Change of the Electronic Properties of Carbon Nanotubes Cause by Three-Dimensional Strain Field

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INTRODUCTION

Since carbon nanotubes (CNTs) have superior properties both mechanically and electronically, there have been many efforts to develop electronic devices or various kinds of sensors based on carbon nanotubes [1-2]. We have revealed the possibility of the high sensitive strain sensor using popular resin in which multi-walled CNTs (MWNTs) are dispersed uniformly [2]. It is a critical issue to understand how the electronic state of CNTs is effected by a deformation [3-4]. In this study, we focused on orbital hybridization, one of the main factor causing the change of the electronic state of CNTs. In order to understand how orbital hybridization occur around strained areas, we analyzed the electronic state of CNTs and graphene nanoribbons (GNRs), unzipped CNTs by using the density functional theory.

CHANGE IN ELECTRONIC STATE OF CNTS AND GNRS CAUSED BY DEFORMATION

We analyzed the electronic structure of armchair GNRs (N = 10, 16, 18, 20) folded on the center line and (n, 0) zigzag CNTs (n = 9, 11, 12, 13) under axial and radial strain. Models of a GNR and a CNT are shown in Fig. 1(a), (b), respectively. The radial strain of the CNTs was considered to the deformation of the circular cross-sectional shape to the deformed elliptical CNT. The semi-major axis of the ellipse can be written $R = (1 + \varepsilon_R) R_0$, where ε_R is defined by the radial strain and R_0 is the radius of the CNT without strain. The amplitudes of the axial and the radial strains were varied 0% to 10% and 0% to 30%, respectively. In order to summarize the results, we used the dihedral angle which is an angle between π orbitals of adjacent atoms as shown in Fig. 1(c).

The analyses were performed by Accelrys' density functional theory (DFT)-code DMol^3. The generalized gradient approximation (GGA) of PW91 was applied in this analysis. The total energy was converged to within 0.5 meV with a Monkhorst-Pack *k*-point mesh of $1 \times 1 \times 50$. The longitudinal direction of the GNRs and CNTs was taken that along *c* axis and vacuum separations along both *a* and *b* axes were more than 50 Å, which was large enough to neglect the interaction of next cells. The length along *c* axis was equal to the transverse vector of CNTs, 4.26 Å in the case of GNRs and CNTs without strain.

The band gap changes of GNRs and CNTs with the increase in the maximum dihedral angle are shown in Fig. 2(a), (b), respectively. As shown in these figures, the band gap remained a small value when a GNR or CNT has initially a small band gap. On the other hand, when a GNR or CNT has a large band gap, the band gap changed drastically. Although band gaps were almost constant when the applied strain was small, band gaps decreased almost linearly as the increase in the maximum dihedral angle when the maximum dihedral angle exceeded the critical value. The decreasing rate of the band gap of CNTs was larger than that of GNRs. This should be because the area of large dihedral angle was larger than that of GNRs, and thus, the orbital hybridization occur at larger areas in the CNTs.

In order to discuss how orbital hybridization occur around the areas of large dihedral angles, the change of the band structure of GNR (N = 10) is

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shown in Fig. 3. As shown in this figure, the highest occupied molecular orbital (HOMO) energy did not change significantly as the increase in the maximum dihedral angle. On the other hand, the lowest unoccupied molecular orbital (LUMO) energies changed significantly. When the maximum dihedral angle was small, the second LUMO energy decreased as the increase in the maximum dihedral angle while the LUMO energy did not changed significantly. After the second LUMO energy merged into the LUMO energy at the maximum dihedral angle of 14 degrees, the LUMO energy started to decrease which resulted in the decrease in the band gap. Because the LUMO and the second LUMO indicate π and σ orbitals, this result indicate that the band gap started to decrease after π orbitals hybridized with σ orbitals and that the decrease in the σ orbital energy caused the orbital hybridization. Therefore, by analyzing the second LUMO energy around strained areas, the estimation of the local band gap of CNTs under complicated strain should be possible.

CONCLUSION

The electronic state of GNRs and CNTs under three-dimensional strain field was analyzed by using the DFT calculation in order to understand how orbital hybridization is induced around strained areas. We found that the decrease in the second LUMO energy resulted in the orbital hybridization which caused the decrease in the band gap. The structural dominant factor which caused the bad gap change was the distribution of dihedral angle.

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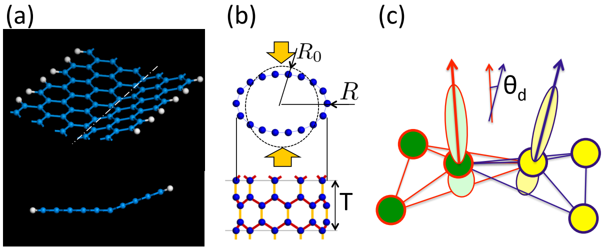

Fig. 1 Examples of the analysis model of (a) GNRs and (b) CNTs, and (c) dihedral angle.

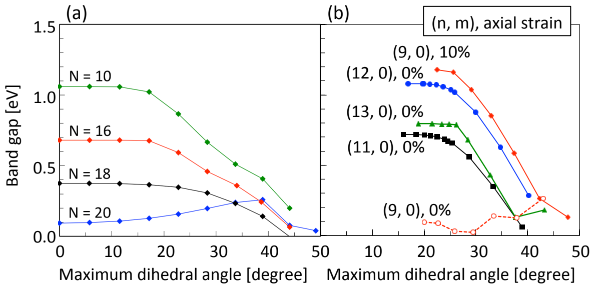

Fig. 2 Change in the band gap of GNRs and CNTs caused by orbital hybridization

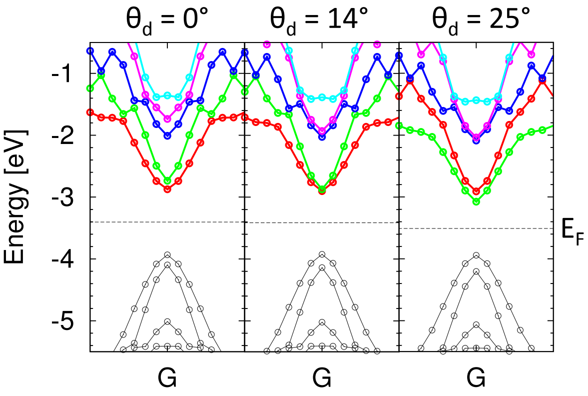

Fig. 3 Change in electronic band structure of AGNR (N=10) with the increase in the maximum dihedral angle