Tuning electronic and magnetic properties of zigzag graphene nanoribbons with a Stone–Wales line defect by position and axis tensile strain

W. X. Zhang,a C. He,ab T. Lia and S. B. Gonga

In this study, the electronic and magnetic properties of zigzag graphene nanoribbons (ZGNRs) with a Stone–Wales line defect (SW LD) under axis tensile strain have been investigated by density functional theory. The calculation results reveal that the axis tensile strain and the position of the SW LD significantly affect the electronic and magnetic properties of the ZGNRs. In the unstrained systems, the SW LD is more stable near the edge, and the antiferromagnetic (AFM) semiconductors have indirect band gaps ($E_g$). With the increasing tensile strain, $\epsilon$, the $E_g$ values of all the AFM semiconducting systems gradually decrease. Moreover, by shifting the SW LD from the center to the edge or increasing the tensile strain, $\epsilon$, semiconductor $\rightarrow$ half-metal $\rightarrow$ metal transition with antiferromagnetic $\rightarrow$ ferromagnetic transfer can be achieved for the systems. The diverse and tunable electronic and magnetic properties enlarge the defective ZGNRs potential applications in electronics and spintronics.

1. Introduction

Graphene consists of a hexagonal monolayer network of sp$^2$-hybridized carbon atoms. When single-layers of graphene were isolated for the first time by mechanical exfoliation,1 the subsequent discovery of its unusual electronic and magnetic properties led to an extraordinary amount of interest and promised a variety of applications.2–5 In addition to some early work,6–7 the possibility of very large one-atom-thick 2D crystals was reported theoretically8–10 and experimentally,11 particularly after large-scale synthesis methods such as chemical vapor-deposition12,13 and epitaxial growth14,15 on metal and SiC substrates were developed.

In addition to extended 2D graphene-like nanosheets, quasi-one-dimensional (1D) graphene nanoribbons (GNRs) with armchair or zigzag edges have also shown unusual electronic,16–24 magnetic,21–26 and quantum-transport properties.27–29 A general method to properly modulate the electronic properties of graphene and GNRs at the nanoscale is chemical functionalization or doping, which has been widely investigated using various techniques.21–23,30–32 Like in other materials, structural defects exist in graphene and can also be deliberately introduced into the host graphene lattice to significantly alter its properties by irradiation or chemical treatments.9,10,33–36 A unique property is that the graphene lattice could reconstruct by forming nonhexagonal rings, which may either introduce curvature in the sheet or leave it flat when the arrangement of the polygons satisfies certain symmetry rules. Furthermore, transmission electron microscopy (TEM)37–39 and scanning tunneling microscopy (STM)40,41 have proven the occurrence of either native or physically introduced defects in graphene by obtaining images of nonhexagonal rings at the atomic scale. Stone et al. reported that the Stone–Wales defect (SW), in which four hexagons are transformed into two pentagons and two heptagons by rotating one of the C–C bonds by 90°, does not involve any removed or added atoms.42 The defected structure retains the same number of atoms as perfect graphene and no dangling bonds are introduced. In graphene, the concept of zero-dimensional point defects is quite similar to bulk crystals, but line defects play a different role.43 It is well-known that defects are not always stationary and that their migration can have an important influence on the properties of a defective crystal. In graphene, each defect has certain mobility parallel to the graphene plane. Generally, the line defects (LD) are tilt boundaries separating two domains of different lattice orientations with the tilt axis normal to the plane, which can be thought of as a line of reconstructed point defects with or without dangling bonds.44–46 Lahiri et al. observed a domain boundary due to lattice mismatch in graphene grown on a Ni surface.44 Banhart et al. proposed that the linear defect corresponding to grain boundaries in graphene should be of paramount importance and grain boundaries may govern the electronic transport in such samples.49 Furthermore, when a linear array of defects are embedded in armchair-GNRs (AGNRs) and zigzag-GNRs (ZGNRs), the hybrid GNRs could exhibit unique electronic and transport properties that differ from

---

*aSchool of Materials Science and Engineering, Chang’an University, Xi’an 710064, China
bState Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, China. E-mail: hecheng@mail.xjtu.edu.cn
perfect AGNRs and ZGNRs. However, a detailed theoretical understanding of the electronic and magnetic properties of these Stone–Wales line defects (SW LD) embedded in ZGNRs remains unclear.

