Multiscale simulations of swift heavy ion irradiation effect on bilayer graphene

Dongdong Zhao, Hongxia Liu\textsuperscript{a)}, Qianqiong Wang, Shulong Wang, Chenxi Fei, and Shupeng Chen
School of Microelectronics, Xidian University, Xi’an 710071, P.R.China
\textsuperscript{a)} hxliu@mail.xidian.edu.cn

Abstract: The swift heavy ion irradiation effect on bilayer graphene is investigated. The radial dose distributions of delta rays produced by bismuth ions are calculated by Monte Carlo method. The radial dose rapidly decreases with increasing the distance from the track center. The energy deposited into the lattice due to electron-phonon coupling is simulated by molecular dynamics method. By given energy to a cylindrical region, the stress accumulates in this area. And then, a pressure wave emanates outwards, which leads to the atoms in the thermal spike region escaping from the upper and lower surface in the form of clusters. As a consequence, the defect configuration is composed of a central pore with radius larger than 0.5 nm and surrounding carbon chain loops.

Keywords: bilayer graphene, swift heavy ion, multiscale simulation

Classification: Electronic materials, semiconductor materials

References

1 Introduction

Since its experimental isolation in 2004 [1], graphene has recently attracted great attention for a variety of novel applications. But, the single layer graphene (SLG) suffers from a major drawback of zero energy gaps, which hinders its application as electronic material [2]. With the ability of controlling band gap, the bilayer graphene (BLG) may lead to new opportunities for electronic devices [3]. To dope graphene with foreign atoms and manipulate its structure, ion irradiation has been shown to be promising [4]. Meanwhile, graphene is naturally sensitive to defects. So, the studies on process of defect formation play significant role in the wide use of graphene-based devices.

Until now, most of the studies are focused on swift heavy ion (SHI) irradiation effect on SLG [5, 6], and few report available for BLG [7]. The study of SHI irradiation effect is absolutely essential to the use of BLG devices in space application, especially field effect transistors [8]. Multiscale simulations can provide a more detailed explanation for the damage formation. To simulate the interactions between incident ions and target atoms, the Monte Carlo (MC) method has been widely used [9, 10]. At the same time, to simulate the energy deposited into the lattice due to electron-phonon coupling, the molecular dynamics (MD) method has been extensively used [11, 12]. Through the combination of MC and MD simulations, this paper gives insight into SHI irradiation effect on BLG.

2 Simulation methods

The transportation processes of swift heavy ions (SHIs) through the BLG are simulated by GEANT4 which is an MC code. For SHIs, the interactions with matter mainly produced energetic electrons, namely delta rays which can excite more electrons. Livermore low-energy electromagnetic models are applied to obtain the radial dose distribution of delta rays. The simulation box implanted with ion beam of bismuth carrying high energy is a cylindrical block with radius of 10 nm and height of 0.67 nm. The SHIs implanted into system are perpendicular to the surface and release delta rays along their paths. Delta rays deposit their energies in a large radius when they transport far away from ion path. The deposited energy of delta rays around ion path is recorded in cylindrical shells with thickness of 1 nm and height of 0.67 nm. Though thermal spike model, the energy deposited into the lattice due to electron-phonon coupling is calculated in LAMMPS, which is an MD simulator. The concrete details of MD simulation can be found in our previous paper [7].
3 Results and discussion

Swift heavy ions predominantly lose energy through inelastic interactions with target electrons, called electronic energy loss (dE/dx). The high density of energy transfer to the electrons along the ion path leads to local states of intense electronic excitation. The deposited energies of delta rays are collected at each cylindrical shell with the thickness of 1 nm. Using GEANT4, the radial dose distributions of bismuth ions in BLG and SLG are calculated and shown in Fig. 1. Since there are no direct simulation results of radial dose distribution in BLG or SLG, this work makes the same simulation with Ref. [9].

