Multiscale simulation of ion beam impacts on a graphene surface

K B Dybyspayeva[1], A Zhuldassov[1], A Ainabayev[1], A F Vyatkin[2], K Alekseev[3] and Z Insepov[1,3,4*]

[1] Nazarbayev University, Astana, 010000, Kazakhstan

[2] Institute of Miscroelectronics Technology, Chernogolovka, Moscow region, Russia

[3] Moscow Engineering Physics Institute, Moscow Russia

[4] Purdue University, West Lafayette, IN USA

E-mail: *zinsepov@purdue.edu

Abstract. Multiscale study of single and multilayer graphene irradiation is presented in this paper. Ab-initio density-functional theory (DFT) was used to study point defects, and a large scale parallel molecular-dynamics (MD) simulations were used for studying formation of gas cluster ion impacts. Moreover, Raman spectra of pure and defect graphene samples were studied from DFT calculations. Threshold energies for creating craters on the surface of graphene were obtained from MD and compared with published papers. The results of simulations were also compared with experimental craters and surface shape.

1. Introduction

Since its first discovery in 2004 graphene has been one of the favored topics in the scientific area [1]. Researchers have published numerous works about the studies of graphene properties and their applications in different fields [2-5]. Despite the fact that graphene is a 2-dimensional thin material it has proven to be mechanically strong and chemically stable [2]. Moreover, it has excellent electrical conductivity properties that are widely used to design graphene-based electronics. It is also applicable for creating graphene-based biomedical devices [3].

Performing and experiment of graphene bombardment is a challenging task. Firstly, experiment is expensive. Secondly, there are several circumstances that prevent from conducting a quality work. Samples of graphene are not perfect: most of the time, the coverage percentage is low. Moreover, during the experiment, bombardment can make graphene flakes merely fly off. Therefore, to study this process there is a need for simulations which can provide some insight on favorable conditions for bombardment, such as, threshold energy, cluster size etc.

Recently, defect formation on graphene surface has been addressed in a considerable number of articles. For instance, Hopster discusses the damages in graphene in the result of irradiation by slow highly-charged ions [4]. However, mechanism of defect formation during HCI interaction with target material is not clear and it requires further investigations. For carbon materials such as HOPG, carbon nanomembranes (CMN) and graphene it is shown that high potential energy (charge state $\sim q > 25$) and low kinetic energy (several keV) required to form induced friction type defect in graphene, hillocks in HOPG and nanopores in CNM [5-6]. In [7] authors propose bombardment by electron and oxygen

plasma treatment for the purposes of building nanopores on the surface of graphene. Plasma treatment can create nanopores in graphene and membranes made of plasma treated graphene shows good results for salt rejection, but plasma treatment do not allow fully control size of nanopores and theirs distribution. Celebi, on the other hand, proposes a method of drilling nanopores on graphene with focused ion beam (FIB) [2]. Although, using FIB drilling allows to create controlled size and uniformly distributed nanopores, but drilling millions nanopores might be formidable task in terms of consuming energy and time. Irradiation of graphene by ions creates single and double vacancies. However, these vacancies tend to reconstruct over time due to the self-healing property of graphene [8]. And this reconstructed graphene lattice still cannot serve as membrane because it still remains impermeable for atoms and molecules as shown in simulations [9]. In the present work, we propose a new method to make nanofilters. We state that irradiation by gas cluster ion beams (GCIB) is a very effective way for building controllable nanopores on the surface of graphene. Such membranes can be used to design water desalination filter with an efficient water transport. We present our preliminary theoretical analysis on irradiation of samples of graphene by GCIB both using density functional theory (DFT) and molecular dynamics (MD).

