# Reaction Kinetics of Stone-Wales Transformations in Graphene

S. T. Skowron[1], V. O. Koroteev[2,3], M. Baldoni[1], S. Lopatin,[4] A. Zurutuza,[5] A. Chuvilin,[6,7*] and E. Bichoutskaia[1*]

[1*] School of Chemistry, University of Nottingham, Nottingham, UK, elena.bichoutskaia@nottingham.ac.uk
[2] Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk, Russia
[3] Novosibirsk State University, Pirogova St. 2, 630090 Novosibirsk, Russia
[4] King Abdullah University of Science & Technology, Thuwal, Saudi Arabia
[5] Graphenea S.A., Donostia-San Sebastian, Spain
[6*] CIC nanoGUNE Consolider, Donostia-San Sebastian, Spain, a.chuvilin@nanogune.eu
[7] IKERBASQUE Basque Foundation for Science, Bilbao, Spain

The Stone-Wales (SW) defect is the simplest topological defect in graphitic materials, consisting of a 90° rotation of a single carbon-carbon bond. Together with electron-beam (e-beam) induced atom emission, the SW rearrangement is responsible for the dynamic behaviour of graphene observed with transmission electron microscopy (TEM) [1,2], and is widely assumed to be induced by the e-beam via a process of direct knock-on damage [3,4]. Due to the complex anisotropic nature of the threshold energy of the rearrangement, a theoretical cross-section of this reaction has not yet been obtained, while the high reversibility of the defect complicates experimental studies.

Beam induced reactions have been considered in the framework of chemical kinetics, and a statistical atomic kinetics approach has been developed for obtaining kinetic parameters of reversible reactions from the bottom-up. Using aberration-corrected TEM, cross-sections of the formation and healing of SW defects in pristine graphene have been calculated from the statistical treatment of large numbers of individual events observed experimentally at the atomic scale. By obtaining information about the lifetime distribution of SW defects, very short-lived defects (invisible to our imaging technique) are accounted for, overcoming a primary barrier to studying the kinetics of reversible reactions using atomic resolution microscopy.

By using experimental image series at a range of electron fluxes, both e-beam and thermally induced reactions were able to be quantified; SW formation and healing were shown to be primarily induced by the e-beam, with a thermally induced mechanism of SW healing that is consistent with theoretical predictions of adatom catalysis [5,6]. SW defect formation was observed at lower accelerating voltages than expected theoretically, for which the energy transferable from the e-beam is expected to be insufficient to induce bond rotation. Additionally, the rate of defect healing is at least three orders of magnitude larger than can be explained by the mechanism of direct knock-on damage. Despite this, the SW rearrangement exhibits a clear dependence on the electron beam, revealing the existence of an unknown and unpredicted beam induced mechanism of rapid atomic structure change in graphene [7].

**References**

[1] A.W. Robertson et al., Nanoscale, 5 (2013) 4079.
[2] S.T. Skowron et al., Chem. Soc. Rev., 44 (2015) 3143.
[3] J. Kotakoski et al., Phys. Rev. B, 83 (2011) 245420.
[4] Z. Wang et al., J. Phys. Chem. C, 116 (2012) 16070.
[5] C.P. Ewels et al., Chem. Phys. Lett., 351 (2002), 178.
[6] C. Wang et al., J. Mater. Chem. A, 1 (2013), 1885.
[7] This research was supported by the ERC Consolidator grant (E.B.), FEI Company (Netherlands) within a collaborative project (A.C.), FP7-PEOPLE-2011-IRSES N295180 MagNonMag project (A.C. & V.K.), and the High Performance Computing (HPC) Facility at the University of Nottingham (M.B. & E.B.).

