Investigation into the effect of doping of boron and nitrogen atoms in the mechanical properties of single-layer polycrystalline graphene

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ABSTRACT

In the present work, classical Molecular Dynamic simulations have been performed to peruse the effect of different grain sizes, temperatures and strain rates for different percentage of boron and nitrogen doping on the mechanical properties of polycrystalline graphene. Therefore, we studied 1%, 3%, 6% and 10% of boron or nitrogen doping for grain sizes of 1, 5, 10, 15, and 20 nm of graphene nanosheets at room temperature. The effect of different temperatures (100, 300, 600 and 900 K) on the mechanical response is investigated for five grain sizes (1, 5, 10, 15 and 20 nm) and 6% of boron or nitrogen doped polycrystalline graphene. Moreover, we studied different engineering strain rates on the mechanical response of six percentage of boron or nitrogen doped polycrystalline graphene for all simulation samples at 300 K. Our findings revealed that the mechanical response of polycrystalline graphene decrease as nitrogen or boron atoms are substituted into the nanosheet. By increasing of nitrogen atoms into polycrystalline graphene, a destructive affect occurs on the ultimate failure strain and tensile strength. Furthermore, the tensile strength tends to increase as the grain sizes increase from 1 to 20 nm. On the contrary, the failure strain has a tendency to decrease. As the temperatures increase in boron or nitrogen doped polycrystalline graphene, the tensile strength decreases as well as the failure strain. An increasing trend has been observed for mechanical properties of boron or nitrogen doped polycrystalline graphene as the strain rate increase. However, the effect of nitrogen on the tensile strength of nanosheet is more significant compared to boron doped nanosheet.

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1. Introduction

Two-dimensional materials like graphene [1] have become an exciting research area in nanomaterials because of their outstanding thermal [2], mechanical [3] and electrical [4] properties [5]. It is evident that the toughest and hardest materials, which have ever been identified, are carbon atoms [6]. Graphene is one of the best candidates in wide variety of applications such as nano-electromechanical systems (NEMS) [7,8], nanoelectronics [9,10] and nanocomposites [11–18], just to name a few. Former experiments by using of atomic force microscope disclosed the theory that pristine graphene nanosheets present a high tensile strength of 130 ± 10 GPa and an elastic modulus of 1 ± 0.1 TPa [3]. Furthermore, single layer graphene (SLG) can possess exceptional high thermal conductivity. It is noticeable that the aforementioned unique characteristics for graphene such as high thermal conductivity, tensile strength and elastic modulus have made this material as an excellent candidate for the reinforcement of thermal, mechanical and micro/nanoscale electronic devices [19,13]. The comprehensive perception of graphene characteristics is also crucial for further applications.

An effective way for the rectification of material characteristics is the chemical doping of materials with other atoms [20]. In fact, for the chemical doping of carbon-based material, nitrogen and boron are considered as the best candidate amid the various material dopants due to having similar atomic structure and strong valence bonds [21]. Graphene and h-BN have the same atomic structure with honeycomb atomic lattices [22]. Pervious studies on graphene have depicted that carbon atoms are subtituted with boron and nitrogen atoms; therefore, the possibility of making n-type and p-type semiconducting graphene [23–25]. Boron or nitrogen doping have been successfully employed in order to rectify the electronic band structure of graphene. Obviously, an energy gap can be made between conduction and valence bonds by adding boron or nitrogen atoms. Consequently, doping of graphene with foreign atoms such as boron or nitrogen could have been utilized in various applications such as nanosensors [24], spin filter devices

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[24], fuel cells and lithium ion batteries [26]. Undoubtedly, it is basal to comprehend the concept of effect of boron or nitrogen doping on graphene properties in their future applications.

Recently, the mechanical and thermal response of polycrystalline graphene nanotubes and nanosheets have been examined by several researchers. For instance, Huang PY et al. [27] performed the first experiment on the mechanical properties of polycrystalline graphene specimen in which the tensile strength and elastic modulus were obtained 35 and 160 GPa, respectively. By contrast, Lee et al. [28] performed experiments where polycrystalline graphene nanosheets with different grain sizes (1–5 nm) achieved a tensile strength and elastic modulus of almost 100 and 965 GPa, respectively. It is clear that the remarkable variation [28] with the first experimental study [27] is found to be due to an inaccurate technique of producing nanomaterial sheets, which weakened the grain boundaries [29]. Thus, the mechanical and thermal response of polycrystalline graphene nanosheets through classical Molecular Dynamic (MD) simulations and density function theory (DFT) have been investigated. Mortazavi et al. [30] studied the mechanical response of boron doped defect-free graphene for a unique strain rate through Molecular Dynamic simulations at room temperature. The result revealed that boron doped graphene can have insignificant reduction efficacy on the graphene properties. As consequence, with 4% boron doped graphene, the tensile strength and elastic modulus decrease by roughly 8 and 5%, respectively. They furthermore studied [31] the mechanical response of nitrogen doped defect-free graphene with different chirality, where the youngs modulus through the expansion of the concentration of nitrogen atoms is not altered whereas the ultimate tensile strength decreased significantly and ductile behavior of graphene is changed to brittle as well. On the other hand, Wei et al. [32] studied the mechanical properties of the h-BN hybridization lateral heterostructure and the GB tilt angles graphene using classical Molecular Dynamics method.

