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Strain effect on electronic structures of graphene nanoribbons: A first-principles study

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We report a first-principles study on the electronic structures of deformed graphene nanoribbons (GNRs). Our theoretical results show that the electronic properties of zigzag GNRs are not sensitive to uniaxial strain, while the energy gap modification of armchair GNRs (AGNRs) as a function of uniaxial strain displays a nonmonotonic relationship with a zigzag pattern. The subband spacings and spatial distributions of the AGNRs can be tuned by applying an external strain. Scanning tunneling microscopy dI/dV maps can be used to characterize the nature of the strain states, compressive or tensile, of AGNRs. In addition, we find that the nearest neighbor hopping integrals between π -orbitals of carbon atoms are responsible for energy gap modification under uniaxial strain based on our tight binding approximation simulations. © 2008 American Institute of Physics. [DOI: 10.1063/1.2958285]

I. INTRODUCTION

Nanoscale carbon materials including fullerenes and carbon nanotubes have attracted a great deal of research interest owing to its versatile electronic properties.^{1,2} Among them, graphene fabricated first by Novoselov *et al.*³ has been studied extensively. Many interesting properties of this kind of layered two-dimensional carbon nanostructure, such as the Landau quantization,⁴ the integer quantum-Hall effect,^{5,6} and the quantization minimum conductivity,⁷ have been investigated by several experimental and theoretical research groups. Now much attention has focused on graphene nanoribbons (GNRs) with various widths, which can be realized by cutting the exfoliated graphene or by patterning graphene epitaxially.^{6,8} The edge carbon atoms of GNRs have two typical topological shapes: namely, armchair and zigzag. The novel electronic, magnetic, reactivity, and transport properties of zigzag and armchair GNRs (ZGNRs and AGNRs) have attracted great research interests.^{9–20} Due to the one-dimensional character, the edge states of GNRs have been comprehensively studied, ranging from the band gap dependence on nanoribbon width,^{12,13} metal-to-insulator transition with addends¹³ to the unique chemical reactivity,^{15–17} and the magnetic coupling.^{18,21,22} Actually, the various spin-polarized electronic structures of ZGNRs and AGNRs can be tuned by the different edge modifications and magnetic impurities.^{14,15,17,23} Son *et al.*²² predicted that ZGNRs become half-metallic when an external transverse electric field is applied, while Rudberg *et al.*²⁴ argued that nonlocal exchange effect removes this half-metallicity. Recently, several groups^{14,23,25} have clearly clarified that the nonlocal ex-

change effect results in a slight quantitative difference from the numerical results at the generalized gradient approximation (GGA) level. Note that the ZGNRs with different symmetries have two distinctly different kinds of transport behaviors,²⁰ and the symmetry breaking of a graphene sheet induces a dipole, leading to a flexoelectric effect.²⁶

The capability to control GNRs' electronic properties is highly desired to build future nanodevice directly on GNRs. For example, the electronic structures of AGNRs can be altered through the chemical edge modification and impurities.^{13–18,27} Another possible effective way is to apply external strain since previous studies have indicated that the uniaxial strain significantly affects the electronic properties of nanoscale carbon material.^{28–30} Existing theoretical works focus on the electronic structure and magnetic and transport properties of GNRs;^{19–24,31,32} nevertheless, more attention should be paid to the geometric deformation effect. Chang *et al.*³³ investigated the deformation effect on the electronic and optical properties of nanographite ribbons using the Hückel tight binding (TB) model. In this paper, we perform a theoretical study on the effect of strain on the electronic structures of GNRs at the density functional theory (DFT) level. The calculated results show that the uniaxial strain does not impact the electronic structures of ZGNRs significantly, while the energy gap, the subband spacings, and the spatial distributions of AGNRs are modified by the external strain. Based on the tight binding simulations, we find that the nearest neighbor hopping integrals between the π -orbitals of carbon atoms are responsible for the energy gap modification under uniaxial strain.

