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Strain effects on the band gap and work function of zigzag single-walled carbon nanotubes and graphene: A comparative study

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ABSTRACT

First-principles local density functional calculation of the electronic structure and work function of zigzag single-wall carbon nanotubes (SWCNTs) and graphene under strain are presented. We found that there is a small circumference strain even for unstrained zigzag SWCNTs that release the curvature energy of the tube. Therefore, we propose that there are two effects contributing to the opening of the band gap of unstrained $(3q, 0)$ SWCNTs: the electron transfer enhancement effect and the circumference strain effect. We show that the band gap and work function of strained zigzag SWCNTs can be successfully estimated from the band structure and work function of strained graphene based on the zone folding method with circumference strain effect. The circumference strain effect is crucial to obtain a correct result. The rate of change of the band gap with respect to the strain for zigzag SWCNTs is almost independent of the value of the strain and the radius of the tube.

1. Introduction

Carbon nanotubes (CNTs) have attracted increasing attention in both theory and application from researchers over the past decade due to their outstanding mechanical and electronic properties [1–4]. Single-walled carbon nanotubes (SWCNTs) are a quasi-one-dimensional nanostructured material. A SWCNT (n, m) denotes a chiral vector of a single sheet of graphite rolled into a cylinder along its two-dimensional lattice vector $\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$ with diameter $D = |\boldsymbol{C}_h|/\pi$, where $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the primitive lattice vectors of a graphene, and m and n are integers. All SWCNTs can be classified according to the chiral vector (n, m) by the zone-folding method [5]. When $(n-m)$ is a multiple of 3, the band gap is zero and the SWCNTs are metallic. If the remainder of $(n - m)/3$ is not zero, the band gap exists and the SWCNTs are narrow- or moderate-gap semiconductors. The band gap of a semiconducting SWCNT also depends on its diameter [2,6]. However, O. Gülseren et al. showed that the radius and band gap relationship is different from that determined by the zone folding method for graphene bands [7]. A large inconsistency in band gaps is found between tight binding and first-principles calculations because of the curvature effects for small radius nanotubes.

The band gaps of nanoribbons and CNTs can be modified under external electric field and mechanical deformations [8–10]. In an *ab initio* study, several authors have reported that the band gaps of CNTs and boron nitride nanotubes may be reduced by applying a transverse electric field through the Stark's effect [11–13]. In addition, the electronic structures of SWCNTs can be changed by deformations [14]. Several tight binding studies have observed that a semiconductor to metal transition (SMT) of SWCNTs takes place under uniaxial strain; the band gap (E_g) varies linearly with strain (σ) [15–17]. R. Heyd et al. found that $|dE_g/d\sigma|$ is about 10.7 MeV/GPa for any $(n, 0)$ SWCNT and the sign of the slope depends on the remainder of n when divided by 3 [15]. Liu et al. showed that the value of $|dE_g/d\sigma|$ for SWCNTs depends only on its chiral angle [17]. They argued that the strain drives the Fermi point K_F to move between and cross over allowed electronic state parallel lines of different quantum numbers, leading to the zigzag pattern of band gap changing with different strains. These observations were confirmed by several first-principles studies. G.Y. Guo et al. focused on this strain effect on $(3q, 0)$ SWCNTs [18]. They found that a small band gap opens due to the curvature effect in unstrained $(3q, 0)$ tubes. The gap decreases linearly with increasing strain, vanishing at a critical strain σ_{crit}, and increasing linearly above σ_{crit} with increasing strain. They found that $dE_g/d\sigma$

