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Effects of Defects on the Fracture Strength of Hexagonal Boron Nitride

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Abstract

Recently, Graphene like 2D nanosheet of hexagonal boron nitride (h-BN) has been attracting a lot of attentions due to its unique mechanical and electrical properties. However, introduction of defects such as mono-vacancy, bi-vacancy, atomistic anti-site and Stone-Wales defects influence the mechanical strength of h-BN. This paper mainly focuses on the effects of various types of pre-existing defects on the mechanical properties of hexagonal boron nitride. Molecular Dynamics (MD) simulations are performed to investigate the effect of varied defect concentration (Number of defect to atom ratio). The results show that both fracture stress and strain are reduced significantly because of the presence of defects. The fracture always initiates from the defect and its propagation is affected by loading direction. Lastly, the fracture phenomenon is observed by atomic images with stress concentration zones.

Keywords: molecular dynamics, h-BN nanosheet, Stone-Wales, atomistic anti-site.

1. Introduction

Monolayer Nanosheet of hexagonal Boron Nitride (h-BN) has a great deal of applications because of its exceptional mechanical, electrical and thermal properties [1-3]. For the past few years, researchers have been investigating various interesting features about the mechanical properties of h-BN.

Kudin et al [4] evaluated and compared the mechanical properties of two dimensional lattices of Carbon, Boron Nitride and Fluorine Carbon compositions using ab initio methods. Peng et al [5] used Density Functional Theory (DFT) calculations to observe the nonlinear elastic deformation of h-BN monolayer up to ultimate strength followed by a strain softening upto failure. Boldrin et al [6] built up a theoretical model and determined the in plane mechanical properties of h-BN nanosheets.

Based on the success of MD to predict mechanical properties at nanoscale, numerous studies are done on the mechanical properties of h-BN [7, 8, 10]. Han et al [8] investigated the effects of temperature and strain rate on the mechanical properties of h-BN nanosheets using MD simulations. They recorded the stress-strain curve in tensile tests and determined the Young's modulus, fracture strength and strain at different temperatures and compared the results. They also observed that a softening effect is exerted on the h-BN nanosheets while raising temperature. Minh Quy and Nguyen [9] used Molecular Dynamics Finite Element Method (MDFEM) to study the effect of a single defect at the center of h-BN and SiC sheets. They found that both the fracture stress and strain reduces significantly for both materials. However, they did not analyze the mechanism of failure extensively and also their method has the limitation of not considering the thermal fluctuation effect of atoms.

However, due to nucleation and evolution of atoms in the nanosheets, presence of defect is a common phenomenon. Hong et al [11] investigated point defects in monolayer molybdenum disulphide by both experimental and theoretical means. Miller et al [12] calculated the minimum energy structure of Graphene and Boron Nitride nanoribbons having a single vacancy using DFT. They found that significant distortion occurs due to the presence of single vacancy defect. Qi lin et al [10] studied the effect of pre-existing defects on the fracture behavior of h-BN nanosheets using MD simulations. However, they only dealt with one defect locating at the center of the h-BN nanosheet. On the other hand, nucleation of defect in a nanosheet is found to form as a cluster. Therefore, the effect of different concentrations of defects such as monovacancy, atomic antisite and Stone-Wallace on mechanical properties of h-BN is an evident necessity.

The main purpose of this paper is to study and investigate the effect of varied concentration of different defects (stone wales defect, atomic antisite defect and mono-vacancy defect) on the fracture strength and strain of h-BN nanosheet under uniaxial tension along armchair and zigzag directions. The nucleation and evaluation of cracks have also been observed by atomic images with stress concentration zones for various defects.

2. Methodology

Atomistic models

To study the effect of defect concentration, we choose defect concentration of 0.25%, 0.50% and 0.75% for each type of defect. Atomistic models of h-BN nanosheets having spatial dimension of 104.4 Å ×100.459 Å and containing 3840 atoms were created. For the single atomic vacancy (SAV) defect, equal number of Boron and Nitrogen were deleted from its regular pristine sheet to acquire the certain defect concentration. Two consecutive Boron and Nitrogen atoms were interchanged to create atomic antisite (AA) defect and stone wales (SW) defect is created by a 90° clockwise rotation of B-N bond; All these defects are shown in figure 1. The defects are distributed uniformly to have equal effect on the whole nanosheet.

