Spatial Distribution of State Densities Dominating Strain Sensitivity of Carbon Nanotubes

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Abstract—In any electronic devices and sensors, internal strain is induced because of the thermal change or the lattice mismatch between different materials. It is, therefore, expected that when carbon nanotubes (CNTs) are used for electronic devices, their electronic properties are changed caused by the deformation. In this study, we study the mechanism of the change in the band gap of CNTs under the radial strain in terms of state density distribution. We found that the spatial distribution of the state density dominates its strain sensitivity, and thus, the strain sensitivity of electronic properties of CNTs. We also calculated the change in the current through the deformed CNTs. The founding indicates that the state density analysis should be useful for the development of novel electronic devices and nano electro mechanical systems and for assuring their reliable performance.

Keywords—carbon nanotube, strain, state density, electronic state

I. INTRODUCTION

In any electronic devices and sensors, internal strain is induced because of the thermal change or the lattice mismatch between different materials [1], [2]. It is, therefore, expected that when carbon nanotubes (CNTs) are used for electronic devices, their electronic properties are changed caused by the deformation. Theoretical [3]-[5] and experimental [6], [7] studies have revealed that both axial and radial strains change the band gap of CNTs.

It is known that the change in the band gap of CNTs under uniaxial strain [3], [4] can be described by the cuttingline theory [8]. The geometrical structure of CNTs can be considered as a graphene sheet in which electrons have the same state when they move along the chiral vector, which corresponds to the vector along the circumference of CNT. The circumferential periodicity confines the movement of electrons and appears as cutting lines in the Brillouin zone of graphene in the reciprocal space. Because the band gap of CNT is determined by the distance of a Fermi point from a cutting line and a uniaxial strain shifts Fermi points from the cutting line relatively, the band gap of the CNT changes under a uniaxial strain. As for the radial strain, the change in the band gap of zigzag CNTs (ZNTs) and armchair CNTs (ANTs) has been studied [5], [9]-[12]. These studies have showed that ANTs, originally metallic, can be shifted to semiconducting while its symmetry breaks under a radial Ken Suzuki, and Hideo Miura Fracture and Reliability Research Institute (FRRI), School of Engineering, Tohoku University, Sendai, Japan {kn, hmiura}@rift.mech.tohoku.ac.jp

strain, while the band gap keeps its metallic characteristics when its symmetry remains [5]. ZNTs, (n,0) type CNTs, are originally metallic or semiconducting when n = 3p or $3p \pm 1$, where p is an integer, respectively. When a radial strain is applied to a ZNT, orbital hybridization is induced and then the band gap is changed. Compared to the mechanism of the band gap change based on cutting-line theory and the symmetry breaking, the effect of orbital hybridization is more complicated, and thus, incompatibility between experimental and theoretical studies still remain [11], [13].

In this study, in order to discuss the relationship between the deformation of CNTs and their electronic properties, first-principles calculation was performed. Firstly, in order to evaluate the change in electronic properties as the increase in strain and to relate geometrical and electronic structures, electronic structures of CNTs and are analyzed. We found that the change in electronic properties under radial strain can be evaluated by using a universal geometrical factor, dihedral angle [14]. Since the more complicated strain field like buckling deformation can be represented by dihedral angle, the effect of local strain field is expected to be evaluated with this factor. Furthermore, the mechanism of the change in the band gap of ZNTs under radial strain is analyzed in detail in terms of the spatial distribution of charge and state density. We electronic properties of CNTs under deformation is dominated by the change in dihedral angle. Finally, the change in current-voltage (I-V) characteristics of CNTs under radial strain is calculated by using nonequilibrium Green's function (NEGF) method based on density functional theory (DFT). Our analysis clarifies how electronic states of CNTs are changed under strain in detail and gives guideline on how to assure the high performance of CNT(s)-based electronic devices.

II. GEOMETRICAL AND ELECTRONIC STRUCTURES

Previous studies have revealed that electronic states of CNTs change significantly under axial, torsional [3], [4] and radial [5], [9] strains. Under axial and torsional strains, the change in bond lengths dominates the change in electronic states of CNTs. The change in the band gap under axial and torsional strains can be solved analytically if a strain is small [3], [4]. It has also been revealed that a radial strain causes orbital hybridization in a CNT which changes the band gap. In spite of these efforts, experimental and theoretical studies

are still not in agreement with each other. Moreover, fully flattened CNTs are found to be more stable than round CNTs recently [15], [16]. Since fully flattened CNTs have similar characteristics to GNRs, that is, they have a band gap, they are prominent candidates for a material of high performance devices. Therefore, understanding of the effect of radial strain is a critical issue to assure the stable and high performance of devices and also to develop highperformance devices. In this section, focusing on radial strain which induces the change in orbital distribution, we analyzed electronic states of ZNTs under a multi-axial strain field to discuss the relationship between geometrical and electronic structures.