of strained semimetallic zigzag SWCNTs [(9, 0), (12, 0), (15, 0) and (27, 0) tubes] is -140 MeV/% for $\sigma < \sigma_{crit}$ and 120 MeV/% for $\sigma > \sigma_{crit}$. Another first-principles study, that of Paran K. Valavala et al. focused on the strain effect on moderate-gap SWCNTs [(10, 0), (13, 0), (14, 0), (16, 0), (17, 0) and (20, 0) tubes] [19]. Their calculations demonstrated that $dE_g/d\sigma$ is 115±10 MeV/% for (3q + 1, 0) SWCNTs and $-(115 \pm 10)$ MeV/% for (3q − 1, 0) SWCNTs. In addition, first-principles studies on the strain effect of (10, 0), (11, 0), (12, 0), (13, 0), (14, 0) and (15, 0) tubes by S. Sreekala et al. confirmed a zigzag pattern of band gap change with strain [20]. Under a compressive strain, they found that the band gap of a (10, 0) tube decreases and becomes near zero (about 0.05 eV) at a strain of 5%. In contrast, the band gap of the (10, 0) tube increases under tensile strain. It reaches a maximum, in a sort of platean or flattened peak then decreases. Using first-principles calculation, it is unclear whether or not a semiconductor to metal transition occurs under uniaxial strain for (3q ± 1, 0) SWCNTs. Moreover, the reason for the flattening of the peak at the strain where the maximum band gap occurs is also unclear.

Another SWCNT property, work function is one of the critical quantities to study the field emission properties of SWCNTs. The work function of small zigzag tubes increases dramatically as the diameter of the tube decreases due to the curvature effect of the tube [21]. The work function of an unstrained zigzag SWCNT can be strongly correlated with the band structure and work function of the unstrained graphene based on the zone-folding method [22]. Recently, first-principle calculations show that the work function can be changed under mechanical deformation [23,24].

In this paper, we systematically study the electronic structure and work function of zigzag SWCNTs and graphene using local density functional approximation. Initially, we examine the relationship between the band gap of strained zigzag SWCNTs and the electronic structure of graphene. We also study the circumference strain effect on the band gap of strained zigzag SWCNTs based on the zone folding method. Finally, we will investigate the dependence of the work function of zigzag SWCNTs on the uniaxial strain. Based on the zone folding method, we can determine the work function of strained zigzag SWCNTs if we know the work function and the electronic structure of strained graphene.

2. Method of computations

In the present first-principles calculations, the local density approximation (LDA) of Perdew and Wang 1991 [25–27] framework using the Vienna *ab initio* simulation package (VASP) were performed [28–31]. In particular we used the projector argumented wave representation [32,33]. A supercell geometry to calculate electronic properties was used. In analyzing free-standing SWCNTs, the infinitely long nanotubes were placed in a square array with intertube distances equal to at least 10 Å. At such a separation, the tube–tube interactions and the overlap of wavefunctions are very small such that the tubes can be treated as decoupled entities. The Brillouin zone **k**-point sampling of SWCNTs was $1 \times 1 \times 24$ for structure optimization and $1 \times 1 \times 80$ for band structure calculation. The length of the unit cell along the tube's z (axial) direction was determined by minimizing the total energy with respect to the cell parameters. The interlayer distance between adjacent graphene in the supercell is 10 Å. The Monkhorst–Pack k-point grid of $16 \times 16 \times 1$ is used for atomic relaxation. A large plane-wave energy cutoff was taken to be 400 eV for simulations. All atoms were wholly relaxed using the conjugate gradient method until the magnitude of the maximum force was less than 0.02 eV/Å.

