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Research Article

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Mechanical properties of boron nitride sheet with randomly distributed vacancy defects

Abstract: Defects and temperature effects on the mechanical properties of hexagonal boron nitride sheet (h-BN) containing randomly distributed defects are investigated by molecular dynamics simulations and the reasons of the results are discussed. Results show that defect deteriorate the mechanical performance of BNNS. The mechanical properties are reduced by increasing percentage of vacancy defects including fracture strength, fracture strain and Young's modulus. Simulations also indicate that the mechanical properties decrease with the temperature increasing. Moreover, defects affect the stable configuration at high temperature. With the percentage of defect increases the nanostructures become more and more unstable. Positions of the defect influent the mechanical properties. The higher the temperature and the percentage of defect are, the stronger the position of the randomly distributed defect affects the mechanical properties. The study provides a theoretical basis for the preparation and performance optimization of BNNSs.

Keywords: defect; temperature effect; mechanical properties; hexagonal boron nitride sheet; molecular dynamics simulations

1 Introduction

Boron Nitride nanosheet (BNNS), which has similar lattice structures that of graphene [1], have been attracted a considerable attention around the world since its synthesized [2]. Because of its excellent properties such as superb thermal and chemical stabilities, highly thermal conductivity, high Young's modulus etc. BNNS is being considered as an excellent candidate for nano-electromechanical systems (NEMS), and is applicable in various ways such as hydrogen storage, gas sensor, biological probes and nanocomposites [2–6]. With the rapid use of BNNSs in nanocomposite structure, it is essential to investigate the mechanical properties of BNNS. There are numerous studies about the mechanical properties of perfect BNNSs [7–10].

The mechanical properties of the BNNSs are analogous to the graphene sheets since BNNs firstly discovered [11]. A value of 0.7-0.9 TPa [12–17] for the Young's modulus of perfect BNNS has been estimated via various methods. However, defects are always inevitably emerged in the synthesizing and fabricating processes of nanostructures [4], which will influence the mechanical properties of the nanostructure [4, 18–20].

The numerical simulation method such as molecular dynamics (MD) is widely used in the mechanical properties investigation because of the difficulty of conduction of the experiments in nano-level and the discrete of the experimental data. The structural properties of defect BNNSs was analyzed by MD simulation, and the energetics of point defects and Stone–Wales defects were obtain [7]. Bending rigid of defective BNNSs were investigated by MD simulations using a tuned Tersoff-type inter-atomic empirical potential [21]. The effects of temperature and defect size on the mechanical response of BNNS were studied [22] using the same method. It was concluded that the initial defect (center crack) reduced both the tensile strength and failure strain, and this reduction was independent of the initial crack length. Later the mechanical performance and failure behavior of h-BN sheets with defects were studied using molecular dynamics methods [23]. Results showed that Young's modulus decrease linearly with the increase of defect size.

While quite a few investigations on defect BNNS's mechanical properties have been reported, only the influence of a certain defects or a small number of defects were studied, there seem to be void in the studies concerning ran-

