An analysis of vacancy clusters and sp2 bonding in natural type IIa diamond using aberration corrected STEM and EELS

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Abstract. The link between brown colour and vacancy structures in natural diamond and has been studied through the techniques of aberration corrected scanning transmission electron microscopy (AC-STEM) and electron energy loss spectroscopy (EELS). Bright field (BF) and high angle annular dark field (HAADF) STEM imaging modes have revealed discrete patches of stronger contrast, of the order of 1nm in size, that are similar to simulated images of vacancy clusters. Core loss spectra show a pre-edge feature for brown diamond corresponding to \(\pi^*\) states. This feature is absent for colourless and heat treated brown diamonds. Additional spectra acquired in regions containing dislocations for both brown and white (colourless) diamonds showed a second pre-edge feature indicating that dislocations have electronic states associated with them and are therefore optically active.

1. Introduction
Type IIa natural diamond is noted for having an extremely low concentration of impurities. In fact the trace amounts of nitrogen (<1ppm) that have been reported in this material are undetectable with IR spectroscopy [1]. Therefore we must look to other crystallographic anomalies to explain the remarkable difference in optical absorption that is observed between brown and colourless diamonds. From transmission electron microscopy (TEM) studies we know that natural diamonds contain many dislocations that have been introduced by geological processes [2]. However it has been demonstrated that these extended defects are not directly responsible for brown colour as they occupy the structure of both brown and colourless diamonds in similar concentrations; although the question still remains as to whether certain types of dislocations are optically active. Further evidence that dislocations are not responsible for brown colour is given by the fact that heat treatment at \(\sim 2500^\circ\)C under a stabilizing pressure of 7GPa removes the brown colour but not the dislocations [3].

In a quest to identify the structural anomaly responsible for the brown colour, density functional theory (DFT) has shown that another extended defect, the spherical vacancy cluster, has the correct electronic properties to allow optical absorption to occur [4]. The motion of jogged dislocations (intersecting dislocations having different slip systems) yields vacancies which coalesce into stable spherical clusters that are lined with pi-bonds. The bonding between the carbon atoms in the localized regions of the vacancy clusters will be sp\(^2\) hybridised and this should be detectable with EELS. It has been demonstrated that the vacancy cluster has a low formation energy and an optical absorption similar to that of brown diamond [5]. In addition, positron annihilation spectroscopy (PAS) studies have shown that the spherical vacancy cluster acts as a deep trap for positrons, which explains why the average positron lifetime is longer for brown diamond than for colourless [6-7].

The aforementioned techniques provide sufficient evidence to support the link between vacancy clusters and brown colouration in type IIa diamonds and negate the possibility that other extended
defects composed of carbon interstitials, (such as those observed in nitrogen containing type 1a diamond), are the dominant defect structures. Ab initio density functional theory has shown that extended interstitial defects can arise in diamonds containing sufficient quantities of nitrogen (~0.2 at. %) but not in chemically pure type IIa diamond [8]. Substitutional nitrogen plays an important role in the trapping of vacancies and the growth of platelet defects. Moreover, interstitial defects do not result in the formation of large quantities of dangling bonds and hence the sp² bonded structures that are evident in brown diamond.

Aberration corrected STEM and EELS are powerful techniques for studying vacancy defects and their associated electronic states. The excellent spatial resolution (<0.1nm) and small depth of focus (~8nm) of the STEM probe allow vacancy clusters to be imaged via BF and HAADF imaging modes. The signal for the BF image originates from the central diffraction disk. Interpreting the contrast in BF images can be difficult as the observed lattice fringes can undergo a reversal of sign with changing crystal thickness and defocus conditions. Additionally, variations in electron phase at defects can distort the structural information of imperfect crystals. As the name suggests the HAADF signal is derived from electrons that are scattered to high angles. The scattering phenomenon is Rutherford like in nature and is approximately proportional to Z², i.e. the HAADF signal increases with atomic number and thickness. Although HAADF images are easier to interpret because of the Rutherford scattering behaviour, unexpected contrast can sometimes be observed due to high-angle scattering contributed by phonons and Bloch wave interference effects [9].

