ELECTRONIC PROPERTIES OF SEMICONDUCTING ZIGZAG (10, 0) CARBON NANOTUBES DUE TO UNIAXIAL STRAIN

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ABSTRACT

In this paper we report the study of the change in electrical properties of zigzag carbon nanotubes (10, 0) under uniaxial compressive and tensile deformation using Density Functional Theory (DFT) calculation. There is an energy gap of 0.972 eV between occupied and unoccupied region in the optimized structure calculation. We found that the band gap of the semi conducting zigzag (10, 0) CNTs decreases as the strain increases for both compressive and tensile deformation. Different profiles of charge density appear for tensile and compressive deformations. The charge density of compressed state is more localized in the z direction of C-C bonds. Meanwhile, charge density of elongated state is localized in the diagonal C-C bonds direction. At the large tensile strain, the C-C bonds break at the z-direction C-C bonds. ICOHP analysis shows that the bond strength of CNT drastically decreases under tensile deformation.

Keyword: band gap, carbon nanotubes, charge density, density functional theory.

INTRODUCTION

The development of science and technology has evolved into the era of nanotechnology. Among the many nanostructured materials, carbon nanotubes (CNTs) have attracted considerable attention. Compared to other nanoscale materials, single-walled carbon nanotubes (SWCNT) possess particularly outstanding physical and electronic properties. Due to the extremely small size of CNTs, the evaluation of its mechanical properties, such as elastic modulus and tensile/compressive strength presents significant challenges to researchers who work in nanomechanics. Electronic states of single-walled carbon nanotubes (SWNCT), such as Density of states (DOS) and band gap, could be correlated with their finite mechanical deformation behavior. The study of this effect is important in view of the ability to manipulate individual nanotubes for many applications.

Recently, Obitayo and Liu [1] have been developed carbon nanotubes as strain sensor its I-V characteristic behavior due to axial change has been explored. In that work, they conclude that for carbon nanotube-based strain sensing applications, the small-gap semiconducting single-walled carbon nanotubes offer the greatest sensitivity.

Even though many research have studied the change of electronics properties of nanotubes under uniaxial deformation [1-3], the theoretical approach in investigating the band-gap changes has not been revealed up completely. Because of the nanoscale size of CNTs, the experiments to measure the properties of individual CNT are quite difficult. Therefore, the ab initio calculations have been regarded as a powerful tool to study properties of CNTs.

In the present report, we calculate the atomic and electronic structure changes of the CNTs under tensile and compressive deformation by using Density Functional Theory (DFT) calculation. We focused on band-gap and bond strength changes due to mechanical uniaxial tensile and compressive deformation.

COMPUTATIONAL DETAILS

We carried out the first-principles calculations on the density functional theory (DFT) level, using the "Vienna ab initio simulation package" [4–6]. The calculation was performed in QC-Cluster at Department of Physics ITB. Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [7] functional is selected in our calculations. A plane-wave basis set was employed within the framework of the projector augmented wave method.[8, 9] K-points ($1 \times 1 \times 17$ Monkhorst-Pack grid) were used in this simulations. One k-point in the two perpendicular directions was enough because the distance between the individual tubes was chosen very large (16 Å) so that the interaction between them was negligible.

We selected zigzag type semiconducting CNTs (10,0). The axial direction (z) of these CNTs was selected as the tensile direction. Before we started the tensile test, the z dimension of the supercells and the initial atomic configuration were completely relaxed. These relaxed z dimensions of the supercells were used as a reference when calculating the applied strains in the following discussion.

The electronic properties of zigzag CNT can be obtained by using electronic density of states calculations. The optimized structure data from SCF calculations can be used to reduce calculation time and neglect structural optimization process. Generally, the mesh K-point sampling for DOS calculation is higher than that of SCF calculations for calculation's accuracy.

To know further the nature of bonding of elongated /compressed CNT, we projected plane waves to local orbital basis functions to extract the crystal orbital Hamilton population (-COHP) [10]. The integration of COHP for all energies up to E_F gives integrated COHP (ICOHP) to render a quasiquantitative interpretation [11] of the net bonding characteristics. This ICOHP were calculated by using the program Local-Orbital Basis Suite towards Electronic-Structure Reconstruction (LOBSTER) [11-13].

