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Strain-induced structural and direct-to-indirect band gap transition in ZnO nanotubes

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ABSTRACT

First-principles calculations have been employed to investigate the structural transformation and direct to indirect band gap transition of ZnO nanotubes under uniaxial strain. The results show that armchair and zigzag nanotubes can be transformed to each other via unusual fourfold-coordinated structures under the applied strain. Both the armchair and zigzag nanotubes exhibit direct band gap while the unusual fourfold-coordinated ones display indirect band gap. The origin of such a direct-to-indirect band gap transition is explained based on the analyses of atomic orbital contributions.

1. Introduction

Zinc oxide (ZnO), an important II–VI semiconductor with a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, has been used for solar cells, transparent electrodes and blue/ultraviolet light emitting devices. Besides, ZnO also exhibits piezoelectric properties that can form the basis for electromechanically coupled sensors and transducers, making it promising for piezoelectric devices and sensors [1]. Recently, low dimensional ZnO nanostructures, such as nanoclusters [2], nanobelts [3,4], nanowires [1,5], and nanotubes (NTs) [6–8], have been studied both experimentally and theoretically due to their potential applications in nanoelectronic, optoelectronic, and photonic devices [9,10].

Experimentally, the synthesized one-dimensional (1-D) ZnO NTs are hollow nanorods with diameter of 10–500 nm and thickness of 5–100 nm [6–8]. Double-walled ZnO NTs with a round outer shape have also been prepared [11]. Theoretically, recent works have verified that single-walled ZnO NTs can exist stably and be regarded as a cylinder rolled up from ZnO graphitic sheet [12,13], similar to carbon NTs. Subsequently, several groups employ first-principles calculations to explore the structural stability, electronic and optical properties of single-walled ZnO NTs [13–16]. It is found that armchair and zigzag ZnO NTs are direct gap semiconductors and their band gaps decrease with the increase of diameter. Interestingly, Wang et al. have successfully converted the nanoscale mechanical energy into electrical energy by means of piezoelectric ZnO NT arrays [17]. These studies have promoted the development of ZnO NTs.

As is well known, the mechanical strain can influence significantly the structural and electronic properties of carbon NTs [18–20]. It also plays an important role in altering the structures and electronic properties of Si and ZnO nanowires [21–23]. For example, it can induce indirect-to-direct band gap transition in [112] Si nanowires [21] and direct-to-indirect band gap transition in [0001] ZnO nanowires [23]. However, very few investigations on how the mechanical strain could alter the structural stability and electronic properties of ZnO NTs have been reported. In this work, we will employ density functional theory calculations to address the structural transformation and electronic properties of single-walled ZnO NTs under uniaxial strain. A brief description of computational methods and models are given in Section 2. We present the simulated results and discussion in Section 3. The main conclusions are summarized in Section 4.

2. Computational methodology

The calculations are performed by Vienna *ab initio* simulation package (VASP) [24,25] based on the projector augmented wave (PAW) method [26] within density functional theory (DFT). The functional proposed by Perdew and Wang 91 (PW 91) with generalized gradient approximation (GGA) [27] is used to describe the exchange correlation interactions. The cut-off of plane-wave energy is set to 500 eV, and the convergence for total energy is con-

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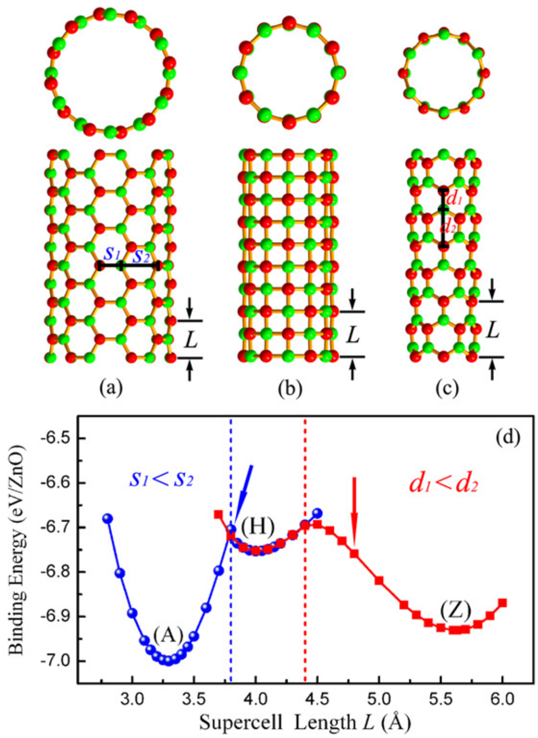

Fig. 1. (Color online.) The equilibrium geometric configurations of (a) A-type $(6,6)$, (b) H-type $(6,\mathrm{H})$ and (c) Z-type $(6,0)$ ZnO NTs. Green and red spheres denote Zn and O atoms, respectively. L is the supercell length. s_1, s_2, d_1, and d_2 are the distances between Zn and O atoms. (d) The binding energy of $(6,6)$, $(6,\mathrm{H})$ and $(6,0)$ ZnO NTs as a function of L. The blue line indicates the structural transition from A-type to H-type NT under uniaxial tension, while the red line indicates Z-type to H-type NT transition under uniaxial compression. Note that for $s_1 < s_2$ ZnO NT is in A-type structure and for $d_1 < d_2$ it is in Z-type structure. Otherwise, for either $s_1 = s_2$ or $d_1 = d_2$ it is in H-type structure. The dash lines and arrows denote the structural and band gap transition points, respectively.

trolled to be smaller than 10^{-6} eV. For Brillouin-zone integrations, a $1 \times 1 \times 11$ k-point mesh with Gamma centered grid is used for all ZnO NTs studied.