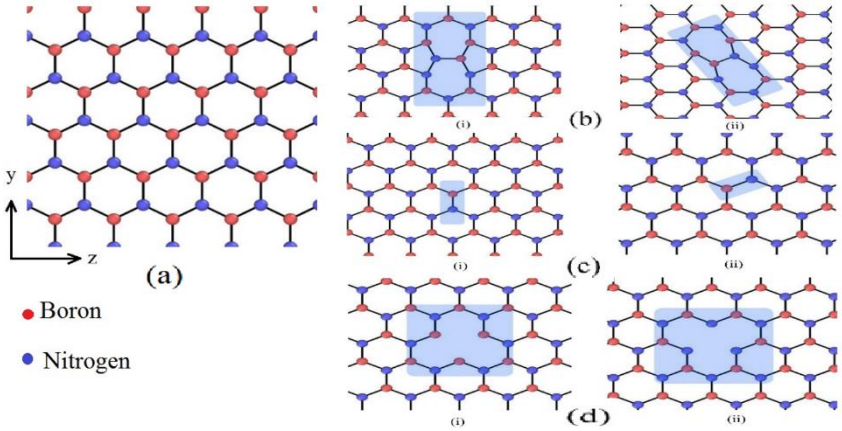

Fig. 1. Hexagonal Boron Nitride nanosheets with various defects. (a) Pristine atomic model. (b) (i) SW defect of type 1 (SW1); (ii) SW defect of type 2 (SW2); (c) (i) AA defect of type 1 (AA1); (ii) AA defect of type 2 (AA2); (d) (i) Single Nitrogen atom vacancy (Nitride SAV); (ii) Single Boron atom vacancy (Boron SAV)

Molecular dynamics simulations

We used LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software package [13] to perform MD simulations and employed Tersoff potential [14] to demonstrate the interaction between the B and N atoms due to its successful use in many studies previous [7, 10, 15, 16]. Periodic boundary conditions were set along all three axis. 1 fs timestep was selected to perform all the simulations. Firstly, the energy of the system were minimized using a conjugate gradient (CG) algorithm. Then the velocity and position of all the atoms in the h-BN nanosheets were updated by performing NVE integration for 50000 timesteps and NPT simulations for 100 ps at 300K. For generating uniaxial tension, a strain rate of 10^9 s^{-1} was applied to the corresponding direction. It is mentionable that in case of SW defects and AA defects, the bond rotation and exchange of atoms respectively create B-B and N-N bonds. So, in order to achieve precise defect configurations, the angular movement of the defected atoms were restricted.

3. Result and Discussion:

Method Validation

In order to validate our simulation method and the potential employed, we developed a model of h-BN nanosheet having the spatial size of approximately 50 Å × 50 Å similar to the size adopted by Zhao and Xue's work [15]. The Young's modulus, yield strain and yield strength were tabulated in Table 1 which are in reasonable agreement with present work.

On the other hand, due to restriction of angular movement for defected atoms in h-BN nanosheets containing SW defects and AA defects, further validation is done for these cases. A model of h-BN nanosheet is modeled with size (206.3 Å × 204.2 Å) containing a type 1 AA defect at the center as modeled by Qi-lin et al [10]. Then, the load is applied along the zigzag direction. The results found by our simulation (ultimate stress 96.1 GPa and ultimate strain 0.19) are in good agreement with the literature [10] (ultimate stress 99 GPa and ultimate strain 0.20 approximately).

Table 1. Comparisons of Young's modulus, yield strength and yield strain between literature and present study

		Young's Modulus E (GPa)	Yield Strength σ (GPa)	Yield Strain ϵ
Armchair	Present Study	733.2	111.1	.28
	Reference [15]	739.9	126.6	.28
Zigzag	Present Study	707.7	107.1	.26
	Reference [15]	692.7	114.1	.27

Effect of concentration of defect:

The uniaxial tensile stress–strain curves of pristine h-BN and the nanosheet containing AA 1 and AA 2 are plotted in figure 2. With the increase of defect concentration the tensile strength is reduced significantly. After relaxation, the B-B and N-N bonds produced due to atomic anticite defects are rearranged. Therefore, a void is produced at each defected zone. AA 1 defects create a void in the armchair direction while AA 2 defects create a void at an angle about 60 degree with armchair direction. So, in case of type 1 atomic antisite defect, the direction of the applied load in zigzag direction is almost perpendicular to the void direction and hence the ultimate stress and ultimate strain are reduced drastically.

