Fast-track Communication

First-principle study of energy band structure of armchair graphene nanoribbons

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First-principle calculation is carried out to study the energy band structure of armchair graphene nanoribbons (AGNRs). Hydrogen passivation is found to be crucial to convert the indirect band gaps into direct ones as a result of enhanced interactions between electrons and nuclei at the edge boundaries, as evidenced from the shortened bond length as well as the increased differential charge density. Ribbon width usually leads to the oscillatory variation of band gaps due to quantum confinement no matter hydrogen passivated or not. Mechanical strain may change the crystal symmetry, reduce the overlapping integral of C–C atoms, and hence modify the band gap further, which depends on the specific ribbon width sensitively. In practical applications, those effects will be hybridized to determine the energy band structure and subsequently the electronic properties of graphene. The results can provide insights into the design of carbon-based devices.

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1. Introduction

Rapid development of integrated circuit technology such as improvement in the integration density, speed, and memory capacity hinges on the continuous reduction of the device size. As the design rule of field effect transistors (FET) has surpassed the 32 nm node, the role of the surface and boundaries is increasingly important. Transport of electrons and phonons can be hindered by random scattering in these regions and the electronic and thermal properties can be adversely affected. Smaller carrier mobility, lower thermal conductance, and reduced stability are critical issues hampering development of next-generation FETs. One alternative is to find new materials to replace single-crystal silicon.

Graphene, a two-dimensional honeycomb crystal consisting of carbon atoms, has extremely high electron mobility (10^5 cm2/V s) [1–3] and excellent thermal conductance (3–5 kW/mK) [4,5] which are far better than those of silicon. Each carbon atom in graphene is bonded to three adjacent ones via strong σ bonds and this leads to the high in-plane strength of 110–121 GPa. Hence, graphene may be a good candidate to replace single-crystal silicon for keeping the rapid development of future microelectronics. However, being a new material, many scientific issues associated with the potential applications are still not well understood according to the ITRS (International Technology Roadmap for Semiconductors). First of all, graphene is in fact a semimetal in that the bottom conduction band and top valence band overlap with each other and there is no energy band gap [1]. It is thus of immense scientific and technological importance to engineer a suitable band gap in order to use graphene as a semiconductor. A great many research works has been performed on this issue from both the experimental and theoretical aspects. It has been demonstrated that when graphene sheets are patterned into nanoribbons, a finite band gap will appear and depend on the ribbon width [6]. The band gap can be modified by exerting mechanical strain [7–9], or edge passivation [10–12]. However, further study is still needed to elucidate the native characteristics of these influencing factors as well as the hybridized effect. For that purpose, first principle calculation is done taking armchair GNRs (AGNRs) as examples in this paper.

2. Simulation model and calculation method

Monolayered graphene is constructed by increasing the lattice primitive vector perpendicular to the layers, c, to 20 Å, which is large enough so that there is vacuum separation and the interactions among layers can be ignored. In this model, graphene has a p6_3mc space group with two in-plane primitive vectors \( a = \sqrt{2} \) Å, as shown in Fig. 1(a) in which two orthotropic axis, \( x \) and \( y \) are perpendicular and parallel to C–C bonds, respectively. The C atoms outside the nanoribbon with a given
width along the x axis are deleted to produce AGNRs and periodic boundary conditions are applied in all three directions. As stated in Ref. [13], the width of the AGNRs is defined by counting the number, \( n \), of C atoms forming a zigzag chain perpendicular to the axis direction, and the graphene nanoribbons are denoted as AGNRs-\( n \). AGNRs-\( n \)-H is used to denote the cases in which the edge boundaries are passivated by hydrogen. As an example, Fig. 1 shows the model of AGNR-10-H. To study the effects of uniaxial tensile strain, the lattice along the length direction (y axis) is stretched to a given strain value and that along the width direction (x axis) is relaxed. For each optimized structure, single-point calculation is performed to obtain the energy band structure. The region enclosed by the dashed lines in Fig. 1(a) is the super cell of AGNRs-H and Fig. 1(b) schematically shows the first Brillouin zone in reciprocal space. The \( K \) point path \( G-K-L \) is sampled with a spacing of 0.15 Å/\( C_0 \) to calculate the energy band structure using the density functional theory (DFT) [14] implemented in Medea-Vasp [15,16]. The generalized gradient approximation with Perdew–Burke–Ernzerhof exchange-correlation potential (GGA-PBE) is used with a kinetic-energy cutoff of 500 eV [17]. The convergence of the total energy is chosen to be 0.01 meV and structure optimization is performed until the force acting on each atom is less than 0.02 eV/Å. Only the energy along the \( K-G \) path is presented here since our main attention is the variation in the band gap.

