Computational Materials Science 144 (2018) 210–215

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Brittle-to-ductile transition in fracture of few-layered black phosphorus ribbons under uniaxial stretching

Lei Wang [a], Kun Cai [b,*]

[a] Department of Engineering Mechanics, Hohai University, Nanjing 210098, PR China
[b] Research School of Engineering, The Australian National University, ACT 2601, Australia

ARTICLE INFO

Article history:
Received 11 September 2017
Received in revised form 11 November 2017
Accepted 14 December 2017

Keywords:
Black phosphorene
Fracture
Molecular dynamics
Brittle-to-ductile transition

ABSTRACT

Owing to excellent electrical properties, few-layered black phosphorene (BP) ribbons will be wide used in nano-electro-mechanical systems. Before acting as a component in the nanosystem, they should be fabricated successfully. During peeling, pulling or cutting in fabrication of a few-layered BP ribbon, the load on it should be controlled to be less than its strength or ultimate strain. Otherwise, the ribbon will be broken which means a failed fabrication. For a deep understanding of the damage process, molecular dynamics simulations are adopted to illustrate the fracture of a few-layered BP ribbon under uniaxial stretching. Influence of both temperature and the thickness of the ribbon are discussed. The brittle-to-ductile transition of the three-dimensional fracture mode is discovered, and the mechanism is revealed.

1. Introduction

Owing to special electron orbits distribution, phosphorus has different allotropic modifications, e.g., white, black, blue, and amorphous red phosphorus at ambient conditions [1,2]. Among the allotropes, black phosphorus (BP) is the most stable one. Monolayer BP has a puckered honeycomb structure, and each phosphorus atom in the structure is covalently bonded with three adjacent atoms. BP attracts much attention recently due to its excellent electrical properties for future application. For example, different from the zero-gap graphene, BP behaves a direct band gap, and the gap can be adjusted from 1.51 eV of a monolayer to 0.59 eV of a five-layer [3]. It has very high carrier mobility up to 1000 $cm^2 V^{-1} s$ [4] and high on/off ratio up to 10^4 [5].

Severing as a component in a nanodevice, the mechanical properties of BP should be deeply understood. Using first-principles calculations, Jiang and Park [6] investigated the mechanical properties of single-layer black phosphorus under uniaxial deformation. The in-plane Young's modulus is 41.3 GPa in the direction perpendicular to the pucker and 106.4 GPa in the parallel direction. They also reported a negative Poisson's ratio in the out-of-plane direction under uniaxial strain [7]. Hu et al. [8] investigated the mechanical and electronic properties of BP ribbon with one or two layers under specified deformation, including uniaxial and biaxial tensions. Wei and Peng [9] recently reported that monolayer phosphorene demonstrates superior mechanical flexibility with ultimate strain up to 30%. Fei and Yang [10] reported the electrical conductance of BP under large strain deformation. However, it is weaker than graphene having Young's modulus of about 1000 GPa and strength of about 100 GPa [11,12], which is a drawback for its potential application. But the compliance of a monolayer BP along the armchair direction (normal to puckered direction) attracts attention on investigation of a nanotube from a BP ribbon [13–19]. As one kind of 2D material, edge may play a key role in mechanical response and performance of single-layer BP ribbon. Sorkin and Zhang [20] investigated the fracture behavior of phosphorene ribbon with different edge structures under uniaxial tension. It is found that the mechanical response is highly anisotropic and bond breaking was analyzed. Sorkin and Zhang [21,22] also explored the structure, elastic property and passivation of phosphorene nanoribbons. The edge passivation can lessen the edge relaxation and reduce the edge stresses and elastic moduli.

Previous studies on the mechanical properties of BP ribbon were based on first principles calculations at 0 K. Two disadvantages for explaining the results. One is that the dimensions of the system in above simulations are limited. Some mechanical properties at structural level cannot be revealed. To carry out a large scale of MD simulation, empirical potential energy function is required. According to the results of first principle calculations on monolayer BP, Jiang [23] fitted the coefficients in the Stillinger-Weber potential [24]. The interlayer interaction in few-layered BP is commonly estimated by traditional Lennard-Jones (LJ) potential [25]. In 2012, Appalakondaiah et al. [26] used dispersion-corrected DFT

* Corresponding author.
E-mail address: kuncai99@163.com (K. Cai).

https://doi.org/10.1016/j.commatsci.2017.12.034
0927-0256/

approaches to modify the van der Waals (vdW) interaction between non-bonding atoms in few-layered BP. Another is the temperature effect being ignored in above simulations. As a matter of fact, the stability of phosphorene is sensitive to temperature. For example, Yang et al. [27] investigated the temperature-dependent mechanical properties of monolayer BP under either uniaxial, biaxial tension or shearing load. Sha et al. [28] evaluated the ultimate strength and strain of monolayer BP at finite temperature up to 450 K. They found that BP becomes weaker at higher temperature. In the work by Cai et al. [29], the critical curvature of a BP ribbon is sensitive to both the curving direction of ribbon and the environmental temperature. Therefore, mechanical properties of few-layered BP ribbon at finite temperature are urgent to be investigated for experiments.