Increasing concentration of defect decreases the tensile strength in all cases except for AA 2 defect in case of loading along zigag direction. In this particular case, the ultimate stress and strain remain almost constant with the increase of number of defects. This can be attributed to the fact that the atomic antisite defect has the ability to annihilate the effect of other nearby defect by acting as void shields. This phenomenon is common in ductile materials and are known as "Dislocation Shield".

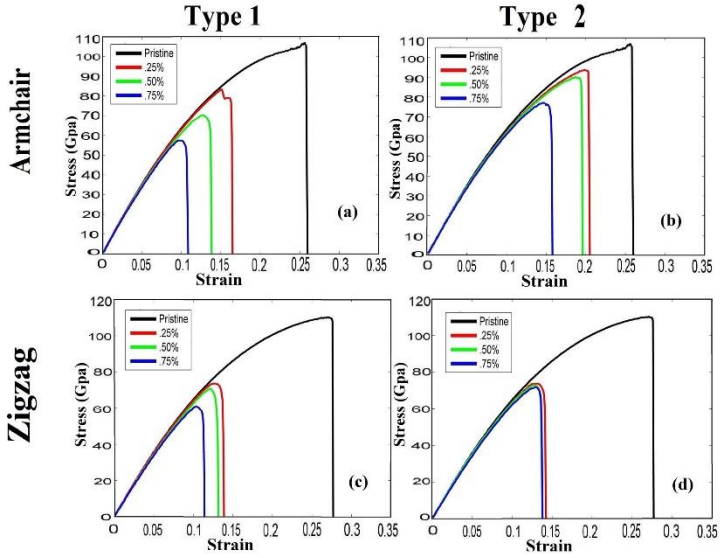

Fig. 2. Uniaxial tensile stress-strain curve of AA defect. (a) Type 1; (b) Type 2, both loaded in armchair direction; (c) type 1; (d)type 2, both loaded in zigzag direction.

In figure 3, the stress-strain plot is shown for SW defects. It is evident that due to the presence of SW 1 defect fracture stress is reduced more prominently than that of SW 2 defect. However, SW 2 defect bascally has negligible effect on tensile strength. From figure 3(d) it is clear that different concentration of SW 2 defect brings almost no change in the properties when load is applied in zigzag direction. On the other hand, it was reported that one SW 2 defect at the centre of the sheet reduces the ultimate stress and strain [10]. On the contrary, in our

study, the ultimate stress increases when the number of defects are increased. This is quite opposite, yet interesting. Because in case of h-BN, we have found an unique annihilation mechanism like dislocation shielding phenomenon [17] as found in ductile material. Most of the sheets with SW 2 and AA defects are loaded at 30^0 angle when they are loaded along the zigzag directions. While the nanosheet with these defects got strained, the bonds and atoms associated with these defects reconfigures to form many tiny cracks due to the mismatch between the loading direction and defect orientation. These tiny cracks nullify each other's effect and consequently get annihilated. For this mechanism, the sheet with these defects behave similarly with pristine sheet as the defects are annihilated and gives almost same fracture stress and strain.

