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Molecular dynamics study on the mechanical properties of carbon doped single-layer polycrystalline boron-nitride nanosheets

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ABSTRACT

In this paper, we study the mechanical behavior of carbon doped polycrystalline boron-nitride under uniaxial loading conditions by Molecular Dynamic (MD) simulations. We determine the influence of doping, grain size and temperature. Therefore, samples of polycrystalline (h-BN) with equivalent grain sizes ranging from 1 to 10 nm are generated, and the effect of doping with concentration of carbon atoms ranging from 1% to 15% on these nanaosheets at room temperature is quantified subsequently. Furthermore, samples with 3% and 6% carbon doping were fabricated and equivalent grain sizes ranging from 1 to 10 nm at room temperature is considered. In the end, we subject the fabricated samples to uniaxial loading in temperatures ranges between 100 and 900 K. Our findings revealed that by substitution of boron and nitrogen atoms with carbon (up to 8%), the ultimate tensile strength and corresponding failure strain of carbon doped polycrystalline h-BN increase. Increasing the grain size in carbon doped polycrystalline h-BN, the ultimate tensile strength increases whereas the failure strain decreases. Although the temperature increment has a negative influence on the mechanical properties of carbon doped polycrystalline h-BN, it still yields excellent mechanical properties, with the ultimate tensile strength of 100–120 GPa at 900 K.

1. Introduction

In recent years, boron-nitride [1,2] and graphene [3–6] have attracted attention of researchers due to their unique properties. For example, graphene with outstanding thermal conductivity [7–9] and mechanical [10–13] properties is considered as a promising material in electronic and diagnosis devices and for robust membranes [11]. However, the zero band-gap [14] of graphene avoids controlling of modulated electrons meaning that electrons can flow at any range of energy [15]. Although many approaches such as adsorption of water and other gas molecules on grephene [16] and reversible hydrogenation [17] have been utilized to solve the band-gap issue, this problem which prevents using graphene in the direct application of electrical application like transistors and electrical insulations [15], remains unsolved [18,19].

In contrast to graphene, hexagonal boron-nitride (h-BN) has a band-gap around $\sim 5.5ev^7$ [20] and due to this outstanding property, it is a noteworthy alternative to graphene [1,2]. Hexagonal boron-nitride in comparison with graphene possesses more stable chemical properties and better resistance to oxidation at high temperature (up to >900 °C) [21]. H-BN also has a high thermal conductivity 390 W/m-K [21], deep Ultraviolet Light-Emitting [22], and noticeable piezoelectricity [23]. These properties of h-BN, especially the electrically insulating characteristic, allows it to be a promising alternative to graphene in electronics and energy storage such as microwave-transparent windows, developing memories, semiconductors and capacitors under extreme conditions [24,25]. It also can be used as structural material for seals and as excellent dielectric in resistive random access memories [26].

On the other hand, the elasticity modulus and tensile strength of graphene are higher than those in boron-nitride [27–29]: the elastic modulus of defect-free boron- nitride is predicted between 770 and 780 GPa [28] and from 800 to 850 GPa [29], whereas the value of the same parameter for defect-free graphene ranges from 960 to 980 GPa [30]. Recently, chemical doping of materials with foreign atoms has been investigated as an effective way for the modification of material properties [31–36]. Since graphene and h-BN possess close atomic size and strong valence bonds [1,37], dopant boron-nitride and carbon is considered as an effective way for the modification of their properties.

There have been several studies on the mechanical and thermal behavior of polycrystalline h-BN nanosheets and nanotubes. Most of

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these concentrated on the mechanical and thermal response of polycrystalline boron-nitride nanosheets through molecular dynamic simulations (MD) and density functional theory (DFT). They revealed that raising the temperature leads to a declined trend in elastic modulus, tensile strength and failure strain[38] and also showed that a decreasing trend in elasticity modulus, tensile strength, and failure strain could be observed by increasing the density of defects along the grain boundaries [38–40]. For example, several researchers studied the mechanical properties of polycrystalline h-BN specimen with different grain sizes (range from 2 to 10 nm) at room temperatures through molecular dynamic simulations [29] predicting elastic moduli and tensile strengths of around 720–750 GPa and 62–85 GPa, respectively. In addition, the result showed that increasing the grain size leads to an increase in the elastic modulus and tensile strength. It is important to simulate enough large materials to be as similar as possible to the real materials. The thermal and mechanical response of large molecular models of boron nitride polycrystalline with random grain configurations were investigated by several researchers reporting an increasing density of defects along the grain boundary lead to a rising thermal resistance and conductivity of hexagonal boron-nitride models [29]. Additionally, these studies proposed that increasing the grain size lead to hexagonal boron-nitride behaving similar to pristine boron-nitride [29]. In [41], the effect of different temperatures and strain rates on the fracture strength of grain boundaries in single-layer polycrystalline boron-nitride nanosheet is considered. The results showed that increasing the temperature yields a declining trend in elastic modulus, tensile strength and failure strain, and a decreasing trend in elastic modulus, tensile strength and failure strain could be observed by increasing the temperature. In addition, the temperature sensitivity is more pronounced for low temperatures below 300 K.

