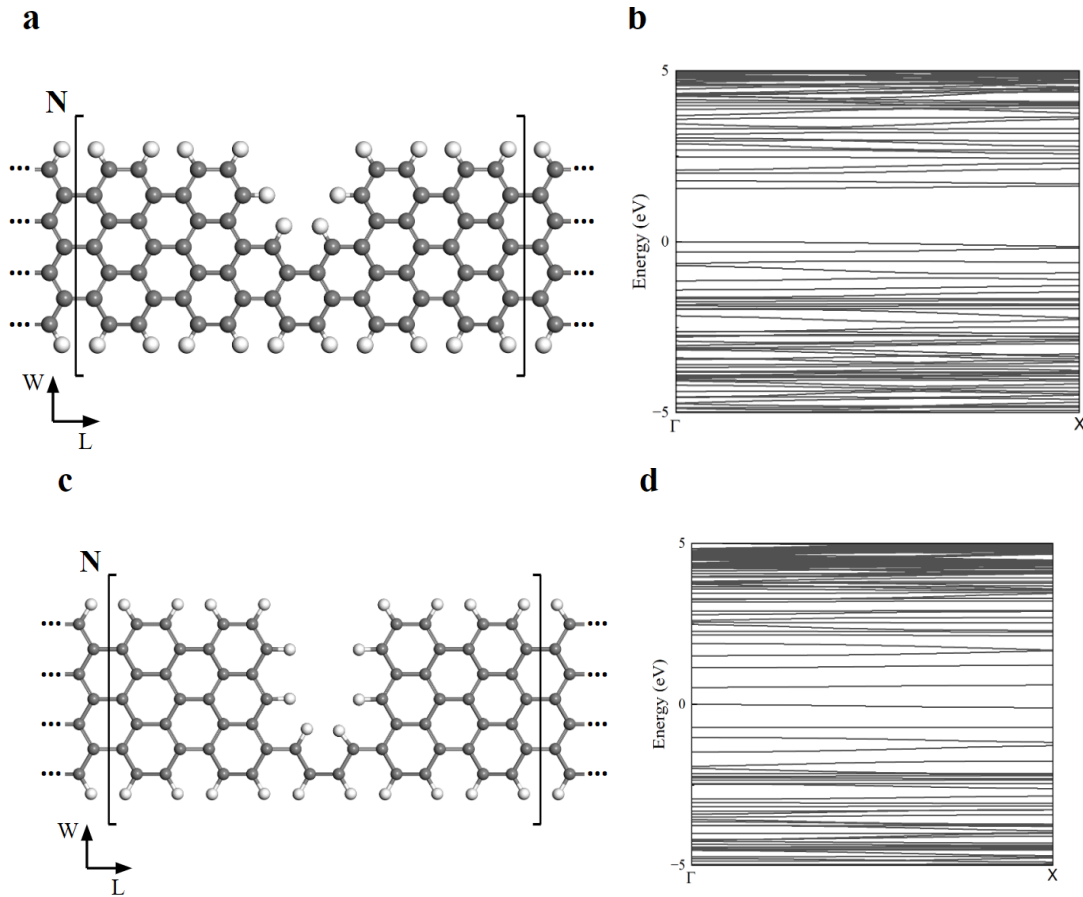

Figure 7. (a) Atomic structure and (b) band structure of 0.935 nm AGNR with a concave of 0.725 nm width and 0.383 nm depth. (c) Atomic structure and (d) band structure of 0.935 nm AGNR with a concave of 0.725 nm width and 0.612 nm depth.

We notice that the band gap decreases significantly with increases in the depth of the concave cut, as shown in Figure 7. However, notice that these periodic depth cuts in the AGNR significantly decrease the mobility of both the electrons and holes as there is very little curvature in k space near the closest point between the valence and conduction bands. In Figure 8, this effect is shown more clearly by looking more closely at the two closest conduction and valence bands of the uncut 7-AGNR and the periodic cut shown in Figure 7 a,b.
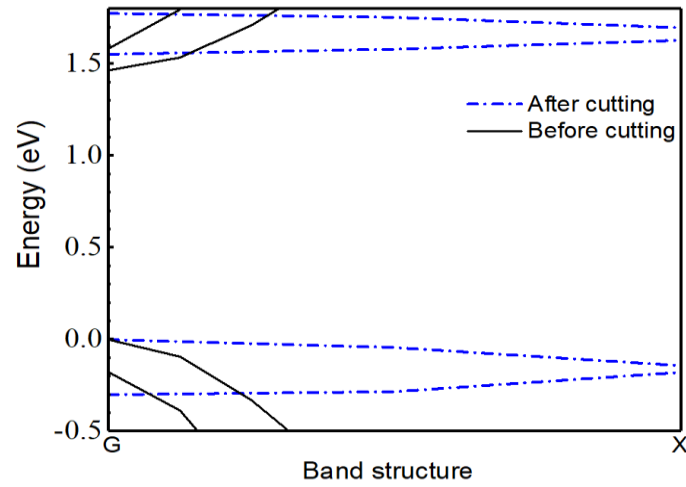
Figure 8. Overlay of two band structures: in blue, the band structure from the cut shown in Figure 7a,b, and in black, the band structure of the uncut 7-AGNR shown in Figure 4.