Evolutions in methods of calculating electronic structure, especially in density functional theory (DFT) [10], combine with the steady increase of available computing capacities; give new opportunities to calculate large systems. Accuracy of DFT technique makes this method an alternative in assisting the design and development of the generation of new devices for nanoscale applications. Unique functional of the electron density is the total energy of the system main principle of DFT. O. Lehtinen, J. Kotakoski used DFT to study the impacts of ion irradiation on production of defects in graphene [8]. In present study DFT was used to investigate graphene lattice reconstruction when single vacancy is introduced in graphene lattice. In addition, we considering DFT as method for calculation Raman spectra of graphene and in present work we show that G peak in graphene changes in position, width and shape with number of layers. It has been shown experimentally [12, 13, 14] and theoretically [15] that the G peak in graphene changes in position, width and shape with number of layers. In [12] the authors investigated variations in the Raman spectrum as a function of the number of graphene layers by using micro Raman spectroscopy and atomic force microscopy (AFM). The variations in the Raman G peak (1580 cm^{-1}), G* peak (2450 cm^{-1}), and 2D peak (2700 cm^{-1}) were observed as functions of the number of graphene layers.

Graf et al. [13] reported on Raman mapping of single- and few-layer graphene flakes resting on a silicon oxide substrate. Lateral resolution of 400 nm allows one to address neighboring sections with various layers of graphene down to a single graphene sheet, previously determined with the scanning force microscope (SFM). Gupta [14] presented the first formal report of Raman scattering studies on nGLs (Graphene Layers), where n is in the range 1 < n < 20, as determined by AFM. An empirical force-constant method has been used by Wang et al [15] to investigate phonon dispersions of graphite and graphene. Their experimental and theoretical results clearly show that certain Raman peaks change with the number of graphene layers (n).

To study electronic and vibrational properties of crystals or molecules Raman spectroscopy is widely used. CASTEP (Cambridge Serial Total Energy Package) [16] is used to compute a Raman intensity. CASTEP delivers a correct symmetry assignment of Raman active vibrational modes and a quantitative measure of the Raman intensity change around the transition.

2. Simulation and modeling

2.1 DFT simulation

2.1.1 The model. Figure 1 shows 5x5x1 graphene supercell and four layer graphene which were used to calculate Raman spectrum of perfect graphene film before ion irradiation. A finite displacements technique was used to calculate the dependence of the graphene G peak position on the layer numbers

of graphene. It is known that the G peak position shifted to lower energies if the number of graphene layers increases.
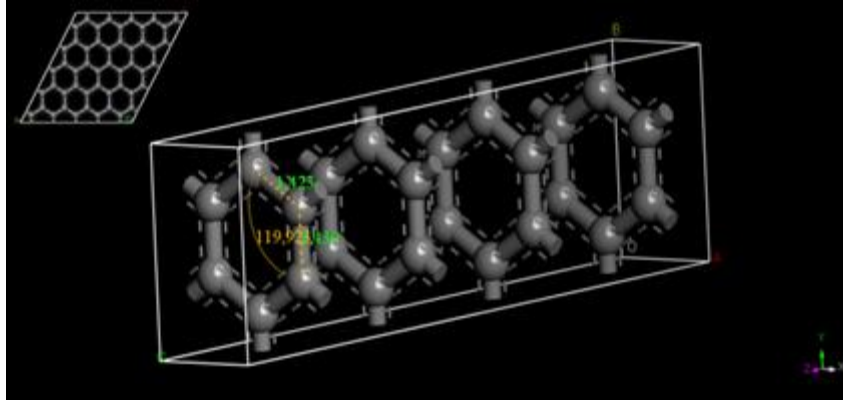

Figure 1. a) - supercell 5x5x1 lattice structure of graphene and b)- four layer grapheme.

2.1.2 Calculation details. We used a first-principles Raman calculation technique based on density functional theory. We used CASTEP which is a first-principles calculation code with using the plane-wave pseudopotential approach. We adopted GGA (PBEsol) [17] as the term exchange correlation with a cutoff energy from 750 to 940 eV and all calculations was performed by norm-conserving pseudopotential (2s22p2). The k-point separation was 0.04 Å-1 Monkhorst-Pack grid is 7x7x1, represented 25 irreducible k-points.

For graphene layers we considered the elementary cell, the distance between layers 0.335 nm, from 1 layer to 10 layers. Layers stacked directly on top of each other (AA stacking) [18].

