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A First-principles Study on the Strain-induced Localized Electronic Properties of Dumbbell-shape Graphene Nanoribbon for Highly Sensitive Strain Sensors

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***Abstract*—The electronic properties of graphene nanoribbons (GNRs) have a function of the ribbon width. It can vary from metallic-like ones to semiconductive-like ones when the width of single GNR is changed. Therefore, the novel structure of GNRs called dumbbell-shape GNR (DS-GNR) was proposed to achieve the development of highly sensitive, reliable, and deformable strain sensors. The DS-GNR consists of one long narrow GNR coalesced by two wide segments of GNRs at its both ends. The wide segments of the original DS-GNR possess the metallic-like electronic properties and the narrow segment of the original DS-GNR has the semiconductive-like electronic properties. In this study, the strain-induced change of the electronic band structure of DS-GNR was analyzed by using the first-principles calculations. The range of the applied uniaxial tensile strain on DS-GNR was from 0% to 10%. When the length of the narrow segment of DS-GNR is longer than 4.3 nm, the effective bandgap located in the narrow segment changes obviously with the change of applied strain. The result indicates that the piezoresistive effect appears in the narrow segment of DS-GNR, and thus high strain sensitivity of its resistivity can be applied to strain sensors.**

Keywords—graphene nanoribbon, dumbbell-shape, strain-induced, first-principles, local electronic properties

I. Introduction

The further aging society requires 24-hour and high-quality nursing cares despite the shortage of caregivers. It is, therefore, indispensable to develop wearable and smart self-health-monitoring systems. Hitherto, conventional strain sensors cannot fulfill the requirements, such as the full range of the large deformation of joints with human body and the detection of fine change of vibration of the heartbeat's pulse. From this point of view, graphene, a two-dimensional (2D) monolayer material is one of the most attractive candidate materials to substitute the conventional components such as silicon utilized in electronic devices. Graphene exhibits unique super-conductive properties, high intrinsic strength, and large deformability [1]. Moreover, narrow armchair graphene nanoribbons (aGNRs) are the candidates for a sensing component of highly sensitive strain sensors owing to its appreciable bandgaps, and thus, piezo-resistance effect [2]. The aGNR manifests semiconductive-like properties with its large bandgaps. While aGNR has relatively small bandgaps exhibiting metallic-like properties. The bandgap monotonically increases when the width of aGNR decreases in all cases [3].

To fabricate highly sensitive, reliable, and deformable strain sensors with low-cost and mass-productivity, the authors have proposed a novel structure, a dumbbell-shape GNR (DS-GNR) structure, as depicted in Fig. 1 [4]. The wide segment of DS-GNR shows metallic-like properties and should have ohmic contact with external metal electrodes. The narrow segment as the sensing element in the DS-GNR shows wide variation of bandgap as a strong function of the total number of carbon atoms along its width direction. Since the DS-GNR consists of three single GNRs with different widths but only carbon atoms, it is readily to be fabricated by a dry-etching process from a large graphene sheet. In our previous study, a smooth-electron-flow existing in the junction area between the wide and narrow segment of DS-GNR has been confirmed [5]. In this study, the strain-induced change of the electronic band structure of DS-GNRs were analyzed by using the first-principles calculations based on density functional theory (DFT) to clarify the strain-induced change of electronic properties under uniaxial tensile strain.

II. Simulation Model

The simulation model of DS-GNR has wide and narrow segments as depicted in Fig. 2. The wide segment was defined to possess metallic-like properties in all cases to simulate wide GNRs or graphene in practical conditions. The narrow

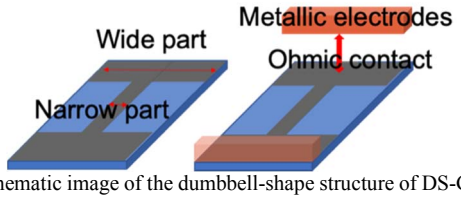

Fig. 1. Schematic image of the dumbbell-shape structure of DS-GNR for the use of strain sensors

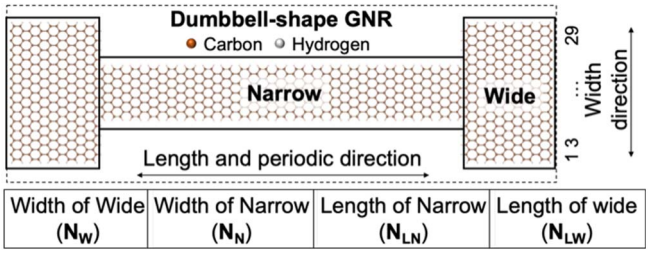

Fig. 2. Simulation model of DS-GNR. One group of six-membered ring of carbon atoms along the length direction is defined as one length of narrow and wide segment. Total number of carbon atoms connected as a dimer line along the width direction was defined as N_W and N_N.

