Atomic structure-colour relationship in natural diamonds

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Abstract. Colour is a physical attribute that can be very difficult to characterise in diamond and consequently it receives regular attention from scientists working in the gem industry. In this work we compare natural brown (the most common colour) and colourless type IIa diamonds containing only trace quantities (< 1 at. ppm) of nitrogen. Numerous attempts have been made to trace the origin of brown tints in natural diamond, with the most likely culprits, i.e. dislocations and nitrogen impurities, ruled out through the application of various analytical techniques. Consequently more emphasis has recently been placed on the study of smaller defects in the diamond structure and their influence on colour. The focus of this research work is the analysis of vacancy defects having a size of the order of 1nm using aberration corrected scanning transmission electron microscopy (AC-STEM). The small electron probe size and depth of focus afforded by this technique allows such defect structures together with their position to be resolved far more readily than with conventional HR-TEM. Small-scale contrast variations are apparent in the lattice images of brown and not of colourless diamonds. These features have been compared to simulated phase contrast images of vacancy clusters in diamond. In addition, both experimental and simulated defocus series indicate that such features are not restricted to the surface of the specimen.

1. Introduction

Some chemically pure natural diamonds have a brown colouration that can only be attributed to inherent crystal lattice defects. One hypothesis is that the brown colour is caused by the presence of single vacant atoms sites and vacancy clusters (small groups of missing atoms). These are believed to form as a result of the movement of dislocations through the diamond lattice, which effectively removes the covalent bonds in localised regions to form sp\textsuperscript{2} type bonds. Dislocation movement occurs during the plastic deformation of the diamond whilst exposed to extreme pressure and temperature beneath the earth’s surface. An extensive survey of defocused bright field (BF) HR-TEM images has revealed the presence of contrasting light and dark features in a number of natural type IIa brown coloured diamonds [1]. In addition, positron annihilation measurements have proven that vacancy clusters exist only in natural brown diamond and are absent from the colourless type [2] [3]. A recent review of research into the cause of brown colour also supports the vacancy cluster hypothesis [4].

Electron energy loss spectroscopy (EELS) measurements have shown small areas (~1nm) where there is increased \pi-bonding intensity in natural brown diamond; \pi-bonding indicates a graphitic type structure and could indicate the presence of vacancy clusters [5].

In this work, using AC-STEM, we reinforce the vacancy cluster theory by assessing accurately the size and depth of the small contrasting features and in the process give far more direct evidence that they are groups of vacancies. Accompanying image simulations indicate that vacancy clusters are visible and show the contrast variation that can be expected.
Experimental

2.1 High Resolution STEM Imaging
Thin electron transparent specimens of untreated brown and colourless natural type IIa diamond were assessed using the high resolution bright field STEM imaging mode on the aberration corrected SuperSTEM at Daresbury Laboratory. The probe size in SuperSTEM is around 1 Å and it can therefore achieve atomic resolution. It is also ideal for observing small scale defects due to its short depth of focus (about 8nm), resulting from the large convergence angle (27mrad). Features of interest such as dislocations and other discontinuities in the crystalline structure can be observed more readily in bright field images due to phase contrast. Phase contrast imaging exploits the change in phase that electrons experience when they pass through and interact with the specimen. The SuperSTEM also provides a simultaneous high angle annular dark field (HAADF) image which highlights localised changes in specimen thickness and also heavier impurities, if they are present. A 40s plasma clean was carried out on all samples prior to loading them in the microscope.

A series of BF and HAADF images were acquired at various positions across the specimens in an attempt to build up a representative picture of their defect structures. In addition, a number of defocus series were acquired in order to observe the way in which the contrast of the features changes with varying amounts of defocus.

2.2 Image Simulation
Image simulation can be a useful aid to understanding the detailed structure that is observed in experimental images. The image simulations employed here use the multi-slice method [6] which transmits and propagates the electron wave function through successive slices of the crystal structure, integrates the electron intensity over the detector area and outputs the proportion of the incident intensity detected as a function of probe position. For STEM image simulation, the multi-slice calculation is performed for each position of the incident electron probe. Experimental parameters were selected for the 100kV VG HB501 SuperSTEM with Nion aberration corrector. BF image simulations of a 54 vacancy cluster in 30nm of perfect diamond crystal lattice were produced over the defocus range, -20nm to +20nm, in steps of 5nm. The angular range of the BF detector was 0-6 mrad.

2. Results and Discussion

3.1 STEM Images
The high magnification BF images of brown and colourless diamond shown in figure 1 reveal some differences between the crystal structures of the two types. The images of the brown specimen show localised regions of different contrast that are absent from those for the colourless specimen. The differences become more apparent at lower magnification as demonstrated by the images shown in figure two, where the magnification has been decreased by a factor of 2. The darker patches that are observed for the brown diamond in figure 2A are of the order of 1nm in size, which correlates with the positron measurements and also agrees with the HR-TEM observations that reveal similar features in a number of natural brown diamonds. Although there is evidence of micro-charging and central beam damage in figure 2B, the contrasting dark patches are not in evidence for the colourless diamond: the micro-charging phenomenon is most problematic for natural colourless diamond specimens in AC-STEM and could provide a clue to the difference in the electronic states found in brown and colourless diamonds, namely a lack of sp² bonds, which would be present on the surfaces of vacancy clusters.

