A Study of the relationship between brown colour and extended defects in diamond using core-loss electron energy loss spectroscopy

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Abstract. There is strong evidence to support the theory that the vacancy cluster, a by-product of dislocation interaction, is the extended defect responsible for brown colour in natural type IIa diamonds. A characteristic of these open volume structures is the hybridised sp² bonding of the 3-fold coordinated carbon atoms that line their cage-like surfaces. When present in sufficiently large concentrations the sp² bonds alter the electronic and optical properties of type IIa diamond dramatically. Similar sp² bond concentrations are found in dark brown CVD diamond, although the defects in this material appear much larger in size than in the natural diamond. In this study we employ core-loss electron energy loss spectroscopy (EELS) and aberration corrected scanning transmission electron microscopy (AC-STEM) to compare the relative sp² content of brown coloured natural type IIa diamonds and dark brown CVD diamonds, using 100% sp² bonded graphite as a reference. The effect of high-pressure high-temperature (HPHT) treatment on sp² content is also investigated.

1. Introduction

Both high resolution electron microscopy (HREM) [1] and positron annihilation spectroscopy (PAS) [2] [3] studies have provided tangible evidence to support the theory that vacancy defects contribute to brown colouration in both naturally occurring type IIa and CVD diamonds. In the case of type IIa diamonds it is probable that large clusters of 50 or so vacancies are the main contributors to the brown colour, as indicated by optical absorption spectroscopy measurements [4]. Annealing studies have shown that the brown colour in type IIa diamond can be removed by heating to >2500°C [5]. However, in the case of CVD diamond it is found that the brown colour is significantly reduced at a comparatively low annealing temperature of 1400°C, presumably due to a reduction in the concentration of smaller nitrogen-vacancy defects through clustering [6] [7]. The exact mechanism for the production of vacancies through plastic deformation of type IIa diamond is not completely understood, however one popular theory is that they are formed by the dissociation of shuffle type dislocations [8]. It is probable that the increased mobility of these dislocations at the elevated temperatures experienced in the earth’s upper mantle provides suitable conditions for the emitted vacancies to cluster together. Density functional theory (DFT) calculations show that both the formation of clusters and the hybridisation of the surrounding carbon bonds lower the overall energy of the crystal [9]. In the case of CVD diamond the dislocation density is very low compared with type IIa diamond, which suggests that the vacancy defects are introduced during the deposition process.

To quantify the sp² content of diamond crystals, a technique that is sensitive to electronic structure is required. One such technique is core-loss EELS, which produces inner shell loss edges that are dependent on the local bonding arrangement of atoms. EELS studies of diamond materials have shown
that the $\pi^*$ peak of the carbon k-edge provides a quantitative measure of the amount of sp$^2$ bonding in a material [10] [11]. The intensity of the $\pi^*$ peak relative to that of the $\sigma^*$ peak (sp$^3$ bonded carbon) can therefore be used to approximate the sp$^2$ content in brown coloured diamonds. In order to provide a means of studying the relationship between brown colour and sp$^2$ content, core-loss EEL spectra were acquired for untreated and HPHT treated brown type IIa diamonds together with dark brown CVD diamonds. The HPHT treatment temperatures were 1900, 2200 and 2500°C.

2. Experimental

Diamond specimens for AC-STEM and EELS analysis were provided by DeBeers research centre. Thinning of these materials to electron transparency was carried out by conventional tripod polishing followed by argon ion milling. A 100kV Vacuum Generators HB501 STEM with Nion aberration corrector was used to acquire high resolution high angle annular dark field (HAADF) and bright field (BF) images. Electron imaging was carried out under UHV conditions ($\sim$1×10$^{-9}$ Torr) and the specimens were free from carbon contamination. EELS measurements were performed with a Gatan Enfina spectrometer. The experimental conditions were: convergence angle 24 mrad, nominal probe size 1.3 Å, collection angle $\sim$19mrad and energy resolution 0.3 eV (measured at FWHM of zero loss peak). Spectrum images were recorded over the energy range 230-364 eV using a dispersion setting of 0.1 eV/channel. The background intensity was removed from the spectra by applying a power-law model. Thickness calculations were performed using the formula given by Egerton [12]. For the purpose of comparing the integrated edge intensity, the acquired spectra were normalised to the maximum intensity at 295 eV. The average integrated intensities corresponding to the $\pi^*$ and $\sigma^*$ excitations were extracted over the energy ranges 282-287 eV and 287-292 eV respectively and used to calculate the sp$^2$ content relative to 100% sp$^3$ bonded polycrystalline graphite.