2.1.3 Results and discussions. Irradiation by single charged ions, in general, produces single or double vacancies in graphene lattice. For high energy ions (1000 keV) graphene is almost transparent. Although single charged ions create defects as vacancies, graphene reconstructs its lattice and remaining flat with sp2 hybridized structure [11].
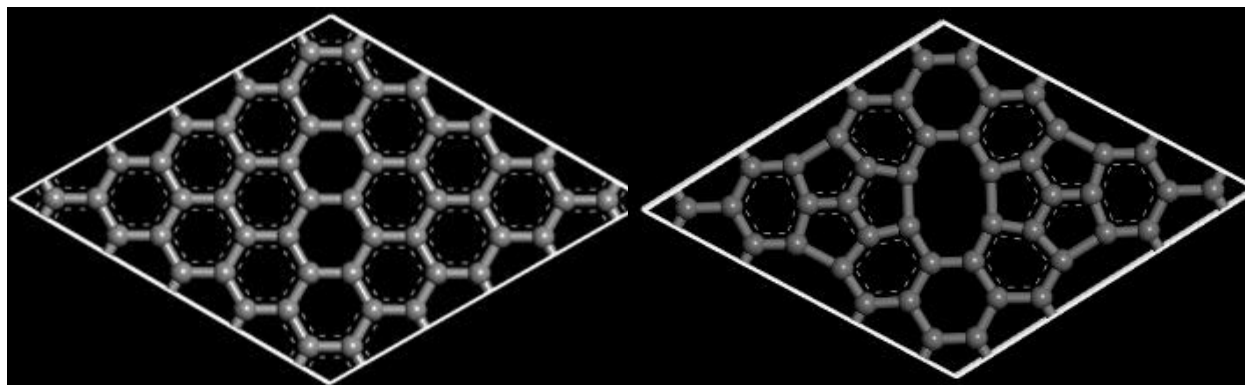

a)   b)

Figure 2. a) -pristine graphene lattice and b) –reconstructed lattice of graphene mainly in the form of a network of pentagons and heptagons after introducing single vacancyin pristine graphene lattice.

In Figure 2, it is shown DFT optimized graphene lattice after removing one atom from its lattice. Reconstructed graphene lattice were obtained by a first-principles technique based on DFT. We used a first-principles calculation code with using the plane-wave pseudopotential approach. We adopted GGA (PBEsol) as the term exchange correlation with a cutoff energy from 750 to 940 eV and all calculations was performed by norm-conserving pseudopotential (2s22p2). The k-point separation was

0.04 Å-1 Monkhorst-Pack grid is 5x5x1, represented 25 irreducible k-points. As can be from Fig. seen lattice of graphene relaxed mainly in the form of a network of pentagons and heptagons with lower density and remaining flat with sp2 hybridized structure. This kind of lattice is still able to hold volatile substances and can serve as volatile substance storage for conduction ion beam analysis [11]. It means that graphene irradiation by single charged ions are not appropriate for creation membranes with few nanometer defects for filtration purposes, for example, for water desalination.