It is well known that the graphene sheet rolled up from different directions will generate carbon NTs with different chiral angle. These NTs are completely specified by a chiral vector given in terms of a pair of integers (n,m) and thus classified into three types, namely armchair (n,n), zigzag $(n,0)$ and chiral (n,m) NTs with $n \neq m$. Here, only single-walled armchair (A-type) and zigzag (Z-type) ZnO NTs are considered. Their initial structures are constructed by rolling up ZnO graphitic sheet. All the NTs are modeled in a tetragonal supercell and infinitely long along their axes by applying periodic boundary conditions. The axial direction is along z-axis and a vacuum region of at least 10 Å is applied in x- and y-axis to avoid the interactions between NTs. Upon starting the uniaxial strain, ZnO NTs are fully relaxed to local minimum configurations by computing the Hellmann–Feynman (H–F) forces [28]. All atoms in the supercell are allowed to move freely until the maximum H–F force is smaller than 0.005 eV/Å. Then, the A-type NTs are subjected to uniaxial tensile strain while the Z-type ones are subjected to uniaxial compressive strain. The uniaxial strain is applied along the axial direction of ZnO NTs. At each strain step, the ZnO NTs are also fully relaxed to obtain their local minimum configurations.

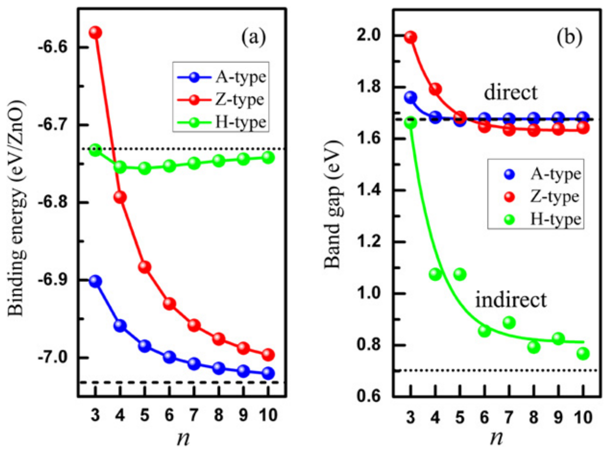

Fig. 2. (Color online.) (a) Binding energies and (b) band gaps as a function of chiral number n for A-type, Z-type, and H-type ZnO NTs. The binding energies, band gaps of ZnO graphitic and rock salt flat sheets are denoted by dash and dot lines, respectively.

3. Results and discussion

In this work, we construct a series of A-type (n,n) and Z-type $(n,0)$ ZnO NTs with $n = 3$–10 and find that the A-type ZnO NTs can transform to unusual fourfold-coordinated (H-type) ones during uniaxial tensile strain. Also, the uniaxial compressive strain can induce the phase transformation from Z-type to H-type ZnO NTs. As a representative example, the fully relaxed structures of A-type $(6,6)$, H-type $(6,\mathrm{H})$ and Z-type $(6,0)$ ZnO NTs are shown in Fig. 1(a), (b) and (c), respectively. The available studies verify that Zn and O atoms in ZnO graphitic sheet are coplanar [12, 29], while they are not located on the same cylinder surface after rolling up the graphitic sheet into a tubule and shift inward and outward along the NT radius, which is similar to the relaxations of surface atoms in [0001] ZnO nanowires [30]. The binding energy of ZnO NTs as a function of supercell length L is presented in Fig. 1(d). One can see that there exist three distinct minima corresponding to the A-type $(6,6)$, the unusual H-type $(6,\mathrm{H})$, and the Z-type $(6,0)$ NTs. As shown in Fig. 1(b), the unusual H-type NT is fourfold, different from the regular threefold coordination in the A-type and Z-type tubes. It is crystallographically similar to the rock salt structure and can be regarded as a tubule rolling up from ZnO rock salt sheet.

As indicated in Fig. 1(d), for structural transformation from $(6,6)$ to $(6,\mathrm{H})$ under uniaxial tension, the supercell length $L = 3.80$ Å marks the transition point, that is, when $L \leqslant 3.80$ Å, s_1 is less than s_2 and ZnO NT belongs to the A-type structure, while $L > 3.80$ Å, s_1 is equal to s_2 and it belongs to the H-type structure. As for the structural transformation from $(6,0)$ to $(6,\mathrm{H})$ under uniaxial compression, $L = 4.40$ Å marks the transition point, i.e., when $L \geqslant 4.40$ Å, d_1 is less than d_2 and ZnO NT is in Z-type structure, while $L < 4.40$ Å, d_1 is equal to d_2 and it is in H-type structure. Either $s_1 = s_2$ or $d_1 = d_2$ means that ZnO NT lies in H-type structure, which is indicated by the side view in Fig. 1(b). Interestingly, Fig. 1(b) also indicates that further uniaxial tensile or compressive strain may induce the structural transformation of ZnO NT from H-type $(6,\mathrm{H})$ to Z-type $(6,0)$ or to A-type $(6,6)$, respectively. It means that both the A-type and Z-type ZnO NTs can be transformed to each other via median phase, i.e. the H-type NT. This structural transformation can also be observed in the thinner and thicker ZnO NTs.

For all the ZnO NTs studied, their binding energies as a function of chiral number n are illustrated in Fig. 2(a). Besides, the binding energies of ZnO graphitic and rock salt sheets are also shown. It is found that, for both A-type and Z-type NTs, their binding energy decreases with increase of n and tends to the value -7.032 eV/ZnO of ZnO graphitic sheet, which is in good agreement with previous study [15]. However, the H-type NT presents completely different behaviors. Its binding energy is irregularly dependent on n and smaller than the value -6.731 eV/ZnO of