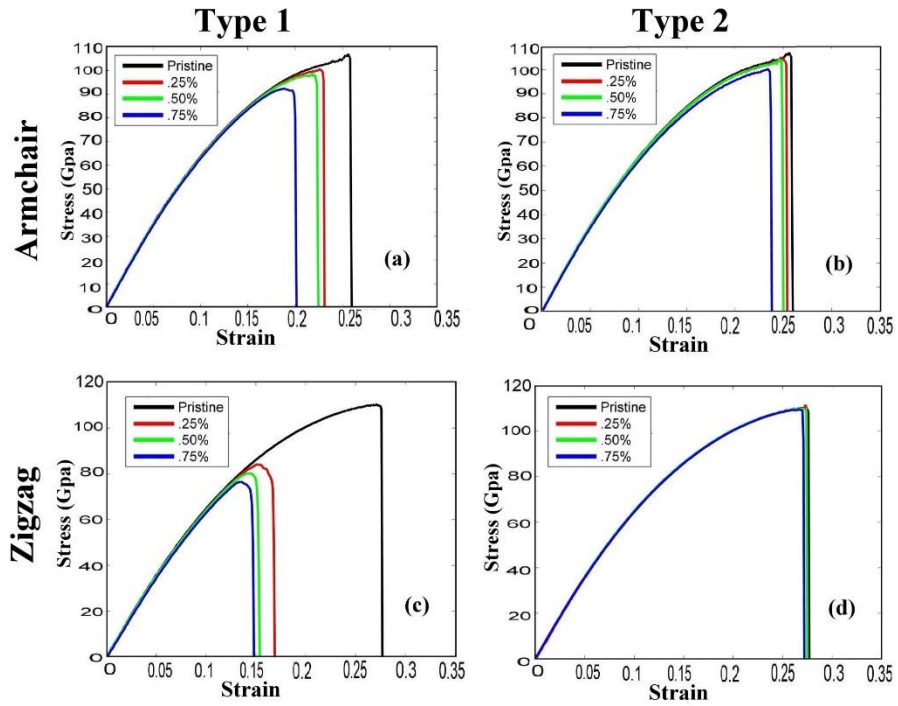

Fig. 3. Uniaxial tensile stress-strain curve of SW defect. (a) type 1; (b) type 2, bothloaded in armchair direction; (c) type 1 (d) type 2, both loaded in zigzag direction.

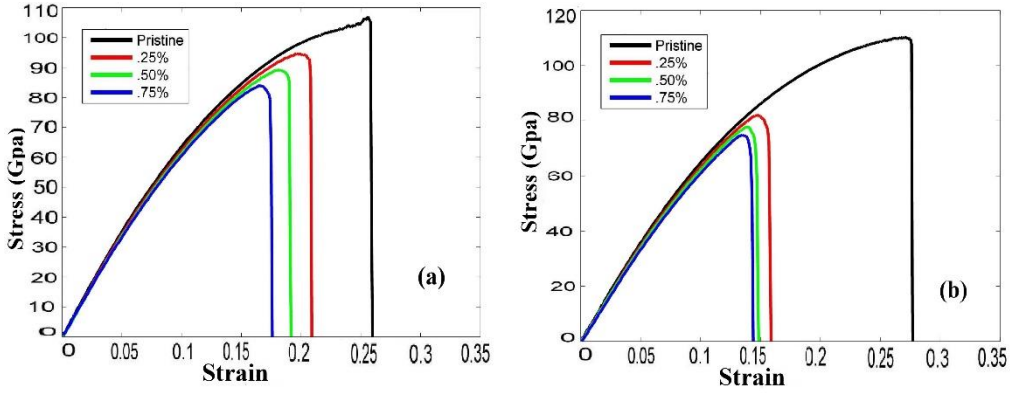

Fig. 4. Uniaxial tensile stress-strain curve of SAV defect. (a) load in armchair direction; (b) load in zigzag direction

The effect of concentration of single vacancy defects on the stress-strain curve of monolayer nanoheet of h-BN is shown in figure 4. The ultimate stress and strain are found to reduce drastically because of the presence of the SAV defects. The main reason is that the single vacancy defects act as individual voids in the nanosheet which start to propagate when loading is applied. However, the armchair direction is more resistant to crack propagation than zigzag direction. Because the direction of void nucleation and evolution are slightly deviated from armchair

direction to facilitate the crack propagation. This deviation requires more energy for crack propagation, hence, armchair direction shows more resistance than zigzag direction.

Effect of loading direction:

To summarize the findings of this study, tensile strength versus defect concentration are plotted in figure 5. The figure shows almost linear relation between strength and defect concentration with negative slope. An interesting observation from the figure 5(d) is that the lines of AA 2 defects and SW 2 defects are almost parallel to x-axis. This indicates that variation of concentration has almost no effect on tensile strength of the nanosheet when uniaxial tension is applied in zigzag direction.

