Computational Materials Science 102 (2015) 258–266

Contents lists available at ScienceDirect

Computational Materials Science

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

Fabrication of nanopore in graphene by electron and ion beam irradiation: Influence of graphene thickness and substrate

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ARTICLE INFO

Article history:
Received 18 October 2014
Received in revised form 17 February 2015
Accepted 23 February 2015
Available online 17 March 2015

Keywords:
Graphene nanopore
Molecular dynamics simulation
Ion beam
Electron beam
Mechanical property

ABSTRACT

In this paper, classical molecular dynamics simulations are conducted to study the fabrication of nanopore in graphene under electron and ion beam irradiation, in which the emphasis is put on the influence of substrate and graphene layers. Firstly, nanopore structures are confirmed to be generated on suspended and supported graphene with suitable incident parameters, while the existing of substrate will induce different phenomena and bring distinguishing results. Then different mechanisms are put forward to explain these distinct phenomena for suspended and supported case. In addition, the optimal parameters for the generation of a high quality nanopore in suspended and supported graphene are derived and the influence of graphene layers is discussed. Specially, the formation of cross-linkings between different layers is examined. Lastly, the influences of the inherent vacancies and sputtered atoms induced vacancies on the mechanical properties of nanoporous graphene are researched by tensile test simulations. These results can help us open the possibilities for better control of nanopore devices.

1. Introduction

Graphene is a honeycomb material made up of carbon with a single layer atom. Motivated by its excellent mechanical [1,2], thermal [3], electrical [4,5] and optical properties [6,7], graphene is receiving explosive attention during the past several years. Consequently, a variety of potential applications, such as field effect transistors and electromechanical devices [8,9] have been expected for this two-dimensional sheet. Among these applications, nanopore sequencing [10] is special for graphene due to its subnanometer thickness (0.34 nm) that is comparable to the spatial interval between neighboring DNA nucleotides. This feature gives graphene the possibility to conduct gene sequencing at a single-base resolution, which is unreachable for the biological, solid-state or biological solid-state hybrid nanopore technology. The feasibility of graphene nanopore used for DNA sequencing at a single-base resolution has already been proved [11–13]. Besides, graphene nanopore has also been demonstrated to have other potential applications, such as water desalination [14] and ion filtration [15]. Moreover, the nanomesh structure created on supported graphene sheet can open up its zero bandgap, which makes graphene a semiconducting film and allows for the rational design of graphene-based devices [16]. In order to realize and expand the applications of graphene nanopore, the finding of an efficient nanopore fabrication technology is essential.

For the fabrication technology of graphene nanopore, the gas clusters [17] and metal clusters [18] irradiation are theoretically proved to be capable of creating nanopore by one shot, while the preparation of the clusters is difficult, which makes these methods in experiment infeasible. Nanoscale lithography [16] and chemical synthesis [19] have been demonstrated to be scalable methods for the throughput fabrication of graphene nanomesh, nevertheless they are limited by the resolution of mask and contamination problems resulted from the contacting masks. Focused beams, mainly refer to focused electron beam and focused ion beam, can be used to generate nanopore of several nanometers (electron beam) [20,21] or tens of nanometers (ion beam) [22]. Though hard to be scaled up due to the complex process, the focused beam irradiation method is being developed towards high efficiency and low cost. Importantly, the focused beam irradiation is still the only method for the effective preparation of graphene nanopore used in DNA sequencing at present [11,23]. So it is important to figure out the phenomena happened during the formation of graphene nanopore under focused beam irradiation. The current work mainly focused on the experimental realization [24] and influence of beam parameters [25], while few attentions are paid

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http://dx.doi.org/10.1016/j.commatsci.2015.02.042
0927-0256/

to the effect of substrate, which may influence the formation mechanisms and properties of nanopore. Meanwhile, the nanopore in multilayer graphene is demonstrated to have advantage in DNA sequencing over monolayer [11,26], but the fabrication mechanisms and influence factors of nanopore in multilayer graphene are still unclear. Besides, the mechanical properties of nanoporous graphene are important for its applications, and they have already been studied with the consideration of size, shape, porosity and edge passivation of nanopore [27–29]. However one should be aware that besides the nanopore structure, the inherent vacancy defects and sputtered atoms induced vacancies during irradiation would also exist in nanoporous graphene, which may affect the tensile properties. This nanopore-vacancies coexisting system is sometimes inevitable during the fabrication of nanopore, nonetheless there are no talks about its mechanical properties.

To this end, a comprehensive study has been carried out on the fabrication of nanopore in graphene under electron and ion beam irradiation by using molecular dynamics simulation methods. Firstly, nanopore structures are confirmed to be generated in suspended and supported graphene, while the properties of nanopore are quite different for two cases. Then different mechanisms are put up to explain the formation of nanopore in suspended and supported graphene. In addition, the optimal parameters (least irradiation energy and dose) for the generation of a high quality nanopore in suspended and supported graphene are derived and the influence of graphene layers is discussed. Lastly, tensile test simulations are proceeded to illuminate the influence of the inherent vacancies and sputtered atoms induced vacancies on the mechanical properties of nanoporous graphene.