On the other hand, mechanical strain could affect the electronic properties of graphene grown on different substrates and thus have significant impact on their device applications. Ferralis et al. reported that the band gap of AGNRs can change in a zigzag manner under uniaxial strain, which shed light on a flexible approach to fabricate electromechanical devices with graphene-like materials.

Therefore, in this study, the effects of the position of SW LD on the structural, electronic and magnetic properties of ZGNRs are comprehensively studied by density functional theory (DFT). Moreover, the influence of the defect location on these properties under tensile strain, has also been considered. These studies provide us with a deep understanding of the novel properties of defective ZGNRs, which is essential to enrich them for future nanodevices.

2. Computational methods

The simulations are based on density functional theory (DFT), which is provided by DMOL. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof scheme (PBE) was adopted for the exchange–correlation potential to optimize geometrical structures and calculate properties for both spin-polarized and spin-unpolarized cases. A similar functional theory has been successfully used to study the structural and electronic properties of GNRs, water, Si and Cu nanowires. The all-electron relativistic Kohn–Sham wave functions (AER) and double numeric plus polarization (DNP) basis set are adopted in the local atomic orbital basis set for DMOL. The Brillouin zone is sampled by 1 \times 8 \times 1 \times 10 \times 1 k-points for all structures in the geometry optimization (electronic) calculations, which brings out the convergence tolerance of energy of 1.0 \times 10^{-5} Ha (1 Ha = 27.2114 eV), a maximum force of 0.002 Ha Å^{-1}, and a maximum displacement of 0.003 Å. Based on the optimized structures, the axis tensile strain, \( \varepsilon \), along the ZGNRs axis direction is modulated by the corresponding lattice parameters. For geometry optimization, both the cell and the atomic positions are allowed to completely relax to find the equilibrium states. Periodic boundary conditions are adopted for all utilized models in this work. To ensure the interactions between the defective ZGNR, the vacuum of 15 Å is added both to neighboring cells and along the width direction. All electronic and magnetic properties of the systems were calculated in their ground states, which were identified by comparing the energies of their nonmagnetic state (NM), ferromagnetic coupling (FM), and antiferromagnetic coupling (AFM). The one with the lowest energy is the ground state.

3. Results and discussion

In our simulation, ZGNRs with \( W = 10 \) (10-ZGNRs) were analyzed, where the nanoribbon width (W) is defined by the number of zigzag chains perpendicular to the axial direction. For 10-ZGNRs with SW LD, two pentagons and two heptagons (SW defect) are symmetrically arranged along the nanoribbon axial direction, which are shown in Fig. 1a–e. As shown in Fig. 1a, when the C–C dimer lines are replaced by SW defect at the middle part of the 10-ZGNRs (4 zigzag chains on both sides of the C–C dimer lines), the SW LD locates at the center of ZGNRs. Thus, this type of defective ZGNR can be considered as two ZGNR parts connected by C–C dimer lines. The structures shown in Fig. 1b–e are constructed by gradually moving the position of the SW LD along the C–C dimer lines from the center to the left edge of the 10-ZGNRs. Here the systems consisting of 10-ZGNRs with SW LD are named \( n \)-SW-\( m \), where \( n \) and \( m \) are the number of zigzag chains on the left and right sides of the C–C dimer lines, respectively. The dangling bonds at both edges are saturated by hydrogen atoms for all systems.