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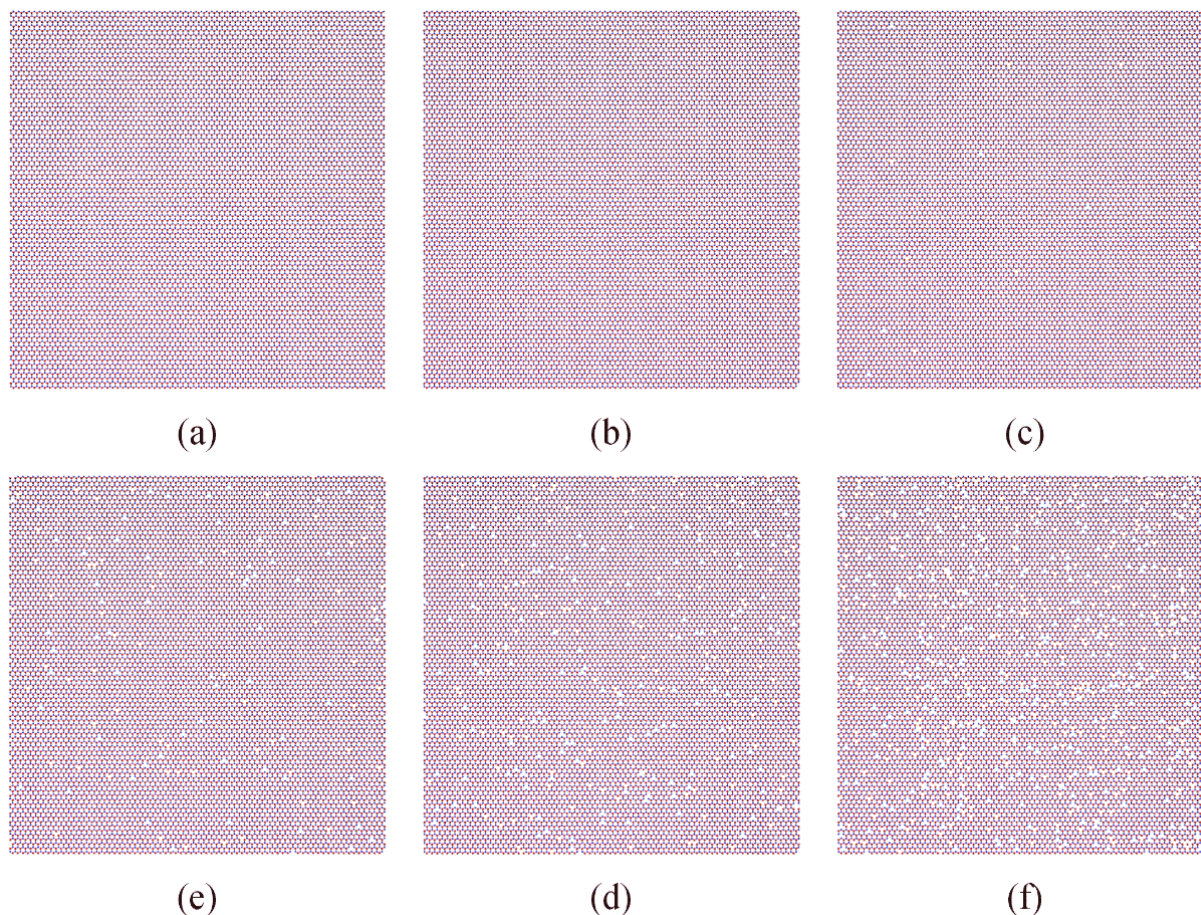
Figure 1: The simulation model of (a) perfect BNNS, (b) BNNS with 1 (0.01%) vacancy defect, (c) BNNS with 13 (0.1%) vacancies defect, (d) BNNS with 127 (1%) vacancies defect, (e) BNNS with 256 (2%) vacancies defect, and (f) BNNS with 636 (5%) vacancies defect and red dots indicate boron atoms and blue dots indicate nitride atoms.

domly distributed defects. However, in the actual industrial manufacturing process different percentages of randomly distributed defects may appear. In this paper, we investigate the effect of temperature and vacancies on the mechanical properties of BNNSs, including the effect of temperature, different percentage defects on elastic modulus, tensile strength and critical strain and so on.

2 Models and simulation methods

It can be concluded from the study of the size effect on the mechanical properties of the nanostructure that the possible model size effect can be neglected when the diagonal length of the square nanostructure is larger than 5nm [24]. So a 18nm×18nm square BNNS, with the diagonal length is greatly larger than 5nm is chosen as the initial perfect model, which does not contain defects. The perfect model

consist of 6363 boron atoms and 6363 nitride atoms, with a total 12726 atoms. In order to investigate the effects of the defects, the randomly distributed vacancies in BNNS structure are created by a random numbers algorithm. 1, 13, 127, 256, 636 atoms are randomly removed from the perfect BNNS, which is also called 0.01%, 0.1%, 1%, 2% and 5% of the total atoms detects as shown in Figure 1. In order to investigate the randomly defect, we create ten models for each percentage defect, respectively. There are totally $10 \times 5 = 50$ models for the defect BNNSs.

A classical molecular dynamics code with the package of Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is used in MD simulation. Newtonian equations of motions governed by the interatomic interactions are solved numerically to determine the trajectories of a large number of atoms. A Velocity - Verlet [25] algorithm is used to integrate the equations of motion. The three-body Tersoff-type potential force field, which had been proved reliable in the description of the BNNS with