Analyses in this study are performed by using the density-functional theory (DFT) within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional implemented in SIESTA package [17]. We use double- ζ plus polarization basis set, norm-conserving pseudopotentials, and a mesh dutoff of 210 Ry. At first, a radial strain was applied to the CNTs and then, a relaxation calculation was performed. During the relaxation calculation, the distance of the facing atoms, d_{ll} , was fixed at the initially applied value. Fixed atoms are colored by blue in an inset in Fig. 1. Strain value is defined as $\varepsilon = |d_{ll} - D_0|/D_0$, where D_0 is the radius of the pristine CNT. The cube size along the tube axis was assumed to be 4.26 Å and the vacuum space at the radial direction was set large enough to neglect the effect of neighbor CNTs. The unit cell consisted of 4n carbon atoms.

The deformation is represented by the dihedral angle [14], an angle between π -orbitals of adjacent atoms as shown in an inset in Fig. 1. The direction of π -orbital of *i*-th atom, $V_{\pi,i}$, is obtained by

$$oldsymbol{V}_{\pi,i} = rac{oldsymbol{V}_{31} imes oldsymbol{V}_{21}}{|oldsymbol{V}_{31} imes oldsymbol{V}_{21}|}$$

where $V_{km} = V_m - V_k$ and V_k (k = 1, 2, 3) is the k-th nearest neighbor atom of *i*-th atom. Dihedral angle, θ_d , can be obtined by

$$\cos \theta_d = \frac{\boldsymbol{V}_{\pi,i} \cdot \boldsymbol{V}_{\pi,j}}{|\boldsymbol{V}_{\pi,i} \cdot \boldsymbol{V}_{\pi,j}|}$$

DFT calculations are performed to evaluate the change in electronic structures of deformed CNTs. The total energy was converged to within 0.5 meV with a Monkhorst-Pack *k*-point mesh of $1 \times 1 \times 50$. Vacuum separations along *x* and *y* axes were more than 20 Å which was large enough to neglect the interaction of next cells. The length of a unit cell along *z* axis was assumed to be equal to the transverse vector of CNTs.

The change in the band gap of ZNTs under the radial strain is shown in Fig. 1. The maximum dihedral angle is taken as x-axis. This figure shows that although any CNTs, which originally have a different magnitude of the band gap, the band gaps of the CNTs starts to decrease at a certain range of the maximum dihedral angle, 25 to 30 degree. Moreover, the band gap decreases at the same rate, approximately 0.07 eV/degree, in every cases. This result shows that the dihedral angle is a universal parameter to



Fig. 1 Change in the relationship between the band gap and the maximum dihedral angle as the increase in radial strain. Insets show analysis model and dihedral angle θ_d .

describe the change in the band gap of CNTs under radial strain. Since the dihedarl angel can be calculated from the positions of an atom and its three neighbors, and thus, it can be used to represent more complicated strain field such as buckling deformation, it is expected to predict the change in the band gap of buckling CNTs by using the dihedral angle.

III. ANALYSIS OF SPATIAL DISTRIBUTION OF STATE DENSITIES

In the previous section, we revealed that when a radial strain is applied to a CNT, its band gap decreases at high curvature regions where the dihedral angle increases. The mechanism of the band gap change, however, has not been yet revealed. In this section, the mechanism of the change in the band gap is discussed in terms of the change in spatial distributions of state densities.

Changes in the electronic band structure of (13,0) CNT are shown in Fig. 2(a)-(c). Figure 2(a) shows the band structure of the CNT under strain-free condition. In this figure, the energy levels between the Fermi energy and the lowest singlet state in the conduction band, state E, are highlighted. All highlighted states except for E are doubly degenerate sates in the original state. In Fig. 2(b) and (c), changes in state D and state B are highlighted for simplicity. While both of state B and D are originally degenerate states, the change behavior of their energy under the radial strain is clearly different: State D is split into state D' and state D" and the energy of state D' decreases drastically as the increase in the strain. On the other hand, state B is not split and its energy did not decrease. The change in state energies at Γ point is summarized in Fig. 2(d). This figure shows that the reduction of state energies starts at the lowest singlet state in the conduction band, state E, and then, the reduction of state energy transmits to lower energy states. Eventually, the band gap starts to decrease when the lowest unoccupied molecular orbital (LUMO) energy, state A in this case, starts to change. It should be stressed that the behavior of the state energy B is clearly different with others and does not decrease. This result indicates that the strain sensitivity of sate energy is varied depending on its state.

The mechanism of the decrease in state energies and the difference of strain sensitivity among states can be well described by analyzing spatial distribution of state densities



Fig. 2 Change in electronic band structure (a-c) and state energies at Γ point (d) of (13,0) CNT under radial stain. Fermi energy is taken to be zero. (a) Dashed and continuous curves show singly and doubly degenerate states, respectively. (b, c) The states D (= D' + D'') and B are highlighted for simplicity. (d) Red-colored state energies decreased as the increase in the strain while the energy of state B did not decrease.



