

Shear Properties of Graphene Containing Nitrogen Atoms and Grain Boundaries Using Molecular Dynamics Simulations

Shingo Okamoto and Akihiko Ito

Abstract—We investigated the shear properties of graphene containing nitrogen atoms and grain boundaries (GBs) via molecular dynamics (MD) simulations. In the MD simulation, we used two types of potential functions: the second-generation reactive empirical bond order (REBO) potential for covalent C–C bonds and the Tersoff potential for covalent C–N bonds. The effects of nitrogen content and different distributions of nitrogen atoms in graphene on its properties were studied. It was found that a nitrogen content of up to 4 % had little effect on the shear properties of graphene except when two nitrogen atoms contained in graphene adjoined each other. In addition, the shear strength depends more greatly on GBs than nitrogen atoms.

Index Terms—graphene, molecular dynamics, nitrogen, shear strength, grain boundary

I. INTRODUCTION

CARBON materials have contributed the weight saving of the air frames, vehicle bodies and sports gears owing to their superior mechanical properties. However, the additional improvement in cost performance has been requested to expand the range of applications. Graphene, which is basic structure in carbon fibers, has been found to have excellent tensile strength (~130 GPa) and the same Young's modulus (~1 TPa) as that of diamond. Therefore, more studies on graphene have recently increased in number [1]. Carbon fibers contain various types of defects, namely, vacancies [2], dislocations [3], grain boundaries (GBs) [4] and heteroatoms [5]. It is crucial to clarify the relations between those defects and the mechanical properties of graphene to develop high-performance carbon fibers.

Carbon fibers derived from raw materials often contain impurities such as oxygen, nitrogen, or hydrogen atoms, and these impurities may affect the mechanical and electronic properties of the materials. Recently, Shen *et al.* [6]

investigated the effects of nitrogen (N) doping on the mechanical properties of ultrananocrystalline diamond (UNCD) films, using molecular dynamics (MD) simulations. We performed the MD simulations on tensile loading of N-containing graphene in order to investigate the effect of N-atoms on mechanical properties of graphene in our previous paper [7]. It was found that N-atoms had little effect on the tensile properties of graphene except when two nitrogen atoms contained in graphene adjoined each other. The tensile properties of graphene with GBs were investigated by Grantab *et al.* using molecular simulations [8]. The shear properties of pristine graphene were estimated by Min *et al.* [9]. However, the shear properties of graphene with N-atoms and GBs have not been clarified so far. In this study, we investigated the influence of N-atom on the mechanical properties of graphene under shear loading, via MD simulations. In addition, we clarified the shear properties of graphene containing both N-atoms and GBs using MD simulations.

II. METHOD

A. Potential Function

In the present study, we used two types of interatomic potentials: the second-generation reactive empirical bond order (2nd REBO) [10] and Tersoff [11], [12] potentials. The 2nd REBO potential for covalent C–C bonds is given by (1):

$$E_{REBO} = \sum_i \sum_{j>i} \left[V_R(r_{ij}) - B_{ij}^* V_A(r_{ij}) \right]. \quad (1)$$

The terms $V_R(r_{ij})$ and $V_A(r_{ij})$ denote the pair-additive interactions that reflect interatomic repulsions and attractions, respectively. The B_{ij}^* denotes the bond-order term.

The Tersoff potential for covalent C–N bonds is given by (2):

$$V = \frac{1}{2} \sum_{i \neq j} \left[f_C(r_{ij}) A_{ij} \exp(-\lambda_{ij} r_{ij}) - b_{ij} f_C(r_{ij}) B_{ij} \exp(-\mu_{ij} r_{ij}) \right], \quad (2)$$

where the parameter b_{ij} is the bond-order term that depends on the local environment.

$$b_{ij} = \chi_{ij} \left(1 + \beta^n \zeta_{ij}^n \right)^{-1/2n_i} \quad (3)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) g(\theta_{ijk}), \quad (4)$$

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$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos \theta_{ijk})^2}, \quad (5)$$

where θ_{ijk} is the angle between bonds ij and ik .