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RESULT AND DISCUSSIONS

Change in density of states during deformation

From the DFT calculation using VASP software, we got the optimized structure of zigzag CNTs (10, 0). The zigzag edge (10, 0) CNT has two different carbon-carbon (C-C) bond length, 1.42 Å and 1.43 Å. The diameter of this optimize structure is 7.89 Å. Our optimized CNTs model was then be compressed and elongated in uniaxial direction (z-direction). There is an energy gap of 0.972 eV between occupied and unoccupied region, which indicates that the system is semiconducting. This result is in agreement with other first principle calculation studies which have been published [14-16].

This result is also supported by experimental and theoretical approach results from other studies. According to the chiral vector information, the pristine zigzag edge (10,0) CNT is semiconducting material [17]. This result is also in a good agreement with experimental result by using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) [17, 18].

The electronic structures of CNTs with various structures under axial strain are evaluated by DFT calculations. To analyze the band gap dependency on uniaxial deformation, we observe the DOS of the deform structure of zigzag edge CNT (10, 0). The band-gap versus strain curves for a zigzag (10, 0) CNTs during the tensile tests are shown in Figure 1. Negative value means that the final deformed structure is shorter than the optimize bulk structure (compressed). Vice versa, the positive value shows that the final deformed structure is longer than the optimize bulk structure (elongated).

Previous work on semiconducting CNTs shows the same result with this work. The band gap for the semiconducting zigzag (10, 0) CNTs displays some variation upon deformation, but most of it decreases as the strain increases [16]. This calculation result also shows that there is semiconductor-metallic transition of the CNTs. The (10,0) zigzag tube has zero band gap like graphene at the strain of -8.3% which means that it possesses metallic electronic properties at this state and returns to the semiconducting state as the strain increases.

Since another work suggests that the small-gap semiconducting single-walled carbon nanotubes offer the greatest sensitivity for the sensor application, we can conclude that CNT (10, 0) can be a good candidate for CNT-based strain sensors.
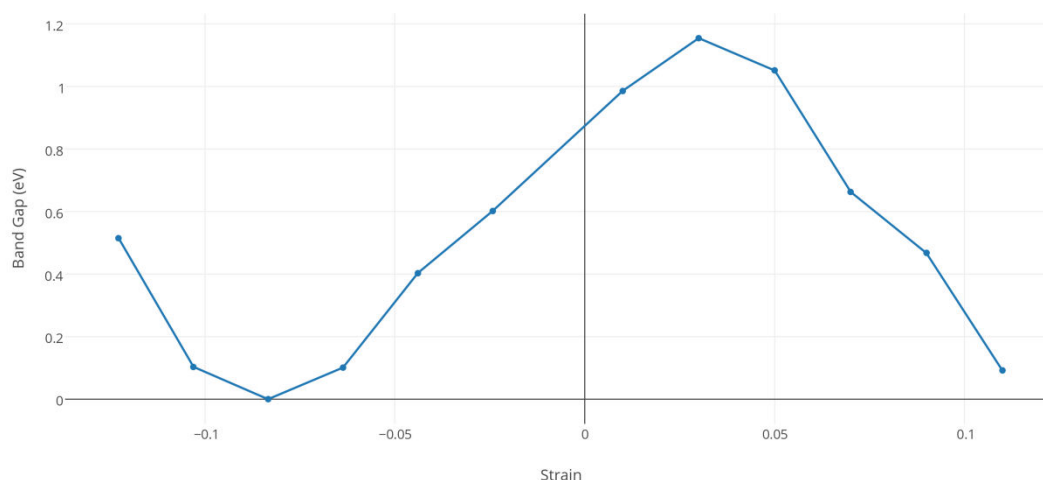

Figure-1. The band gap versus strain for semi-conducting zigzag (10,0) CNTs.