segment was selected to have both large bandgaps and small bandgaps. The dashed line indicates supercell and it had periodic condition along the length direction, the horizontal direction in the inset. All the dangling bonds of carbon atoms on the outer frame of the structure were terminated by hydrogen atoms. Four parameters are defined to describe the structure of the DS-GNR. The width of the wide segment, N_W, the width of the narrow segment of N_N, the length of the narrow segment N_{LN}, and the length of the wide segment, N_{LW}. N_W and N_N indicate the number of carbon atoms connected as a dimer line along the width direction. N_{LN} and N_{LW} indicate two dimer lines as one unit along the length direction. The length of each segment was modelled to be longer than 10 six-membered rings because it was found that the length of the interaction area around the junction between the narrow and wide segments was about 5 six-membered rings [6]. To estimate the effect of strain, the position of each atom along the length direction was stretched uniformly from 0% to 10%.

The VASP for GPU code was utilized for fully optimizing the large dumbbell-shape structure by the RMM-DIIS method with the maximum force between two atoms less than 0.1 eV $Å^{-1}$. The SIESTA package was used for the calculations of electronic band structure and the local density of states by utilizing the conjugate gradient (CG) method. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form was used in both codes. In this study only the structure with 0% strain was fully optimized. The structures with applied strain were calculated by single-point CG method.

III. Strain-induced Change of Electrlnic Band Sturcture

Fig. 3 shows the example change of the electronic band structure of DS-NGR (N_W = 17, N_N = 07, N_{LN} = 20, N_{LW} = 05), the local density of states (LDOS), under the application of uniaxial tensile strain. The change of the LDOS in the representative two regions, line 1 (ln 1) and line 15 (ln 15), which were the center regions of the wide and narrow segments, respectively. The upper graph of LDOS in Fig. 3 describes the change of electronic band structure in the wide segment. The bottom graph of LDOS indicates that in the narrow segment. In the center region of the wide segment, the bandgap between the most inner peak of the LDOS increased with strain. It indicates that the electronic properties in the wide segment changed from metallic-like ones to semiconductive-like ones with the increment of the applied strain. On the other hand, the electronic band structure in the narrow segment changed from semiconductive-like ones to metallic-like ones with strain. The change rate of LDOS in the narrow segment was larger than that in the wide segment as indicated by the color arrows.

Similar change appeared in the DS-GNR (N_W = 29, N_N = 11, N_{LN} = 20, N_{LW} = 05) as shown in Fig. 4. In this structure, however, the effective bandgap in both segments increased monotonically with strain. Thus, the electronic properties in both regions changed from metallic-like ones to semiconductive-like ones.

These results clearly indicate that piezoresistive effect appears in the narrow segment as was expected, and therefore, high strain sensitivity of its resistivity can be applied to strain sensors. To assure the reliable operation, however, it is important to minimize the strain in the wide segment, which should show metallic properties.

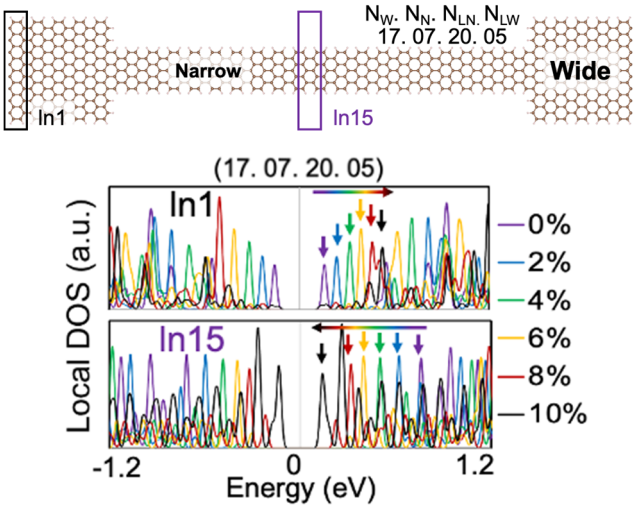

Fig. 3. Change of the electronic band structure in the center regions of the wide (ln 1) and narrow (ln 15) segments of DS-GNR (17, 07, 20, 05) under strain