An additional cut was made to the AGNR shown in Figure 7 a,b to flatten to slope into the depth cut, and this periodic cut is shown in Figure 9. Note that the band gap is decreased, and that the curvature of the energy band at the gamma point is higher. This is highlighted in Figure 10 where the band structure of these two cuts are superimposed. Note that the second cut (shown in the green-dotted line in the figure) has a higher curvature in the energy (E) with respect to the wave number (k) and therefore has a higher mobility of both electrons (conduction band) and holes (valence band).
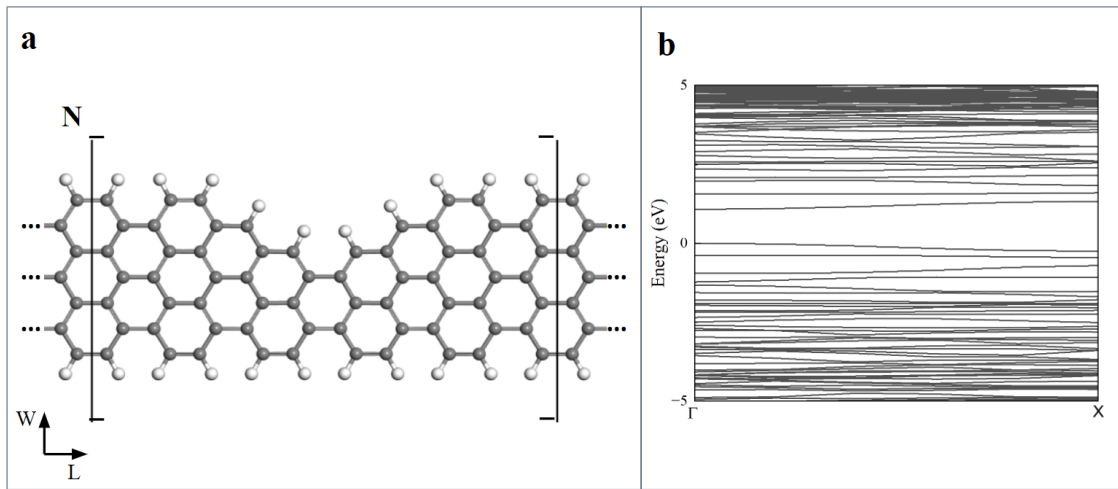

Figure 9. (a) Atomic structure and (b) band structure of 0.935 nm AGNR with a concave of 1.14 nm width and 0.371 nm depth. The resulting bandgap is 1.07 eV.
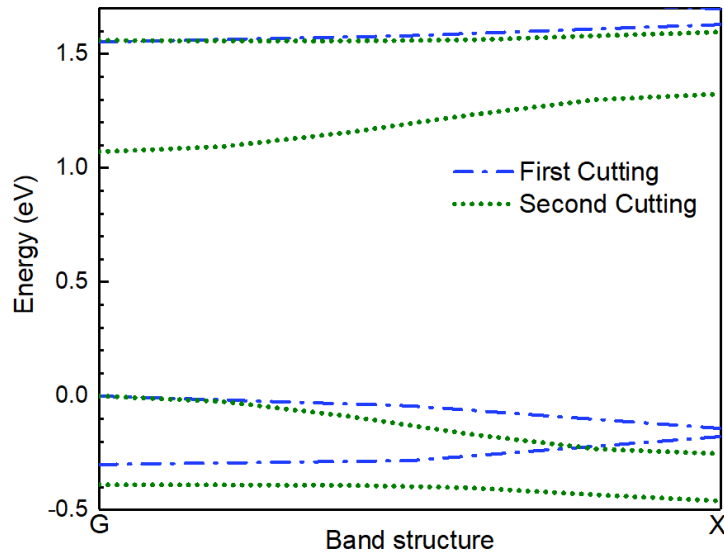
Figure 10. Overlay of two band structures: the initial depth cut 7-AGNR as shown in Figure 7a,b (dashed blue line labeled "First Cutting"), and the more gradual sloped cut shown in Figure 9a,b (dotted green line labeled "Second Cutting").

The impact of concave cuts was also tested on zigzag GNRs (ZGNRs), which occur when the graphene sheet is cut along its primary axis. In all of the periodic cuts where the depth, width, and slope of the cuts were varied on ZGNRs, no band gap was opened and they remained conductors.

4. Conclusion

The DFT based simulation studies conducted here replicated prior published characteristics of graphene sheets, and those of both armchair and zigzag nanoribbons. A range of types of concave cuts to these nanoribbons were tested showing periodic cuts in the armchair graphene nanoribbons change the size of the band gap, but also can adversely affect the mobility of charge carriers. When an additional slope transition into the cut was made an increase in carrier mobility was observed. This suggests that more gradual periodic cuts to armchair graphene nanoribbons may provide a useful means to adjust the bandgap while preserving the carrier mobility.

These results are important as we are currently reaching the limits in size reduction of traditional silicon-based integrated circuits. Ideally, it is useful to construct narrower GNRs that have a band structure that is optimal for the transistor and have high carrier mobility – this research makes progress towards this goal.

A new GNR-based FET could be constructed that uses ZGNRs as conductors and AGNRs with a depth cutout, to create a smaller band gap, between a pair of conductors to create a transistor. The graphene sheet with this type of pattern could be sandwiched between two insulator layers made from silicon dioxide (SiO_2) and additional ZGNR conductors in layers above and below; these insulators could act as a capacitor that turns on the gate.

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