Core-loss EELS is sensitive to electronic states originating from defects and the pre-edge structure can reveal defect states in the band gap for diamond [10-11]. The predominant feature of the diamond k-edge is the ionization that occurs at 290eV due to k-shell electrons being promoted to σ* states. Features appearing before the ionization edge in the range 282-288eV have been assigned to π* states [12].

2. Vacancy cluster contrast
Thin electron transparent specimens of untreated brown, annealed brown and colourless type IIa diamond were assessed using the aberration corrected SuperSTEM at Daresbury Laboratory. Electron imaging was carried out under UHV conditions (~1x10⁻⁹ Torr) and the specimens were free from carbon contamination. The high magnification BF and HAADF images shown in Figure 1 reveal some differences between the crystal structures of the three specimens. It is important to note that the distortions observed in the images of the colourless and heat treated samples are due to micro charging under the highly focused electron probe. This phenomenon is most problematic with insulating materials in the AC-STEM and is indicative of the electronic properties of the material. In the case of colourless diamond the contribution from sp² bonding is negligible and the band gap contains fewer electronic states accordingly. The BF images of the brown diamond show localised regions of stronger contrast that are absent from those for the colourless and annealed specimens. The darker patches that are observed for the brown diamond are of the order of 1nm in size, which correlates with the PAS measurements and also agrees with the HR-TEM observations that reveal similar features in a number of natural brown diamonds [13].
Brown IIa – heat treated 2500°C

![Figure 1](image)

**Figure 1.** Comparison of BF and HAADF image contrast for brown, heat treated brown and colourless natural type IIa diamonds.

The corresponding features that are observed in the HAADF images have a bright intensity which is unexpected, i.e. one might expect to see weak contrast of opposite sign where there are clusters of vacancies. However, this phenomenon can be explained by considering the effect that a relaxed structure of vacancies might have on the relative excitation of s-type and p-type Bloch states in the diamond crystal. Channelled p-type states that would normally pass through a defect free crystal without scattering interact with the displaced atoms around the vacancy cluster causing s-type states to be excited. The resultant scattered waves add cumulatively giving rise to bright intensity and strong contrast in the HAADF image. A detailed explanation of Bloch wave interference effects in imperfect crystals is given by Perovic et al. [9].

2.1. *Through-focal image series*

By acquiring a through-focal image series in both BF and HAADF it was possible to study the contrast of the vacancy clusters in more detail. This involved acquiring a number of images at different values of defocus, starting at -20nm underfocus and moving to +20nm overfocus, with focus being at the beam entrance surface. The thickness of the specimen in the region of interest was determined from the number of electron mean free paths acquired from EELS measurements and was found to be approximately 80nm. Concentrating on one of the vacancy clusters in the BF series (Figure 2), we observe strong contrast of bright intensity at -20nm underfocus, very little contrast approaching focus and then stronger contrast of opposite sign at +20nm overfocus. This effect is not unexpected as the contrast displayed by a cluster 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. The fact that the feature is invisible at around -10nm defocus means that it is in-focus at a depth probed 10 nm below the beam entrance surface and hence is positioned at this depth. The feature may therefore be disregarded as a surface asperity.

By comparison the HAADF series shows strong contrast of bright intensity throughout and does not display any reversal of sign.
Figure 2. Through-focal image series acquired between -20nm and +20nm, showing how the contrast of a vacancy cluster changes in BF and HAADF.

2.2. STEM Image Simulation

Image simulations were performed to determine the contrast that one would expect from a multi-vacancy structure in experimental images. The simulations employed here use the multi-slice method [14] 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 SuperSTEM with Nion aberration corrector. BF and HAADF simulations of a 54 vacancy cluster positioned at an arbitrary depth of 7nm below the beam entrance surface of a 30nm crystal were produced. A defocus range of -20nm to +20nm was selected, in keeping with the experimental conditions. The angular range of the BF and HAADF detector was 0-6 mrad and 70-210 mrad respectively. The output from the multi-slice calculations is shown in Figure 3 below.