The parameters A_{ij} , B_{ij} , λ_{ij} , and μ_{ij} depend on the atom type, namely, carbon or nitrogen. For atoms i and j (of different types), these parameters are

$$A_{ij} = (A_i \times A_j)^{\frac{1}{2}}, \quad B_{ij} = (B_i \times B_j)^{\frac{1}{2}} \quad (6)$$

$$\lambda_{ij} = \frac{(\lambda_i + \lambda_j)}{2}, \quad \mu_{ij} = \frac{(\mu_i + \mu_j)}{2}, \quad (7)$$

where the parameters with a single index represent the interaction between atoms of the same type.

The parameter χ_{ij} in (3) takes into account the strengthening or weakening of the heteropolar bonds. There is no data for the determination of χ_{ij} for C–N interaction at present. In our model, this χ_{ij} is set to 0.8833 to obtain the lattice constants a and b of the graphitic- C_3N_4 orthorhombic structure as 4.10 and 4.70 Å, respectively similar to the previous work [7]. From discussions on the N–N interaction, we know that the N molecule does not interact with other atoms, because of its high binding energy (9.8 eV) and that it diffuses through the crystal and exits the surface. In our model, to keep the nitrogen molecule stable inside the crystalline structure, χ_{N-N} is set to zero [6], [12].

In this work, the cutoff length R_{min} in the cutoff function $f_c(r)$, given by (8) of both the 2nd REBO and the Tersoff potentials is set to 2.1 Å to avoid the dramatic increase in interatomic forces similar to the method in our previous paper [7].

$$f_c(r) = \begin{cases} 1, & r < R_{min} \\ \left\{ 1 + \cos \left[\frac{\pi(r - R_{min})}{R_{max} - R_{min}} \right] \right\} / 2, & R_{min} < r < R_{max} \\ 0, & r > R_{max} \end{cases} \quad (8)$$

B. Analysis model

The analysis model of pristine graphene employed under the shear loading of armchair direction consists of 588 carbon atoms with dimensions identical to those of a real crystallite in typical carbon fibers [13], as shown in Fig. 1(a). In the case of the shear loading of zigzag direction, the analysis model consists of 576 carbon atoms with the same dimensions, as shown in Fig. 1(b).

The analysis model of graphene containing tilt GBs under the shear loading consists of 730 carbon atoms as shown in Fig. 2. There are many possible GB angles (the angles represent the total mismatch angle between the left and right grains) for graphene models with GBs. In the present study, we adopted the model with the GB angle of 21.7° which has the largest tensile strength among the models with each GB angle [8]. In this case, the five-membered rings and seven-membered ones are present in the GBs.

The periodic boundary condition is imposed in only the Y direction in the calculations of shear loading. The analysis models consist of two parts. One part is referred to as the active zone, in which the atoms move according to their

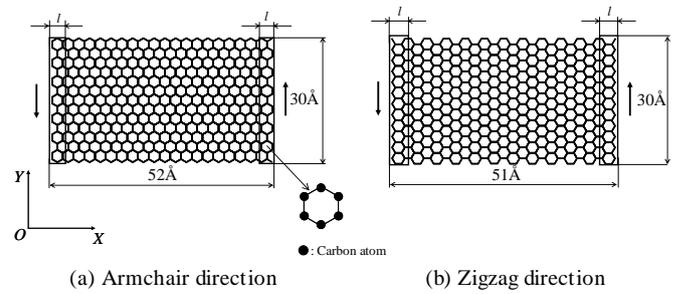


Fig. 1. Configuration of pristine graphene without GBs used under shear loading

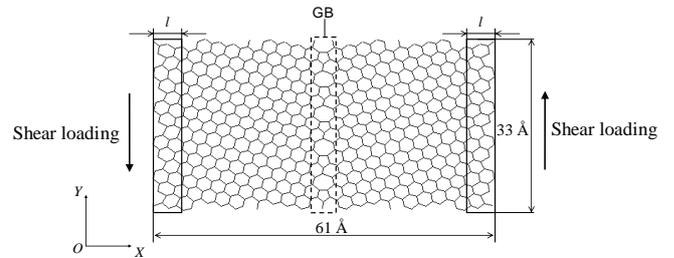


Fig. 2. Configuration of graphene containing armchair GBs with the GB angle of 21.7° used under shear loading.