(a) armchair

(b) zigzag
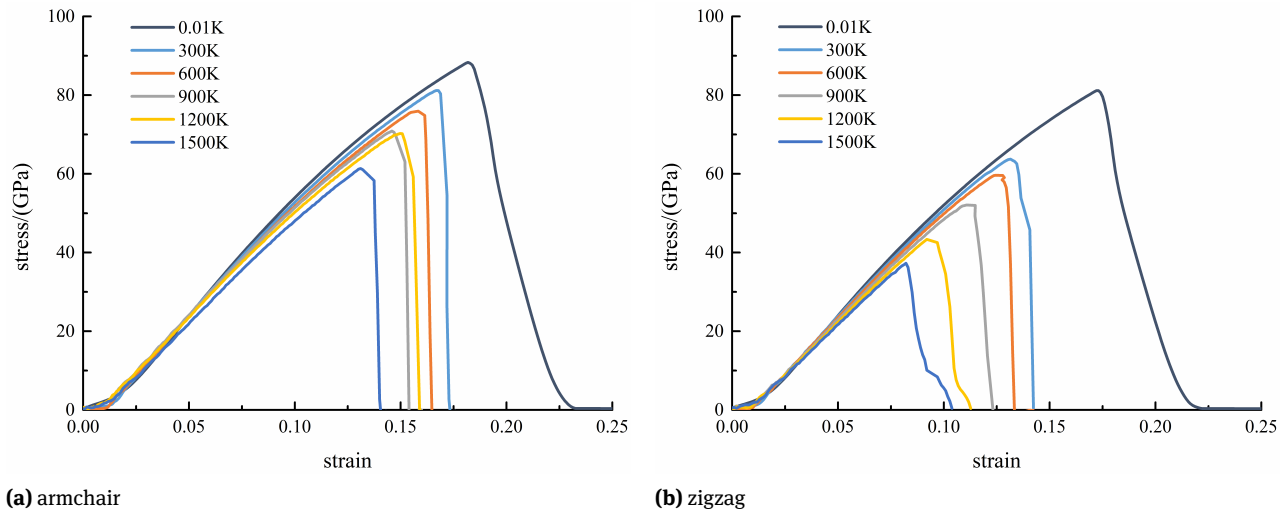
Figure 2: Stress-strain curve of perfect BNNSs.

or without defects is used to model the molecular interactions in BNNSs.

A relaxation process is carried out to minimize the total potential energy of the entire BNNS with steepest descend algorithm before applying the external loads. A stable configuration is obtained at a fully relaxed process at a certain temperature. In order to clarify the temperature effect on the mechanical properties the simulation, thermally equilibrated to 0.01K, 300K, 600K, 900K,1200K and 1500K respectively, in a canonical ensemble, so-called NVT using Nose–Hoover thermostat ensemble is carried out at present study. During the uniaxial tension simulation, a constant tension strain rate of $1{\times}10^{-9}s^{-1}$ is adopted, which is applied by displacement of the atoms at the top end of the BNNSs and fixed at the other end.

3 Results and discussion

In this section, the effects of the defect and temperature on the mechanical properties of BNNSs with and without randomly distributed vacancy are analyzed and compared. The stress-strain curves of zigzag and armchair BNNSs are plotted according the uniaxial tension simulation. The mechanical properties such as the Young's modulus, the critical fracture stress and the fracture strain of the BNNSs are calculated based on the stress-strain curves.

Figure 2 shows the stress-strain relation of the pristine zigzag and armchair BNNS models without defect. The temperature effect is also illustrated. The Young's modulus of the BNNSs are 631(armchair) / 601(zigzag) GPa at room temperature. The critical strength stress and the failure critical strain are 81GPa and 17% for armchair, whereas those values are 64GPa and 13% for zigzag which are in good agreement with those reported in previous literatures using DFT [26] or MD [23] method.

Figures 3-4 show the stress-strain curve of the BNNSs with defects. In general, the mechanical performance of armchair is better than zigzag according to the fracture strength, fracture strain and Young's modulus. Unlike graphene, which the stress-strain curves exhibit two linear stages in the case of less defect and at temperature 0.01K [27], the brittle fracture mechanism of BNNSs is observed for all the cases. Firstly the stress increases linearly with the strain increasing due to the elastic deformation of nitride-boron bonds. With the stretching continuing, the deformation is aggravated. Then the stress increases with the strain increasing with a nonlinear relation due to the nonlinear deformation of the nitride-boron bond and the change of the bond angle. A material damages whereas the critical stress achieved. In addition, with the increase of the percentage of defect and the temperature, the stress-strain curves of the BNNNS exhibited a more non-liner characteristic. The BNNSs do not show the second linear stage like graphene because the asymmetry nitride-boron bonds aggravate the lattice vibrations, whereas for the graphene only a few groups of the acoustic mode excited at very low temperature.