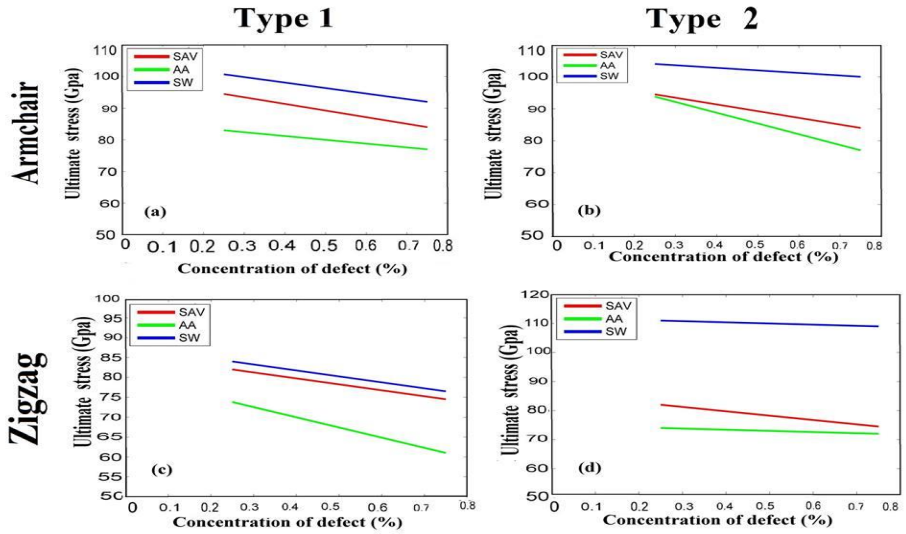

Fig 5 . Variation of ultimate stress with concentration of various defects. (a) Type 1 of SW, AA and SAV defects in armchair loading (b) Type 2 of SW, AA and SAV defects in armchair loading (c) Type 1 of of SW, AA and SAV defects in zigzaag loading (d) Type 2 of SW, AA and SAV defects in zigzag loading

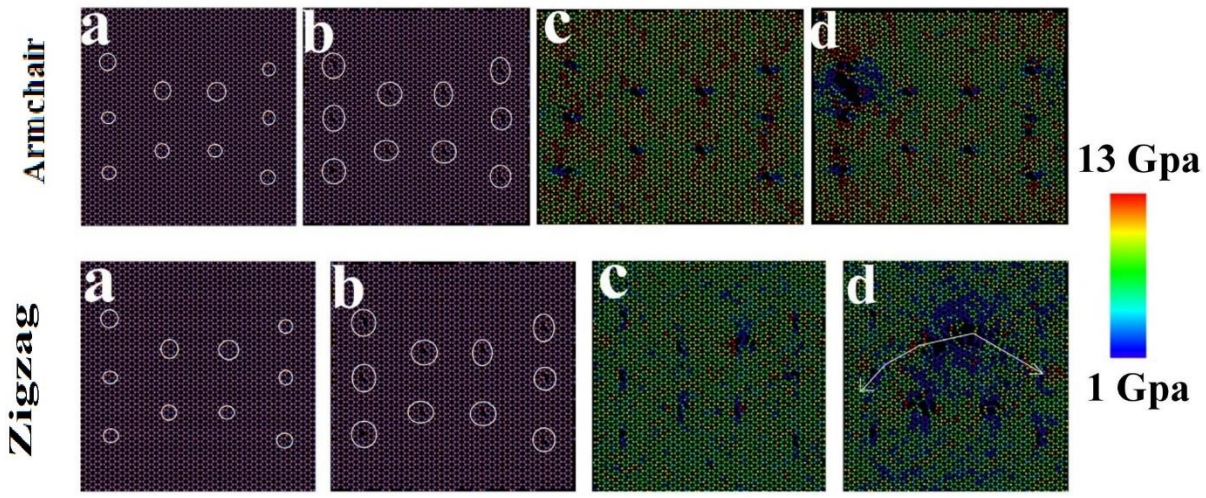

Fig. 6: Atomic stress concentration of h-BN nanosheet containing AA2 defect of 0.5% concentration in the tension of armchair and zigzag direction. (a) Initial condition; (b) Creation of cracks after equilibration process; (c) Just before fracture; (d) Immediately after fracture.

Fracture Mechanism

Figure 6 shows the snapshots of stress distribution for AA2 defect in armchair and zigzag loading respectively. After relaxation, voids are formed at 60^0 angle with armchair direction. At the onset of the fracture, we observe that the zone around these voids are highly stressed as shown in the figure 6. Due to this highly localized stress near the void, B-N bonds near the void break which initiate the imminent failure of the h-BN nanosheet. In case of zigzag direction, during the fracture, these voids combine with each other and create a bow shaped crack before fracture. The main reason behind that is the voids are at an angle of 60 degree with armchair direction. Therefore, the zigzag loading introduces a crack propagation perpendicular to the void direction.

4. Conclusion:

The effect of varied concentration of various defects are studied by Molecular Dynamics simulation method. The results obtained in our study are summarized below:

- Hexagonal Boron Nitride is found to exhibit brittle failure. Due to the introduction of defect, the fracture stress and strain are reduced significantly. Moreover, with the increase of concentration of defects, both fracture stress and strain shows decreasing trend.
- AA2 and SW 2 defects show an interesting "Void shielding" mechanism when load is applied along zigzag direction for h-BN.
- It is also found that bonds in armchair direction resist more fracture than in zigzag direction.
- The mechanisms of failure indicates a prominent zone of localized stress concentration around the voids. Finally, a bow shaped crack formation is found in case of AA2 defect when loaded in zigzag direction.

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