In order to study the preferred coupling of these moments, we calculated the energies of NM, FM, and AFM for the 4-SW-4, 3-SW-5, 2-SW-6, 1-SW-7, and 0-SW-8 systems. The calculated energies of the AFM state for the 4-SW-4, 3-SW-5, 2-SW-6, and 1-SW-7 systems are comparatively lower than those of the FM and NM states. Thus, the ground state in these systems is the AFM state. For the 0-SW-8 system, the FM state is more energetically favorable. The results demonstrate that when a SW LD is introduced, the position of the SW LD has a great effect on the magnetic configurations of the \( n \)-SW-\( m \) systems. As the SW LD moves from the center to the left edge, the systems experience a transition from the AFM to FM state.

Once their ground states were confirmed, the relative stability of these \( n \)-SW-\( m \) systems was subsequently investigated to search for the most stable structure. Their total energies by choosing the energy of the 4-SW-4 system as a reference are shown in Fig. 1f. The results show that the total energies of the \( n \)-SW-\( m \) systems become more and more negative and thus the system becomes increasingly stable as the SW LD shifts away from the center. Particularly, there is a large drop in energy from the 2-SW-6 to 0-SW-8 system, which indicates that the SW LD near the edge is more favorable.

Fig. 2a–e displays the spin-polarized band structures of the five \( n \)-SW-\( m \) systems. It can be seen that the band structures of the \( n \)-SW-\( m \) systems vary with the different locations of the SW (55–77) LD in the ZGNRs. The energy bands of the 4-SW-4 system for both spins degenerate, whereas for the other \( n \)-SW-\( m \) systems, the energy bands near the \( E_f \) split into two sub-bands (spin up and spin down) and exhibit some deformation. When the SW LD shifts away from the center, the degree of splitting and deformation becomes stronger. The band gap of the \( n \)-SW-\( m \) systems is defined by the energy difference between the conduction band minimum (CBM) and the valence band maximum (VBM), i.e., \( E_g = CBM - VBM \). CBM and VBM are each characterized by a certain crystal momentum (\( k \)-vector) in the Brillouin zone. As shown in Fig. 2a–c, because the \( k \)-vector of the CBM and VBM are different, the three systems of 4-SW-4, 3-SW-5, and 2-SW-6 are semiconductors with indirect \( E_g \). As the SW LD moves gradually to the left edge, the \( E_g \) values for the three semiconductors decrease gradually and the corresponding \( E_g \) values of each semiconducting \( n \)-SW-\( m \) system are 0.297 eV, 0.217 eV and 0.054 eV. Compared with our calculated \( E_g \) value of...
0.38 eV for perfect 10-ZGNRs, the $E_g$ values of these three semiconducting systems decrease because the impurity states near the $E_f$ is induced by the SW LD. When the SW LD appears near the edge in the other two systems (1-SW-7 and 0-SW-8), their electronic properties exhibit unusual features, which differ from the characteristic semiconducting features. In Fig. 2d, the 1-SW-7 system exhibits a half-metallic character, where the spin up and down states show its semiconducting and metallic behaviors, respectively. For the 0-SW-8 system, as shown in Fig. 2e, there is no $E_g$ opening for both the spin up and down states, which displays a distinguished metallic behavior. In addition, compared with the other $n$-SW-$m$ systems, the energy bands of the 0-SW-8 system significantly change near the $E_f$.

Next, we studied the influence of axis tensile strain, $\epsilon$, on the electronic properties of these $n$-SW-$m$ systems. For the semiconducting systems, the axis tensile strain, $\epsilon$, always reduces $E_g$ to zero rapidly, where a transition from semiconductor to half-metal appears. The corresponding $\epsilon_c$ values for the electronic transition (semiconductor $\rightarrow$ half-metal) are 2.5%, 2.0%, and 1.2% for the 4-SW-4, 3-SW-5, and 2-SW-6 systems. On further increasing the axis tensile strain, $\epsilon$, the transition from AFM half-metallic to FM metals for the three systems will occur quickly. The spin-polarized band structures of the three semiconducting systems were calculated to better understand the effects of axis tensile strain, $\epsilon$, on their electronic properties, which are shown in Fig. 3. With an increase in axis tensile strain, $\epsilon$, the electronic distributions of the bands near the $E_f$ become apparently asymmetric between the spin up and down bands. When the three systems become AFM half-metals, the spin up and down channels show semiconducting and metallic behaviors, respectively, as shown in Fig. 3. As $\epsilon$ further increases to the critical transition value (AFM half-metallic to FM metals) for each system, the bands near the $E_f$ experience stronger spin splitting, as shown in Fig. 4.