Since the vacancy defects are randomly distributed in BNNSs, one determined model is not sufficient to represent most of the possible situation of the vacancy defected BNNSs of certain percentage. Each set of the model for a certain percentage defect consist of ten models of the ran-
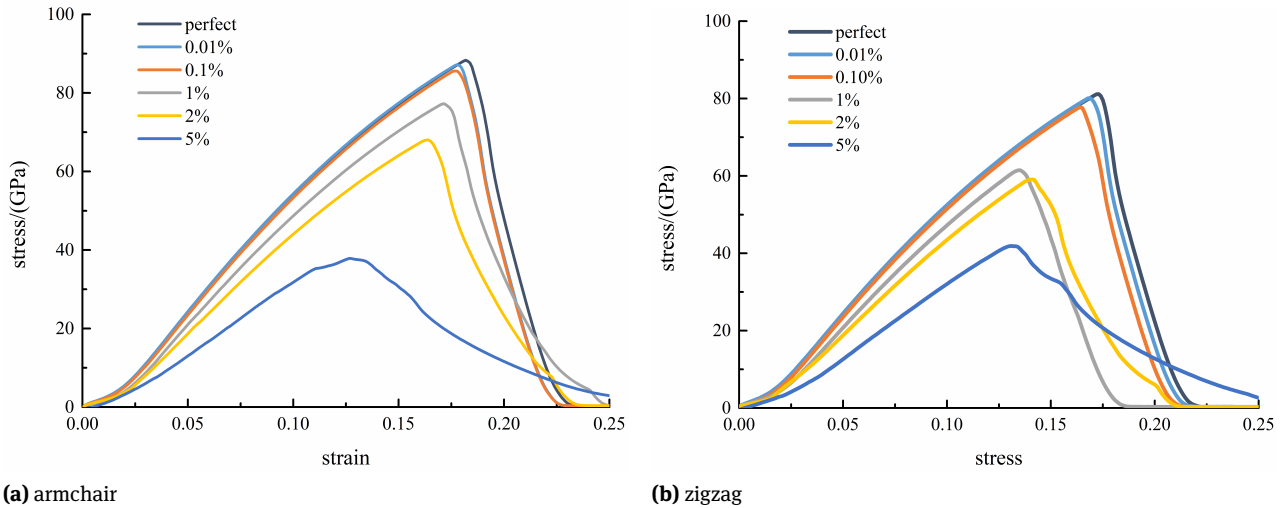
(a) armchair

(b) zigzag

Figure 3: Stress-strain curve of BNNS at 0.01K.

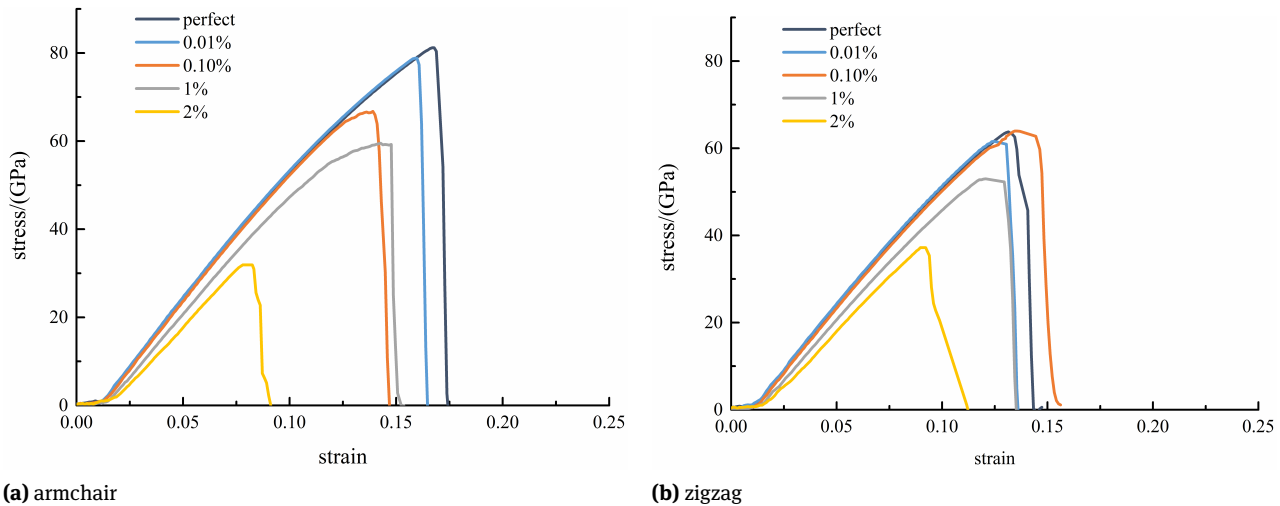

(a) armchair

(b) zigzag

Figure 4: Stress-strain curve of BNNS at 300K.

domly distributed vacancy defected BNNSs. In ten models the locations of the vacancy defect are different because the atoms are deleted by a random numbers algorithm. In order to clarify the random defect effect on the mechanical properties the variance of the values for each set of models are obtain. The mean values of the critical stress, critical strain and the equivalent Young's modulus can be obtained for the respective of the mechanical properties of certain percentage of defect. Figure 5 demonstrates the critical stress of the ten different models with 0.01% defect zigzag BNNS. According to Figure 5(a) for a certain percentage of vacancy defects, the critical stress remains nearly the same for most of the models at 0.01K. In another words, the critical stress is independent to the position of the randomly distributed defect when the temperature is

very low. When the temperature rises to 1500K, as shown in Figure 5(b), the critical stress of the ten models scatters. It is obvious that the position of the randomly distributed defect strongly affect the mechanical properties of BNNSs at high temperature.