The shift of Raman spectrum G-peak was obtained in our DFT calculations of a multilayer graphene stucture with 1-10 layers (Figure 3) by using CASTEP software. The results of these calculations were in accordance with the statement that as number of graphene layers increases G peak position shifted to lower energies. Figure 2 shows comparison of the calculated (this work) and experimental (this work) Raman G-peaks with other experimental and calculated G-peaks means [12-15]. It can be seen from the comparison that CASTEP result in a good agreement with other experimental and theoretical works which means that CASTEP are reliable tool to conduct Raman shift related calculations.
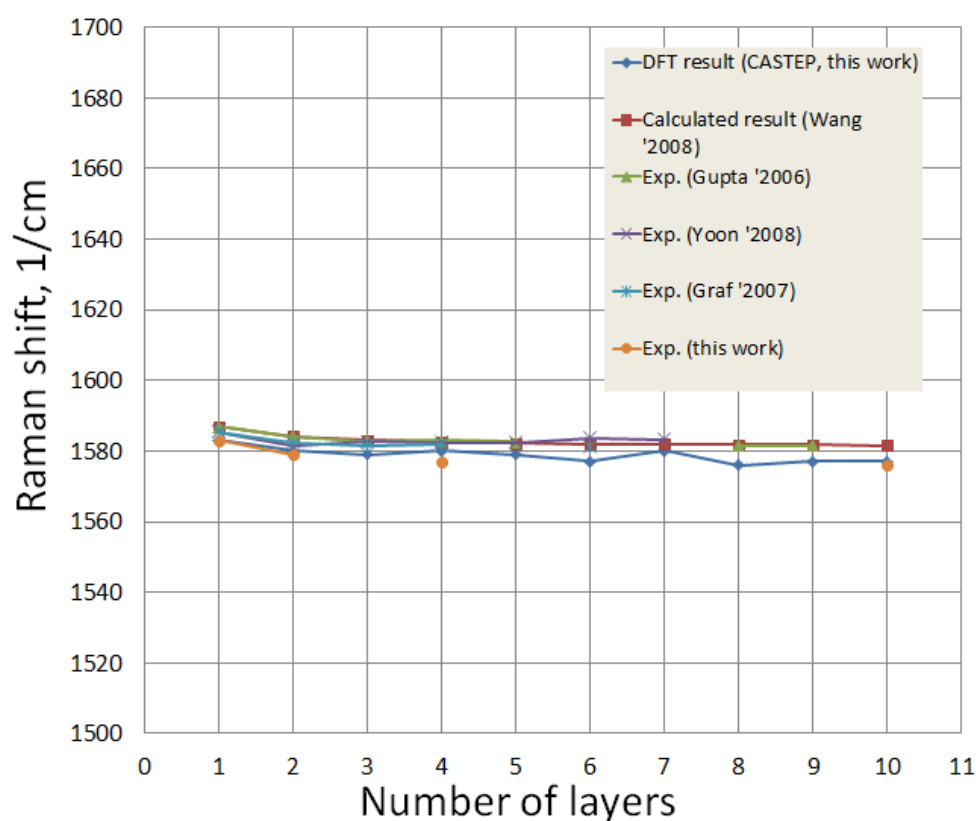

Figure 3. G-peak displacement calculated with DFT versus the number of graphene layers.

One of the main future goals of using CASTEP for calculation Raman spectra of a defect containing graphene sample is to determine different types of defects (vacancies, craters, holes) created by ion irradiation by evaluation of Raman spectra of irradiated graphene. Thus, by comparing experimental Raman spectra of GCIB irradiated graphene samples with calculated defect containing graphene, one can understand the kind of defects GCIB produces in the graphene structure. This study is still underway and the results will be published elsewhere.

2.2 MD Simulation
Many papers have been dedicated to the MD study of graphene irradiation with ions. In their models, scientists examine bombardment processes of single layer [6] and multi-layer graphene sheets [7] as

well as graphene on various substrates such as SiC [8]. In the present work, we developed the simulation model of a single layer graphene irradiated with argon cluster in the result of which we observe formation of nanopores on the surface of the material. By controlling the fluency of irradiation and the size of the cluster, it is possible to create pores of a desired diameter. We believe that such technology can be useful to create energy efficient filters for water desalination. It has also been tested and discussed in [9] where the experimental material was MoS2.

2.2.1 The model. Irradiation of graphene with argon cluster was studied using large-scale molecular massively parallel simulator (LAMMPS) package [19]. The simulation model consisted of an individual argon cluster and a single layer graphene sheet. Incident energy of the cluster was varied between 2.8 eV/atom to 28 eV/atom in –z-direction, and size of the graphene sheet was chosen between about 100×100 Å^2 and 1000×1000 Å^2. Size of the cluster was chosen to be between 10 and 1070 atoms in the cluster. Tersoff potential is applied to describe carbon-carbon interactions of the graphene sheet, placed in the *xy*-plane at $z = 0$. Lennard-Jones and Buckingham potentials were used for Ar-Ar and Ar-carbon interactions, respectively.