Moreover, in order to deeply describe the electronic structure of the $n$-SW-$m$ systems, the corresponding electronic distributions at the Gamma point have been explored. For the three semiconducting systems (4-SW-4, 3-SW-5, and 2-SW-6) and the half-metallic system (1-SW-7), the electronic distributions of bands display similar behaviors. Thus, taking the 3-SW-5 system as an example (in Fig. 4a), the highest occupied molecular orbital (HOMO) is mainly localized on the edge C atoms and the lowest unoccupied molecular orbital (LUMO) is primarily localized on the defect C atoms, where the $E_g$ of this system is determined by the two sub-bands. More interestingly, for HOMO $- 4$ (the fourth orbital under HOMO), the electronic states mainly distribute on the left edge and defect site, which indicates that a strong interaction exists between the left edge and defect site due to serious deformation as the SW LD moves to the left edge. Moreover, LUMO + 4 (the fourth orbital up LUMO) is completely localized on the right edge of the defective...
ZGNRs. Both of the electronic distributions for HOMO – 4 and LUMO + 4 also distribute along C–C bonds.

According to the total density of states (DOS) and partial DOS for the 3-SW-5 system in Fig. 4b, the electronic states near the $E_f$ are determined by both the defect C atoms and the two edges of the ZGNRs, which correspond to the former results which show that the impurity states appear near the $E_f$. The results of the calculated ground states and the partial DOS demonstrate that the SW LD introduces impurity states within the $E_g$ of the perfect ZGNRs, thus leading to the reduction of the $E_g$ for the semiconducting 4-SW-4, 3-SW-5, and 2-SW-6 systems.

For the metallic 0-SW-8 system, as shown in Fig. 4c, the HOMO orbital is only localized on the right edge of the ZGNRs and the LUMO orbital distributes on the defect sites. The
HOMO − 4 and LUMO + 4 charge densities are mainly centered at single C atoms. However, the densities are inhomogeneous over the whole region.

In addition, the HOMO − 4, HOMO, LUMO and LUMO + 4 for 3-SW-5 with ε = 5.0% are shown in Fig. 4d for comparison. For the 3-SW-5 system at the FM state, the HOMO orbital is mainly localized on the right edge C atoms and the LUMO orbital is completely contributed by the defect C atoms. For HOMO − 4, the electronic states mainly distribute on the left edge and defect sites along the periodic direction, whereas LUMO + 4 are localized along C–C bonds in a uniaxial direction.

The results of the magnetic properties for these n-SW-m systems are shown in Fig. 5. As shown in Fig. 5a and b, for the 4-SW-4 and 3-SW-5 systems, the two edges of the ZGNRs are still antiferromagnetically coupled, and the magnetism on the atoms connected to the C–C dimers is also antiferromagnetically aligned. Because ZGNRs with SW LD could be considered as a combination of two ZGNR parts aligned C–C dimers, the atoms connected with the C–C dimers are antiferromagnetically coupled, which is similar to the case of perfect ZGNRs. Moreover, the half-metallic system and the semiconducting systems exhibit a similar magnetic ordering and the rest of their magnetic moments are zero. However, for the metallic system 0-SW-8 [Fig. 5c], the ground state is FM and the magnetic alignment on the two edges of the system becomes FM ordering, which results in a net magnetic moment of 1.17 μB. This clearly indicates that the magnetic moment is mainly contributed by the C atoms on the right edge.

Considering the symmetrical characteristic of the SW LD, a similar effect of the defect location on the electronic and magnetic properties could be drawn as the SW LD moved to the right edge.

