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Growth of nitrogen-doped graphene on copper: Multiscale simulations

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We used multiscale simulations to model the growth of nitrogen-doped graphene on a copper substrate by chemical vapour deposition (CVD). Our simulations are based on *ab-initio* calculations of energy barriers for surface diffusion, which are complemented by larger scale Kinetic Monte Carlo (KMC) simulations. Our results indicate that the shape of grown doped graphene flakes depends on the temperature and deposition flux they are submitted during the process, but we found no significant effect of nitrogen doping on this shape. However, we show that nitrogen atoms have a preference for pyridine-like sites compared to graphite-like sites, as observed experimentally.

1. Introduction

The fundamental necessity for the development of graphene-based technologies lies in the control of its properties. Effective application of this two-dimensional material for devices like field effect transistors and transparent electrodes require the modification of its electronic properties. The insertion of charges in graphene layers is one route towards this goal. One of the most promising ways of controlling the concentration and the type of carriers in graphene is chemical doping with foreign atoms (*e.g.* nitrogen) [1–3].

Several techniques are being used in order to dope graphene with nitrogen, like chemical vapour deposition (CVD) [4], arc discharge [5] and N plasma treatment [6]. The CVD deposition method stands out in this scenario, with remarkable advances since the first report of using this method to produce N-doped graphene [7]. CVD is widely applied to produce carbon materials, combining a source of carbon and/or nitrogen-containing molecules (CH_4, NH_3, C_5H_5N) and a metal providing the catalytic sites for the dissociation and further adsorption of the C and N atoms [7,8]. This is a low-cost and efficient method to produce N-doped graphene yet comprehension of the elementary steps of the growth is still lacking. The control of the nucleation on these stages is a critical issue for experimentalists, since it can determine the quality of the sample and its use in future application on optoelectronic devices. The atomic description of these first steps, concerning the competition between diffusion events of C and N atoms on the metallic surface is then necessary.

Concerning the pristine graphene, there are some theoretical studies that propose models of the early stages of its growth on metallic surfaces [9–11], but the effect of doping was not explored.

Making use of *ab-initio* calculations and Kinetic Monte Carlo (KMC) simulations, we obtained the energy barriers for C and N diffusion on Cu(111) and simulated the growth of N-doped flakes. This allowed us to understand the effects of nitrogen in the growth of doped graphene. We show that the free and dimer diffusion as well the attachment events are very likely compared to the inverse detachment ones. The different natures of C and N provide different energy barriers for these events and this determines slight differences between the pristine and doped samples, such as the concentration of structural defects. We also find that nitrogen atoms tend to have less nearest neighbours, which corresponds to a prevalence of pyridine-like sites that persists during growth and for various deposition parameters.

The article is organized as follows. In Section 2, the *ab-initio* calculations and the energy barriers obtained for a wide range of diffusion events are discussed. Section 3 covers the Kinetic Monte Carlo model and presents the results we obtained considering the effects of macroscopic parameters, such as temperature, deposition flux and nitrogen proportion. Finally, in Section 4 conclusions on our computational work have been drawn.

2. DFT simulations

The DFT calculations were carried out with the VASP code [12] using the PAW method to describe the core electrons. The electron exchange and correlation effects were described by the Perdew–Burke Ernzerhof (PBE) functional [13], with van der Waals correction within the method of Tkatchenko and Scheffler [14]. The copper surface is modelled as a supercell with finite number of Cu(111) layers, corresponding to a lattice parameter of 3.63 for bulk Cu (kept fixed throughout the

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calculations), and adsorbed C and N atoms plus a vacuum region larger than 17 Å to avoid interactions between adjacent images. A dipole correction was applied to eliminate spurious interactions between neighbouring slabs [15]. The supercell used contains nine Cu layers in the growth direction and a 3 × 3 structure in the adsorption plane. It was increased for specific events, like vacancy and edge diffusion. Different sites of Cu(111) surface can be considered for the adsorption of carbon and nitrogen. The most common adsorption sites are *fcc*, *hcp* and *top*. In the *top* configuration, the adsorbed atom is located right over the Cu of the topmost surface, while for *hcp* and *fcc* configurations, the adsorbed atom is placed over the Cu atom of the second and third Cu topmost layers, respectively. It has been shown that small graphene islands have a higher binding energy in *fcc*–*hcp* configuration [16], which will be considered in this work. The top and side views of a single layer of graphene adsorbed in the *fcc*–*hcp* sites of Cu(111) surface are shown in Fig. 1. The Cu surface was fully relaxed in a first step, and further fixed for energy barriers calculations. Brillouin zone sampling was performed with a 7 × 7 × 1 Automatic k-mesh points and the kinetic energy cutoff for the plane waves were set to 420 eV. The electronic self-consistent criterium was set to 1×10^{-5} eV and the residue force components are converged below 25 meV/Å.

