Combined TEM and STEM study of the brown colouration of natural diamonds

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Abstract. A range of natural brown, colourless and HPHT-treated single crystal diamonds are analysed via Transmission Electron Microscopy (TEM). Graphitic inclusions are found only in specimens originating from diamonds with brown colour. The inclusion sizes range from slivers of around 50nm by 5-10nm, to regions around 10µm in diameter with undefined boundaries. The suspected proportions of graphite to diamond were confirmed by micro-RAMAN spectroscopy. The orientation relationship, measured via diffraction and lattice imaging, was found to be diamond \{111\} and \{110\} planes parallel to graphitic basal and \{2\{11\}0\} planes respectively, where three diamond \{111\} planes coincide with two graphitic basal planes. This orientation, suggesting diamond 111-vacancy platelets, is consistent with defects associated with a featureless optical absorption spectrum similar to brown diamond. Vacancies and dislocations in diamond and their link to brown colouration will continue to be studied.

1. Introduction
Natural brown diamonds are the most abundant of mined diamonds, accounting for around 98%. Diamonds retailed as precious stones are type IIa, which do not contain a measurable concentration of elements other than carbon. The brown diamonds studied here are also type IIa, narrowing the possibilities of the cause of the brown colour to defects in the diamond lattice. However, the mystery continues as type IIa brown diamonds lose their colour under high-pressure and high-temperature treatment.

In contrast to previous beliefs, dislocations do not seem to show sufficient optical activity to be the sole cause for the colouration. Recent investigations into the colouration have revealed strong links with vacancies on two counts. Firstly, the concentration of vacancies has been shown to decrease with the decrease of the brown colour [1]. Also, theoretical calculations indicate that vacancy 'platelets' in the \{111\} planes will exhibit featureless optical absorption spectra similar to brown diamond [2].

A range of natural brown, HPHT treated and colourless diamonds has been studied by transmission electron microscopy, revealing regions of graphitic character only in samples with brown colour. All samples were identically prepared by laser cutting and subsequent ion beam milling. The graphitic regions do not have distinct boundaries, and they range in size from diameters of several micrometers to sliver-like 'islands' of around 50 nm by 5-10nm. Although the orientation of the graphite relative to the diamond is easily determined via the TEM, the boundaries and organisation of the graphite appears complicated.
2. Experimental Procedure

Each sample has been laser cut to 70 - 100µm by DTC Maidenhead, then Argon ion beam milled to electron transparency (usually around 50nm). Each diamond is thinned to give an approximate <110> axis in the TEM. The plate is mounted on a copper ring for security in the TEM specimen holder.

A range of natural diamond samples (3 brown, 1 brown HPHT treated, 1 pink HPHT treated, 3 colourless HPHT treated and 2 colourless) was analysed using a combination of the following transmission electron microscopes: Philips 400T 120KeV; Philips CM200 200KeV; FEI Tecnai F30 FEGTEM 300keV. The Tecnai, in particular, was used for high-resolution lattice imaging.

Micro-RAMAN spectroscopy was performed on the TEM sample A490-146-02B to confirm the presence of graphite in particular areas. The system used is a Renishaw micro-RAMAN system with an Ar-ion laser of laser line 514.5nm.

The SuperSTEM has been used to study electronic states of dislocations by high-resolution imaging and EELS on dislocation cores in brown diamond, continuing previous work [3]. The SuperSTEM is a VG 501 FEG STEM fitted with a corrector for spherical aberrations. The accompanying Enfina EELS system is capable of atomic column resolution EELS analysis.

3. Results & Discussion

The smallest ‘islands’ of graphite are easily visible in the TEM, as in figure 1a, due to the large concentration of strain contours in the surrounding diamond. Strain contrast is also present at the boundary of larger regions; where the graphite seems to ‘dissolve’ into small islands, see figure 1b.

These regions of graphite were found in 3 out of 4 natural brown diamonds, and were not found in any other treated or colourless samples. Bearing in mind the identical preparation, the likelihood of this occurring by coincidence is around 2.4%.

Electron diffraction in the regions of both diamond and graphite revealed that the orientation relationship is consistent over all graphite-including regions in every sample. The diffraction patterns were indexed at three zone axes (<<111>>, <<110>>, <411>>) allowing only one solution to the orientation relationship, which is {111} and {110} planes of diamonds parallel to graphitic basal planes and {2110} respectively. A model has been built to show the relative positioning of the two carbon structures (figure 2).

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Figure 1  a) Presence of graphitic ‘islands’ (approx. 100nm) revealed by horizontal strain contrast features and long vertical contours down the image. b) The boundary between diamond (top) and graphite, the large strain shows up in dark contrast patches.

Figure 2 Orientation relationship between diamond and graphite seen along the <110>-zone axis of diamond. Diamond is shown in white bonds and the black lines to the right of the image represent diamond {111} planes. Graphite is displayed in dark bonds, and the light lines to the right show basal planes.