2. Simulation models

In order to investigate the fabrication of graphene nanopore under electron and ion beam irradiation, empirical molecular dynamics simulations [30] are performed using the code LAMMPS [31]. The potential energy from which the interatomic forces between the carbon atoms in graphene for each simulation is determined by the adaptive intermolecular reactive bond order (AIREBO) potential [32] with 2.0 Å as the cutoff distance. This potential allows for the breakage and creation of covalent bond and can take the no-bonded interactions into consideration as well, which enables the simulations on the variations of bond breaking and formation during the fabrication of graphene nanopore.

For the case of ion beam irradiation, Ar is chosen as representative ion due to its easily accessible feature in the experiments [33,34]. In order to describe the interaction forces between carbon atoms in graphene and Ar ions, the Ziegler–Biersack–Littnark (ZBL) potential [35] is used due to there are no chemical bonds formed between carbon atoms and Ar ions. The ZBL potential, also known as the universal repulsive potential, is the most widely used analytical potential describing the collisions between focused beam and carbon nanomaterials [36–38]. However, because this potential has a classical feature which cannot include the charge effects, we treat the incident ions as neutral Ar atoms rather than charged ions, as in other researches of collision process [37,38]. For the supported cases, graphene is supported by (0001) plane cleaved from SiO2 substrate with O termination. The initial distance between graphene layer and the surface of SiO2 is set to be 2.9 Å. The interactions between the atoms in SiO2 are described by Tersoff potential, which is smoothly joined with the ZBL potential at short distance to realistically describe energetic collisions. The interactions between carbon atoms in graphene and substrate atoms are described by Lennard–Jones (LJ) potential. As a van der Waals (vdW) type potential, the interatomic interactions are depicted by $V_{ij}(r) = 4\varepsilon_{ij}\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$, where i = C, j = Si or O, r is the interaction distance, the parameters ε_{ij}, σ and cutoff distance are from Ref. [39].

The simulation models of suspended system are depicted in Fig. 1. As shown in Fig. 1(a) and (b), the graphene sheets used in these studies have a dimension about 10 × 10 nm. The irradiated Ar ions are initially located in a cylinder region 40 Å above the plane of graphene, and then each ion will be irradiated vertically to the graphene plane every 500 simulation steps by assigning a kinetic energy to the ion. The incident energy of ion beam varies from 20 to 1000 eV and the incident dose (number of the total incident ions) varies from 20 to 600 to find the suitable parameters for the nanopore fabrication process. Besides, the layer of graphene sheet is increased from monolayer to five layers to consider about the fabrication of nanopore in multilayer graphene. The diameter of the cylinder is set as 2 nm to obtain a nanopore which can be used in DNA sequencing or water desalination. The irradiation radius of the ion beam can be controlled by a nano-mask [40] in actual experiments, as shown in Fig. 1(d). The supported cases have similar models except for the 3.6 nm SiO2 substrate.

The simulation method of electron beam irradiation is similar to that used in the collision researches of carbon nanotubes [41,42]. The electron irradiation process is mimicked by periodically assigning a velocity to a PKA (the primary knock-on atoms) in the graphene sheet. Even though the physical way of assigning of energies and momenta involves a significant fraction of "side collisions", the energy transferred due to "side collisions" is very little. Thus we consider only the "head-on" collisions from the beam direction where most of the energy and momentum is transferred. The kinetic energy assigned to the PKAs is increased from 0.5 to 500 eV. The PKAs are selected randomly from the irradiated area of graphene, which also has a diameter of 2.0 nm as displayed by the red area in Fig. 1(a), and one PKA receives the energy every ten steps for 2 ps followed by 1 ps of the system relaxation. For the whole electron beam irradiation process, we use 20 cycles of this irradiation-relaxation process. The influence of electron dose, referring to the number of cycles, is also discussed.

During the irradiation process, the outer areas of the four borders are fixed to reflect the fixed boundaries in Fig. 1(c) and (d), as depicted by the gray areas in Fig. 1(a) and (b). Besides, a thermostat region adjacent to the fixed area is also applied to allow for the dissipation of the energy associated with the collision events, as shown by the [1]red areas in Fig. 1. The size of the thermostat region is tested and rationally chosen. For the thermostat region, we choose the Langevin thermostat to keep a temperature of 300 K to absorb the energy waves generated by the irradiated beams. Before all the simulation cases, the system is equilibrated at 300 K for 10 ps to insure the graphene is fully relaxed. Then the graphene sheets are irradiated by ion or electron beam with different irradiation doses and energies. After each set of irradiation events, the system is annealed at 2000 K for 10 ps (the structure of graphene would not change anymore after this annealing time and temperature). Finally, the system is cooled to 300 K and kept at this temperature for enough time.

In order to characterize the mechanical responses of the fabricated graphene nanopore during the service process, we also perform the tensile test simulations as illustrated in Fig. 2. The nanopore system and nanopore-vacancies coexisting system are studied respectively. The vacancies are mainly monovacancies, which are randomly distributed in graphene. For the tensile tests, the dimension of the model used is 20 × 20 nm (we have increased the size from 15 × 15 nm to 30 × 30 nm, the results are little influenced by these changes). The right two layers of carbon atoms in

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.