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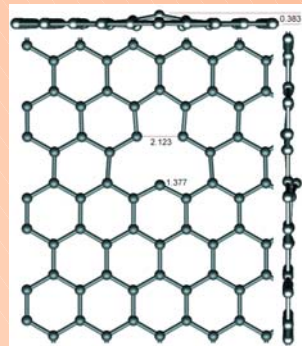
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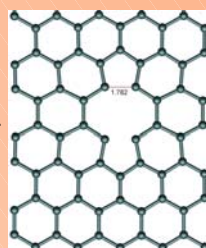
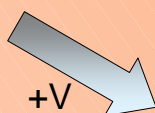
Material processing requires detailed understanding of the diffusion and aggregation of defects and impurities. A standard assumption in models of aggregation is that the free energy decreases monotonically as defects approach one another. We show here that this assumption is invalid for carbon materials, and indirectly for isoelectronic first row compounds. Defects which give rise to under-coordinated atoms have an **important metastable minimum as a pair at third neighbour**, where these atoms **rehybridise** (from sp^2 to sp in **graphite**, sp^3 to sp^2 in **diamond**).

This leads to a **new regime in the material phase diagram** where defects are mobile but not yet able to combine into their ground state configurations, and predicts a new class of metastable defect structures at odd neighbour distances.

The isolated vacancy undergoes weak bond reconstruction between two C neighbours, leaving the third atom neighbouring the vacancy under-coordinated (migration barrier 1.45eV).



Conventional model for vacancy aggregation with annealing at increasing temperature



Calculations

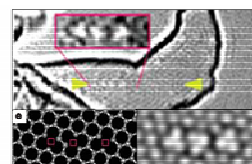
DFT-LDA supercell calculations using AIMPRO. BHS pseudo-potentials. Migration barriers determined using DFTB with nudged elastic band, followed by single point energy calculations with AIMPRO.

Two vacancies at 1st neighbour form a stable 5-8-5 complex with reconstructed C-C bonds. This migrates with a barrier of around 7eV, and is hence effectively immobile until high temperatures.

Thus in the conventional vacancy aggregation model, vacancy loop growth can only occur through trapping of further mono-vacancies. This is inconsistent with AFM observations of asymmetric vacancy-based objects which anneal out before 1473K.

Experimental Support

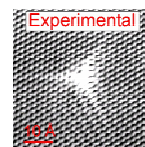
First observations of individual vacancy defects in single walled nanohorns by HRTEM show vacancies at 3rd neighbour. Further studies by the same group (publication in preparation) show this to be a common occurrence.



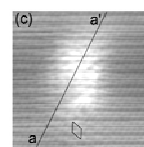
A Hashimoto et al, Nature **430**, 870-873 (2004)

3 vacancies – two at 3rd neighbour, 3rd at 5th neighbour.

AFM studies of Ar⁺ irradiated HOPG under annealing see smaller asymmetric vacancy-related defects, followed by formation of 'domelike protrusions' that show Ostwald ripening like behaviour (typical height ~1-1.5 angstroms):



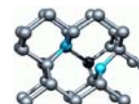
Typical room temperature monovacancy STM image
J. G. Kushnir et al., J.Phys.Chem. **103** (1999) 1619



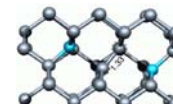
"The number of these hillocks decreased slightly up to 1473K and significantly decreased above 1473K"

B. An, S. Fukuyama, K. Yokogawa, M. Yoshimura, J. Appl. Phys. **92** 5237 (2002)

In diamond, the N4 and W7 EPR centres have been assigned to two substitutional N atoms at third-neighbour sites.

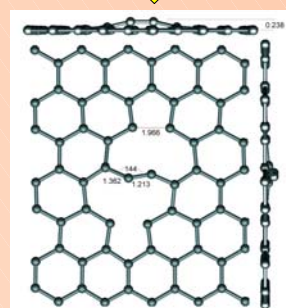


The A Centre

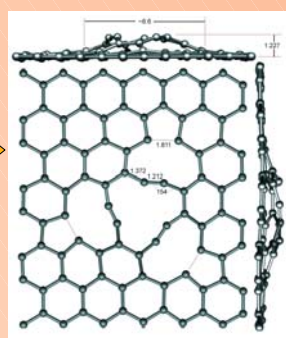
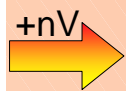


3rd neighbour N_s

Improved model incorporating metastable intermediates



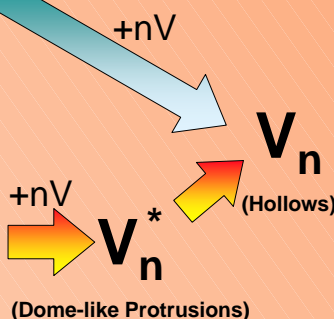
V₂^{*}



V₄^{*}

When two vacancies reach 3rd neighbour spacing their under-coordinated C atoms can form a strong triple bond (1.21Å), binding energy of 2.79eV compared to the isolated pair. The barrier for this defect to collapse to the V₂ ground state is ~2.2eV.

Further aggregation leads to multiple vacancy metastable complexes (e.g. V₄^{*} is 2.43eV more stable than two isolated V₂^{*}). V₄^{*} forms a 'hillock', lifting ~1.2Å out of the graphite plane. This is because the -C≡C- unit in V₂^{*} is mechanically constrained by the surrounding lattice, and elongates the parallel C-C bonds in the neighbouring pentagons. However the three triple bonds in V₄^{*} can relieve this strain through a concerted lifting of the defect core. This is consistent with AFM observation of hillocks rising 1.2-1.5Å out of plane.



(Dome-like Protrusions)

The increased stability of V_n^{*} metastable defects will increase the activation energy that must be overcome in order to collapse into V_n. At increased temperatures other processes should activate (vacancy release and recapture from V_n^{*} allowing Ostwald ripening and increased aggregate symmetry). Ultimately the barrier to 1st neighbour combination will be overcome and the defects will collapse into circular vacancy hollows.

Metastable defect complexing due to third neighbour rehybridisation is a general effect.

The importance of this result is that it is **general**. The formation of metastable defect pairs is not limited to vacancies in planar hexagonal materials; all that is required is **two defects which create under-coordinated host atoms, in a material that is able to rehybridise**. Thus we expect a range of metastable intermediate species, for example for **substitutional nitrogen-vacancy defects in graphite and BN**, or possibly involving **cross-linked interstitials**. We have calculated its effect for vacancies in hexagonal-BN.

Odd neighbour defect stabilisation is also possible in non-layered **crystalline materials**, e.g. **nitrogen pairs in diamond**. The stable substitutional nitrogen pair in diamond is the A-centre present in high concentrations in natural type IaA diamond (N on neighbouring sites). The A-centre is very stable compared to two isolated substitutional N donors (bound by 3.9eV). However, placing N at a third neighbour site once again leads to a surprisingly stable defect complex (just 2.5eV higher in energy than the A-centre). The two central carbon atoms, both three-fold coordinated, rehybridise giving a strong -C≡C- double bond (1.33Å cf diamond bond-length of 1.54 Å). There is some experimental evidence for such metastable nitrogen pairs. The N4 and W7 EPR centres have been assigned to N-pairs at third-neighbour sites.

We would also expect such an effect in many crystalline compounds where rehybridisation is possible such as AlN, GaN and InN.