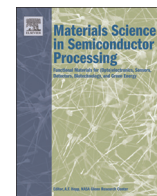




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Kinetic Monte Carlo simulations of vacancy evolution in graphene

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ABSTRACT

Kinetic lattice Monte Carlo simulations, implementing *ab initio* calibrated energetics, are applied to study the evolution of vacancy systems in graphene. The evolution of the under-coordinated atomic layer proceeds, in general, by island nucleation and growth. However, the first stage (nucleation) is strongly influenced by the stability of small aggregates (e.g. di-vacancies) and by the effective coalescence/attachment barriers. Quantitative predictions of the system kinetics in terms of crystal state and defects' morphology as a function of the initial state and the temperature can be obtained and readily compared with experimental structural characterization of processed samples.

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1. Introduction

The control and prediction of the evolution of edges and structural defects in graphene are crucial issues for any graphene-based technological development. Indeed, they have an essential role in the mechanical [1], chemical [2], electrical [3] and magnetic [4] properties of this two dimensional (2D) material. The character of the planar sp^2 carbon bonds makes vacancies (Vs) the most important class of intrinsic defects in graphene and a “vacancy engineering” has been proposed as a viable route for tailoring the functionality of this material [5]. Moreover, the behavior of extended vacancy-type defects has a strong affinity with the conformation of edges [6,7], which in turn is a fundamental aspect for the understanding of the kinetics of graphene growth processes [8,9].

The reliable prediction of the evolution of a given density of Vs in graphene could efficiently support the “vacancy engineering” techniques (e.g. a sequence of irradiation and annealing processes). However, the current simulation tools in this emerging field are not designed for applications on large space-time scales and their predictions are limited to the early stage of the interaction of few-vacancy systems [10].

Here we present a stochastic method for the large-scale simulation (both in space and time) of under-coordinated graphene systems using the kinetic lattice Monte Carlo (KLMC) scheme. The implemented KLMC model allows for a generic energetic mapping which considers the stability of several local configurations.

Simulation results are discussed, demonstrating the consequence of the different calibration choices in the long-time evolution. In particular, the mapping of *ab initio* energetics results in a large effective coalescence barrier which slows down the hole formation.

2. Methodology

The diffusive motion of vacancies is modeled by the displacement of under-coordinated carbons with respect to the ideal threefold coordination of the next-neighbor shell. No preferential direction of the diffusive jumps (given the hexagonal symmetry of graphene) and the zero probability of diffusion to a site already occupied by a carbon atom are imposed. The evolution of the vacancy system is studied through an activation energy model in our kinetic lattice Monte Carlo approach. This method allows for the evolution of the system through a sequence of stochastic events occurring with a rate ν_i . In our case, an event is the jump of a carbon atom to any of the unoccupied first neighbor sites. The event rate ν_i is correlated to the probability of that particular event to occur and is given, according to the transition state theory, by a Boltzmann weight:

$$\nu_i = \frac{1}{\tau_i} = \nu_0 e^{-(E_i/k_b T)} \quad (1)$$

where k_b is the Boltzmann constant, T the absolute temperature, E_i is an activation barrier energy and ν_0 a prefactor which accounts for any contribution not included in the energy barrier. This rate form implies within the KLMC model that events that are more

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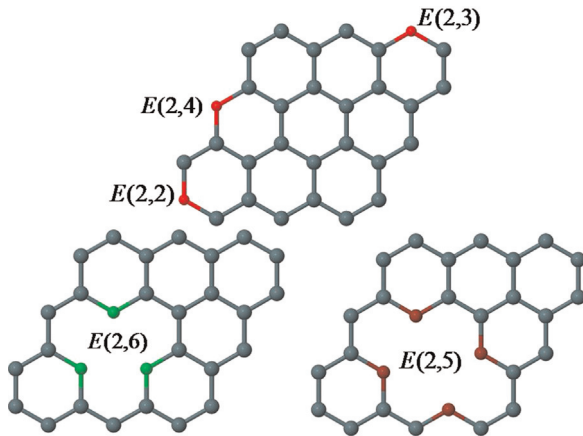


Fig. 1. Examples of carbon atoms in defective configurations and related energy parameters.

Table 1

Model energy parameters and relevant related configurations. Note that $E(2, 6)$ is the vacancy migration energy calculated by DFT [10], while larger values of $E(2, 4)$ and $E(2, 3)$ (e.g. $\sim 2 \times E_b$) do not modify substantially the results discussed here.