The most striking feature is that the deformation of defect is highly limited in graphene at temperature below its melting point due to high stability of graphene sheets at room temperature [33]. Consequently, it is noticeable that defects are chiefly produced during the fabrication of graphene sheets. Presently, several methods have been utilized, including evaporation of surface layer Si on SiC, graphite sonication in a proper liquid medium, and chemical vapor deposition (CVD) on metals. However, an effective way to generate large-area graphene sheets in industry-scale is chemical vapor deposition (CVD) technique [34,35]. The fabrication of polycrystalline graphene nanosheets are as a consequence of growing crystal during the CVD process. The grain boundaries in polycrystalline graphene sheets generated by the CVD technique may decline the thermal conductivity and electrical [36] as well as stability of graphene structure under mechanical loading [37]. Hydrogenation has been extensively taken as an effective way to manipulate the thermal [38], electronic [39], magnetic [40] properties of graphene and GBs for hydrogenation [35]. Although, a theory has been disclosed that hydrogenation can exacerbate the fracture strength of graphene structures because of weakening effect of sp³ hybridization [41–43,35]. To our best knowledge, the mechanical response of boron and nitrogen doped polycrystalline graphene through Molecular Dynamic simulation has not been surveyed yet. In the present paper, we will concentrate on the effect of boron or nitrogen doping on the mechanical response of polycrystalline graphene comprehensively in order to extend former studies.

2. Computational models and methods

In this paper, all simulation are performed with the open-source software LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator) package [44]. We visualized the output results from

LAMMPS by OVITO [45]. The optimized Tersoff potential proposed by Lindsay and Broido [46] was used for the bonding interaction between carbon and carbon atoms rather than the original Tersoff potential [47,48]. The ultimate tensile strength obtained through the optimized Tersoff potential for single layer graphene [6] agree better with experimental results [3]. The optimized Tersoff potential parameters for boron, nitrogen [49] and carbon [46,49] are provided in Table 1. The boron, nitrogen and carbon bonding interaction parameters are computed from Eq. (10) [50]. Eq. (1) demonstrates the potential energy (E) between two adjoining atoms i and j.

$$E = \sum_i E_i = \frac{1}{2}\sum_{i \neq j} V_{ij} \tag{1}$$

with,

$$V_{ij} = f_c(r_{ij})\left[f_R(r_{ij}) + b_{ij}f_A(r_{ij})\right] \tag{2}$$

$$E = \frac{1}{2}\sum_i \sum_{j \neq i} f_c(r_{ij})\left[f_R(r_{ij}) + b_{ij}f_A(r_{ij})\right] \tag{3}$$

$$f_R(r_{ij}) = A_{ij}\exp(-\lambda_{ij}^I r_{ij}) \tag{4}$$

$$f_A(r_{ij}) = -B_{ij}\exp(-\lambda_{ij}^{II} r_{ij}) \tag{5}$$

The cutoff function $f_c(r_{ij})$ is given by:

$$f_c(r_{ij}) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{r-R}{D}\right), & R - D < r < R + D \\ 0, & r > R + D \end{cases} \tag{6}$$

where, the bond order term b_{ij} is given by:

$$b_{ij} = (1 + \beta_i^{n_i}\zeta_{ij}^{n_i})^{-1/2n} \tag{7}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_i k).\omega_{ik}.g(\theta_{ijk}) \tag{8}$$

$$g(\theta_{ijk}) = \gamma_{ijk}\left(1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{\left[d_i^2 + (cos\theta_{ijk} - cos\theta_0)^2\right]}\right) \tag{9}$$

$$\lambda_{ij} = (\lambda_i + \lambda_j)/2, \quad \mu_{ij} = (\mu_i + \mu_j)/2, \quad A_{ij} = (A_iA_j)^{\frac{1}{2}},$$
$$B_{ij} = (B_iB_j)^{\frac{1}{2}}, \quad R_{ij} = (R_iR_j)^{\frac{1}{2}}, \quad S_{ij} = (S_iS_j)^{\frac{1}{2}} \tag{10}$$

where the cut off function is denoted by f_C; f_R and f_A are repulsive and attractive pair potentials, and b_{ij} is the bond function. The cut off parameter is utilized for interactions for the distances of atoms between 1.8 Å and 2.1 Å [48,47,46]. It is undeniable that during

Table 1
The optimized Tersoff interamotic potential parameters for boron and nitrogen [49] and carbon [46] (R (Å) and D (Å) are not optimized).

Elements	B [49]	N [49]	C [46]
A (eV)	277.02	11,000	1393.6
B (eV)	183.49	219.45	430
λ (Å^{-1})	1.9922	5.7708	3.4879
μ (Å^{-1})	1.5856	2.2115	2.2119
β	0.0000016	0.10562	0.00000015724
n	3.9929	12.4498	0.72751
c	0.52629	79,934	38,049
d	0.0015870	134.32	4.384
h	0.5000	–0.9973	–0.930
R (Å)	1.95	2.15	1.95
D (Å)	0.15	0.15	0.15