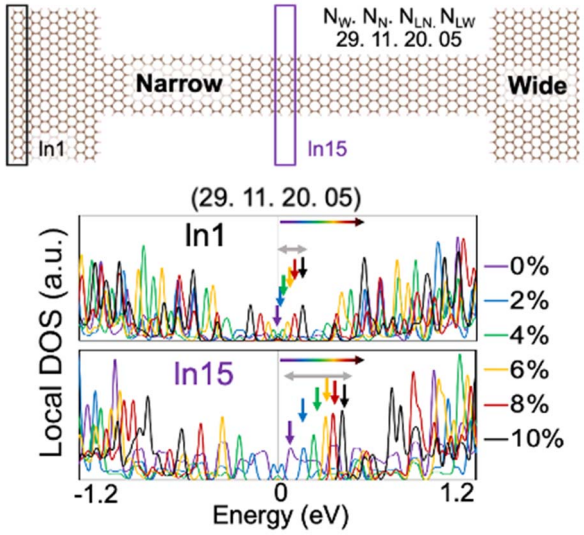

Fig. 4. Change of the electronic band structure in the center regions of the wide (ln 1) and narrow (ln 15) segments of DS-GNR (29, 11, 20, 05) under strain

IV. Strain-induced Change of Electron Orbital Distribution

Figs. 5(a) and 5(b) show the electron orbital distribution of DS-GNR (29, 11, 20, 05) on the highest occupied molecular orbitals (HOMO). Yellow region indicates positive phase of the movement of electrons and green region indicates that of negative phase. As shown in the Figs. 5(a) and 5(b), the colored region is located in the wide segments of DS-GNR with 0% and 10% strain. The results reveal that the possibility of the movement of electrons in the wide segment of DS-GNR is higher than that of in the narrow segment under strain, and thus the strain sensitivity of the narrow segment of DS-GNR is higher than that of in the wide segment owing to its large resistivity. The figures of electron orbital distribution of DS-GNR with strain from 0% to 10% have identical pattern at the HOMO 1, thus, those are not shown here.

In particular, the electron orbital distribution of DS-GNR with 10% strain exhibits a gradient transition region around the junction between the wide and the narrow segment. It

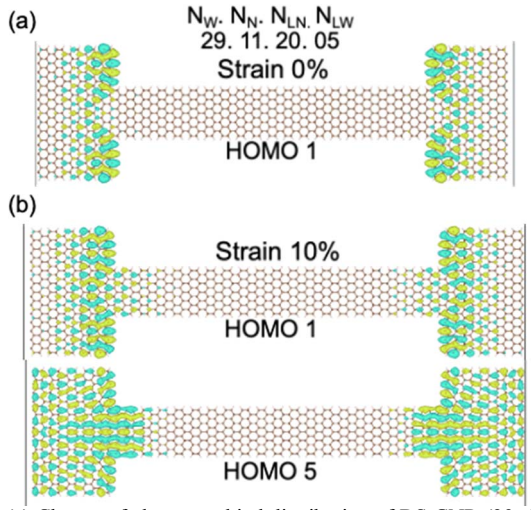

Fig. 5. (a) Change of electron orbital distribution of DS-GNR (29, 11, 20, 05) at the first HOMO (HOMO 1) with 0% strain (b) Change of electron orbital distribution of DS-GNR (29, 11, 20, 05) at the HOMO 1 and the fifth HOMO (HOMO 5) with 10% strain

indicates that electrons transfer smoothly from the wide segment to the narrow segment of DS-GNR with 10% strain. In addition, the electron orbital distribution of DS-GNR with 10% strain exhibits localized pattern on the fifth HOMO (HOMO 5). This result indicates that piezoresistive effect has more impact in the narrow segment with 10% strain than that of 0% strain, and thus, higher strain sensitivity of its resistivity can be achieved for use in strain sensors with applied strain.

V. Strain-induced Change of Electrlnic Band Sturcture with Fixed Bonding Length in the Wide Segment of DS-GNR

In this sub-section, another condition is hypothesized that the DS-GNR is suspended for use in highly deformable strain sensors. Since the widths between the wide and the narrow segment are relatively different, the stress appeared in two segments should be different with the same force applied in DS-GNR under uniaxial tensile strain. Therefore, the strain deformation in the wide and the narrow segments is different in this condition. When the width of wide segment becomes much wider than that of narrow segment or the wide segment becomes large area graphene, the carbon-carbon bonding length in the wide segment of DS-GNR should show negligible change during the applied strain, in other words, no strain appears in the wide segment. Therefore, the strain-induced change of electronic band structure with the fixed carbon-carbon bonding length in the wide segment of DS-GNR was also analyzed by the first-principles calculations here. It is, likewise, applied to the condition which the DS-GNR has suspended GNR in the narrow segment but with deposited metal electrodes on the wide segment (no strain in the wide segment).