Modeling graphene sheet was implemented by building a lattice with 4 basis atoms in a rectangle crystal cell. Lattice parameters and coordinates of the basis atoms used in LAMMPS are presented in the Table 1. Parameters of Tersoff potential are taken from LAMMPS BNC.tersoff data file, which was then converted to LAMMPS "real" units.

Initially, cluster temperature was set to 0K. The simulations were performed in NVE ensemble. Boundary conditions were set to periodic in *x, y,* and *z*.

Table 1. The parameters of Tersoff potential used in MD simulations [13].

Parameter	Value/Coordinates
Lattice constant	1.421 A
Lattice vector a1	(3, 0, 0)
Lattice vector a2	(0, 1.732, 0)
Lattice vector a3	(0, 0, 2.357)
Basis atom 1	(0, 0, 0)
Basis atom 2	(0.333, 0, 0)
Basis atom 3	(0.5, 0.5, 0)
Basis atom 4	(0.833, 0.5, 0)

2.2.2 Results and discussions. Upon irradiation, one can observe defect formation on graphene sheet, when the incident energy is higher than the threshold one. The purpose of this computational method is to explain cluster ion-solid interaction on a molecular level and to provide guidelines in determining optimal conditions to achieve desired material processing results in further cluster ion beam irradiation experiments.

Threshold energy was obtained from this simulation study, which was compared with the experimental data obtained by irradiation of graphene and graphene oxide films with Ar and Ar+O$_2$ mixture cluster ion beams at Exogenesis Corp., USA. The simulation data was also compared with the similar research study by Zabihi et al [6].

It was observed that threshold penetration energy of the cluster depends on the cluster radius as well as on the graphene sheet area. Figure 4 shows snapshots of our molecular dynamics simulations

of argon cluster bombardment on a graphene sheet with the cluster energy of 10.12 eV/atom for graphene area of $100x100\text{Å}^2$ and $1000x1000\text{Å}^2$ at various time instants.

Figure 6 shows comparison of our simulation results for threshold values with the simulation data in [6]. Both set of simulation values have the same orders of magnitude for the $100xa100\text{Å}^2$ graphene area for small cluster sizes. However, the present study shows that the threshold energies per atom are higher for Ar_{50}, and lower for less number of atoms in the cluster.

t = 0 fs

t = 450 fs

t = 750 fs

t = 2250 fs

Figure 4. Simulation snapshots of argon cluster bombardment on a graphene sheet with the cluster at different timesteps. Images are processed using Atomeye.
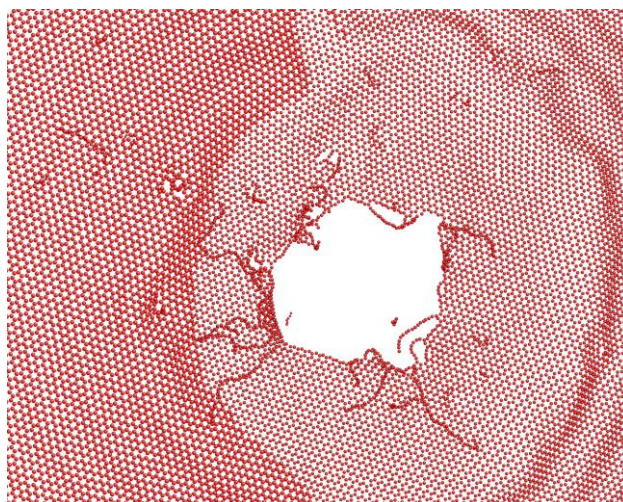
Figure 5. Top view of the crater formed in the result of GCIB bombardment at t = 3000 fs.
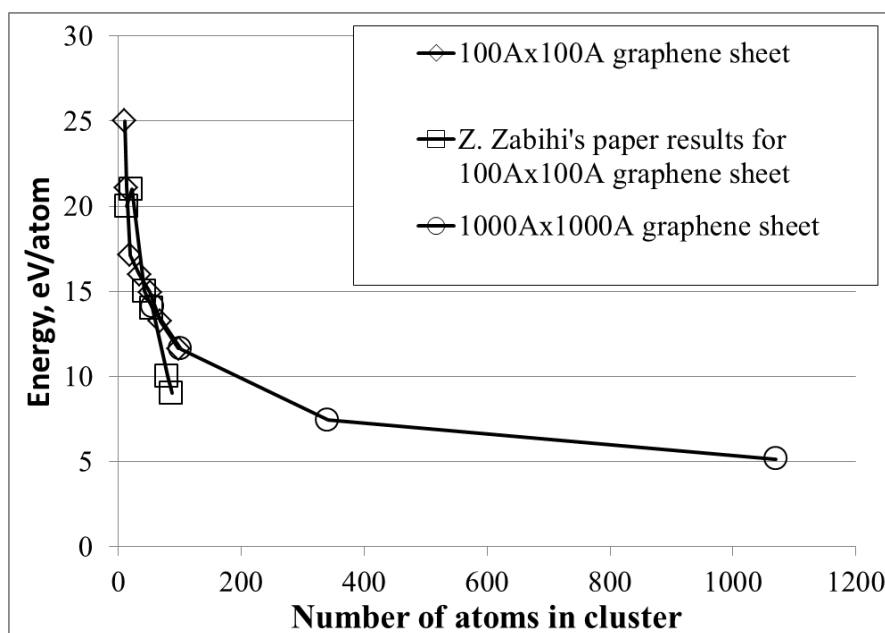