3. Results and discussion

The core-loss spectra for type IIa brown and colourless diamonds are shown in figure 1, along with spectra for type IIa brown diamonds that have been HPHT treated to 1900°C, 2200°C and 2500°C. A characteristic k-edge is visible at 290 eV corresponding to the 1s to $\sigma^*$ transition that is associated with sp$^3$ bonded tetrahedral carbon. In addition, a prominent pre-edge peak is observed at $\sim$286eV for the untreated brown diamond signifying the presence of sp$^2$ bonds in the crystal. This feature is absent from the spectrum for the colourless diamond. This characteristic feature correlates with low-loss EELS measurements that have identified a $\pi$-$\pi^*$ transition at 6-7eV in brown type IIa diamond, which is indicative of a graphitic type structure and hence sp$^2$ bonding [1]. Employing the integrated intensity comparison method, the sp$^2$ content of the untreated brown diamond was found to be 16 %.

The spectra for the HPHT treated type IIa brown diamonds reveal that the effect of annealing on sp$^2$ content does not become apparent until temperatures in excess of 1900°C are reached. A significant pre-edge peak remains after annealing at this lower temperature, with the calculated sp$^2$ content ranging from 10 % - 20 % depending on the region sampled. One possible explanation for this non-uniformity is that the mono-vacancy population starts to decrease through the growth of larger vacancy clusters and / or the elimination of interstitial carbon atoms, thereby creating a dispersed sp$^2$ network. Annealing studies show that there

![Figure 1. K-edge spectra for type IIa brown and colourless diamonds together with spectra for brown type IIa diamonds heat treated at 1900°C, 2200°C and 2500°C.](image-url)
is no apparent change in the brown colour at this temperature. By comparison, the colour is observed
to lighten considerably when the annealing temperature is raised to 2200°C and this coincides with a
corresponding drop in sp² content to between 0 % and 6 % depending on the region sampled. It is
possible that the larger vacancy clusters become unstable when their energy of formation reaches a
critical level, at which point they collapse to form inactive dislocation loops. This might explain the
marked reduction in the pre-edge peak intensity at 2200°C. Increasing the annealing temperature still
further to 2500°C has the effect of completely eliminating the sp² absorption peak from the core-loss
spectrum which corresponds with the removal of the brown colour. Additional studies have shown
that there is a correlation between the disappearance of contrasting features from STEM images, the
removal of the sp² peak and the elimination of the brown colour at 2500°C [13].

Furthermore, there is evidence to suggest that the dislocations found in both brown and colourless
type IIa diamonds contribute additional electronic states to the band structure of diamond. This is
demonstrated by the spectra shown in Figure 2 which show a separate absorption peak at ~284 eV
near to dislocations in both brown and colourless natural diamonds.

![Figure 2](image2.png)

**Figure 2.** Additional pre-edge feature at ~284 eV at dislocations in brown and colourless type IIa diamonds.

![Figure 3](image3.png)

**Figure 3.** EEL spectra showing increased sp² content at crater-like defect in dark brown CVD diamond.
An investigation of large (10-15 nm) crater-like defects in dark brown CVD diamond has revealed that significant quantities of sp² bonds exist around the perimeter of the defects, figure 3. The exact origin of these open volume structures is unknown, however it is likely that they have been introduced during the deposition process and are in fact much larger versions of the vacancy clusters observed in the natural brown diamonds. This hypothesis would be consistent with the PAS measurements which show increased positron lifetime components for brown CVD diamond [7]. It is important to note that these crater type defects are not found in all dark brown CVD material and that the EEL spectra exhibit a background sp² contribution regardless of their presence.

4. Conclusion
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 286 eV originates from sp² states associated with the π-bonded lining of vacancy clusters. However, the 284 eV peak can be attributed to electronic states at dislocations in both brown and colourless natural diamonds. Large open volume defects of the order of 10nm have been identified as sites of sp² bonding in dark brown CVD diamond.

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