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Absorption and temperature effects on the tensile strength of a black phosphorus ribbon in argon environment

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ABSTRACT

Due to its excellent electrical properties, a few-layer black phosphorus (BP) ribbon has wide potential application in nano-devices. Its strength is essential for fabrication of the nano-devices. However, BP suffers from severe performance degradation in ambient conditions. In the present study, using argon as shielding gas, we investigate the tensile strength of a few-layer ribbon with consideration of both temperature and gas absorption via molecular dynamics simulations. Results demonstrate that the tensile strength of a BP ribbon is weakened at high temperature. If the ribbon has full relaxation before stretching, its tensile strength can be improved slightly by the argon membrane absorbed onto its surfaces. At 300 K, the strength is improved obviously due to gas absorption. The conclusions can be used for potential application in fabrication of few-layer BP ribbons.

1. Introduction

Phosphorus has many allotropes [1–5], among them black phosphorus (BP) has the most stable structure via $3sp^3$ bonds within the same layer and van der Waals interaction between layers [6–7]. In particular, the few-layer BP is a semiconductor material [8–11] due to its unique electronic properties, e.g., over 10^4 of drain current modulation, up to 10^3 $cm^2/(V\,s)$ of charge-carrier mobility, etc. Hence, wide application in nanodevices of the new two-dimensional material becomes possible.

However, the stability of a BP ribbon is far less than that of a ribbon from graphene due to the strength of a $3sp^3$ bond being weaker than that of a $2sp^2$ in graphene. Decades ago, people have found that BP is instable at high temperature and high pressure [1–3]. BP also has weak stability in chemistry. Due to chemically activity of the atoms at edge of a BP ribbon, they tend to be bonded with foreign molecules. Therefore, BP is instable when exposed in air or water [12,13]. Island et al. [14] investigated the instability of few-layer BP exposed to ambient conditions. It was reported that the strong affinity of BP for water not only leads to a volume change due to the condensation of moisture from air, but also greatly modifies the performance of BP-base field effect transistors by a layer-by-layer etching process. Using first principles calculations, Boukhvalov et al. [15] studied the stability of phosphorene after chemical modifications of hydrogenation, fluorination and oxidation. To improve the chemical stability, one can reduce the number of edge atoms in the ribbon by three approaches. The first one is to covalently bond the atoms with other atoms [16,17]. The second method is to covalently bond the opposite edges of a ribbon, i.e., to form a BP ribbon into a nanotube [18–28]. In the nanotube, those atoms on the two sides become as stable as the internal atoms. The final method is to protect the BP with graphene [29]. The mechanical stability of the BP ribbon contains two aspects, i.e., mechanical strength and ultimate compression of buckling. The former one determines the process of its fabrication, and is essential for its application in a nanodevice. Wei and Peng [30] discussed the ideal tensile strength and critical strain of a monolayer BP. 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 [31] studied the edge stress of phosphorene using density functional tight binding calculations. Sorkin and Zhang [32] investigated the fracture behavior of phosphorene ribbon with different edge structures under uniaxial tension. Using molecular dynamics approach with the Stillinger-Weber potential proposed by Jiang [33], Sha et al. [34] and Yang et al. [35] separately investigated the strength of a monolayer BP under different loads at finite tem-

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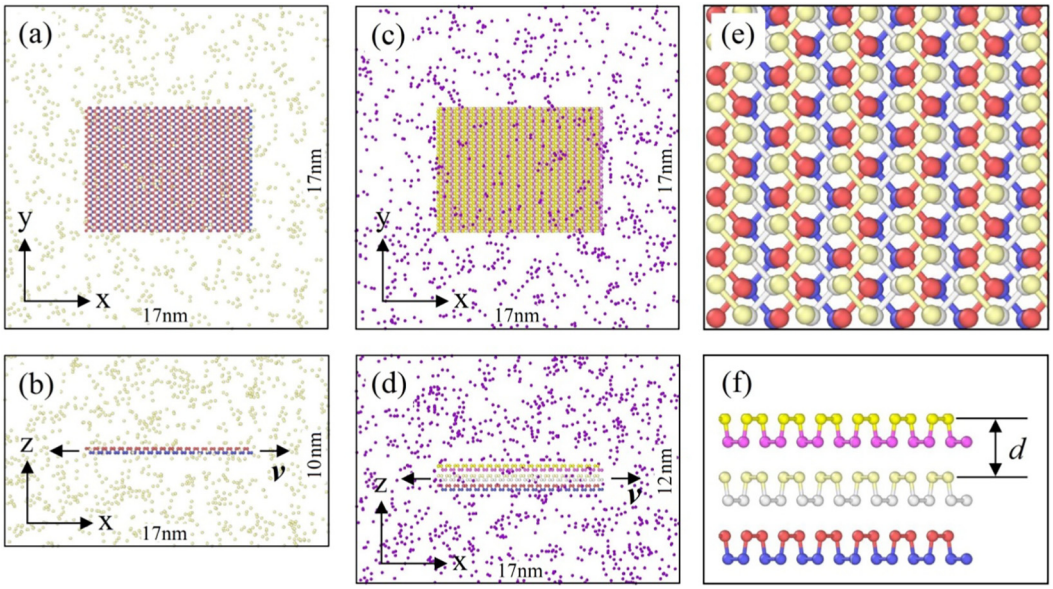