In order to obtain the energy barriers, we employed the nudged elastic band (NEB) method [17], as implemented in VASP. In these calculations, the in-plane coordinates for C and N atoms were kept fix and the *z* coordinates were fully relaxed. The energy barriers for more than 25 events were obtained and were further used as the activation energies in KMC simulations. The simplest event considered was the free diffusion of carbon and nitrogen atoms, which consists of moving one atom between the *fcc* and *hcp* sites. The N free diffusion energy barrier is presented in Fig. 2 as an example. We observed that the *fcc* site is 0.1 eV more stable than the *hcp* site. This asymmetry in the energy barrier means that the activation energy necessary for the nitrogen atom to move from the *hcp* site to *fcc* one (0.39 eV) is smaller than the activation energy to move it along the inverse path (*fcc* to *hcp*, 0.49 eV). If full relaxation of the Cu atoms is considered, the values are 0.16 eV and 0.23 eV, respectively, showing the same relative asymmetry. In case of carbon, previous calculations showed a symmetric energy barrier of 0.5 eV, with the difference between the energy of *fcc* and *hcp* considered negligible [11]. The other events considered include several possibilities, such as free and dimer diffusion, attachment and detachment of atoms, edge diffusion and migration of vacancies.

Table 1 comprises the events and the respective energy barriers calculated by NEB/DFT and the values considered as the activation energies in our KMC simulations. The simple events for carbon atoms and pristine islands were previously reported by our group [11].

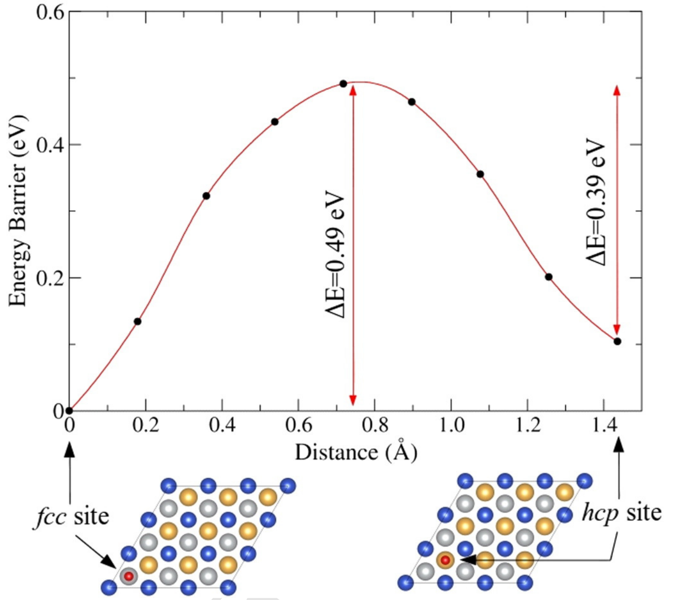

Fig. 2. Energy barrier of N free diffusion on Cu(111) surface. The red spheres on the left and right pictures indicate the N atom on the *fcc* and *hcp* sites, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

According to values presented on Table 1, both free diffusion and dimer diffusion events have low energy barriers. Thus, these diffusions are very likely and fundamental for the first nucleation stages of graphene flakes. This dimer is formed by two C atoms bonded covalently and its diffusion has a lower energy barrier than the diffusion of a single atom of carbon. This fact can be explained in terms of their binding energy. When just one atom of C is adsorbed on the *fcc*(*hcp*) site of Cu(111) surface, the distance between the C and the top layer of Cu is of 1.05 Å (1.04 Å) and the binding energy is −4.93 eV (−4.88 eV) [16]. The C–C dimer allocated over the *fcc-hcp* site, however, is at a height of 1.45 Å and the binding energy is −3.31 eV. This shows that the interaction between the substrate and the carbon atom is larger than the one with the dimer and hence the dimer has a higher mobility than the single atom. This decay of copper–carbon interaction was also reported previously by Mi *et al.* [18].

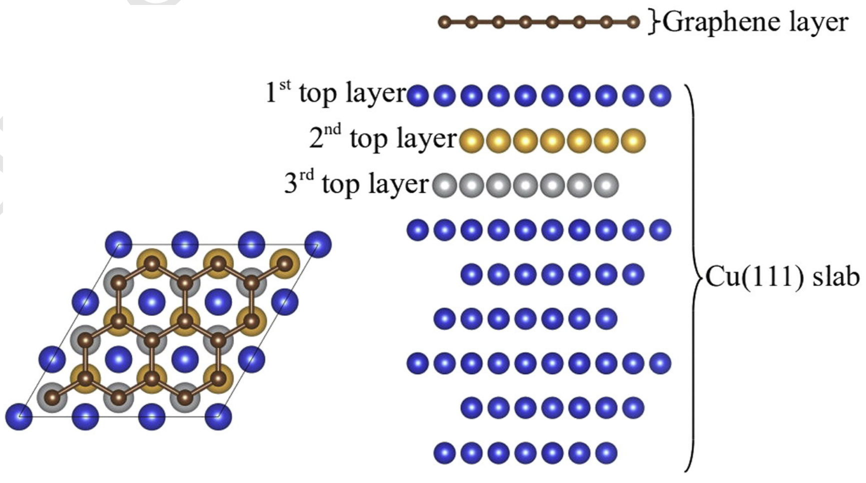

Fig. 1. Top (left) and side (right) view of a 3 × 3 supercell of single layer graphene adsorbed on Cu(111) slab. Brown spheres represent the C atoms, while the blue, yellow and grey represent the Cu atoms on different layers. For clarity in the side view, the first, second and third layer are indicated in order to identify the *top* (blue), *fcc* (grey) and *hcp* (yellow) sites where the C atoms can be adsorbed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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