Figure 3. Simulated BF and HAADF image series of v54 cluster positioned 7nm below beam entrance surface. The diamond crystal thickness is 30nm. An rms amplitude of vibration of 0.02Å was applied.

Comparing the small scale features highlighted in the experimental images and the simulated vacancy cluster shown in Figure 3, we observe similar characteristics. Between -20nm underfocus and focus in the BF series the contrast is weak and the cluster is barely visible. However, on moving through focus to +20nm overfocus the contrast becomes stronger and the cluster appears dark.
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 one correlates the defocus condition under which weak contrast is observed in both the experimental and simulated images, then the approximate position of the defect within the volume of the specimen can be determined. For example, one could ascertain from the simulated image series that a cluster positioned 10nm below the surface of the specimen would be largely invisible in the electron image. In comparison to the BF series, the contrast observed in the HAADF series is always of the same sign and is of similar intensity to that seen experimentally.

3. Core-loss EELS pre-edge structure
Core-loss EELS measurements were carried out to investigate sp$^2$ states in brown, heat treated brown and colourless natural diamond specimens. The diamond k-edge spectra presented here were acquired with a GATAN Enfina spectrometer having a collection angle of up to 19mrad. Spectrum images were acquired with a pixel dwell time of 0.5 s over the energy loss range 248 eV to 382 eV. The energy resolution determined from the FWHM of the zero loss peak was 0.3 eV.

Figure 4 shows the difference in the pre-edge structure for treated and untreated natural diamonds. Interestingly, two peaks are observed for the brown diamond (a), one at ~284eV and another at 286eV. By comparison the 286eV peak is absent for the colourless diamond (b), although a small contribution is seen at 284eV. The double feature before the main ionisation edge has been reported previously in nanocrystalline diamonds by Okada et al [12] and has been...
attributed to sp\(^2\) states. However, evidence exists in this research and previous studies of low-loss EELS [15] of diamond to suggest that the 284eV peak originates from electronic states at dislocations. The fact that dislocations have electronic states associated with them begs the question as to why they do not contribute to the brown colouration. In the absence of further quantitative information, it is assumed that these optically active dislocations are not present in sufficient concentration to cause brown colour.

Comparing the spectra for the natural brown diamonds heat treated to 1900°C (c) and 2500°C (d), there is still evidence of the sp\(^2\) states in the former but not the latter. This finding agrees with the annealing studies which show that the brown colouration is not removed until temperatures in excess of 2000°C are reached. In fact the brown colouration becomes less and less prominent until it finally disappears at around 2500°C [3]. Furthermore, PAS measurements have demonstrated that the disappearance of the brown colour at the higher treatment temperature coincides with a reduction in the average positron lifetime [6]. One hypothesis is that the spherical vacancy structure grows by the uptake of mobile vacancies at elevated temperature until a critical size is reached where the structure collapses and forms an optically inactive dislocation loop. A similar mechanism for the removal of brown colour has been discussed by Hounsome et al [5].

4. Conclusion
A correlation exists between the contrast observed at vacancy clusters in experimental STEM images of type IIa natural brown diamond and the contrast predicted by simulated images of similar vacancy structures. Phase contrast is the principle mechanism for observing contrast in the BF image, whereas high angle scattering due to Bloch wave interference is the probable cause of contrast of opposite sign to that expected in the HAADF image. Core-loss EELS shows a double pre-edge peak for brown diamond that is annealed out by heat treating to 2500°C. The peak at 286eV originates from sp\(^2\) states associated with the \(\pi\)-bonded lining of the vacancy clusters. However, the 284eV peak can be attributed to electronic states at dislocations in both brown and colourless natural diamonds.

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