By comparison, the HAADF images taken at both magnifications are not intuitive, since channelling of the electron probe along the [110] zone axis will have a marked effect on the intensity detected at the exit surface and the contrast from a defect will depend on its position within the thickness of the specimen.
The interpretation of these contrast variations is complicated by the possibility that they could originate from surface contaminants. A useful way of determining whether a feature is restricted to the surface or extends further into the specimen is to perform a through-focal series. This involves acquiring a number of images at various defocus values, as displayed in figure 3. The short depth of focus of the STEM probe allows the position and extent of a feature in the specimen to be investigated. The experimental series shown in figure 3 was acquired over a defocus range of -12nm to +16nm, starting at underfocus and moving to overfocus, with focus being at the beam entrance surface. The thickness of the specimen in this region was measured using electron energy loss spectroscopy (EELS) and found to be approximately 80nm. Prominent light and dark features are observed to gain and lose contrast as the defocus becomes more positive. This effect is not unexpected as the contrast displayed by a vacancy defect will vary depending on its position relative to the electron probe and therefore will not necessarily be visible when the surface of the specimen is in focus. As an example, the circled feature is absent at underfocus, becomes more visible at focus and then gradually darker with increasing overfocus. The fact that the feature is invisible at around -12nm defocus means that it is in-focus at a depth probed 12 nm below the beam entrance surface and hence is positioned at this depth; this effect is comparable with that observed in the image simulations shown in fig. 4. The feature may therefore be disregarded as a surface asperity.

Figure 1. High magnification BF and HAADF STEM images of (A) brown diamond (B) colourless diamond.

Figure 2. Lower magnification bright field STEM images of (A) brown diamond and (B) colourless diamond. The dark patches of contrast are circled.

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Figure 3. Bright field through-focal series of natural brown diamond demonstrating how the contrast of the circled feature becomes darker on moving from underfocus to overfocus.
3.2 Image Simulations
A comparison can be made between the small scale features highlighted in the STEM images and the contrasting central feature that appears in the simulated through-focal series shown in figure 4. The 54 vacancy cluster shown in the simulation lies at a depth of 7nm below the beam entrance surface. On moving from underfocus to overfocus the contrast of the simulated cluster is observed to change from light to dark. In addition, very little contrast is seen when the electron beam is focused on the defect rather than on the specimen surface, i.e. when the defocus is set to -5nm and -10nm. The change in appearance of the simulated cluster with defocus correlates with that observed in the experimental images (figure 3). Although the feature in figure 3 does not display a complete reversal of contrast it does appear less prominent at underfocus and this agrees with the simulation. Furthermore, if the disappearance of the feature in both the experimental and simulated images can be correlated, then the approximate position of the defect within the volume of the specimen can be determined. For example, one could ascertain from the simulated images that defects lying between 5nm and 10nm below the surface of the specimen would be largely invisible to the electron probe.

![Figure 4. Simulated bright field focus series of a 54 vacancy cluster in 30nm of pure diamond lattice.](image)

3. Conclusion
There is evidence to suggest that the patches of contrast observed in BF STEM images of brown diamond are vacancy clusters. When electrons from the incident probe interact with the vacancies it is expected that they will change phase and thereby impart a degree of contrast to a corresponding localised region of the BF image. The scale of the observed features is in keeping with the findings of positron annihilation experiments. Through-focal series show that the contrasting features are not confined to the surface of the specimen. The small depth of focus afforded by the SuperSTEM allows defects to be imaged at various positions through the thickness of the specimen; this is an advantage over the conventional TEM. Image simulations predict that vacancy clusters should be visible over a range of defocus in bright field STEM images.

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5. References
[1] Barnes R, 2007 PhD Thesis Manchester
[2] Tuomisto F, Mäki J-M, Kelly C J, Fisher D and Martineau P M, Origin of the brown colouration in high purity natural diamond, Submitted to Physical Review Letters on 27.11.2008
[3] Avalos V and Dannefaer S, 2003 Vacancy-type defects in brown diamonds investigated by positron annihilation, Physica B 340-342, 76-79
[4] Fisher D, 2009 Brown diamonds and high pressure high temperature treatment, Lithos, doi: 10.1016/j.lithos.2009.03.005
[5] Barnes R and Bangert U, 2006 Journal of Physics: Conference Series 26 157-160
[6] Kirkland E J, Advanced Computing in Electron Microscopy, Plenum, New York, 1998.