As shown in Fig. 1, because of limited range and energy distributions of delta rays, the radial dose sharply reduces with increase of radius around the ion trajectory. The distribution of energy deposited by an ion to an atom among the larger number of ionized electrons decreases their individual energies and leads to a lack of high energy electrons. The energies of most ionized electrons are below 100 eV, which makes the energy deposition along the path only confined to a small area as the range of 100 eV electrons is about 2 nm. At the same time, the maximum transferred energy to delta rays is determined by a relative velocity $\beta$ which equals the ratio of ion velocity to velocity of light according to Equation (1) [9]:

$$\omega_m = \frac{2mc^2\beta^2}{1 - \beta^2}$$  \hspace{1cm} (1)

where $m$, $c$ and $\omega_m$ are the mass of electron, the velocity of light and maximum transferred energy to delta rays. For both BLG and SLG, the maximum transferred energy from 700 MeV bismuth ions to delta rays is about 7.35 keV. In other words, there are still few delta rays with high energies transporting a long distance which can reach tens or even hundreds of nanometers. That is the reason why the dose of delta rays is far greater than zero at the edge of BLG and SLG. For the same energies of ions implanted into different matters, the dose of delta rays in BLG is approximately twice as much as the dose in SLG, which can be attributed to the difference between their thicknesses.

Fig. 1. Radial dose distributions of bismuth ions both in BLG and SLG. The inset is used to compare the results of this work with the Ref. [9], which aims to demonstrate the simulation method of this work is credible.

As shown in Fig. 1, because of limited range and energy distributions of delta rays, the radial dose sharply reduces with increase of radius around the ion trajectory. The distribution of energy deposited by an ion to an atom among the larger number of ionized electrons decreases their individual energies and leads to a lack of high energy electrons. The energies of most ionized electrons are below 100 eV, which makes the energy deposition along the path only confined to a small area as the range of 100 eV electrons is about 2 nm. At the same time, the maximum transferred energy to delta rays is determined by a relative velocity $\beta$ which equals the ratio of ion velocity to velocity of light according to Equation (1) [9]:

$$\omega_m = \frac{2mc^2\beta^2}{1 - \beta^2}$$  \hspace{1cm} (1)

where $m$, $c$ and $\omega_m$ are the mass of electron, the velocity of light and maximum transferred energy to delta rays. For both BLG and SLG, the maximum transferred energy from 700 MeV bismuth ions to delta rays is about 7.35 keV. In other words, there are still few delta rays with high energies transporting a long distance which can reach tens or even hundreds of nanometers. That is the reason why the dose of delta rays is far greater than zero at the edge of BLG and SLG. For the same energies of ions implanted into different matters, the dose of delta rays in BLG is approximately twice as much as the dose in SLG, which can be attributed to the difference between their thicknesses.
Based on the thermal spike model, the effect of intense electronic excitation inducing a latent track formation is simulated by LAMMPS. Fig. 2 shows the changes of system structure along with the time. It is found that the carbon atoms are pulled out from the BLG plane due to the thermal spike. Since the nuclear stopping cross sections are negligible, the defects in BLG are not merely a direct result of the atomic collisions in the thermal spike region. It is demonstrated that the ejection of atoms is restricted to the thermal spike region, which is comparable to the case of localized electronic excitations induced by SHIs. This behavior is interpreted in terms of emission due to a pressure-driven jet or a pressure pulse built up inside the track core, which led to a rapid expansion of particles in the track both laterally and upward and finally gives rise to the sputtering of particles [5]. In consideration of these conclusions, it can be inferred that the stress initiated from the track region should play an important role in the process of damage formation. As shown in Fig. 1, it is found that the damage of BLG is in the form of small clusters but not single atoms, which suggests that the damage of BLG is the result of collective motion of all the atoms in the track region.