II. COMPUTATIONAL METHOD AND MODEL

We apply DFT with GGA implemented with the DMol³ package.³⁴ The Becke exchange gradient correction and the

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FIG. 1. (Color online) Schematic of an AGNR with width $W=13$. Here, the one-dimensional unit cell distance between two dash-dotted lines is represented by r . The blue atoms denote that hydrogen atoms passivate the edge carbon atoms (black dots). Four kinds of carbon-carbon bond lengths are labeled with a_1 – a_4 .

Lee–Yang–Parr correlation gradient correction (BLYP) are adopted.³⁵ The basis set consists of the double numerical atomic orbitals augmented by polarization functions. The calculations are all-electron ones with scalar relativistic corrections. Self-consistent field procedure is carried out with a convergence criterion of 5.0×10^{-5} a.u. in energy and electron density. Geometry optimizations are conducted with convergence criteria of 5×10^{-3} in the gradient, 5×10^{-3} in the displacement, and 5×10^{-5} a.u. in energy. Medium grid mesh points are employed for the matrix integrations, the real-space global cutoff radius of all atoms is set to be 5.5 Å, and uniformly 128 K points along the one-dimensional Brillouin zone are used to calculate the electronic structures of the AGNRs and ZGNRs. As a fundamental issue with DFT-based calculations, it is worth to examine the sensitivity of the numerical results to the adopted exchange and correlation approximation. Fortunately, previous calculations^{14,23,25} have shown that the results based on the hybrid density functional and local density functional plus Hubbard parameter U methods are qualitatively consistent with the GGA ones. Here, we adopt the BLYP exchange-correlation functional in the present work.

In our calculations, AGNRs with widths $W=12$, 13, and 14 are chosen to represent three typical families (corresponding to $3n$, $3n+1$, and $3n+2$, respectively), similar to the previous theoretical studies.^{12,13} As an example, the schematic of an AGNR with width $W=13$ is shown in Fig. 1. To avoid the effects of the σ electronic states near the Fermi level, the dangling bonds of edge carbon atoms ZGNRs and AGNRs are saturated by hydrogen atoms. All atomic positions of GNRs atoms are allowed to relax by using a rectangular supercell, in which a GNR is set with its edge separated by at least 10 Å from the neighboring GNRs.

III. RESULTS AND DISCUSSION

As a benchmark, the electronic structures of AGNRs with zero strain are calculated. The energy gaps are 0.55, 0.90, and 0.19 eV for the AGNR with widths $W=12$, 13, and 14, respectively, which agree nicely with the previous DFT results.¹² The deformation of AGNRs can be represented by the strain (ϵ), defined as $\epsilon = (r - r_0)/r_0$, where r and r_0 are the deformed and initial equilibrium lattice constants ($r_0 = 4.287$ Å) along the axial direction of AGNRs.³⁶ Note

FIG. 2. (Color online) (a) Band structures of AGNRs with width $W=13$. Here, the uniaxial strains (ϵ) are set as -4.0% , -0.8% , 0.0% , 3.0% , 7.3% , and 10.0% and are labeled A, B, C, D, E, and F, respectively. (b) The spatial distributions and energy variations of these subbands (v1, v2, c1, and c2) near the Fermi surface of the deformed AGNRs with different strains. Four lines are sketched to track energy level variations.

that the symmetry of AGNRs remains invariant during the deformation. For example, the AGNRs with width $W=13$ keeps the D_{2h} symmetry regardless of strain, which is much lower than D_{6h} , the symmetry of infinite two-dimensional graphene layer.