Figure 6. Threshold penetration energy *versus* cluster size, NVE ensemble.
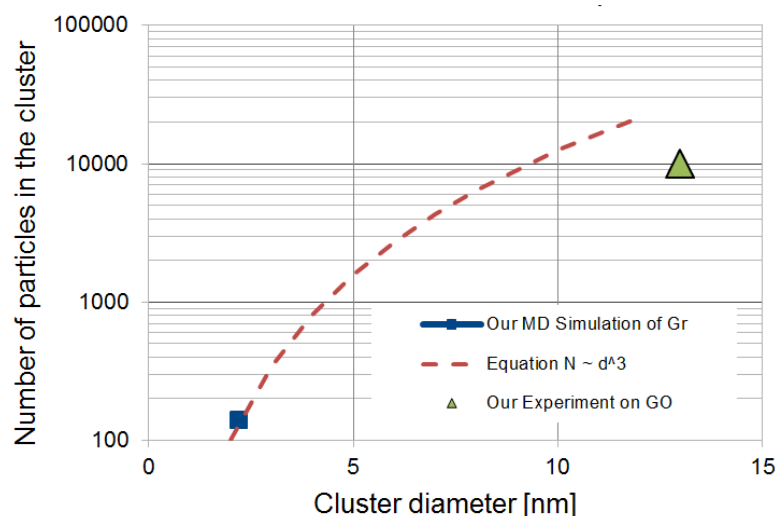
Figure 7. Cluster diameter versus number of particles.

Figure 7. shows how cluster diameter changes with number of particles in the cluster which is described by equation N ~d3. Our simulation results for holes diameter formed in graphene after cluster collision in agreement with graph line described by equation N ~ d3.

3. Conclusion

DFT calculation was conducted for obtaining the dependence of Raman spectra on the number of graphene layers: single layer and multilayer graphene were studied. DFT calculations are in good agreement with the Raman spectra measurements for graphene.

Large-scale atomistic MD simulations were used for obtaining threshold energies for pore formation in graphene with Ar cluster ions. The obtained threshold energies are in good agreement with the previous MD simulations by Zabihi et al [6] of small cluster irradiation on graphene. However, the threshold energies depend on the cluster size and for realistic experimental gas cluster sizes of 1070 atoms in cluster, the threshold energies are higher. It was also shown that small substrate sizes may lower threshold energies. Our MD simulations showed a high stability, strength and resistance of an ideal graphene film against making holes with cluster ion bombardments. Small holes were able to self-healing after the cluster atoms leave the graphene surface.

Acknowlegments

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