Point defect generation by plastic deformation in diamond

F.H.J. Laidlaw[1,2], *R. Beanland*[1], *D. Fisher*[3], *P.L. Diggle*[3]

[1]Department of Physics, University of Warwick, CV4 7AL, UK
[2]Centre for Doctoral Training in Diamond Science and Technology, University of Warwick, Coventry, CV4 7AL, UK
[3]De Beers Group Technology, Maidenhead, SL6 6JW, UK

The origin of the brown colouration in diamond has been the subject of much investigation over the past few decades, pushed forward by the discovery that the brown colouration could be removed by High Pressure High Temperature (HPHT) treatments, increasing the value of the stone. Since all brown diamonds are plastically deformed, dislocations were an early candidate for the origin of the colouration. Subsequent studies have since shown that dislocations cannot be responsible for the colouration[1]. Vacancy clusters are the likely origin of the colouration after being detected in brown diamond, and not in colourless diamond, by Positron Annihilation Spectroscopy (PAS)[1,2]. The vacancy clusters anneal out with the colouration following HPHT treatment, while DFT modelling and optical excitation spectroscopy shows these vacancy clusters have absorption spectra which can account for the brown colouration[3–6]. Although not directly responsible for the brown colouration, the dislocations are thought to play a secondary role in the formation of the colour by generating vacancies during plastic deformation. Multiple electron microscopy techniques have been employed to investigate the link between the plastic deformation and the brown colouration. The dislocation microstructures observed by TEM imaging indicate point defect generation has occurred however, rather than finding evidence of vacancies being generated (the vacancy clusters are invisible in TEM imaging), we find evidence that a large concentration of interstitials have been generated.

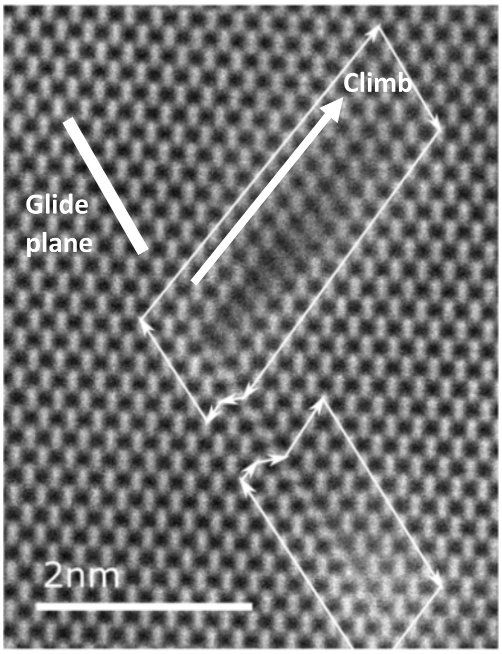

Figure 1: A dissociated 60° dislocation in untreated brown diamond. Top Burgers circuits surround a 90° partial dislocation which has undergone climb while the bottom circuit surrounds a 30° partial dislocation

Atomic resolution images of dissociated dislocations and faulted dipoles show that large numbers of interstitials have condensed into dislocation loops attached to the 90° partial dislocation, Figure 1 and 2. Rough estimates of the number of condensed interstitials suggest a concentration of approx. 10^{17} – 10^{19} cm^{-3} has been generated by plastic deformation and subsequently absorbed onto the dislocations. This value is similar to the monovacancy concentration in brown diamond measured by PAS[2,7] of $10^{18} cm^{-3}$ and suggests that plastic deformation produces almost equal numbers of both interstitials and vacancies. While the interstitials condense on the dislocations, the vacancies likely aggregate into the vacancy clusters.

The plastic deformation behaviour observed in diamond has been seen in many other simple fcc metals and semiconductors, such as Cu[8], Si[9], etc, all of which have been studied in far more detail. Apart from the extreme conditions required to plastically deform diamond, it does not appear to behave differently from other fcc materials.