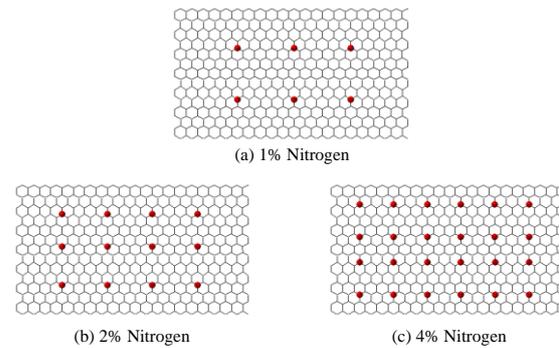


Fig. 3. Analysis models for N-containing graphene at each N-contents.

interactions with neighboring atoms. The other part enclosed by the boxes as shown in Figs. 1 and 2 is referred to as the boundary zone, in which the atoms are restrained. The thickness l of the boundary zone is $1.5 \times \sqrt{3}a$ and $1.5a$ for the model without GBs used under shear loadings in the armchair and zigzag directions, respectively, where a is the length of C=C bond of graphene. The l of the analysis model with GBs is 4.23 Å.

The analysis models for uniformly distributed N-atoms in graphene are shown in Fig. 3. The carbon atoms in the active zone of the graphene model used in the armchair direction, as shown in Fig. 1(a), are replaced with the N-atoms such that the distance between neighboring N-atoms can be consistently uniform.

Three cases with differing N-contents, namely, 1 %, 2 %, and 4 %, are investigated.

In the analysis models of randomly distributed N-atoms in graphene, random carbon atoms in the active zone are replaced with N-atoms using pseudorandom numbers so that any N-atoms can not adjoin each other.

C. MD simulation

All the MD calculations employ the velocity Verlet method to calculate the time integral of the equations of motion of

atoms. The velocities of all atoms are adjusted simultaneously using the velocity scaling method [14] in order to control the temperature of the analysis models by the preset temperature T_{SET} . The mass of carbon atoms, m_C , and the mass of N-atoms, m_N , are 1.9927×10^{-26} kg and 2.3253×10^{-26} kg, respectively. The time step is 0.2 fs.

The atomic stress acting on each atom is calculated to obtain the stress-strain curves and visualize stress distribution during shear loadings. The atomic stress σ_{IJ}^i which is a component in the J direction in the I -plane is given by calculating the kinetic energies of, the interatomic force acting on, and the volume occupied by atom i , as given in (9):

$$\sigma_{IJ}^i = \frac{1}{\Omega^i} \left(m V_i^i V_{IJ}^i + I^i F_{IJ}^i \right), \quad (9)$$

where, Ω^i denotes the volume occupied by atom i , which is referred to as the atomic volume. This volume is calculated by averaging the volume of all atoms in the initial structure of each system. The m can be either m_C or m_N . The F_{IJ}^i denotes the interatomic force acting on atom i from the neighbouring atoms. The global stress of an analysis model is calculated by averaging over all atoms in each system.