In 2D crystalline materials structure such as boron-nitride and graphene, the number of defects are created during the fabrication process. These dominant defects directly affect the mechanical and thermal properties and reduce the elastic modulus, tensile strength and failure strain. Currently, chemical vapor deposition (CVD) is an effective way to fabricate graphene and boron-nitride nanosheets [42–44]. During the fabrication process of polycrystalline (CVD), different types of topological defects mostly at grain boundaries are created [30]. In this process, two atoms rotate 90° with respect to the midpoint of the bond yielding defects of pentagon-heptagon (5/7) and square-octagon (4/8) form [45,46]. They act as dislocation cores leading to an increasing stress concentration along the grain boundaries [30], resulting in a deterioration of mechanical and thermal properties compared to the single-crystalline structures.

Due to the mechanical advantages of carbon in comparison with boron-nitride, the mechanical properties of polycrystalline h-BN are expected to be modified by doping carbon atoms in boron-nitride. To our best knowledge, the mechanical response of carbon doped boron-nitride through molecular dynamic simulations has not been studied so far. In the present paper, we therefore investigate the effect of carbon doping on the mechanical response of single-layer polycrystalline h-BN through molecular dynamic simulation.

2. Computational methods

We performed all MD simulations using the open-source software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) and use OVITO (Open Visualization Tool) for visualization [47,48]. A Tersoff type potential [49,50] was utilized in this paper. We used the optimized Tersoff potential developed by Lindsay and Broido [51,48] to define the interaction between atoms. In this optimized Tersoff potential, the phonon dispersion curves of graphene and bulk h-BN could be predicted conforming to experimental measurements. The combining rule explained in Ref. [49] was performed to display the bonding interaction between boron, nitrogen and carbon atoms. It is a function of the distance between two neighboring atoms i and j and given by

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

where E and r_{ij} are the potential energy and distance between two neighboring atoms respectively, f_c is a smooth cutoff function, and f_R and f_A denote the repulsive and attractive pair potential, respectively.

As suggested for instance in [40,41,52–54], we utilized the Voronoi cell [55,56] method in order to fabricate four models of 2D hexagonal boron nitride nanosheets. Doped polycrystalline hexagonal boron nitride is constructed subsequently. When atoms along the grain boundary are too close to each other, an unwanted repulsion can occur in the Voronoi method. Therefore, the atoms with a distance less than 0.1 nm must be removed. In order to remove the finite length effect and local stress concentrations, periodic boundary conditions (PBC) are employed along the x and y directions. In our modelling, carbon dopants were randomly distributed along the whole polycrystalline h-BN structure [57,58]. We used large-scale classical molecular dynamics simulations to create the grain boundaries. It is worth mentioning that the limited reactivity of Tersoff potential prevents the creation of complex grain boundaries. However, this can be easily prevented by a method proposed in [59]. Therefore, in order to fabricate the grain boundaries, we replaced nitrogen and boron atoms with carbon atoms and then along with a number of other researchers instead of Tersoff potential a similar technique is utilized by performing the second-generation reactive empirical bond order (REBO) potential [60,61]. We first equilibrate the initial structure of graphene for 10 ps at 300 K. Next, the structure is heated and then equilibrated in order to increase the mobility of atoms and rearranging their positions. Then the structure is heated up to 3000 K for 100 ps uniformly keeping the temperature of system for another 100 ps and by cooling the system to 300 K, atomic positions were rearranged. It is worth mentioning that we used the Nose Hoover thermostat method (NVT)[54,62] for heating, relaxing and cooling the initial structure. These processes eventually form the grain boundaries and their junctions lead to the fabrication of a new (polycrystalline) structure. In the following, we replaced the carbon atoms with native boron and nitrogen atoms in order to generate the desired polycrystalline h-BN. In order to ensure the accurate relaxation state of the polycrystalline h-BN structure and prepare it for the evaluation of experimental studies, we used the Nose- Hoover barostat and thermostat method (NPT) to equilibrate the structure to zero stresses at room temperature and zero pressure for 50 ps before using the loading conditions. The previous experimental studies reveal that during the fabrication process (CVD) of polycrystalline h-BN, different types of topological defects form, mostly along the grain boundaries. These defects mostly include pentagon-heptagon (5/7) and square-octagon (4/8) pairs [46].In accordance with experimental observation, theoretical studies by Liu et al. [63] and Wang et al. [64] also suggests the (5/7) pairs and (4/8) pairs mainly form in polycrystalline h-BN grain boundaries. As shown in Fig. 1, grain boundaries in the reconstructed polycrystalline h-BN models in this work also mostly consist of pentagon-heptagon and square-octagon pairs, which agrees well with previous experimental and the theoretical findings. They act as dislocation cores leading to an increasing stress concentration along the grain boundaries [30], resulting in a deterioration of mechanical and thermal properties compared to single-crystalline structures. Samples of polycrystalline boron-nitride nanosheets with size of 25 nm × 25 nm with different grain sizes of 1, 5, 7 and 10 nm have been fabricated. Two samples of polycrystalline boron-nitride nanosheets with grain sizes of 5 and 10 nm including grain boundaries are illustrated in Fig. 1. After creating the polycrystalline boron-nitride nanosheets, 1%, 2%, 3%, 5%, 6%, 7%, 8%, 10%, 12% and 15% of boron and nitrogen atoms were replaced by carbon atoms. Fig. 2 illustrates one sample of 5% carbon doped polycrystalline h-BN with grain size of 5 nm.

The mechanical response of carbon doped polycrystalline boron-nitride with grain sizes of 1, 3, 7 and 10 nm was studied.The length of