Theoretical Investigation of the Graphene Monovacancy

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Recent experimental work by Robertson et al. 2013 [1],imaging the graphene monovacancy with aberration corrected transmission electron microscopy (AC-TEM), has proposed a vacancy diffusion mechanism alternative to the theoretically predicted 'straight swap' mechanism shown in Fig. 1. Previous theoretical work on the diffusion of the monovacancy has lead to the prediction of two main saddle point structures (Fig. 1b and 1c). In addition to the different views on the saddle point structures, there is also a wide discrepancy in the values for barriersto vacancy migration ranging from 1.0 eV to 1.7 eV [2-4]. Our study was set out to clarify which saddle point structure had the lower diffusion barrier and to validate theoretically the experimental mechanism proposed by Robertson et al.

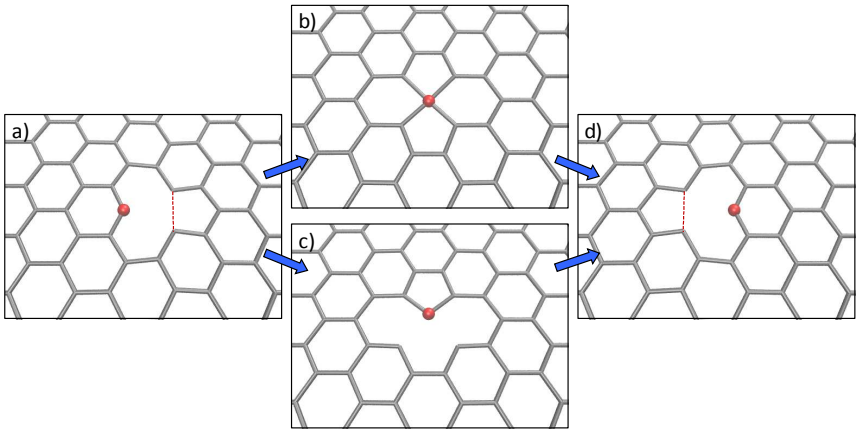

Figure 1: Literature saddle point structures for the migration of a monovacancy in graphene, where a) and d) are initial and final 5-9 configurations. The red C atom is the migrating atom and the reconstructed bond is shown as a red dashed line.

The AIMPRO code [5] was used with periodic boundary conditions to model an infinite sheet of graphene. Calculations were run with density functional theory (DFT) using both LDA and GGA functionals on an 8x8 hexagonal supercell with HGH pseudopotentials and atom centred Gaussian basis functions. The nudged elastic band (NEB) method [6] was used within AIMPRO to calculate the diffusion profile of the monovacancy through a force projection scheme.

The minimum energy configuration of the graphene monovacancy is a 5-9 vacancy, which undergoes a Jahn-Teller distortion so that two of the three C atoms with dangling bonds form a reconstructed bond with a longer bond length (~1.9 Å) than a typical C-C bond. There are three equivalent 5-9 orientations as the reconstructed bond switches between the three C atoms with a barrier of ~0.15-0.20 Å.

For the diffusion of the 5-9 vacancy, we found that the 5-13 saddle point structure (Fig. 1c) has a lower diffusion barrier than the in-plane spiro saddle point (Fig. 1b) for both LDA and GGA functionals. However, a variation on the in-plane spiro saddle point with an out-of-

plane distortion to the neighbouring C atoms(Fig. 2) resulted in a much lower barrier for diffusion. The barrier for the non-planar spiro structure is 0.56 eV (LDA) and 0.87 eV (GGA). The GGA result agrees well with the frequency of migrations observed during experiment at room temperature, when we would expect to see one diffusion pass every 15-20 seconds.

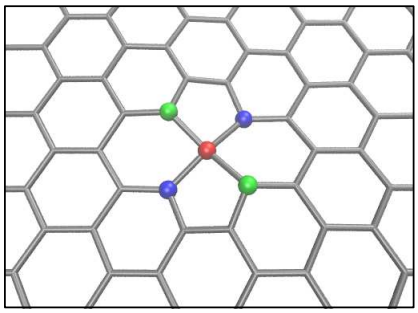

Figure 2: The low barrier out-of-plane spiro saddle point structure for the migration of a monovacancy in graphene. The red C atom is the migrating atom, with the green atoms raised up out of the plane and the blue C atoms down.

The experimentally observed diffusion mechanism outlined in the Robertson et al. 2013 paper suggests that instead of the 'straight swap' mechanism calculated theoretically in Fig. 1, the vacancy undergoes a rotation around a fixed atom. NEB calculations show that this pathway is energetically unfavourable, and is very unlikely to be detected experimentally with the observed frequency of migrations. Also, the NEB diffusion profile shows a stable transition structure of an additional 5-9 vacancy, which is not observed experimentally. A possible explanation is that anad-atom might bepresent on or near a vacancy defect. This would alter the migration pathway and result in different diffusion barriers changing the mechanism for vacancy diffusion.

In conclusion, it was found that along with the widely reported monovacancy saddle point structures for diffusion, an out-of-plane spiro saddle point structure resulted in the lowest barrier for diffusion. This barrier is 0.56 eV and 0.87 eV for LDA and GGA functionals, respectively. Applying this to the recent experimental results from AC-TEM, the most likely explanation for the observed monovacancy diffusion is due to the presence of ad-atoms [7].

References

[1] A.W. Robertson et al., ACS Nano,7 (2013) 4495.
[2] G.D. Lee et al., Physical Review Letters, 95 (2005) 205501.
[3] A.V. Krasheninnikov et al., Chemical Physics Letters, 418 (2006) 132.
[4] A. El-Barbary et al.,Physical Review B, 68 (2003) 144107.
[5] P. Briddon and R. Jones,Physica Status Solidi (B), 217 (2000) 131.
[6] G. Henkelman and H. Jonsson, Journal of Chemical Physics, 113 (2000) 9978.

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