The initial positions of the atoms are given such that the analysis model can become identical to the crystal structure of N-containing graphene at 300 K. First, the atoms of the analysis model are relaxed until the stresses are stabilized for 14,000 MD simulation steps. The atoms in the active zone are relaxed in all the directions. The atoms in the left-hand side boundary zone are relaxed in only the Y direction. The atoms in the right-hand side one are relaxed in only the X and Y directions. After the atoms are relaxed, constant displacements are applied to the atoms in the boundary zones to calculate the shear loading in the Y direction. The atoms in the boundary zones are restrained in all the directions. The atoms in the active zone of the analysis model are relaxed for all the directions for 7,000 MD simulation steps. The shear strain increment $\Delta \gamma_{xy}$ is 0.0023. The shear moduli are obtained from

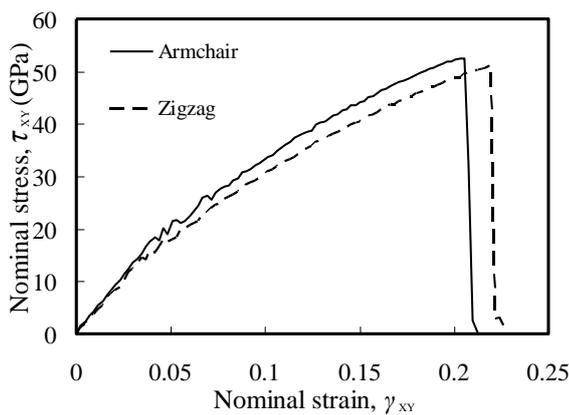


Fig. 4. Stress-strain curves of pristine graphene under shear loading.

TABLE I
SHEAR PROPERTIES OF PRISTINE GRAPHENE

Direction	Shear strength (GPa)	Shear modulus (GPa)
Armchair	53	442
Zigzag	51	408
Average	52	425

the slopes of the straight lines in the range, where the relation between the stress and strain is linear, and the shear strengths are given by the peak of the nominal stress–nominal strain curves.

III. RESULTS AND DISCUSSION

A. Validation of calculation method

We performed the MD simulations on shear loadings of pristine graphene at 300 K to verify the propriety of our calculation method. The results of shear loadings are shown in Table I and Fig. 4. The average shear strength is 52 GPa, which nearly agrees with the 60 GPa calculated by Min *et al.* [9] using MD simulations. The average shear modulus is 425 GPa, which also nearly agrees with the experimentally obtained value of 434 GPa by Blaklee *et al.* [15].

B. Shear properties of nitrogen-containing graphene without GBs

MD simulations on shear loadings were performed in order to investigate the effect of N-atoms on the shear properties of graphene without GBs. In all the MD calculations, the shear loadings were applied in the armchair direction using the analysis model as shown in Fig. 1(a). Examples of the stress-strain curves of graphene containing uniformly distributed N-atoms are shown in Fig. 5. The calculated shear strengths and moduli are listed in Table II.

It was found that the shear strength and modulus of the graphene sheet do not change much with a change in the N-content.

Snapshots taken during the shear loadings are shown in Fig. 6. In all the cases, fractures occur because of cleavage of the C–C bond, which is in proximity to a C–N bond. This behavior was also found during the tensile loadings as reported in our previous paper [7].

Examples of the stress-strain curves of graphene containing randomly distributed N-atoms that do not adjoin each other, are shown in Fig. 7. The calculated shear strengths and moduli are listed in Table III. The shear strength and modulus do not change much with a change in the N-content.

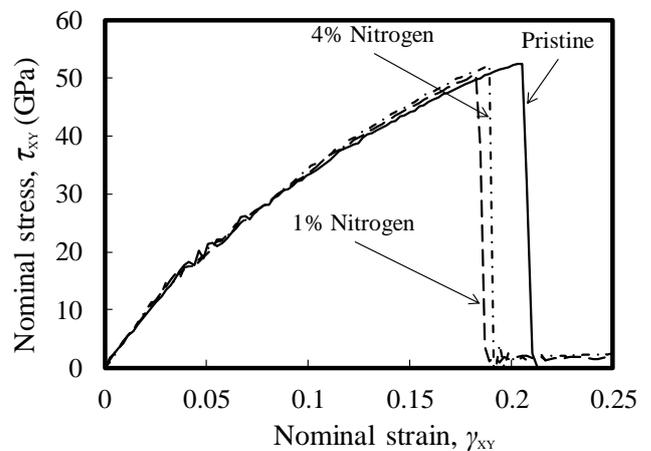


Fig. 5. Stress-strain curves of graphene containing uniformly distributed N-atoms.

