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Local equilibrium configurations and minimum energy path of carbon nanotubes with Stone-Wales defects and their related pentagon-heptagon lattice defects

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ABSTRACT

The energy landscape over configurational change of defects in carbon nanotube (CNT) is clarified for a variety of distributions of Stone–Wales defects and pentagon–heptagon (5–7) defects using the Peierls–Nabarro dislocation model. Based on the theoretical model, the configurational energy is estimated by relative displacement without fatal loss of accuracy, but the calculation of energy during the configurational change of defect is simplified with reduced degrees of freedom in the displacement field. The equilibrium configurations are obtained using the conjugate-gradient method, and the saddle point on the minimum-energy path between two equilibrium configurations for evolution of defects, such as the nucleation/annihilation and movement of defects, is estimated using the nudged elastic-band method. Many equilibrium configurations stably exist because of the lattice trapping of the 5–7 defects due to the relatively large Peierls–Nabarro barrier. The total energy does not only depend on the mean value of the relative displacement, but also on the complexity of the configurations of the defects, and we draw a directed graph which shows the possible paths of the configuration change of the defects. The results provide fundamental information related to the stability of the thermal activation of defects in CNT.

1. Introduction

Carbon nanotubes (CNTs) are applied to nano-sized electronic and electromechanical devices such as nano-sensors [1,2], nano-medicinal therapy [3], conductive materials [4], and energy storage [5], because of their distinctive electronic and mechanical properties such as ultra-high stiffness and strength [6]. According to scanning tunneling microscopy and transmission electron microscope observations, topological defects such as vacancies, metastable atoms, pentagons, heptagons, Stone–Wales (SW) defects, and pentagon–heptagon (5–7) defect pairs commonly exist in CNTs [7–9]. Lattice defects typically behave as weak points in most materials, however, they sometimes bring good characters due to the local disorder. Some appropriate distribution of lattice defects in nano materials could provide a breakthrough for increasing the electrochemical capacitance [10], and the deformation mechanism map of CNTs with defects is drawn as a function of temperature and bending curvature[11]. Different types of defects commonly exist in nano-materials, and they play an important role in determining the shape of nano-structures during the generation process: The defects formed by rotation of carbon–carbon (C–C) bonds usually reduce the stiffness of CNTs [12], but they can control the chirality for nanotube growth [13]. The defects alter the conductivity determined by chirality, determine new forms of deformation [14], and construct junctions by connecting two zigzag tubes with different helicities and diameters [15]. The large energy barrier at room temperature prevents from the translational motion of defects, but thermally activated process at elevated temperature makes it possible with the help of displacement of the crystalline structure [16]. Active defects in nano-carbon have been observed [17], and plastic deformation of CNT caused by dynamical motion of defects has been reported [18,19].

Theoretical approaches and simulations are useful to understand the detailed mechanism of processes from viewpoints of energy and force that may not be captured straightforwardly by experiments. It is clarified that a 5–7 defect pair is more stable than a local Haeckelite structure based on the first-principles density functional theory [20], and by calculation the total energy, the 5–7 defect pair is found to be more highly reactive than pristine

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tube walls [21]. According to molecular dynamics (MD) simulations, the chirality of CNTs is partly changed during reconstruction [22], and the topological defects affect the buckling behaviour [23,24]. The process of adsorption, reflection, substitution, penetration and damage in CNT with defects have been researched using the MD method [25]. The activation energy of defects impedes the formation of localized predominant instability [26], and an activation energies are required for the nucleation of SW-defect and the motion of 5–7 defect pair [27,28].

Theoretical analysis is an attractive tool that can summarize basic characters that are commonly observed for active defects in experiments, and it can reduce the time required for large-scale atomic simulations, while enabling us to obtain fundamental knowledge to design and control the defect structure from qualitative and quantitative perspectives. Plastic deformation due to slip-motion of the 5–7 defect pair and pseudo-climb [29], and the efficiency of use of the relative displacement on the slip-plane in theoretical approach have been reported [30]. The SW defect as a dipole of dislocation and anti-dislocation in graphene has been studied analytically based on the free-energy function principle [31]. The activation energy is important for the excitation of intrinsic localized modes (ILMs), which can be a trigger of SW-defect transformation [32,33].