We first investigate the electronic structures for AGNR with width $W=13$ under a series of uniaxial strains, as shown in Fig. 2(a), where $\epsilon = -4.0\%$, -0.8% , 0.0% , 3.0% , 7.3% , and 10.0% were labeled A, B, C, D, E, and F, respectively. They all exhibit direct band gaps at the Γ point. It is clear that the subband spacings and energy gap of the deformed AGNRs are tunable with uniaxial strain. The obvious difference among band structures of the deformed AGNRs under six different given ϵ values is the energy positions of two upmost valence subbands (v1 and v2) and two lowest conduction subbands (c1 and c2). Since the energy of a specific band depends on the C–C overlap integrals and the C–C bond geometries, it is expected that these subbands will respond to the applied uniaxial strains differently. Four subbands (v1, v2, c1, and c2) separate at the Γ point when the applied strain (ϵ) is -4.0% (case A). We observe that two valence subbands (v1 and v2) and two conduction subbands (c1 and c2) nearly degenerate and the gap reaches the maximal energy gap of 1.0 eV when the compressive deformation is -0.8% (case B). The subbands separate gradually and the gap decreases almost linearly as the tensile strain increases (case C–D). When the strain increases continuously to 7.3% (case E), the subband separation between v1 and c1 decreases to 0.03 eV, which corresponds to the minimal energy gap case. When ϵ further increases to 10.0% (case F), four subbands will separate again.

Figure 2(b) presents the spatial distributions of wave functions literally corresponding to the four subbands (v2, v1, c1, and c2) under six different uniaxial strains at the Γ

FIG. 3. (Color online) Simulated STM dI/dV maps of the deformed AGNRs with width $W=13$. (a) and (b) stand for dI/dV maps of the AGNR with $\varepsilon=-4.0\%$ at $E=0.36$ and -0.36 eV, (c) and (d) for $\varepsilon=3.0\%$ at $E=0.28$ and -0.28 eV, respectively. Here, the deformed AGNRs are modeled with a 1×3 superlattice and the tip-sample distance is $4 \text{ \AA}$.

point. These subbands can be classified into two kinds of states: the vertical bonds along the periodic direction (denoted as VB) and the parallel bonds perpendicular to the periodic direction (denoted as PB). Two subbands c1 and v2 are VB states, two subbands c2 and v1 are PB states for the AGNRs with strain $\varepsilon=-4.0\%$ (case A), while the AGNRs is elongated ($\varepsilon=3.0\%$, case D), c2 and v1 are tuned to be VB states, and c1 and v2 have PB features. Clearly, the spatial distributions of frontier subbands can be significantly manipulated by the external strain.

Since a scanning tunneling microscopy (STM) dI/dV spatial map is approximately proportional to the local density of states (LDOS) at a specific energy,^{37–39} the energy-resolved STM dI/dV mapping technique is expected to explore the LDOS of the AGNR with different strains. Here, we adopt the Tersoff–Hamann model.⁴⁰ This method has been successfully applied to explain the experimental results,³⁸ which allows us to obtain STM dI/dV maps based on the LDOS of the sample surface. The theoretical dI/dV maps of the deformed AGNRs with width $W=13$ (case A, $\varepsilon=-4.0\%$) at $E=0.36$ and -0.36 eV are shown in Figs. 3(a) and 3(b), while (c) and (d) are the simulated dI/dV maps of the AGNRs with $\varepsilon=3.0\%$ (case D) at $E=0.28$ and -0.28 eV, respectively. It is clear that the STM dI/dV maps are energy dependent. For the AGNR with compressive strain ($\varepsilon=-4.0\%$), the STM dI/dV map at $E=0.36$ eV has twofold symmetry with the highlighted edges and some bright spots at the central region, which are mainly contributed by the subband c1. The dI/dV map of this compressive AGNR at $E=-0.36$ eV is dominated by short bright stripes, manifesting the orbital that corresponds to the subband v1, perpendicular to the periodic direction. Interestingly, the spatial character of these simulated dI/dV maps shows a strong contrast to those of AGNR under tensile strains with $\varepsilon=3.0\%$ (case D). The dI/dV maps of the elongating AGNR (case D) at $E=0.28$ and -0.28 eV are close to the results of case A at $E=-0.36$ and 0.36 eV, respectively. These observations show that it is possible to utilize STM dI/dV maps to characterize the nature of the strain states, compressive or tensile, of AGNRs.⁴¹

FIG. 4. (Color online) Variation of the energy gaps (E_g) for the AGNRs with widths $W=12$, 13 , and 14 as a function of the strain (ε). Variation of E_g as a function of ε for three family structures with different widths, (a) $W=3n$, (b) $W=3n+1$, and (c) $W=3n+2$ ($n=4, 6$, and 8).

