Dynamics of Single Fe Atoms Embedded into the Graphene Lattice

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While graphene has a great potential for applications in spintronics, the control over magnetism in graphene remains challenging. The magnetism in graphene is related to the presence of lattice defects, such as vacancies, edges or covalently bonded impurities [1]. While properties of some of these defects have been extensively studied, their controllable incorporation into the grapheme lattice remains challenging. Also, the studies of dynamics of these defects are very limited. The control of the introduction of such defects into the lattice and understanding their dynamics is a key for the success of spin-based graphene devices. One of the promising ways for inducing local magnetic moments in graphene is incorporation of transition metal (TM) atoms into the lattice [2,3]. Recently, electron beam irradiation has been used to facilitate the incorporation of single Fe atoms into graphene mono and divacancies (Fe@MV and Fe@DV, respectively) [3]. The dynamics of these defects has then been studied in real time using aberration corrected transmission electron microscopy (TEM) at 80 keV. The authors observed reversible transformations of Fe@MV to Fe@DV as well as the migration of the defects. However, theoretical studies of Fe atoms embedded into the mono and divacancies in graphene predict the migration barriers of 3.6 eV for Fe@MV and about 5 eV for Fe@DV, suggesting the high stability of these defects [2]. Therefore the experimentally observed transformations have been proposed to be caused by electron beam irradiation. In the present work we have performed ab-initio molecular dynamics simulations to investigate effects of electron irradiation on the dynamics of Fe@MV and Fe@DV complexes.

Elastic scattering of fast electrons on atomic nuclei results in the transfer of momentum to the nuclei and their subsequent motion. The maximum energy that can be transferred to Fe and C atoms from 80 keV electrons is T^{Fe}_{max} = 3.4 eV and T^{C}_{max} = 15.8 eV, respectively. Our calculations show that elastic scattering of 80 keV electrons on Fe atoms is unlikely to induce significant structural changes to the Fe@MV or Fe@DV defects. However, the C atoms covalently bonded to Fe can get enough energy to break Fe-C and C-C covalent bonds. The threshold energy for emission of a C atom from the Fe@MV has been calculated to be 15 eV, which is below the T^{C}_{max}, indicating that the transformation of Fe@MV to Fe@DV can readily occur under 80 keV electron irradiation. The removal of a C atom from the Fe@DV defect require an energy higher than 15.7 eV, suggesting that Fe@DV has a higher stability against the electron irradiation. These results agree with the experimental observations [3]. Transformations of Fe@DV to defects comprising of a Fe atom bound to larger vacancy clusters have not been reported. It can be expected therefore that under 80 keV electron beam all Fe@MV defects will be transformed to Fe@DV. Such transformation is highly desirable, since Fe@MV is diamagnetic while Fe@DV shows paramagnetic moment. However, our calculations shows that in the presence of C adatoms Fe@DV spontaneously transforms back to Fe@MV. The transformations of Fe@DV to Fe@MV have also been observed experimentally [3].

We also show that electron irradiation can induce migration of Fe@MV and Fe@DV defects. This process occurs via the ejection of a C atom from the defect by the electron collision and formation of intermediate structures comprising of Fe@DV (Fe@TV) with the C adatom. These structures, however, do not survive for a long time within MD simulations and

spontaneously recombine to Fe@MV (Fe@DV). Snapshots of molecular dynamics simulation showing migration of the Fe@MV defect are presented in Figure 1.

Our work facilitate understanding of dynamics of metal atoms embedded into the graphene lattice and, particularly, effects of electron irradiation on structural transformation and migration of such defects.

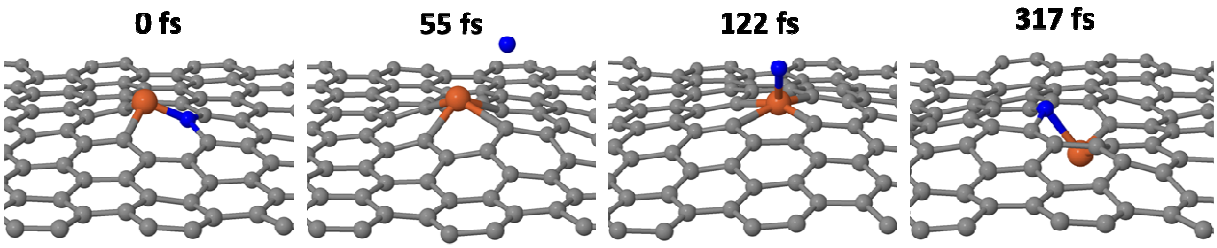

Figure 1: Snapshots of molecular dynamics simulation showing migration of the Fe@MV defect. The carbon atom shown in blue color has been given a momentum that corresponds to a collision event with 80 keV electron.

References

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