TABLE II
SHEAR PROPERTIES OF GRAPHENE CONTAINING UNIFORMLY DISTRIBUTED N-ATOMS

Nitrogen content (%)	Shear strength (GPa)	Shear modulus (GPa)
0	53	442
1	51	458
2	51	473
4	52	477

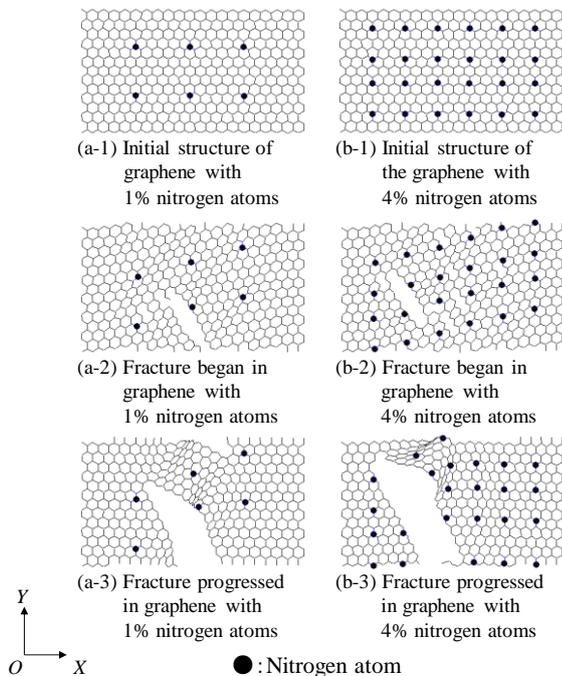


Fig. 6. Structures before tensile loading and after fracture for graphene containing uniformly distributed N-atoms at each N-content. 1 % nitrogen ((a-1)–(a-3)), 4 % nitrogen ((b-1)–(b-3)).

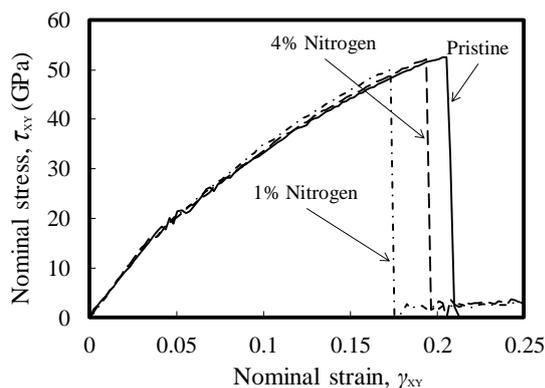


Fig. 7. Stress-strain curves of graphene containing randomly distributed N-atoms that do not adjoin each other.

TABLE III
SHEAR PROPERTIES OF GRAPHENE CONTAINING RANDOMLY DISTRIBUTED N-ATOMS THAT DO NOT ADJOIN EACH OTHER

Nitrogen content (%)	Shear strength (GPa)	Shear modulus (GPa)
0	53	442
1	52	465
2	51	479
4	50	466

Snapshots taken during the shear loadings are shown in Fig. 8. Fractures occur because of cleavage of the C-C bond, which is in proximity to a C-N bond. Those results are similar to the case of graphene containing uniformly distributed N-atoms.

Examples of the stress-strain curves of graphene containing randomly distributed N- atoms and including two adjoining N-atoms are shown in Fig. 9. The calculated shear strengths and shear moduli are listed in Table IV. The decline in shear strength is larger than in the case of the random distribution in