To be more exact, the variances of the fracture critical stress are divided by the mean values of the critical stress as the ratio of the variances which is illustrate in Figures 6 and 7.

It can be concluded from Figures 6 and 7 that the ratio of the variances increases with the temperature and defect percentage increasing. In another words the higher the temperature is, the stronger the position of the randomly distributed defect affects the mechanical properties of BNNS. It is well explained by Figure 7 that the position of
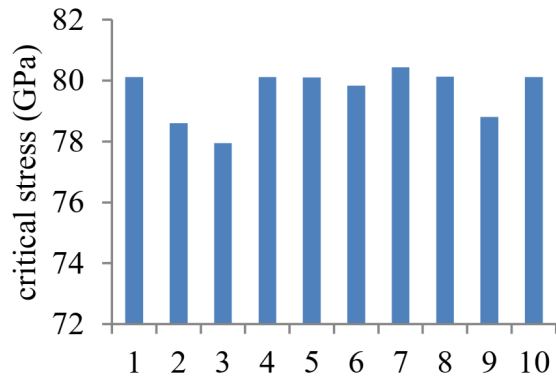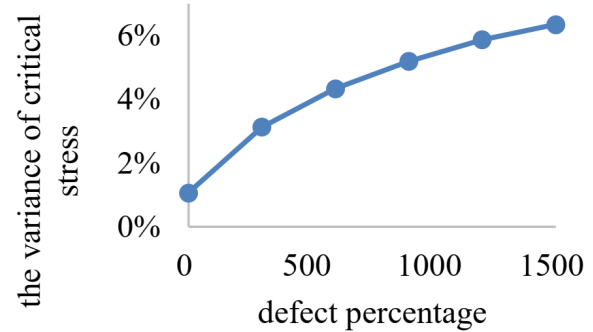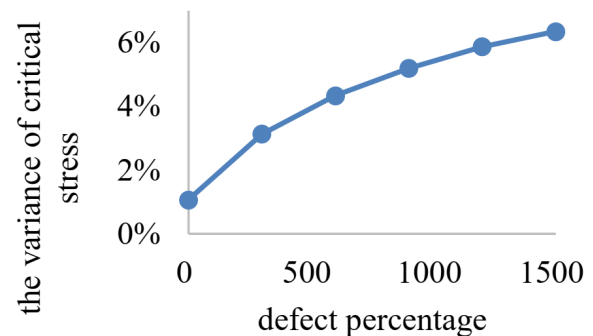
(a) 0.01K
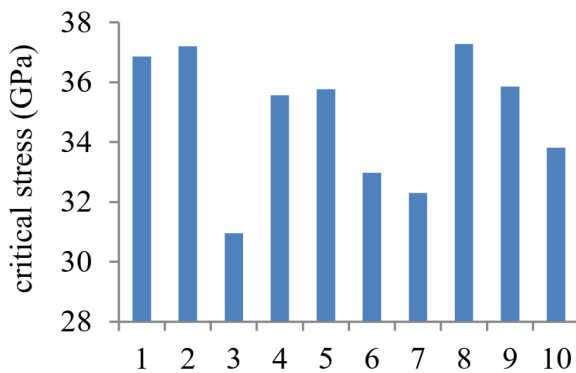
(b) 1500K

Figure 5: Fracture critical stress with 0.01% defect zigzag BNNS.

Figure 6: The variances of the critical stress for 0.01% defected zigzag BNNS at different temperature.

Figure 7: The variances of the critical stress for different percentage defect of zigzag BNNS at 0.01K.

the randomly distributed defect has a strong influence on the mechanical properties of BNNSs when the percentage of the defect goes higher.

Subsequently, the temperature effect and the defect effect on the mechanical performance of both armchair and zigzag BNNS are studied. The Young's modulus is obtained with the slope of the linear part of the stress-strain curves (strain from 0.5% to 5%). The critical fracture stress and fracture strain are obtained according to the highest point of stress in the stress-strain curve. The mean values of the critical stress, critical strain and the equivalent Young's modulus are obtained for average the values of those in ten models as illustrated in Figure 8, 9 and 10, respectively.

