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Molecular dynamics simulations of defect production in graphene by carbon irradiation

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ABSTRACT

We present molecular dynamics simulations with empirical potentials to study the type of defects produced when irradiating graphene with low energy carbon ions (100 eV and 200 eV) and different dose rates. Simulations show the formation of very stable structures such as dimers, single chains of carbons and double chains of carbons. These structures are similar to those described in the literature, observed experimentally when irradiating graphene. For high doses or dose rates, the formation of nanopores is observed, similar to previous results by other authors for higher energies of the implanted ions. These simulations show how tunning the different parameters of irradiation conditions can be used to selectively create defects in graphene.

1. Introduction

Graphene is, undoubtedly, one of the most promising materials, with applications in many different fields [1], from energy storage [2] to microelectronics [3] or biological applications [4] among many others. In the field of radiation effects, graphene has a special interest due to the possible changes of electrical and mechanical properties of this system induced by defects [5] and the formation of very stable structures under some types of irradiation [6]. Modification of the graphene layer by electron [6,7] or ion implantation [8] has increasing attention since it could be a way of controlling the production of defects. For these methods to be efficient and feasible it is important to understand the type of defects produced under the different irradiation conditions, such as irradiation type (electrons or ions), temperature, energy and dose.

In this work we use molecular dynamics simulations with empirical potentials to study the effect of low energy collisions by carbon atoms on a graphene sheet. Molecular dynamics simulations have been used extensively to study carbon nanostructures [9]. In graphene the main focus has been on studying vacancy and vacancy clusters due to their effect on the electrical properties of this material [5] as well as fracture and mechanical behaviour [10] due to its enhanced properties. But there is also an important number of publications related to irradiation of graphene under different conditions [7,11–13]. In particular, irradiation of graphene with carbon atoms has been studied by Bellido and Seminario [11]. They performed simulations of individual implantation of single carbon ions with energies between 0.1 eV and 100 keV and observed the formation of single vacancies and double vacancies. Li et al. [12] studied the continuous irradiation of graphene with different ions. Defects produced by electron irradiation have also been studied using molecular dynamics [13]. In our work we focus on understanding the type of defects generated by low energy carbon atoms and high dose irradiation and compare to those observed experimentally under different irradiation conditions.

2. Methodology

We have performed molecular dynamics simulations of irradiation of graphene with carbon ions using two different interatomic potentials, Tersoff [14] and Brenner [15]. Both potentials have been fitted to the Universal potential for short distances, required for irradiation simulations. Calculations with the Tersoff potential were done using the MD code LAMMPS [16] and the MDCASK code [17] was used for the Brenner potential calculations.

The simulations consist of a single graphene layer of surfaces between 5 nm × 5 nm and 17 nm × 17 nm. In one direction the borders of the simulation cell are fixed while they are free in the other two directions. For the small simulation cells the system is coupled to a thermal bath that consists of two atomic layers at the border of the simulation cell where the temperature is rescaled every time step. The temperature in these calculations is 10 K. For the larger system size, the simulation cell is first relaxed at 300 K before the energetic atom is launched towards the graphene layer and no thermal bath is used. Energies of the carbon ion of 100 eV

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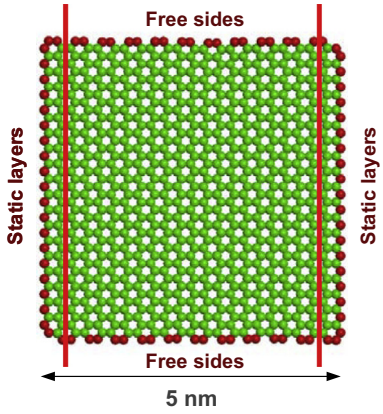

Fig. 1. Simulation cell. Single graphene layer of a 5 nm × 5 nm surface. Borders along one of the directions are fixed and free on the perpendicular direction.

and 200 eV are used. In these calculations the electronic energy loss was neglected since at these low energies this contribution is very small. The coordination of the atoms in the graphene layer is obtained to identify the presence of defects such as vacancies. Fig. 1 shows, as an example, the initial conditions for the simulation of a 5 nm × 5 nm graphene layer, showing the location of the static layers and the free boundaries.

Ions are introduced in the sample at different rates, between 0.05 picoseconds and 1 picosecond per ion and in areas that go from about 4–54 nm^2. Any of the dose rates used in these simulations are orders of magnitude higher than those expected in an ion irradiation experiment. A simulation that reproduces the exact experimental conditions will require times between ions of milliseconds, which is not feasible with molecular dynamics simulations. For such a direct comparison, a combination of molecular dynamics and kinetic Monte Carlo calculations would be needed. However, the purpose of this work is not to directly compare with the experimental results in terms of dose and defect population, but to explore if simulations can reproduce some of the structures observed experimentally and under which conditions.