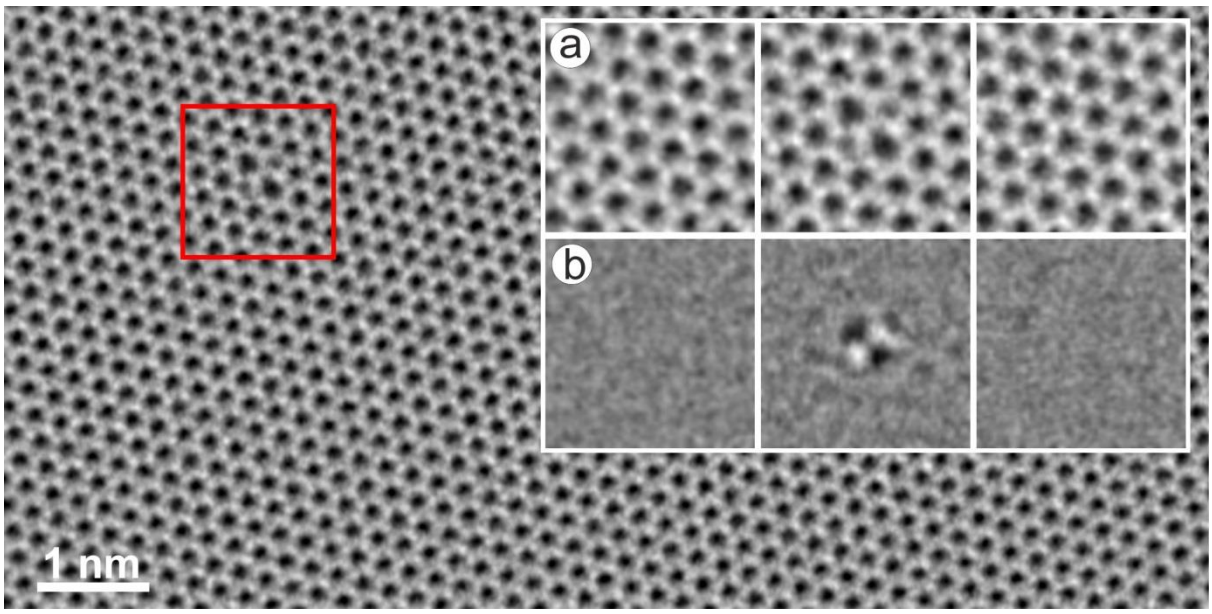


Figure 1: Example image of a SW defect in pristine graphene from an image series at 80 kV. Inset shows area bordered in red: (a) example sequence of a SW defect forming and then healing to return to pristine graphene over 3 seconds (1 second per image); (b) the same images with the graphene lattice removed by Fourier filtering, showing the characteristic 'dumbbell' signal of a SW defect.

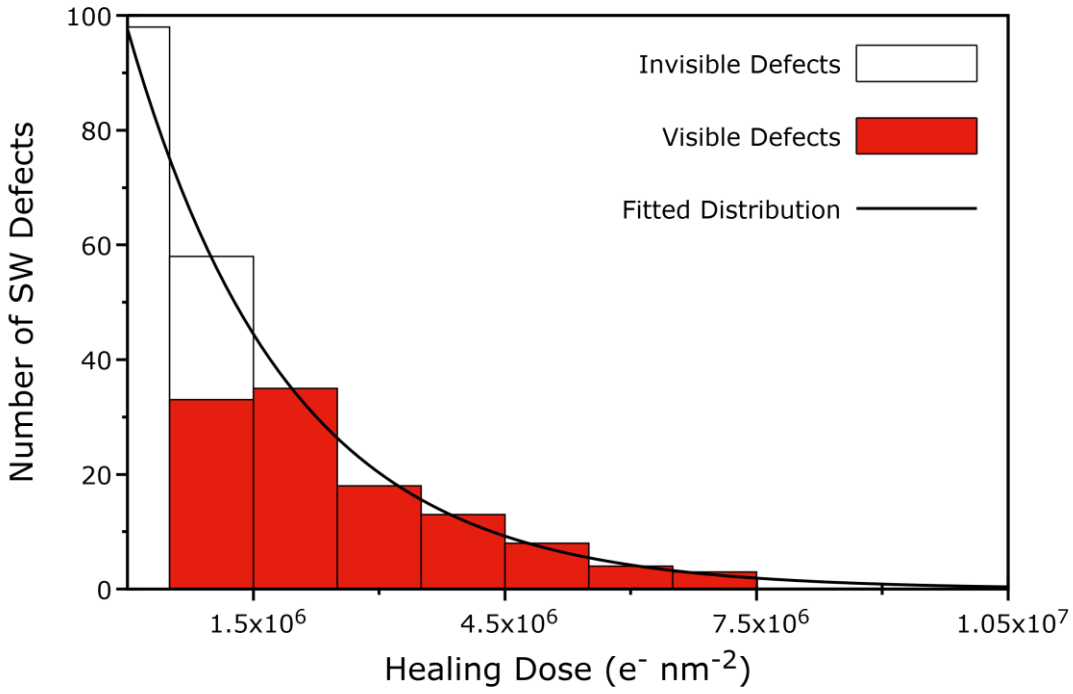


Figure 2: By fitting the distribution of the electron dose required to heal each experimentally observed SW defect to the geometric distribution, the true cross-section of SW formation can be found, accounting for defects that healed too quickly to be imaged by TEM.