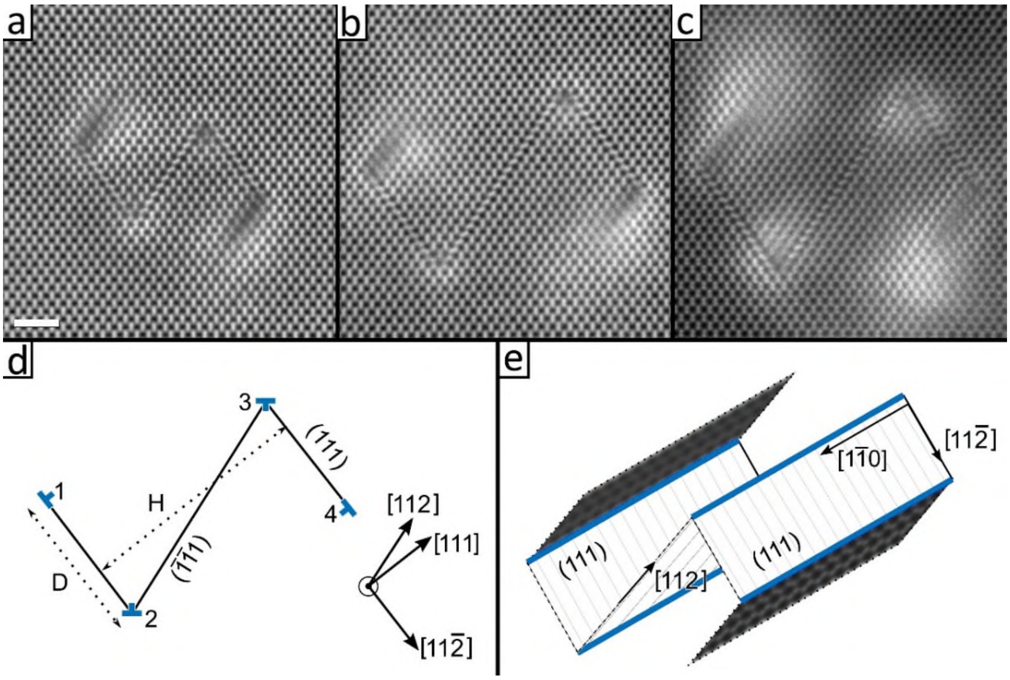

Figure 2: (a), (b), (c) ADF-STEM images of faulted dislocation dipoles in an untreated brown diamond that have undergone climb through addition of interstitial atoms (scale bar 2 nm). (d) Schematic showing the structure of a faulted dipole, Dislocations 1 and 4 are 90° partial dislocations, dislocations 2 and 3 are stair rod partial dislocations. (e) 3D schematic of the faulted dipole showing the climbed sections.

References

1. Fisher, D. Brown diamonds and high pressure high temperature treatment. *Lithos* **112**, 619–624 (2009).
2. Avalos, V. & Dannefaer, S. Vacancy-type defects in brown diamonds investigated by positron annihilation. *Phys. B Condens. Matter* **340–342**, 76–79 (2003).
3. Mäki, J. M., Kuittinen, T., Korhonen, E. & Tuomisto, F. Positron lifetime spectroscopy with optical excitation: A case study of natural diamond. *New J. Phys.* **14**, (2012).
4. Jones, R., Hounsome, L. S., Fujita, N., Öberg, S. & Briddon, P. R. Electrical and optical properties of multivacancy centres in diamond. *Phys. Status Solidi Appl. Mater. Sci.* **204**, 3059–3064 (2007).
5. Hounsome, L. S. *et al.* Optical properties of vacancy related defects in diamond. *Phys. Status Solidi Appl. Mater. Sci.* **202**, 2182–2187 (2005).
6. Fujita, N., Jones, R., Öberg, S. & Briddon, P. R. Large spherical vacancy clusters in diamond - Origin of the brown colouration? *Diam. Relat. Mater.* **18**, 843–845 (2009).
7. Maki, J.-M., Tuomisto, F., Kelly, C. J., Fisher, D. & Martineau, P. M. Properties of optically active vacancy clusters in type IIa diamond. *J. Phys. Condend. Matter 21* **46**, 24–28 (2009).
8. Décamps, B., Cherns, D. & Condat, M. The climb of dissociated dislocations in a quenched Cu-13·43 at.% Al alloy. *Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop.* **48**, 123–137 (1983).
9. Thibault-Desseaux, J., Kirchner, H. O. K. & Putaux, J. L. Climb of dissociated dislocations in silicon. *Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop.* **60**, 385–400 (1989).