It can be concluded from Figures 8-10 that the mechanical properties are reduced by increasing percentage of vacancy defects and increasing temperature, whereas the defects dramatically degrade the mechanical performance of BNNSs. The defects deteriorate the mechanical properties of the BNNS by reducing their tensile strength, failure strain and elastic modulus.

One of the characteristics of nanomaterials is that they can be used at high temperature. One of the advantages of BNNSs is that they are stable at high temperature. It is obvious that perfect BNNS is stable at 1500K but when the percentage of defect increases the nanostructures become more and more unstable. When the percentage of defect reaches to 1%, the nanostructure is unstable and cannot exist at the temperature higher than 900K. Moreover, when the percentage of defect is 2% and 5%, the nanostructures is unstable at the relaxing process at 600K and 300K, respectively. Defect affects the stable configuration at high temperature.

As shown in Figure 8 the fracture strength, for both zigzag and armchair BNNS, drops with the increase of temperature and the percentage of defect. When the percentage is less than 0.01%, the fracture strength drops by about 35% and 55% for armchair and zigzag BNNS with the temperature increasing from 0.01K to 1500K. When the percentage defect reach 0.1%, the value of the fracture stress drops dramatically by about 72% and 64% for armchair
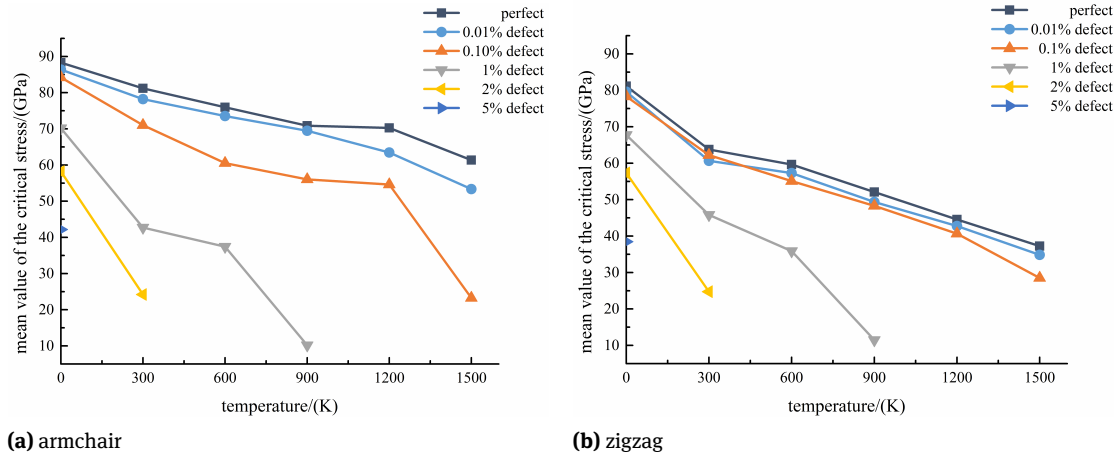
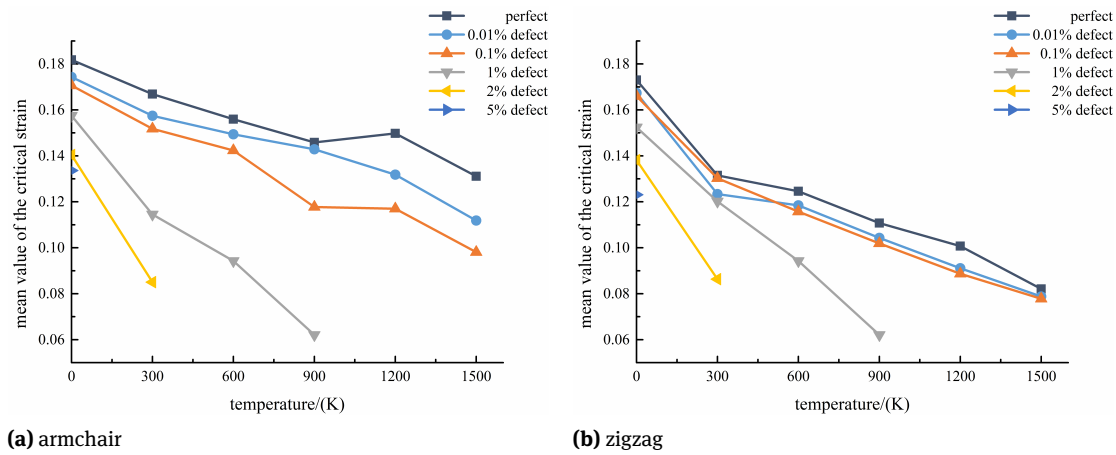**Figure 8:** Mean fracture stress as a function of temperature with different percentage of vacancy defect.