The view along the columns of diamond in the [110]-directions shows the {111} planes of diamond, in white, and the {0001} basal planes of graphite, in black, running
horizontally across the image. This model demonstrates a repeated coordination of three diamond \{111\} planes to two graphitic basal planes, an organisation also seen in annealed polycrystalline CVD diamond [4]. This coordination is equivalent to a \{111\} plane of vacancies replacing one in three diamond planes. This ties in with the aforementioned work on vacancy clusters [2], which linked \{111\} vacancy platelets to optical absorption spectra features similar to brown diamond. The exact boundaries of the graphite are unknown; therefore bonds between the structures are not specified.

High-resolution lattice images of both diamond and graphite confirm the presence of the two structures in natural brown diamond TEM samples. However, in the regions of the graphitic slivers, which are surrounded by strain contrast, the lattice images are not as straightforward. Although the strain extends over 500nm, the disturbance to the diamond lattice is only around 4-5nm (figure 3a). Moiré fringes appear as brighter planes every third diamond \{111\} plane, where the graphitic basal planes coincide with diamond \{111\} planes.

The reason there are several sets of Moiré fringes is unknown, however it is possible that numerous graphite inclusions placed at different depths in the specimen could be responsible. If this were the case it would be unlikely that the graphite would start on the same \{111\} plane of diamond looking in this direction, therefore explaining the staggered fringes.

**Figure 3** Image of disturbed diamond lattice within one sliver of strain contrast (Image approximately (5nm)²). Part of one set of Moiré fringes are highlighted by black lines.

Simulations, based on the orientation relationship between diamond and the graphitic regions above, have been performed for a supercell constructed of planes perpendicular to the <110> beam. Images of varying proportions of \{110\} diamond and \{2\overline{1}10\} graphite layers were generated for a conventional TEM by the TEMSIM program [5]. Moiré fringes appear at the same periodicity as lattice images of slivers in figure 3. For an equal proportion of diamond and graphite, the simulation reveals the diamond \{111\} planes as visibly separate between the fringes as can be seen in figure 4a. Figure 4b taken from the image in figure 3 and filtered, displays how this appears in the TEM. Another image taken from figure 3 has less defined planes between the fringes, which corresponds to the simulation for an increased graphitic concentration, as demonstrated in figure 4c and d.

**Figure 4** TEMSIM simulations using a diamond/graphite supercell constructed of unit cell layers d (diamond) and g (graphite) in the ratio d/g with defocus 9.6nm and thickness around 40Å (these values were found to best mimic experiment), and accompanying TEM images taken from figure 3 a) d=4, g=4 with b) the best matching filtered TEM image; c) d=4, g=8 with d) the best matching TEM image. The measured diamond/graphite orientation relationship was used. The beam direction was <110>\textsubscript{diamond}. The simulation assumed a 300keV conventional TEM.

Micro-Raman spectroscopy with a spot diameter of 1µm was performed on the areas of the diamond specimen A490-146-02B, where graphite inclusions were thought to be. The graphite Raman shift (~1580cm\textsuperscript{-1}) was combined with the diamond Raman shift (~1330cm\textsuperscript{-1}) in varying proportions in different areas suspected of containing graphite. The results confirmed all suspected inclusions as graphite with the proportions of the peaks
corresponding to the assumed concentrations.

It is important to consider all defects in diamonds to fully understand the cause of the colouration. Previous studies [3] of electronic states of dislocation cores were pursued using the EELS facilities with ultra-high resolution. The dislocation in figure 5 and similar dislocations in brown diamond A490-146-02B were imaged and low- and core-loss EELS performed to atomic column resolution both on the core, and in surrounding areas.

Figure 5 a) End-on dislocation core in brown diamond A490-146-02B with extra plane highlighted in b).

Initial results show no significant difference between on and off core spectra. Yet, earlier work [3] showed a difference between on and off dislocation spectra in brown diamond. These results, however, had much poorer spatial resolution suggesting the effect of electronic states of dislocations could be delocalised over an area much larger than the immediate core.

It is quite certain that graphite inclusions appear in the 3 of the 4 brown diamond TEM specimens considered in this research. However, the question is whether these specimens are representative of the bulk diamond, and if they are not, how did these regions form in only the brown diamond samples? The preparation procedure should not affect the diamond structure, however this assumption is based on perfect diamonds. How would diamond with defects, such as plagued with vacancy clusters, be affected? These graphitic regions could be a major clue in the determination of how brown diamonds differ from their colourless counterparts.

4. Conclusion
The existence of graphitic inclusions was confirmed through transmission electron microscopy, in specimens originating from diamonds with brown colour. The inclusion sizes range from slivers of around 50nm by 5-10nm, to regions around 10µm in diameter with undefined boundaries. The suspected proportions of graphite to diamond were confirmed by 1µm spot size micro-RAMAN spectroscopy. The orientation relationship, measured via diffraction and lattice imaging, was found to be diamond \{111\} and \{110\} planes parallel to graphitic basal and \{2110\} planes respectively, where three diamond \{111\} planes coincide with two graphitic basal planes. This orientation agrees with work on diamond \{111\}-vacancy platelets [2], which are suggested to cause featureless optical absorption spectra, which is associated with brown colour.

If defects such as vacancies are responsible for the brown colour, it is important to understand their distribution in brown diamonds in dislocations as well as apparently perfect regions, through all stages of the high-temperature, high-pressure treatment. For this reason, research into these regions will continue with high-resolution imaging and EELS analysis.

5. References
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