3. Results and discussion

Fig. 1 displays (a) the atomic structure, (b) Brillouin zone, and (c) the band structure of graphene from the Γ point to M point under different x-strains. The intersection of band 4 (π) and band 5 (π^*) determines the Fermi point K_F. The vertex point K_V is the high symmetry point of the irreducible Brillouin zone and is located at the intersection of the first Brillouin zone boundaries. The Fermi point K_F sits on the vertex point K_V at zero strain. A (n, 0) zigzag SWCNT is rolled up from a single sheet of graphene along the vector $\mathbf{C}_h$ (y axis in Fig. 1(a)). Because of the periodic boundary condition along the circumference, the wave vector k_y in circumferential direction on the graphene is quantized by the rule $k_y = 2\pi m/C_h$ with $m = 0, 1, 2, \ldots, 2n - 1, 2n$. Due to the symmetry of the Brillouin zone, the first $n + 1$ line segments are sufficient to describe the eigenvalue spectrum of the zigzag SWCNTs, as shown in Fig. 1(b). The spacing between the line segments is given by $\Delta_k = 2\pi/C_h$. The band gap of the (n, 0) SWCNT is given by $E_g = E_5^{min} - E_4^{max}$, where E_5^{min} (E_4^{max}) is the minimum (maximum) of the eigenvalue of the 5th (4th) band in the $n + 1$ line segments of graphene. Although the position of the Fermi point will be affected by the strain, it is always on the line of $k_x = 0$ [34]. This means that the maximum of the 4th band and the minimum of the 5th band always occur along the line of $k_x = 0$. Therefore, the band structure along $\Gamma - M$ in graphene under strain is sufficient to study the effect of strain on the band gap of zigzag SWCNTs. The strain along the tube direction (x-axis in Fig. 1(a)) in the honeycomb lattice is denoted by x-strain (σ_x). The x-strain is given by $\sigma_x = (l - l_0)/l_0$, where l_0 and l are the equilibrium length of unstrained SWCNT and the corresponding length of strained SWCNT in the axial direction, respectively. Fig. 1(c) shows the band structure of graphene under different x-strains. The positions of K_V point and M point are given by $(1 + a_y^2/a_x^2) \cdot \pi/(2a_y)$ and π/a_y, respectively. Under zero strain, a_y^2/a_x^2 equals 1/3 and the K_V point sits at 2/3 the way from Γ to M. The K_V point moves toward Γ point for stretching strain and moves away from Γ point for compression strain. It is interesting to note that the Fermi point also moves toward Γ point during stretching and moves away from Γ point during compression. Because the magnitude of the shift of Fermi point and the K_V point for a given x-strain are different, the Fermi point moves away from the K_V point under x-strain, as shown in the inset of Fig. 1(c).

Zigzag SWCNTs can be classified as $n = 3q$ and $n = 3q \pm 1$. The y components of the K_F point are given by $2q\Delta_k$ and $(2q \pm 2/3)\Delta_k$ for unstrained (3q, 0) and (3q ± 1, 0) tubes, respectively. Therefore, the Fermi point sits on the $m = 2q$ line for the (3q, 0) tube and sits between $m = 2q$ and $m = 2q \pm 1$ line segments for (3q ± 1, 0) tubes. For example, a (10, 0) SWCNT, when $q = 3$, will have 11 line segments in the $\Gamma - M$ region and the Fermi point will sit between the 6th and 7th line segments, as shown in Fig. 1(b). E_n^L (E_n^R) denotes the eigenvalue of the nth band at k^L (k^R) where k^L (k^R) is the k point in the first line segment from the left (right) of the Fermi point along the line of $k_x = 0$. The distance Δk_F^L (Δk_F^R) from k^L (k^R) to the Fermi point defines the band gap of the tube. For the case of (3q + 1, 0) SWCNT under zero strain, Δk_F^L is $2/3\Delta_k$ and Δk_F^R is $1/3\Delta_k$. The band gap of the tube is given by the gap value at k^R, which is $E_g^R = E_5^R - E_4^R$. Under stretching strain, the Fermi point moves away from k^R (as shown in Fig. 1(c)) and therefore the gap increases until the point when $E_g^R = E_g^L$ is reached, after which the gap becomes defined by E_g^L and decreases under further stretching until it reaches zero when K_F reaches k^L. During compression strain, the Fermi point moves toward k^R and the gap decreases until it reaches zero when K_F reaches k^R. For unstrained (3q − 1, 0) SWCNTs, Δk_F^L is $1/3\Delta_k$ and Δk_F^R is $2/3\Delta_k$, respectively. The gap of the tube is determined by E_g^L. Under stretching strain, the Fermi point moves toward k^L and therefore the gap decreases until it reaches