Parameter	Value (eV)	Configuration
$E(2, 6)$	1.2	Vacancy
$E(2, 5)$	$E(2,6)+1.4$	Di-vacancy
$E(2, 4)$	$E(2,6)+1.9$	Zig-zag edge
$E(2, 3)$	$E(2,6)+1.8$	Armchair edge
$E(2, 2)$	$E(2,6)+0.9$	Carbon chain core
$E(2, 1)$	$E(2,6)+0.8$	Carbon chain edge

likely to occur will happen more frequently. The energy barrier E_i for the migration of a particular atom is imposed to depend on the initial local configuration only. Such interaction energy is further modeled as dependent only on the number of occupied sites on the next-neighbor (n.n.) and second-neighbor (s.n.) shells. Thus rates depend only on the coordination of the C atom by the formula:

$$E_i = E(j, m) \quad (2)$$

where j and m are respectively the number of occupied n.n. and s.n. lattice sites of the migrating atom. Thus the model depends, in general, on the 21 energy parameters $E(j, m)$ to be determined through comparisons with density functional theory (DFT) results. We note that the extension of the energy parameter to the s.n. shell allows the mapping of the stability of relevant V-type defect configurations. For example in Fig. 1 we indicate the energy parameters associated at atoms in: zig-zag $E(2, 4)$, armchair $E(2, 3)$, kink $E(2, 2)$, single vacancy $E(2, 6)$ and di-vacancy $E(2, 5)$ configurations. Note that all these local configurations are characterized by twofold coordinated atoms in the n.n. shell and, in a simplified n.n. bond counting rule, they should have the same event rate. Conversely with the more general rule of Eq. (2), we could consider also the configuration's gain/cost and correlate different configurations with their relative stability. For example according to DFT calculations [5,10] the di-vacancy complex is a very stable configuration with an energy gain of ~ 8 eV with respect to the two isolated Vs: using parameters reported in Table 1 and assuming a energy cost for the n.n. C-C bond breaking of $E_b = 2.5$ eV [5] we obtain a V-V coalescence energy gain of 8.1 eV. Note that the displacement of any $E(2, 5)$ C atoms in the di-vacancy state (see Fig. 1) leads to unstable one-fold coordinated configurations (i.e. $E(1, 6)$ in this case) which have a higher energy ($E(1, X) \sim E(2, X) + E_b$) in our calibration.

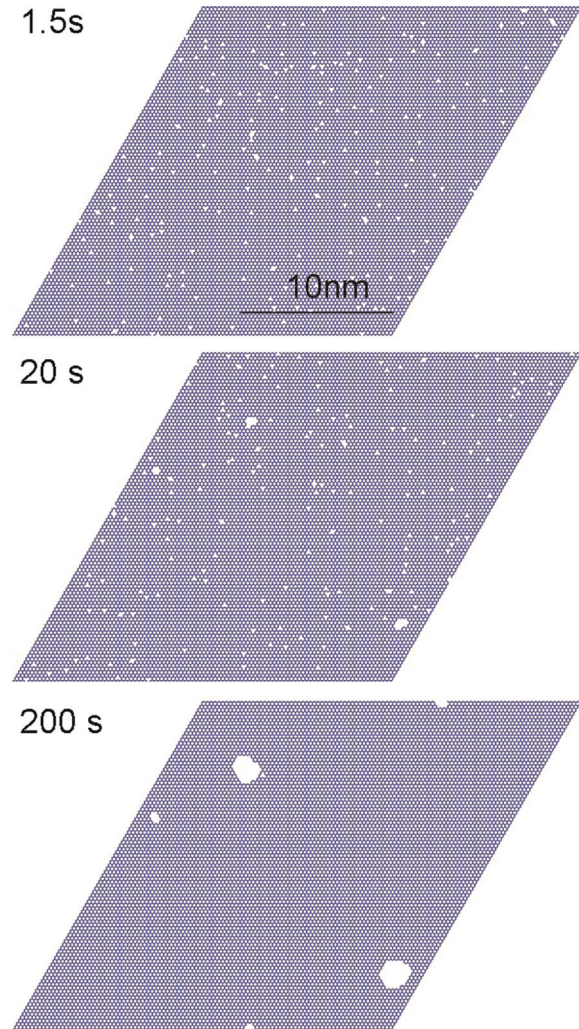


Fig. 2. Snapshots of the simulated evolution of a system with initial 1% V density at $T=500$ °C. Here the calibration with fixed configuration energies ($E(2, X) = 2.0$ eV) for the twofold coordinated C is considered.

At each time step, rates are calculated for any possible transition, then a total transition rate $\nu = \sum_i \nu_i n_i$ is evaluated, where the sum is extended to all possible local configuration and n_i is the number of atoms sharing the same i -th configuration. A transition is randomly chosen, using as weight the relative frequencies $w_i = n_i \nu_i / \nu$ and then a given atom is chosen randomly with uniform distribution among those who share that particular coordination. The atom is then moved on the lattice to a site chosen randomly with uniform distribution among first neighbors not already occupied by another atom. The time clock is then elapsed by a time $\delta t \approx 1/\nu$, the average time needed for another diffusion event to occur. The KLMC code repeats the above steps until the clock reaches a limiting time. This method allows to preserve atomic accuracy, while exploring long simulation times.

3. Results

In all the simulation results discussed here we considered a graphene lattice with an initial configuration of random vacancies on which periodic boundary conditions are applied. The frequency pre-factor is $h/2k_bT$ [11] where h is Planck's constant. Evaporation is also considered with an additional energy cost of 2.0 eV. However, evaporation events predominantly occur in the case of isolated atoms simulating the detachment events of C adatoms

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