In this research, we investigate the equilibrium configurations and stability of a series of distributions of 5–7 defect pairs in zigzag CNTs. There is related literature on dislocation motions in graphene using experiment and simulation methods, but there has been little published work on theoretical studies of the energy landscape and the minimum energy path (MEP) for different defect configurations in CNTs in a systematic and effective way. We use the theoretical formulation based on the Peierls–Nabarro model proposed by Wang et al. [30,31], in which the total energy is described in terms of the relative displacements on atoms in the upper and lower layers on a slip region. To estimate the total energy of the CNT with high accuracy with limited the degree of freedom, the parameters in the model are fitted to reproduce the generalized stacking fault energy obtained by *ab initio* calculation based on density functional theory. First, we find the equilibrium points using the conjugate gradient (CG) method. Then, we find the MEP on which the transition between local equilibrium configurations occurs via saddle-point configuration. We utilize the nudged elastic band (NEB) method [34,35], to determine the MEP to obtain fundamental understanding for the temporal evolution of defect structures. We search for the saddle-point configuration and determine the energy landscape. We quantitatively estimate the energy change during the elemental process on the motion of defect pairs, and obtain the activation energy and released energy. Finally, we draw a directed graph to show the possible path between two equilibrium configurations. The mathematical graph theory is efficiently used to study in chemical applications [36]. The obtained graph shows the combinations of two equilibrium state that can be transformed from one to the other, and it can predict the deformation path of CNTs.

2. Mechanical analysis model of CNT with defects

SW defects can be regarded as a conjunction of 5–7 defect pair by local rearrangement of atoms [37,38], which is shown in Fig. 1 (a). The position of an atom is identified by three components of displacement, and it is useful to take radial, axial and circumferential directions according to the geometry of CNT. The distribution of the radial component of displacement field is not only related to the out-of-plane deformation but also the strain in the circumferential direction. During the nucleation/annihilation of SW defect and motion of 5–7 and 7–5 defects, however, breaking of a C–C bond and lattice rotation to create a new bond occurs. In such inelastic deformation with topological change of atomistic structure, the deformation is mainly represented by the relative displacement on the slip plane along the circumferential direction.

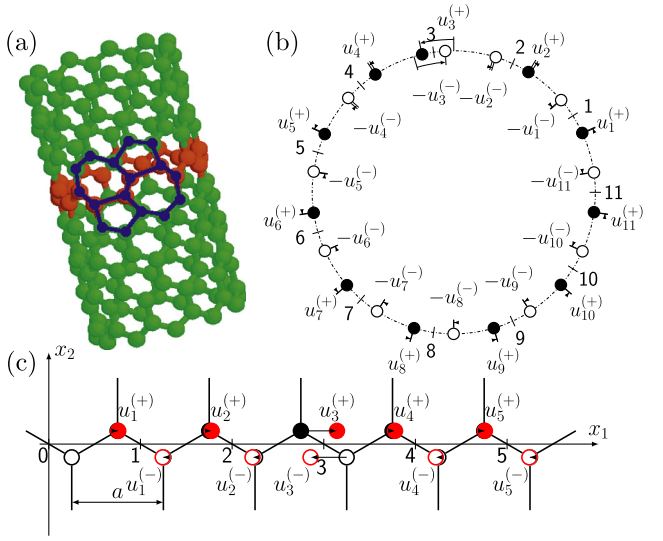

Fig. 1. (11, 0)–CNT including a Stone–Wales (SW) defect: (a) Bird's-eye view of the model: representative atoms are indicated (painted in red). The SW defect are characterised by pentagon–heptagon defects (5–7) defects (painted in blue). The total energy are represented as a function of the relative displacement on slip region (painted in red). (b) A cross-section view of the slip region. (c) A development view of the model. The slip region on which the relative displacement are studied. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this research, the circumferential component of the relative displacement, which is the largest contributory to evaluate the strain energy, is taken into account explicitly. Indeed, the other components of displacement is not negligibly small to the representative dimensions of CNT, but they do not affect the strain energy, because the corresponding components of stress vanish [39]. The bond rotation and rearrangement in the vicinity of the defect which are important for the migration of defect are taken into account implicitly, because the generalized stacking fault energy obtained by *ab initio* calculation based on density functional theory is fitted as a function of relative displacement u, i.e. γ-surface $\gamma(u)$ [31]. We study the circumferential migration of 5–7 and 7–5 defect pairs on a zigzag CNT, where the chiral vector is (11, 0). Fig. 1(b) shows schematics of the cross-section of a CNT with a SW defect. The lattice constant a (=2.46 Å) is measured in circumferential direction. The deformation can be expressed by the relative displacement of atomic sites, $u_1, u_2, \ldots, u_{11}$ on the interface of a cross section. Open and solid circles in Fig. 1(b) indicate the positions of the upper and lower atoms, respectively. The relative displacement,

$$u_l = \frac{1}{2}\left(u_l^{(+)} - u_l^{(-)}\right), \tag{1}$$

is defined by the difference of upper and lower displacements, $u_l^{(+)}$ and $u_l^{(-)}$, at l-th site, as shown in Fig. 1(c). The value of u_l is normalized by the lattice constant a. Based on above mentioned assumption, the total energy E_{total} is a function of the relative displacements

$$\boldsymbol{u} = (u_1, u_2, \ldots, u_n), \tag{2}$$

where the component u_l denotes the l-th atomic sites, and $n = 11$ for (11, 0)–CNT. Considering the periodicity, we use an expression

$$u_{[l]} = u_{\text{MOD}(n+l-1,n)+1}. \tag{3}$$