Deformation electron density

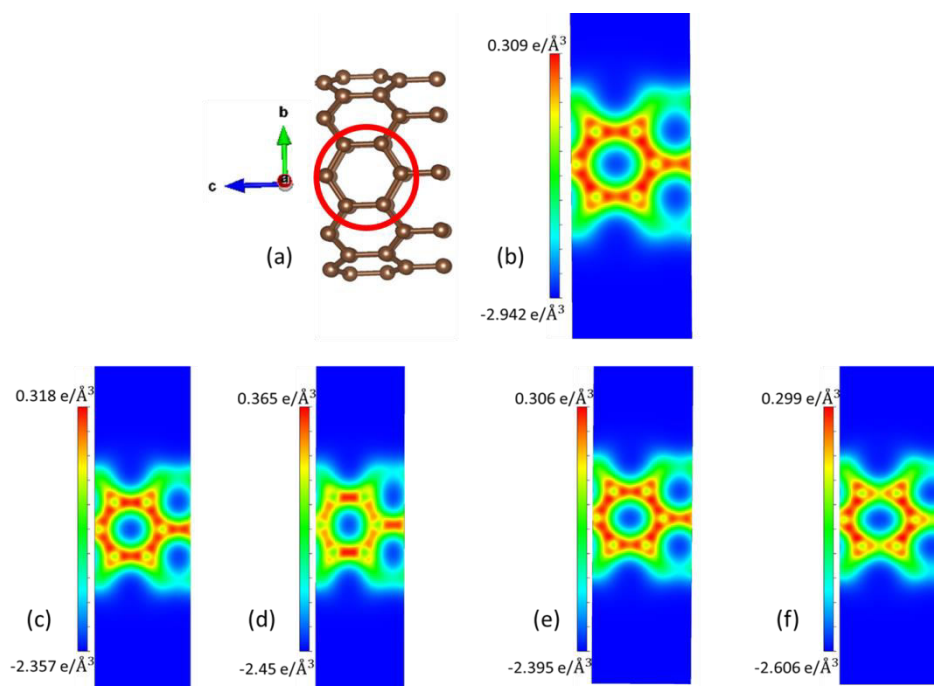ARPN Journal of Engineering and Applied Sciences

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Figure-2. (a) Focused area for charge density analyzing; Charge density of the (10,0) zigzag CNT under: (b) 2% (c) 10% compressive and (e) 1% (f) 10% tensile strain.

Figure-2 shows change in the charge density of the (10,0) zigzag CNT under compressive and tensile strain. We analyze the two dimensional charge density slice of the semiconducting zigzag (10, 0) CNTs focusing on the red circle area shown in the Figure-2(a). Charge density of the CNT before imposed by uniform stretching or compressed of the initial atomic configuration in the z direction is shown in Figure-2(b). Charge density during the compressive deformation is shown in Figure-2(c) and (d), it can be seen that the charge density becomes more localized in the -z direction C-C bonds and the angle of the hexagonal carbon formation decreases. The amount of localized charge density also increases as the compressive strain increase.

The different profile appears during tensile deformation. The charge density, as shown in Figure-2(e) and (f), decreases as the tensile strain increase. The Charge density is localized in the diagonal C-C bonds. At large strain, i.e. 7% for tensile and 5% for compression, the C-C bonds break at the z-direction C-C bonds. This indicates that for more than 7% tensile and 5% compressive strain, CNT starts to break and no longer efficient to be used as a sensor. Because when some C-C bonds are broken, the CNT is in plastic region, so when it is strained, it will not return to its original shape. For the strain sensor application, CNT should be able to return to its original shape, it means that the CNT should be in the elastic region. From our charge density analysis, the elastic region of CNT (10, 0) might be below 7% tensile and 5% compressive strain.

From this figure also we can conclude that the bond strength of the CNT under compressive deformation is higher compared to that of tensile deformation. It is indicated by the higher value of the electron density in compressive deformation compared to tensile deformation at the same strain. To study further about this bond strength, we perform the ICOHP calculation.