3. Results and discussions

Fig. 2 depicts the energy band structure of AGNRs without hydrogen passivation as a function of the ribbon width. The positions of the two lowest conduction subbands (\( c_1 \) and \( c_2 \)) and two highest valence subbands (\( v_1 \) and \( v_2 \)) change dramatically due to the quantum confinement effects, leading to considerable band gaps compared to those of two-dimensional graphene sheets. The top valence band and bottom conduction band are at the \( G \) and \( K \) points, respectively, indicating an indirect band gap. The gap varies with the ribbon width from 5 to 12. In AGNRs-5, \( c_1 \) and \( c_2 \) as well as \( v_1 \) and \( v_2 \) appear as individual energy levels, \( c_1 \) is close to \( v_1 \), and the minimum band gap of 0.29 eV is obtained (Fig. 2(a)). In AGNRs-7, \( v_1 \) and \( v_2 \) are degenerate at the \( G \) point and the energy levels of \( c_1 \) and \( c_2 \) at the \( K \) point move upward to nearly 1.0 eV yielding the maximum band gap of 0.91 eV (Fig. 2(c)). \( c_1 \) and \( c_2 \) become closer to each other with increasing ribbon width and are even degenerate in the whole path from \( K \) to \( G \) for AGNRs when the ribbon width is larger than 10.

Hydrogen passivation changes the energy band structure significantly, as illustrated in Fig. 3. The most remarkable change can be observed from the bottom conduction band and top valence band located at the \( G \) point in reciprocal space, implying that the indirect band gap changes into direct ones. Hydrogen passivation redistributes the electrons and the interactions between the electron clouds and nuclei should be enhanced at the edge boundaries of AGNRs according to our analysis (to be presented later). Consequently, the energy of the conduction band at the \( G \) point is lowered thereby promoting the transformation of indirect band gaps to direct ones. A direct band gap improves the carrier mobility because no phonon emission or annihilation is required to satisfy momentum conservation during the electronic transition. Fig. 4 displays the band gaps of AGNRs-H as a function of ribbon widths and oscillating variations with a period of 3 can be discerned, they can be classified into three groups. In general, the band gap decreases gradually and approaches zero when

![Fig. 1. (Color online) Schematic model of a graphene nanoribbon with armchair boundaries.](image1)

![Fig. 2. Energy band structures of AGNRs with different widths: (a) 5, (b) 6, (c) 7, (d) 8, (e) 9, (f) 10, (g) 11, and (h) 12.](image2)
AGNRs-H becomes infinitely wide, that is, into an ideal two-dimensional graphene sheet. The results can be understood qualitatively by tight-binding approximation in which the band gap of the AGNRs-H can be expressed as

$$E_g = \min_{p=1,2,\ldots,n} \left( \frac{-2\sqrt{3}t_0}{n+1} - p_0 \right)$$

$$p_0 = \frac{1}{2} - \frac{\sqrt{3}}{2n}(1+\nu)\sigma$$

where $\sigma$ denotes the uniaxial strain, $t_0$ is the nearest neighbor hopping integral in the absence of strain, $n$ represents the ribbon width, $p$ is the band index from 1 to $n$, and $\nu$ is Poisson’s ratio. $p/n+1$ can be regarded as equally spaced points along the axis. In the unstrained state, $\sigma = 0$, and so $p_0 = 2/3$. Only when $n+1$ is equal to an integer multiples of 3 will the minimum value of $|p/n+1 - p_0|$ be zero. In the other case, $|p/n+1 - p_0|$ is not equal to zero. The smaller the value of $n$ is, the larger it is, leading to periodic dependence of the band gap.