In order to further clarify how the BLG is damaged at the $dE/dx$ (11.8 keV/nm) while the kinetic energy per atom is nearly 3.94 eV/atom, the time evolution of kinetic energy and atomic stress in the z direction ($\sigma_{zz}$) of the system are analyzed. Four parameters are shown in Fig. 3 when the damage of BLG is initiated. Deep insight into the damage mechanism of BLG can be gained from the distribution of per-atom stress in z direction. As shown in Fig. 3(d), the high stress is mainly localized in the track core region. In order to distinguish the effects of kinetic energy transfer and atomic stress distribution on the damage process, the time evolution of $k_{e_{\max}}$ and $|\sigma_{zz}|_{\max}$ of all the carbon atoms is provided in Fig. 3(a) and (b), respectively. The $k_{e_{\max}}$ of all the carbon atoms is always below 20 eV in the damage process, while $|\sigma_{zz}|_{\max}$ is as high as 3292 GPa around 0.04 ps after the introduction of the thermal spike. During the initial stage of the thermal spike, the $|\sigma_{zz}|_{\max}$ is seen to be as high as 3000 GPa. According to experimental results, the intrinsic stress of graphene is $130 \pm 10$ GPa [5]. Consequently, the damage in BLG results from the stress accumulation in the track region. A flow of constituent atoms
from the center of the track to the surrounding regions caused by the pressure wave can be seen. More atoms can be pushed out by the pressure wave as the presence of the surface, which can be identified in Fig. 2 from (b) to (f). And then, the high per-atom stress corresponds to the ejection of carbon atoms, which means those carbon atoms in the spike area are knocked out from their equilibrium positions. Finally, a small pore is formed in the BLG and the per-atom stress is lowered.

As can be seen in Fig. 2 from (b) to (f), those atoms which escaped from the upper and lower surfaces are in the form of clusters instead of single atoms. This observation further supports the conclusion that the damage of BLG results from the evolution of pressure waves initiated at the center of ion track. The average distributions of the (c) per-atom $k_e$ and (d) per-atom $\sigma_{zz}$ along the radial distance from the center of the track are also plotted. The track radius is located at 3 nm, as indicated by the dashed line.

**Fig. 3.** The temporal evolution of the (a) maximal kinetic energy and (b) maximal atomic stress in the z direction extracted from all the carbon atoms of BLG when $dE/dx$ is 11.8 keV/nm. The average distributions of the (c) per-atom $k_e$ and (d) per-atom $\sigma_{zz}$ along the radial distance from the center of the track are also plotted. The track radius is located at 3 nm, as indicated by the dashed line.
structure shown in Fig. 4(a), which displays a pore in the center along with surrounding carbon chain loops.

Fig. 4. The fine structure of system (a) and the normalized density as a function of distance from the track center (b) at the end of simulation. The simulation results in this work can be compared with the previous MD simulation results in Ref. [7].

As shown in Fig. 4(a), a relatively small central pore and surrounding mesh-like structure with lots of carbon chains can be seen, which also supports the conclusion that the damage of BLG results from the evolution of pressure waves initiated at the center of ion track. As a function of distance from the track center, the density profile of system is shown in Fig. 4(b). A low density core and a high density shell fine structure can be seen. The normalized densities are calculated at each cylindrical shell with the thickness of 0.5 nm. The density of central cylinder with a radius of 0.5 nm falls to zero, which means the radius of central pore larger than 0.5 nm.

4 Conclusion

The radial dose distributions of delta rays both in BLG and SLG are calculated through GEANT4. The radial doses which have a direct relationship with the thickness of matter rapidly decrease along with increasing the distance from the track center. By computing the time evolution of kinetic energy and atomic stress in the z direction, the process of defect formation is simulated in LAMMPS. At the initial stage of thermal spike, the stress accumulates in the track region. Along with the pressure wave emanating outwards, the atoms in the track region begin to escape from the surfaces in the form of clusters. Consequently, a structure of central pore surrounding with carbon chain loops can be clearly seen.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 61376099, 11235008, 61434007) and the Specialized Fund for the Doctoral Program of Higher Education (Grant No. 20130203130002).