Now we turn to an energy gap modification, which has technique importance. For instance, the extensive work committed to tune the energy gaps of GNRs and silicon nanowires by various means.^{13,42} To present clearly the energy gap modification, we have shown the variations of energy gap of AGNRs with widths $W=12$, 13 , and 14 as a function of ε in Fig. 4(a) with filled square, circle, and triangle symbol lines, respectively. The calculated maximal values of E_g for the AGNR with widths $W=12$, 13 , and 14 are 1.07 , 1.00 , and 0.97 eV appearing at $\varepsilon=5.0\%$, -0.8% , and 9.5% , respectively, while the minimal values of E_g are 0.02 , 0.03 , and 0.03 eV, which occur at $\varepsilon=-4.5\%$, 7.3% , and 1.3% , respectively. The shapes of the calculated curves display a zigzag feature for three different ribbon widths and the energy gaps change almost linearly between two neighboring turning points by changing the ε . It is clear that the energy gap is sensitive to the external strain (ε). This delicate electromechanical coupling of AGNRs suggests one interesting application of AGNRs as strain sensors.

The variations of the energy gaps of three family structures with different widths ($W=3n$, $3n+1$, and $3n+2$, where $n=4, 5$, and 6) as a function of ε are shown in Figs. 4(b)–4(d), respectively. Obviously, the following are several common features for all AGNRs. (1) The energy gap decreases when the width of AGNRs increases without external strain. (2) The minimal energy gaps of all deformed AGNRs are of the order of several meV, while the maximal energy gaps are sensitive to the width of the deformed AGNRs and the values decrease as the width of AGNRs increases. For example, the maximal values of energy gaps are 1.07 , 0.74 , and 0.56 eV for the deformed AGNRs with width $W=3n$ ($n=4, 6$, and 8), which appear at $\varepsilon=9.5\%$, 6.6% , and 4.8% , respectively, as shown in Fig. 3(b). (3) The zigzag feature here is universal for all deformed AGNRs. (4) Clearly, the separation of strains between two turning points becomes shorter when the width of AGNR increases, which suggests that the tunability of the energy gap becomes weaker for the

FIG. 5. (Color online) (a) Four kinds of C–C bond lengths of the deformed AGNRs with width $W=13$ as a function of ε . (b) The variation of the band gap obtained by TBA method for AGNRs with $W=12, 13$, and 14 as a function of the nearest neighbor hopping integral t_1 . (c) The maximal value of energy gap of AGNRs obtained from TBA results vs the ribbon widths with three family structures ($W=3n, 3n+1$, and $3n+2$, where n is an integer).

wider AGNRs. (5) The previous TB studies reported that the uniaxial strain could lead to the semiconductor-metal transition for the AGNRs.³³ Here, it should be pointed out that the exact semiconductor-to-metal transition is not achieved from DFT calculations by either elongating or compressing the AGNRs. To observe such a semiconductor-to-metal transition, the crossing of subbands $v1$ and $c1$ is required. However, the special geometry of AGNR and orbital interaction prevent this type of interband crossing. The tendency of metallic transition can lead to appreciable structural distortion, which is the origin of the slight kinks located at about $\varepsilon=7.3\%$ in Fig. 5(a).

TB simulations of hydrogen-passivated AGNRs could reproduce the DFT results through the introduction of an additional hopping parameter to incorporate edge effects.^{12,13} It is worth exploring the possibility of studying electronic structures of the deformed AGNRs using the TB model. According to the optimized geometry data, we find that there are four kinds of carbon-carbon bond lengths in the deformed AGNRs, as labeled by a_n ($n=1-4$) in Fig. 1, where a_1 and a_2 stand for the inner C–C distances and a_3 and a_4 describe the edge C–C separations. For example, the variation of four kinds of bond lengths as a function of the strain