In fabricating a piece of few-layered BP ribbon by peeling from a block of BP, the ribbon must be under uniaxial tension. To obtain a few-layered BP successfully, 5 major steps are required. First, a BP bulk should be prepared by cutting, and is fixed on a substrate. Second, probe attaches to an edge of the cut bulk. Third, the probe is fixed on the edge by such method as chemical vapor deposition of phosphorus gas. Fourth, pull the probe away from the BP bulk with a relative small speed. Final, a few-layered BP ribbon is removed from the bulk and goes together with the probe. Frankly, the bending deformation must happen during peeling process because the interlayer friction of BP is much higher than their (vdW induced) attraction along the normal direction of layer. To avoid breakage of the ribbon attached to the probe during peeling, the edge should be pulled normal to the layer. In pulling, the BP ribbon is mainly under bending deformation. Thus, bending property of BP ribbon also attracts many attention. For example, based on a density functional potential, Verma et al. [30] studied the flexibility of single-layer phosphorene along an arbitrary direction and found a directional dependent thickness. When the length of the ribbon from the bulk is higher, the ribbon is mainly under tension, which is discussed in our present work. In other words, if the breakage in a BP ribbon is avoided, the mechanism for fracture should be understood to avoid the breakage of BP in fabrication. For a monolayer BP ribbon, Sha et al. [28] have found that the fracture propagates along the groove of the puckered structure when the ribbon is under uniaxial tension along the armchair direction. Obviously, the damage process can be considered as a two-dimensional (2D) fracture. Up to now, no result is published to show the mechanism for damage of few-layered BP ribbon. In the present study, we study the mechanism for the three-dimensional (3D) fracture in few-layered BP ribbon under uniaxial stretching, and temperature effect is majorly considered.

2. Model description and methodology

In this paper, four kinds of models, those are double-, triple-, four- and five-layer, are considered for few-layered BP ribbon, which can be considered as a stacking of single layers according to a specified order. Geometrical structure of a triple-layer BP ribbon prototype is presented in Fig. 1. The four phosphorene structures take the stacking sequence of AB, ABA, ABAB, and ABABA, respectively [9], as shown in Fig. 1(b), and the interlayer distance (rather than surface distance) is chosen to be 5.235 Å. The armchair and zigzag directions of each sheet are oriented along the X and Y axes, respectively. There are 20 periods along both X and Y directions and thus the dimensions of a model in simulation is 76.16 Å × 73.31 Å in XY plane. Simulation box is set to be 400 Å × 400 Å × 400 Å and BP ribbon is placed in the center of the simulation box. In other words, the BP ribbon is far from the box boundaries. Periodic boundary conditions (PBC) are applied on both X and Y directions, while free surface boundary is applied on the normal direction (Z) of the plane. Two rows or columns of atoms at four edges are defined as boundaries where external loading is applied.

The initial geometrical structure of few-layered black phosphorus is optimized using conjugate gradient method on the potential energy of the system, and then the system is relaxed in NVT (constant number of atoms, system volume and temperature) ensemble for 50,000 time steps to reach an equilibrium and minimum energy state at a desired temperature. Temperature control is performed by time integration on Nose-Hoover style equations of motion and the thermo-statting is achieved by introducing some dynamic variables coupled to velocities of atoms. The equations of atomic motion are integrated with a time step of 1.0 fs. Thereafter, the uniaxial tensile loading is applied in either X or Y direction by increasing a displacement of 0.01 Å along the loading direction and subsequently accompanied by 2000 steps (i.e. *2* ps) of relaxation in a step-by-step manner, ensuring a quasi-static deformation in simulation. Hence, in the present work, the value of the strain rate equals (0.01 Å/76.16 Å)/2ps, i.e., 6.57×10^{-5}/ps.

The MD simulations are performed using the open source software package LAMMPS [31]. The bonding interactions between phosphorus atoms within the same layer are described by the Stillinger–Weber (SW) potential with the parameters proposed by Jiang et al. [23], while the non-bonding vdW interactions between phosphorus atoms across adjacent layers are modeled by the 12-6 type LJ potential with the related parameters of σ = 3.438 Å, and ε = 15.94 meV. In simulation, the atomic stress is adopted to evaluate the strength of a BP ribbon under stretching.

3. Results and discussion

3.1. Effect of layer number

Before discussing the temperature effect, we compare the ultimate stresses and strains of few-layered BP ribbons under uniaxial stretching at 1 K. At a low temperature close to absolute zero, thermal vibration of atoms is very small and interlayer interaction (vdW interaction) is stable. For convenience, we just provide the relative stresses for comparison. In Fig. 2, it can be found that the ultimate strains stretched along either armchair or zigzag direction have slight difference with respect to the number of layers in BP ribbons. It suggests a conclusion, i.e., the ultimate strain of a BP ribbon depends slightly on the thickness of ribbon. By comparing the ultimate stresses (or the maximum values of relative stresses), one can find that the monolayer BP ribbon has the maximum strength. The relative differences among the stresses could reach 20% when stretching along the armchair direction or over 20% along zigzag direction. Fortunately, the differences among the ribbons with 3 or more layers are not high. And the 4-layered BP ribbon is weaker than the 5-layered ribbon, which indicates that a BP ribbon with more than 5 layers should be stronger than the 4-layered ribbon but weaker than the monolayer ribbon.

3.2. Temperature effect on 3-D fracture of BP ribbons

To clarify the effect of temperature, a 3-layered BP ribbon is chosen to be a prototype and its mechanical behavior is investigated under tension along either the armchair or zigzag direction at different temperature, as provided in Fig. 3. It can be observed that both rupture strain and peak stress drop monotonically with the increase of temperature. For example, if considering the strength of BP ribbon at 1 K as the ideal strength, the strength of the BP ribbon at 100 K is only 40% of the ideal strength along the armchair direction. At 200 K, the strength decrease to be about 20% of the ideal strength. At normal temperature, the strength is less than 10% of the ideal strength. When the ribbon is stretched