Figure 9: Mean fracture strain as a function of temperature with different percentage of vacancy defect.
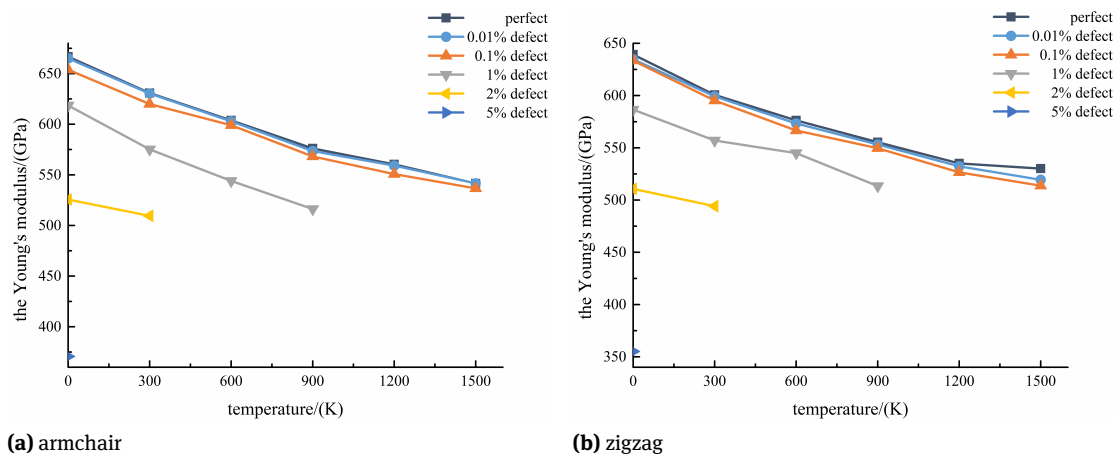

Figure 10: Young's modulus as a function of temperature with different percentage of vacancy defect.

and zigzag BNNS at the temperature from 0.01K to 1500K. However, at a fixed temperature, the change of the fracture strength of zigzag BNNS is minor when the percentage of defect is less than 1%. The fracture strength decreases rapidly when the percentage increase to 1%.

Compared to the change of fracture strength, that of the fracture strain is minor. It is shown from the relationship between the fracture strain and the temperature, as illustrated by Figure 9 that the fracture strain drops about 53% from 0.01K to 1500K, for both armchair and zigzag BNNSs, when the percentage of defect less than 0.1%. Similarly, when the percentage of vacancy defect is higher than 1%, the fracture strain drops sharply.

As shown in Figure 10, the Young's modulus decreases linearly with the temperature increasing. The Young's modulus verse temperature curves are nearly coincident as the percentage defect less than 0.1%. It makes no great difference to the defect effect on the Young's modulus when the defect is small. It is obvious that temperature and defect has a greater influence on the failure strength and strain of BNNSs than on their Young's modulus.

4 Conclusions

Defects in the structure of BNNS are always inevitably emerged in the synthesizing and fabricating processes. In the present work, the effects of temperature and randomly distributed defects on the mechanical performance of BNNSs are investigated. The mechanical properties reduce by increasing percentage of vacancy defects and increasing temperature. In another words the defects deteriorate the mechanical properties of the BNNS by reducing their tensile strength, failure strain and elastic modulus. Moreover, when the percentage of defect is higher than 1%, the mechanical performances degrade dramatically. Temperature and defect has a greater influence on the failure strength and strain of BNNSs than on their Young's modulus. The Young's modulus decreases linearly with the temperature increasing. The findings also indicate that unlike graphene, which the stress-strain curves exhibit two linear stages in a specific case, the brittle fracture mechanisms of BNNSs are observed for all the cases. The reason for it is that the asymmetry nitride-boron bonds aggravate the lattice vibrations, unlike graphene which only a few groups of the acoustic mode excited at very low temperature. The results also show that the position of the randomly distributed defect strongly affect the mechanical properties of BNNSs at high temperature and high percentage of vacancy defect. Moreover, defects affect the stable configuration at high temperature. This study provides a theoretical basis for the preparation and performance optimization of BNNSs.

References

[1] Kalavakunda V., Hosmane N.S., Graphene and its analogues, Nanotechnology Reviews, 2016. 5(4), 369-376.

[2] Kim J.H. et al., Mechanical properties of two-dimensional materials and their applications, J. Phys. D: Appl. Phys., 2019. 52(8), 083001.