Fig. 1. Initial configuration of BP ribbons in a box filled with argon atoms. (a) and (b) are top and front views of the monolayer BP ribbon, while (c) and (d) are top and front views of the triple-layer BP ribbon. Both ribbons have the same sizes of 7.62 nm × 7.33 nm in xy-plane. (e) ABA stacking style is adopted to arrange the layers in the triple-layer BP ribbon, (e) with average thickness of $d = 0.5235$ nm of each layer (along z-direction). After relaxation, the ribbon will be stretched with a constant velocity ($\boldsymbol{v}$) at its right edge and fixed at the left edge.

perature.

One fact is that there is only BP in above discussions, i.e., no other atoms are involved in the experiments. Usually, a few-layer BP ribbon is usually operated under inert environment or exposing in air rather than vacuum [36–38]. A vacuum condition is hard to achieve and severely restricts commercial application of BP-related devices. Operating few-layer BP in inert gas, e.g. argon, is popular [37,38]. When using argon gas as a protective and processing media, we have to face a fact that argon molecules are absorbed onto the surface of the BP ribbon. What may happen to the strength of the BP ribbon? To answer this question, we present a series of numerical experiments on a monolayer and a triple-layer BP ribbon at finite temperature. It is known that, at finite temperature, the argon atoms in the box shown in Fig. 1a–d have initial velocities. For the atoms in the BP ribbon, they have to vibrate at their equilibrium positions. Meanwhile, the argon atoms can move with certain free path. The chance of collision of the argon atoms with the surface atoms in the ribbon becomes higher at higher temperature. Hence, some surface phosphorous atoms may depart from the ribbon after collision, and therefore, results in defect(s) on the ribbon. When the defect(s) propagate into the ribbon, the ribbon will be broken immediately. Hence, the temperature of the system is significant for the tensile strength of the ribbon. The major task is to reveal the temperature effect on the strength of a few-layer BP ribbon with consideration of absorption of the argon atoms.

2. Models and methodology

2.1. Models

Fig. 1 a-d gives the simulation boxes, and each box contains a BP ribbon and certain number of argon atoms. The temperature of the system is between 1 K and 300 K in the following numerical experiments. The number of argon atoms will be set of 0, 200, 500, 1000, or 1500. According to the ideal gas law, for example, the pressure in the simulation box with 1000 argon atoms is ~14.66 bar (or ~1.48 Mpa) at 300 K. It is feasible in an experiment. Details will be illustrated before each discussion.

2.2. Methodology

To obtain the strength of a BP ribbon under tension along armchair direction, molecular dynamics simulation approach is used by way of the open source code LAMMPS [39]. In a simulation, the covalently bonding interaction among the P atoms in the ribbon is evaluated by Stillinger-Weber potential [40] with the parameters presented recently by Jiang [33] through the first principle calculations. The non-bonding interaction between atoms is assessed using the 12–6 Lennard-Jones (L-J) potential [41]. For the interaction between neighbor layers or when the ribbon is broken, the L-J parameters for describing the interaction between two non-bonding P atoms at the new edge are of $\varepsilon = 15.94$ meV and $\sigma = 0.3438$ nm, respectively [33]. And the L-J parameters for argon atoms are 10.3236 meV and 0.3405 nm, respectively [42,43]. Using Lorenz-Berthelot rules, the L-J parameters for the non-bonding interaction between the argon atoms and the P atoms are 12.828 meV and 0.34215 nm.

Each simulation contains following steps:

Step 1: Build the system containing specified BP ribbon and argon atoms, all the boundaries of the box are periodic.
Step 2: Reshape the ribbon and the relative positions of argon atoms by minimizing the potential energy of the system using steepest decent algorithm.
Step 3: Initiate the velocities of the atoms in the box in Nosé-Hoover thermostat (NVT ensemble) [44,45].
Step 4: Relax the system for a period of time.
Step 5: Fix the left edge of the BP ribbon, and move the right edge with specified velocity as tensile loading along the armchair direction.