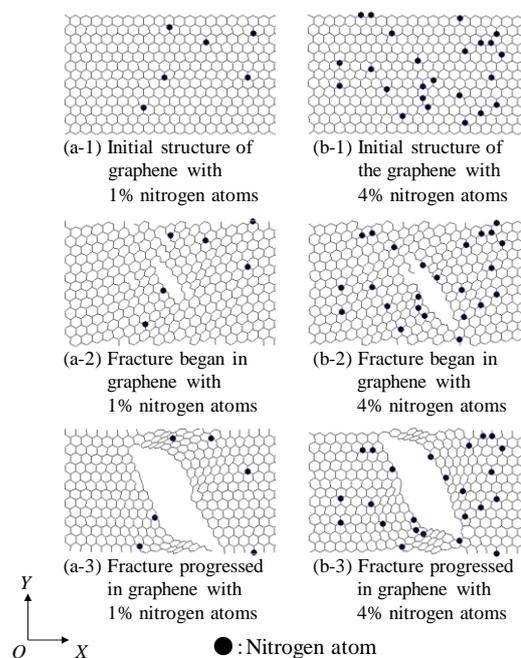


Fig. 8. Structures before shear loading and after fracture for graphene containing randomly distributed N-atoms that do not adjoin each other at each N-content. 1 % nitrogen ((a-1)–(a-3)), 4 % nitrogen ((b-1)–(b-3)).

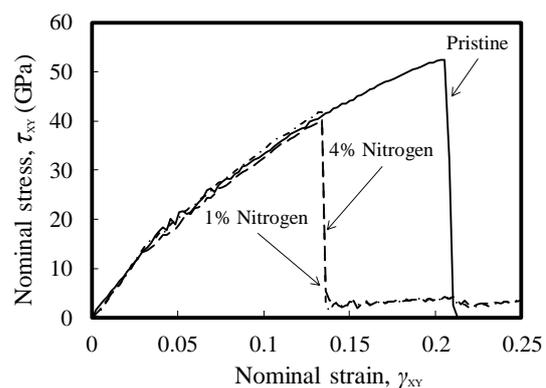


Fig. 9. Stress-strain curves of graphene containing randomly distributed N- atoms and including two adjoining ones.

TABLE IV
SHEAR PROPERTIES OF GRAPHENE CONTAINING RANDOMLY DISTRIBUTED N-ATOMS AND INCLUDING TWO ADJOINING ONES

Nitrogen content (%)	Shear strength (GPa)	Shear modulus (GPa)
0	53	442
1	40	452
2	41	462
4	42	466

which N-atoms do not adjoin each other.

Snapshots taken during the shear loadings are shown in Fig. 10. In all the cases, fracture occurs at the point where two N-atoms adjoin each other (marked by the circle), similar to the case of tensile loading as previously reported by the authors [7].

The relation between the shear strength and the N- content is shown in Fig. 11. The shear strength in the case of the randomdistribution including two adjoining N-atoms is lower than that in the other cases when N-content is over 1 %. From these results, it was found that the presence of two adjoining N-atoms in graphene affect the shear strength considerably. Then, those results are similar to the case of tensile loading.

C. Shear properties of nitrogen-containing graphene with GBs

MD simulations on shear loadings of graphene containing the tilt GBs and N-atoms were performed in order to investigate the effect of GBs and N-atoms on the mechanical properties of