[3] Choyal V., Choyal V.K., Kundalwal S.I., Effect of atom vacancies on elastic and electronic properties of transversely isotropic boron nitride nanotubes: A comprehensive computational study, Comput. Mater. Sci., 2019, 156, 332-345.

[4] Weston L., et al., Native point defects and impurities in hexagonal boron nitride, Phys. Rev. B, 2018, 97(21), 214104.

[5] Ryou J., Park J., Hong S., Investigations of Vacancy Structures Related to Their Growth in h-BN Sheet, Nanoscale Res. Lett., 2017, 12(1), 445.

[6] Yang Z.C., et al., Nonlinear in-plane buckling of fixed shallow functionally graded graphene reinforced composite arches subjected to mechanical and thermal loading, Appl. Math. Model., 2019, 70, 315-327.

[7] Slotman G.J.,Fasolino A., Structure, stability and defects of single layer hexagonal BN in comparison to graphene, J. Phys. Condens. Matter, 2013, 25(4), 045009.

[8] Griebel M., Hamaekers J., Heber F., A molecular dynamics study on the impact of defects and functionalization on the Young modulus of boron-nitride nanotubes, Comput. Mater. Sci., 2009, 45(4), 1097-1103.

[9] Thomas S., Ajith K.M., Valsakumar M.C., Directional anisotropy, finite size effect and elastic properties of hexagonal boron nitride, J. Phys. Condens. Matter, 2016, 28(29), 295302.

[10] Mortazavi B., Rémond Y., Investigation of tensile response and thermal conductivity of boron-nitride nanosheets using molecular dynamics simulations, Physica E: Low-dimensional Syst. Nanostr., 2012, 44(9), 1846-1852.

[11] Corso M., et al., Boron Nitride Nanomesh, Science, 2004, 303(5655), 217.

[12] Peng Q., Ji W., De S., Mechanical properties of the hexagonal boron nitride monolayer: Ab initio study, Comput. Mater. Sci., 2012, 56, 11-17.

[13] Le M.Q., Size effects in mechanical properties of boron nitride nanoribbons, J. Mech. Sci. Technol., 2014, 28(10), 4173-4178.

[14] Oh E.S., Elastic Properties of Various Boron-Nitride Structures, Met. Mater. Int., 2011, 17(1), 21-27.

[15] Bosak A. et al., Elasticity of hexagonal boron nitride: Inelastic x-ray scattering measurements, Phys. Rev. B, 2006, 73(4), 041402.

[16] Zhao S., Xue J., Mechanical properties of hybrid graphene and hexagonal boron nitride sheets as revealed by molecular dynamic simulations, J. Phys. D: Appl. Phys., 2013, 46(13), 135303.

[17] Oh E.S., Elastic properties of boron-nitride nanotubes through the continuum lattice approach, Mater. Lett., 2010, 64(7), 859-862.

[18] Setoodeh A.R., Badjian H., Mechanical behavior enhancement of defective graphene sheet employing boron nitride coating via atomistic study, Mater. Res. Express, 2017, 4(12).

[19] Jiang J.W., Wang B.S., Park H.S., Topologically protected interface phonons in two-dimensional nanomaterials: hexagonal boron nitride and silicon carbide, Nanoscale, 2018, 10(29), 13913-13923.

[20] Lin X., Han Q., Huang J., Effect of defects on the motion of carbon nanotube thermal actuator, Nanotechnology Reviews, 2019, 8(1), 79-89.

[21] Thomas S. et al., Temperature dependent structural properties and bending rigidity of pristine and defective hexagonal boron nitride, J. Phys. Condens. Matter, 2015, 27(31), 315302.

[22] Abadi R. et al., Investigation of crack propagation and existing notch on the mechanical response of polycrystalline hexagonal boron-nitride nanosheets, Comput. Mater. Sci., 2017, 131, 86-99.

[23] Li N. et al., Mechanical properties and failure behavior of hexagonal boron nitride sheets with nano-cracks, Comput. Mater. Sci., 2017, 140, 356-366.

[24] Zhao H., Min K., Aluru N.R., Size and Chirality Dependent Elastic Properties of Graphene Nanoribbons under Uniaxial Tension, Nano Lett., 2009, 9(8), 3012-3015.

[25] Swope W.C. et al., A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters, J. Chem. Phys., 1982, 76(1), 637-649.

[26] Mortazavi B.,Cuniberti G., Mechanical properties of polycrystalline boron-nitride nanosheets, RSC Adv., 2014. 4(37), 19137-19143.

[27] Liang Y., Han Q., Huan S., The Effects of Temperature and Vacancies on the Elastic Modulus and Strength of Graphene Sheet, J. Thermal Stresses, 2015, 38(8), 926-933.