Fig. 3. Strain-dependence of the spatial distribution of state density at Γ point. Side views and their schematic image of the pristine CNT are shown on the first column, and cross-sectional views of the state density distribution of strained CNTs are shown on the other columns. Strain value is shown on the top of each panel. The cross-sectional views are represented by contour lines. The most outer line is 0.02 [$e/(a.u.)^3$] and the contour interval is 0.02. The blue (red) lines indicate plus (negative) phase of the wave function.

at Γ point. The change in state density distributions of state D', strain-sensitive state, and state B, strain-insensitive state, are shown in Fig. 3. The figure clearly shows the difference between the spatial distribution of state D' and state B: State density D' and B expands along the axial direction and the circumferential direction at the original state, respectively, as shown on the first column in Fig. 3. State density D' is localized at high-curvature regions when the redial strain is applied (see the case in $\varepsilon = 0.20$). Under larger strain, state density distributions move toward the center due to the interaction of opposing walls ($\varepsilon = 0.50$). On the other hand, spatial distribution of state density B does not change significantly even under large strain. The results show that the spatial distribution of the state density dominates its strain sensitivity, and thus, the strain sensitivity of electronic properties of CNTs. The founding indicates that the state density analysis should be useful for the development of novel electronic devices and nano electro mechanical systems (NEMS) and for assuring their reliable performance.

IV. CHANGE IN I-V CHARACTERISTICS OF CNTS UNDER RADIAL STRAIN

Based on the above results, we can expect that by applying a radial strain, the current value can be modified. This characteristics can be used various applications such as strain sensors, actuators, and nanoscale switches. Thus, in this section, the change in the current through CNTs under radial strain is analyzed.

Current-voltage (I-V) characteristics of (n,0) CNTs (n = 10, 11, 13, 14) are analyzed by using nonequilibrium Green's function (NEGF) method implemented in the TRANSIESTA code [18]. In this method, analysis model is divided three parts; device region and left and right electrodes. The Green's function, G_D , of device region is given by

$$G_D = [ES_D - H_D - (\Sigma_1 + \Sigma_2)].$$

where H_D and S_D are Hamiltonian and overlap matrices of the device region, E is the energy of the incident electron to the device region, and Σ_1 and Σ_2 are the self-energy matrix of left and right electrodes, respectively, which represent the connection of each electrode with the device region. The transmission function from the right electrode to left electrode is obtained by

$$T_{12}(E, V) = \operatorname{Tr}[\Gamma_1 G_D \Gamma_2 G_D^{\dagger}]$$

$$\Gamma_j = i[\Sigma_j - \Sigma_i^{\dagger}], (i, j = 1, 2)$$

The current value under bias voltage from the right electrode to the left electrode is obtained from the transmission function.

$$I(V) = \frac{2e}{h} \int T_{12}(E,V) [f_2(E,V) - f_1(E,V)] dE,$$

where $f_{1,(2)}$ is Fermi function of left (right) electrode, *e* and *h* are an elementary charge and Planck's constant.

In this analysis, the same radial strain as Fig. 4 is applied to both device region and electrodes homogeneously. Such strain field should be introduced because of the deposition of metallic electrodes or an insulator layer. Device region contains seven unit cell. +0.5 V and -0.5 V bias voltage are applied to right and left electrode, respectively. The change in voltage in the device region is obtained self consistently in this analysis. To assure the accuracy of the analysis, a unit cell of each electrode is included in the device region during the calculation.

The change in transmission function of electron moving from right to left electrodes is shown in Fig. 4. This figure shows when 20% strain is applied, the transmission function increases at high energy region, more than 1.2 eV, while the transmission function of energy less than 1.2 eV does not change significantly. The increase in the transmission at high energy region corresponds to the decrease in the energy of unoccupied states as shown in Fig. 5. Further strain causes the increase in the transmission at whole energy region ($\varepsilon =$ 50%). The increase in the transmission at low energy corresponds to the decrease in the LUMO energy, which



Fig. 4. Change in the transmission function of (13,0) CNT under 1.0 V bias. The average potential of both electrodes is assumed to be 0 eV. Electrons of energy from -0.5 eV to 0.5 eV mainly contribute to the current flow. Inset shows the analysis model. Unit bias voltage is applied to the device region consisting of seven unit cells.



Fig. 5. Change in the current through CNTs under radial strain. Dihedral angle is used to summarize the results.

occurs after the decrease in energies of higher levels. The change in current caused by the change in transmission is summarized at Fig. 5. This figure shows that the current value increase as the increase in the radial strain, and then, decreases drastically when the radial strain exceeds a certain value. These results show that the localization of state densities generates the path of electrons at high curvature regions and that the interaction of the upper and lower walls cause a drastic decrease in the current. The founding of this study indicates that the control of the strain field is required to assure the stable function of electronic devices, and, at the same time, we can develop both strain-sensitive and insensitive devices and sensors by using CNTs.

V. CONCLUSION

In this study, we discussed the change in electronic structures of CNTs under radial stain in terms of the spatial distribution of state density. We revealed that when a radial strain is applied to CNTs, their state densities localize at high curvature regions. Because the localization of state density decreases its energy, when the LUMO energy decreases the band gap starts to decrease. Moreover, the analysis of I-V characteristics revealed that the current value increases as the localization of state densities. On the other hand, the interaction of walls causes the drastic decrease in the current. These analysis results indicate that CNTs have a various electronic features which can be used in electronic devices or

sensors, such as strain sensors, nanoscale switches, and actuators.

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