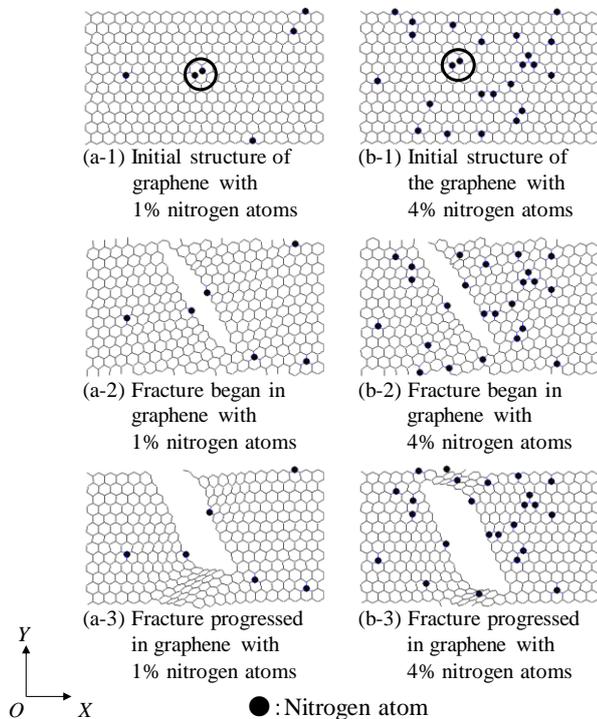


Fig. 10. Structures before shear loading and after fracture for graphene containing randomly distributed N-atoms at each N-content and including two adjoining ones. 1 % nitrogen ((a-1)–(a-3)), 4 % nitrogen ((b-1)–(b-3)).

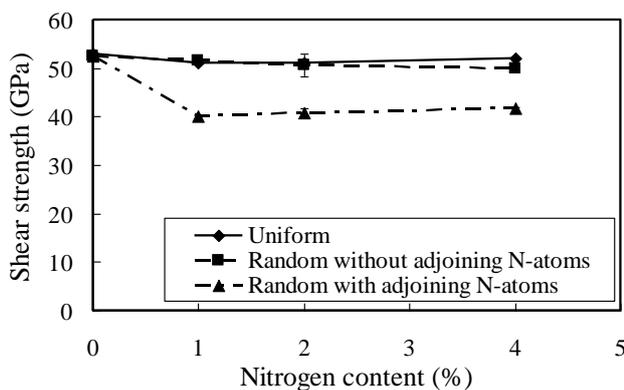


Fig. 11. Shear strength with N-content in graphene containing N- atoms on each distribution.

graphene. Examples of the stress-strain curves of graphene with the tilt GBs containing randomly distributed N-atoms are shown in Fig. 12. The calculated shear strengths and moduli are listed in Table V.

It was found that the shear strength slightly decreases when the N-content is 4 %.

Snapshots taken during the shear loadings of graphene with the tilt GBs not containing N-atoms are shown in Fig. 13.

The shear stress concentrates around the GBs, especially on the seven-membered rings. A fracture began at that point and progressed in the right hand side of the sheet. The progressing direction of fracture is zigzag one, similar to the case of graphene without GBs. However, the fracture does not progress in the left hand side of the sheet differing to the case of graphene without the GBs.

Snapshots of graphene with the tilt GBs containing

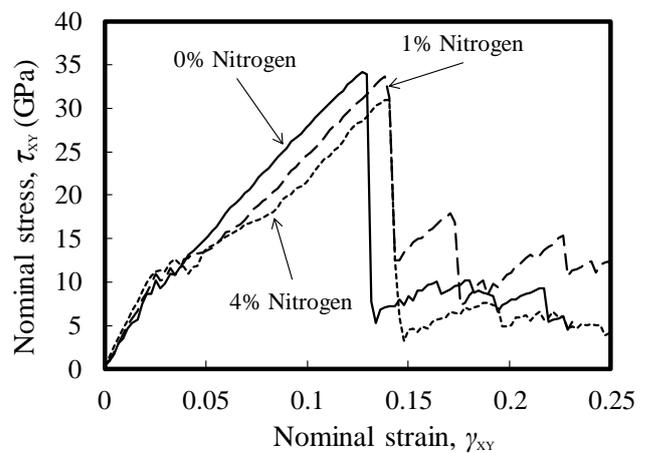


Fig. 12. Stress-strain curves of graphene with the armchair GBs containing randomly distributed N-atoms.