ε is shown in Fig. 5(a) for the deformed AGNRs with width $W=13$. It is clear that the C–C separations change almost linearly with the strain and the deformation leads to the largest change in the inner C–C bond length (a_1). The changes in the C–C distance affect the hopping parameter (t) between two neighboring carbon atoms in the deformed AGNRs. For simplicity, we assume that the change in t (Δt) is proportional to Δa linearly. Compared with the change in t_1 (Δt_1), the changes in other three hopping integrals are set as $\Delta t_2=0.15\Delta t_1$, $\Delta t_3=0.40\Delta t_1$, and $\Delta t_4=0.13\Delta t_1$, respectively. The coefficient before Δt_1 is determined by the relative slope, as shown in Fig. 4(a). Four initial hopping parameters for the optimized strain-free AGNRs are set as $t_1=-2.7$ eV, $t_2=-2.65$ eV, $t_3=-3.2$ eV, and $t_4=-2.75$ eV. Figure 5(b) presents the changes in the energy gaps of AGNRs versus t_1 . We find that the TB results reproduce the main features of DFT calculations. This observation shows that the change in the hopping parameters between the π -orbitals of carbon atoms in the deformed AGNRs is the microscopic origin for the variation of energy gaps. In other words, the electronic structures of the deformed AGNRs can be well presented by adding the hopping parameter t_1 in the TB scheme.

Recently, Han *et al.*⁴³ have measured the energy gaps of GNRs with various widths from 10 to 100 nm. Of course, the geometric structures GNRs are somewhat deformed due to the stress from the substrate. We now apply the TB to investigate the variation of maximal value of E_g as a function of the width of AGNRs (W), as shown in Fig. 5(c). It is clear that $E_{g\max}$ decreases smoothly as the width of AGNRs increases, which is independent of the family structures. By fitting the calculated curve, we find a simple empirical formula, $E_{g\max}(\text{eV})=14.06/W$, as plotted in Fig. 5(c) with the green line. We propose that this nice scaling relation can be more useful to calibrate maximal energy gaps of AGNRs with large widths. For example, the maximal value of energy gap of AGNR with $W=100$ (about 12 nm) is found to be 0.14 eV from TB calculation. Noteworthy, our proposed scaling relation gives the value of 0.14 eV as well, which agrees quite nicely with the reported experimental value.⁴³

It has been suggested that the ground state of hydrogen-saturated ZGNRs is antiferromagnetic.^{14,22} The localized edge states on each edge have opposite spin orientations. Clearly, it is interesting to examine the electronic structures of the deformed ZGNRs by performing spin-polarized calculations. Figure 6 presents the calculated band structures of ZGNR ($W=13$) with and without the presence of uniaxial strain. We observe that the states of opposite spin orientation are degenerate in all bands regardless of the strain condition. The shape of the band structure and band gap (0.31 eV) of ZGNR without deformation agree well with the previous results.^{14,22} The band gaps are 0.29 and 0.35 eV for the ZGNR with -5.0% and 5.0% strain, respectively. This result shows that the deformed ZGNRs are semiconductor and that the energy gaps are tuned less significantly than AGNRs by the external strain. Another interesting aspect is that the ordering of all subbands remain unchanged during deformation. Therefore, the uniaxial strain does not affect the topological character of the electronic structures of ZGNRs.

FIG. 6. The spin-polarized band structures of the ZGNR ($W=13$) with and without deformation.

IV. CONCLUSION

In summary, the electronic structures of deformed GNRs are calculated using *ab initio* methods and TB methods. The electronic properties of ZGNRs are not sensitive to the uniaxial strain, while the energy gaps of AGNRs are predicted to change with zigzag shape as a function of the applied uniaxial strain. The tunable window of the energy gap becomes narrower when the width of ANGRs increases. The subband spacings and the spatial distributions of the deformed AGNRs are modified by the external strain. It is possible to utilize STM dI/dV maps to characterize the nature of the strain states, compressive or tensile, of AGNRs. Our TB approximation (TBA) simulations reproduce these results by first-principles calculations. We find that the change in the hopping integrals between the π -orbitals of carbon atoms are responsible for the variation of the energy gap of deformed AGNRs. These findings are helpful to construct and design graphene-based nanoelectronic devices in the near future.

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