3. Results

Fig. 2 shows the results obtained for system sizes of 5 nm × 5 nm with the interatomic potential from Brenner [15] and irradiation with 200 eV carbon atoms. The ions are sent perpendicular towards the surface from random locations in a surface of 4.5 nm × 4.5 nm, that is, the dose per ion is on the order of 5×10^{12} ions/cm^2 A total of 80 ions are launched. The time between ions in this case is 1 picosecond. Four snapshots are shown in Fig. 2 after the irradiation with 10, 20, 30 and 40 ions (Fig. 2a–d, respectively). Red spheres represent undercoordinated atoms, that is those atoms at the border of the simulation cell

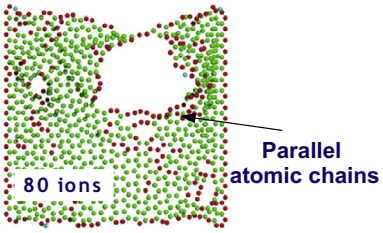

Fig. 3. Formation of parallel atomic chains at high implantation dose (80 ions).

and atoms surrounding vacancies and vacancy clusters. Fig. 2a shows that after 10 ions a di-atomic chain is formed. Di-atomic chains have been observed experimentally after electron irradiation [6]. Such chain is remarkably strong. After 40 ions, the chain is still present, even though collisions are produced close to this chain and other defects are formed around it. In fact, the vacancy cluster grows significantly without breaking this chain.

Higher doses show the formation of more complex structures, also observed experimentally [6]. One of such structures is a parallel chain, close to a large void, as shown in Fig. 3. The formation of nanopores in suspended graphene has been studied by molecular dynamics simulations by Li et al. [12]. In those simulations irradiation was confined to a smaller area (1.5 nm radius) and higher energies were used (500 eV to 100 keV). Our simulations show that nanopores can be created even at lower energies. Like in the case of reference [12], these pores produced by carbon ions do not have smooth edges and many carbon chains are formed.

It is important to mention that for this small system size, the implantation of carbon atoms produces a buckling in the graphene layer, as shown in Fig. 4. In this figure we show a transversal view of the graphene layer after irradiation with 10, 20, 30 and 40 carbon ions of 200 eV, corresponding to the same conditions as in Fig. 2. The buckling of the graphene layer starts to be apparent after 20 ions, and it is very clear after 40 ions. In fact, deflection of a graphene layer by the implantation with ions has also been studied by molecular dynamics by Terdalkal et al. [18]. However, in this case the bucklings seems to be enhanced by the small size of the simulation box and the large number of defects produced at this high dose rate.

We have performed simulations with larger system sizes (17 nm × 17 nm) and 100 eV carbon ions with the interatomic potential of Tersoff [14] coupled to the Universal potential [11]. In this case the ions are also sent perpendicular towards the surface from random locations. Two different areas have been sampled. When the ions are launched in a small area, 3.5 nm^2, that is a dose per ion of about 28×10^{12} ions/cm^2 (six times higher than the case above, Figs. 2–4) and at a very high dose rate (one ion every 15 fs) a nanopore is formed similar to those observed in the simulations by Li et al. [12]. Note that in the work of Li higher energies of the carbon ion are used (500 eV to 100 keV), similar

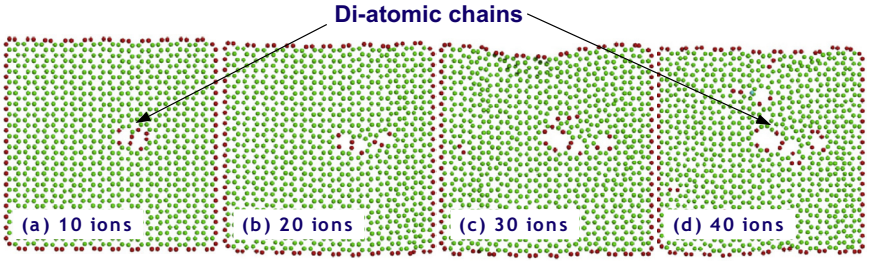

Fig. 2. Defects produced in the graphene layer for doses of 10, 20, 30 and 40 carbon ions of 200 eV. Note the formation of a very stable di-atomic chain after 10 ions and how it remains even after the implantation of 40 ions.