TABLE V
SHEAR PROPERTIES OF GRAPHENE CONTAINING THE ARMCHAIR GBs AND RANDOMLY DISTRIBUTED N- ATOMS

Nitrogen content (%)	Shear strength (GPa)	Shear modulus (GPa)
0	34	390
1	34	412
2	35	414
4	31	460

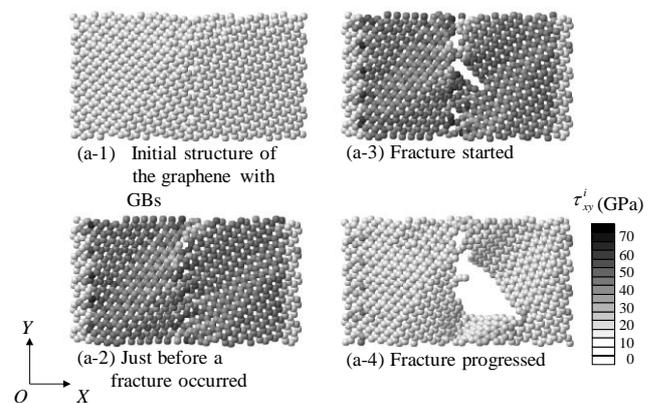


Fig. 13. Stages of fracture progress in graphene with the armchair GBs not containing N-atoms.

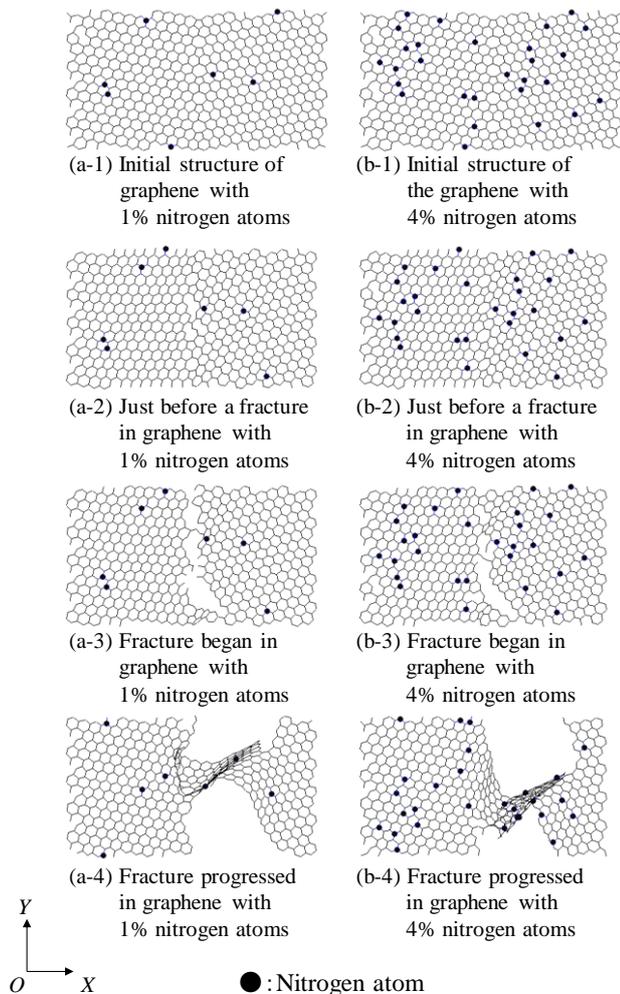


Fig. 14. Stages of fracture progress in graphene with armchair GBs at each N-content. 1 % nitrogen ((a-1)–(a-4)), 4 % nitrogen ((b-1)–(b-4)).

randomly distributed N-atoms are shown in Fig. 14. Fractures begin at the GBs and not at the C-C bond, which is in proximity to a C-N bond differing to the case of graphene without the GBs. Thus, the strength of graphene depends more greatly on the GBs than N-atoms, unless two N-atoms present in graphene adjoin each other.

IV. CONCLUSION

We performed MD simulations on shear loadings of graphene containing N-atoms and grain boundaries (GBs) in order to investigate the effect of the N-atom and GBs on the shear properties of graphene. As a result, it was found that in the case of graphene without the GBs, both the shear strength and modulus do not change much for N-content of up to 4 %, unless two N-atoms present in graphene adjoin each other. Those results were similar to the case of tensile loading previously reported by the authors. Then, the shear strength of graphene is affected more extensively by the GBs than N-atoms.

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