Similarly, the magnetic properties of these n-SW-m systems with or without axis tensile strain, ε, are also discussed. The energy difference ΔE between the EFM and EAFM of the n-SW-m systems has also been calculated. For the half-metallic 1-SW-7 system in the unstrained case, the ground state favors the AFM configuration. When ε ≥ 1.5%, the system changes into the FM state. On further increasing ε, the metallic 0-SW-8 system does not change the FM ground state and still remains in the FM configuration, even though the initial spin configuration is set as the AFM state. For the three semiconducting systems (4-SW-4, 3-SW-5, and 2-SW-6), when ε = 0, ΔE > 0 and their ground states are of AFM configurations, which are discussed above. As ε increases, ΔE decreases gradually. Then, at the critical ε (εc) of 2.8%, 2.6%, and 1.9%, the AFM → FM transitions take place with ΔE < 0 for the three systems. In addition, it is clear that εc for this magnetic transition decreases gradually as the SW LD shifts away from the center. Further increasing axis tensile strain, ε, will lead to the ΔE becoming more negative, which indicates that the FM states for these systems become more stable. Moreover, for the three semiconducting systems, the magnetic alignment on the edges and the defect site under ε are similar. The spin density distributions (Δρ = ρup − ρdown) for 3-SW-5 under different strain (the axis tensile strain ε = 1.0%, 3.0%, and 5.0%) are shown in Fig. 6. In the AFM state (ε = 1.0%), the spin ordering is antiferromagnetically coupled between the two edges, but ferromagnetically coupled along the C atoms connected to the C–C dimers, and the total magnetic moment is small. With the increasing axis tensile strain, ε, when ε ≥ εc, the magnetic configuration of the system becomes the FM state, in which the magnetic coupling between the two edges changes from antiparallel to parallel. Moreover, the spin densities on the two edges and the SW LD increase with increasing ε, which is consistent with the enhanced stability of the FM state. The situation for the other semiconducting systems, 4-SW-4 and 2-SW-6, is similar.

The total magnetic moments of all the n-SW-m systems under ε were also studied. The calculated results demonstrate that the magnetism is mainly contributed by the two edges and the SW LD. As ε increases, the total magnetic moments of these systems change from 0.72 to 2.1 μB, and the magnetic moments on the two sites increase slowly.

Finally, we summarize the computed properties for n-SW-m versus axis tensile strain, ε, in Fig. 7. Clearly, the intriguing and diverse transformation in the electronic and magnetic properties of the novel SW LD systems remarkably depends on the line defect sites. As the SW LD moves from the center to the edge, in the unstrained systems, semiconductor → half-metal → metal.
(AFM → FM) transitions can be achieved. Under axis tensile strain, $\varepsilon$, the $E_g$ values of all the semiconducting systems decrease gradually. The critical transition $\varepsilon$ values of each system are also shown in Fig. 7. Our results predict that effectively controlling the LD sites is a tunable way to modulate the electronic and magnetic properties of ZGNRs.

4. Conclusions

In summary, we have investigated the modulation of structural, electronic and magnetic properties by changing the SW LD locations and axis tensile strain of 10-ZGNRs by density functional theory. In the unstrained systems, the SW LD is more stable near the edge and AFM semiconductors have indirect band gaps. As the SW LD moves from the center to the edge, a semiconductor $\rightarrow$ half-metal $\rightarrow$ metal (AFM $\rightarrow$ FM) transition can be achieved. With the increasing tensile strain, $\varepsilon$, the $E_g$ values of all the AFM semiconducting systems gradually decrease and AFM semiconductor $\rightarrow$ AFM half-metal $\rightarrow$ FM metal transitions also occur for each system. These diverse properties are of fundamental significance and they open up exciting opportunities for the design of novel nanoelectronic spintronic devices.

Acknowledgements

The authors acknowledge supports by the National Natural Science Foundation of China (NSFC, nos 51177006, 51301020 and 51471124), the Natural Science Foundation of Shaanxi province, China (2014JQ6196), PhD Programs Foundation of Ministry of Education of China (Grant no. 20110201120002), the special fund for basic scientific research of central colleges of Chang’an University (no. 2013G1311053) and State Key Laboratory for Mechanical Behavior of Materials.

References