The bonding length between the wide and the narrow segment changed abruptly in this study as the pre-calculation in order to simplify the cumbersome simulation factors. Thus, only the position of each atom along the length direction in the narrow segment of DS-GNR was stretched uniformly from 0% to 10% in this condition.

Fig. 6 shows the example change of the electronic band structure of DS-GNR ($N_W = 29$, $N_N = 11$, $N_{LN} = 20$, $N_{LW} = 05$), the LDOS, under the application of uniaxial tensile strain with

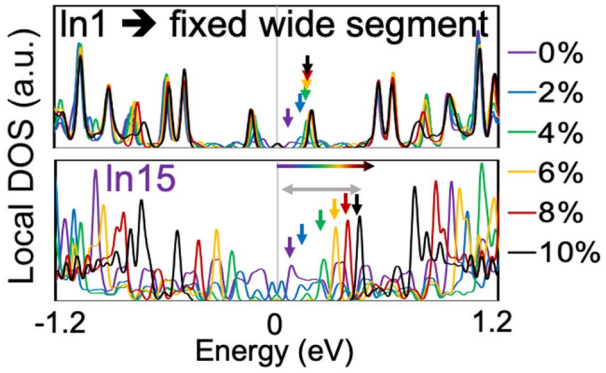

Fig. 6. Change of the electronic band structure in the center regions of the wide (ln 1) and narrow (ln 15) segments of DS-GNR (29, 11, 20, 05) with fixed carbon-carbon bonding length in the wide segment under strain

fixed carbon-carbon bonding length in the wide segment. The upper graph of LDOS in Fig. 6 describes the change of electronic band structure of DS-GNR with the fixed wide segment. In the center region of the fixed wide segment, the peaks of bandgap are superposed practically under strain. It indicates that the electronic properties in the wide segment has nearly no change with the increment of the applied strain which was metallic-like properties. The bottom graph of LDOS in Fig. 6 presents the change of electronic band structure of DS-GNR with uniaxial strain in the narrow segment. However, the electronic band structure in the narrow segment changed from metallic-like ones to semiconductive-like ones. The change is identical to that of DS-GNR without fixed carbon-carbon bonding length in the wide segment which already indicated above as shown in Fig. 4.

The results clearly indicate that piezoresistive effect appears in the narrow segment even there is no piezoresistive effect in the wide segment, and therefore, high strain sensitivity of its resistivity can be applied to strain sensors by utilizing DS-GNR.

Fig. 7 expresses the change of effective bandgap between single GNRs and DS-GNRs with fixed carbon-carbon bonding length in the wide segment under strain. The solid line with square points (ln 1) indicates the change of effective bandgap in the wide segment of DS-GNR. The slope of it is nearly flat with strain close to 10%. It indicates that the strain sensitivity of wide segment is low which should show metallic properties continuously under strain. Whereas, the strain sensitivity is still high in the narrow segment (solid line with triangle points, ln 15) regardless the low strain sensitivity in the wide segment. It has great potential for enhancing the reliability of strain sensors utilizing DS-GNRs with multi-GNRs in the narrow segment due to its high strain sensitivity of its resistivity when the length of the narrow segment is longer than 10 N_{LN} (4.3 nm).

The dumbbell-shape structure has stable ohmic contact to the external metal electrodes owing to its metallic-like properties in the wide segment under strain in this condition. In addition, the DS-GNR consists of only carbon atoms, hence, it has the smooth-electron-flow between the wide segment and the narrow segment.

VI. Conclusions

The change of the local electronic band structure of DS-GNRs under uniaxial strain was analysed by applying the first-principles calculation. High strain sensitivity was validated in

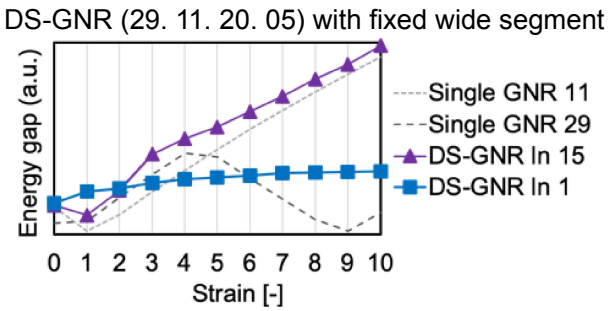

Fig. 7. Change of the effective bandgap in Single GNRs and in the center region of the wide (ln 1) and the narrow (ln 15) segments of DS-GNR with fixed carbon-carbon bonding length in the wide segment under strain

the GNR narrower than 70 nm. The sensitivity was found to increase with the decreases in the width of GNR. Therefore, the DS-GNR exhibits great potential to be applied to highly sensitive, reliable and deformable strain sensors.

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