Fig. 3 presents the bond length distribution along some typical paths perpendicular to the axis direction of the AGNRs. In the nanoribbons with an even number of C atoms in the width zigzag chains, such as 10 and 12, the bond length along any path is asymmetrically distributed (Fig. 5(a), (d), (c) and (f)), whereas it is symmetrical in the nanoribbons with an odd number of C atoms in the width zigzag chains, e.g., 11 (Fig. 5(b) and (e)). The longitudinal C–C bonds at the edges, for instance, bond 1 in Path 1 and bond 5 in Path 2 of the AGNRs-10-H and bond 1 and bond 6 in Path 1 of the AGNRs-11-H, shrink considerably from 1.42 Å to 1.37 Å, but those located at the armchair back, bond 5 in Path 1 and bond 1 in Path 2 of the AGNRs-10-H as well as bond 1 and bond 5 in Path 2 of the AGNRs-11-H, expand slightly on the contrary. The bond length in the interior of AGNRs-H oscillates around the equilibrium value of 1.42 Å due to extension of the edge effect. This induces the crystal lattice changing from symmetric into asymmetric locally, in particular, near the edge boundaries of AGNRs-H. The lowered crystal symmetry often leads to the split of degenerated energy levels at bottom conduction subband and top valence subband, and thus modifies the energy band structure to some degree. This can also be evidenced from the differential charge density which describes the variation in the charge density accompanying the change in the atomic configuration.

Uniaxial strain can change the separation between atoms, reduce the overlapping integral of C–C atoms, and affect the interactions between electrons and nuclei. In this case, the energy band structure, particularly the lowest conduction subbands and the highest valence subbands, should be changed. The direct band gap of AGNRs-H is retained in spite of the application of large uniaxial strain. The AGNRs-H can usually be classified into three families according to the ribbon widths. Fig. 6 shows two groups of band gaps as a function of the applied strain, with three AGNRs-H of different widths being involved in each group, such as AGNR-7-H, AGNR-8-H, and AGNR-9-H (Fig.6(a)) as well as AGNR-10-H, AGNR-11-H and AGNR-12-H (Fig. 6(b)). The dependence of the band gap on the applied uniaxial strain is sensitive to the ribbon width. In AGNR-10-H, the band gap decreases initially from 1.16 eV at zero strain to nearly 0 eV at a strain of 0.08. It then increases linearly to 1.2 eV at a strain of 0.2. In AGNR-12-H, the band gap increases from 0.51 eV to 1.08 eV when
the strain is increased from 0.0 to 0.06, decreases to 0.04 eV at a strain of 0.12, and then increases again. In AGNR-11-H, the band gap decreases slightly at small strain, increases to 1.09 eV at a strain of 0.10, and decreases gradually afterwards. As for the group of AGNRs-7-H, AGNRs-8-H and AGNRs-9-H, the band gaps change in a similar manner as illustrated by Fig. 6 (a). The difference between the maximum and minimum band gaps decreases gradually with increasing ribbon widths. It is evidenced from Eq. (1), if a uniaxial strain $s$ is applied, $p_0$ will be altered, and subsequently the band gap oscillates with the applied strain, similar to the size effect stated above. In brief, hydrogen passivation mainly affects the edge states and changes the band gap characteristics. The ribbon width often leads to oscillatory band gaps due to quantum confinement. Strain usually changes the crystal symmetry as well as the overlapping integral of C–C atoms, and modifies the band gap further. In practice, all these influencing factors should combine to determine the energy band structure of the AGNRs-$n$-H, which should be paid more attention in the applications of relevant carbon-based devices.

4. Conclusions

Graphene, a two-dimensional honeycomb crystal of carbons, boasts high carrier mobility and thermal conductance but band gap engineering is needed for applications to nanoelectronics. First-principle calculation is performed to determine the influence of hydrogen passivation, ribbon width, as well as mechanical strain on the energy band structure of armchair graphene nanoribbons. Hydrogen passivation can change the nature of the band gap from indirect to direct because the enhanced interaction between electron clouds and nuclei near the edge boundaries will

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**Fig. 5.** (Color online) Bond length distribution of AGNRs-H after structural optimization with the ribbon width of (d) 10, (e) 11 and (f) 12 along the path in (a), (b) and (c), respectively.

**Fig. 6.** (Color online) Energy gaps of AGNRs-H with the different ribbon width as a function of applied uniaxial strain. Panels (a) and (b) show two typical groups of AGNRs-H.
lower the energy of bottom conduction subband at G point. The band gaps vary with the ribbon width due to quantum confinement no matter hydrogen passivated or not and can be classified into three groups. As a whole, the band gaps decrease with the increasing ribbon width. The crystal symmetry as well as the overlapping integral of C–C atoms may be altered through exerting uniaxial strain, which can also induce the alteration of band gaps. We should take into consideration their hybridized effect upon designing relevant microelectronic devices.

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