Bond strength

Integrating - COHP over energy produces an integrated COHP (ICOHP) value, which indicates the order of covalent bond strength [19,20]. The average - ICOHP value for each C-C bonds of the deform structure of zigzag edge CNT (10,0) is depicted in Figure-3.
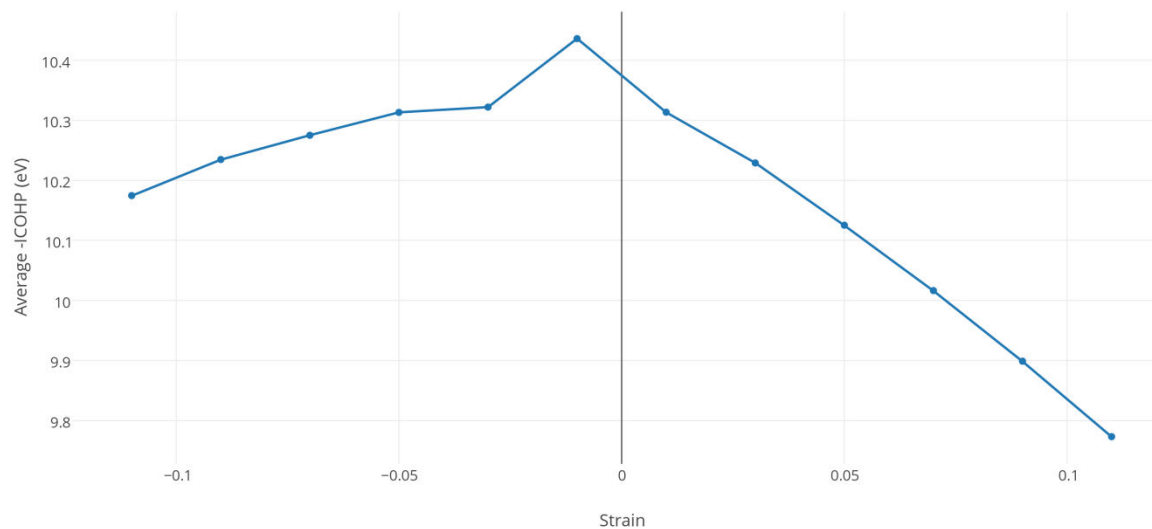
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Figure-3. The average - ICOHP value for each C-C bonds versus strain for semi-conducting zigzag (10,0) CNTs.

The higher - ICOHP indicates stronger orbital interactions. The bond strength for the semiconducting zigzag (10, 0) CNTs displays some variation upon deformation, but most of it decreases as the strain increases. This result confirms that the charge density of deform CNT correlates with the bond strength. The bond strength of the CNT under compressive deformation is higher compared to that of tensile deformation.

From Figure-3 we can see that the bond strength of CNT under tensile deformation drastically decreases compared to that of compressive deformation. It explains the finding of higher compressive strength compared to tensile strength of nanotube composite obtained in experimental works [21, 22].

CONCLUSIONS

The band gap of the CNTs displays some variation upon deformation, but most of it decreases as the strain increases. This work also shows that there is semiconductor-metallic transition of the CNTs at -8.3% of strain which indicates that it possesses metallic electronic properties at this state and returns to the semiconducting state as the strain increases.

During the compressive deformation, the charge density becomes more localized in the -z direction C-C bonds. Amount of this localized charge density increases as the compressive strain increases. During tensile deformation, the localized charge density decreases as the tensile strain increases. Meanwhile, the charge density under tensile deformation is localized at the diagonal C-C bonds. At the large tensile strain, the C-C bonds break at the z-direction C-C bonds. Our charge density result shows that the elastic region of CNT (10,0) might be at below 7% tensile and 5% compressive strain.

Bond strength of the CNT under compressive deformation is higher compared to that of tensile deformation. It is indicated by the higher value of the electron density in compressive deformation compared to

that of tensile deformation at the same strain. ICOHP analysis also shows that the bond strength of CNT under tensile deformation drastically decreases compared to that of compressive deformation.

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