Brown colour in natural diamond and interaction between the brown related and other colour-inducing defects

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D Fisher, S J Sibley and C J Kelly

Diamond Trading Company, DTC Research Centre, Maidenhead, Berkshire SL6 6JW, UK

Abstract
Absorption spectroscopy results on a range of type II diamonds are presented which enable the electronic states associated with them to be mapped out. High pressure, high temperature treatment of brown type IIa diamonds has enabled an activation energy for the removal of the brown colour of 8.0 ± 0.3 eV to be determined and this is consistent with expectations associated with the currently accepted vacancy cluster model for the defect. Theoretical calculations suggest that this defect will generate partially filled gap states about 1 eV above the valence band. Data on the photochromic behaviour of bands producing pink colour and their relation to brown colour are presented; these suggest that the pink bands are produced from two independent transitions with ground states close to each other just below the middle of the band gap. Compensation of neutral boron by charge transfer from states associated with brown colour is demonstrated via the correlated increase in neutral boron and decrease in brown colour on high pressure, high temperature treatment to remove the defects causing the brown colour.

1. Introduction

The commercial and technical importance of diamond has stimulated significant research into its optical and electronic properties. Such studies have tended to focus on high purity, high quality material or, in the case of gemstones, on the point defects that impart desirable colours. The wide band gap of diamond provides great scope for the production of a wide range of colours via the introduction of defect induced electronic gap states. One colour of diamond that received relatively little interest, perhaps due to its low commercial value, was brown, with references to this rarely going beyond a probable link with plastic deformation and speculation as to the nature of the defects responsible for the observed wavelength dependent absorption [1–3]. This has changed significantly in recent years with a desire to understand brown colour in synthetic diamonds grown via chemical vapour deposition [4–6] and a search for the fundamental cause of brown colour in natural diamond prompted by the discovery that high pressure, high temperature (HPHT) treatment of such stones could remove the brown, so significantly enhancing their appearance and increasing their commercial value [7–9].

As part of our study into the colour changes induced by HPHT treatment in different diamond types we have looked extensively at the absorption features associated with brown diamonds and also those of the final products of treatment. The work presented here concentrates on low nitrogen (type II) diamonds, the behaviour of the absorption associated with brown colour on HPHT treatment and the interaction of the defect responsible for the brown colour with other defect centres to produce charge transfer effects and photochromic behaviour. These include pink and blue diamonds. The colour changes induced by HPHT treatment in type I diamonds tend to be dominated by the strong absorption features associated with nitrogen containing point defects and will not be considered in detail here.

1.1. Type IIa brown diamonds

Type IIa brown diamonds have been studied extensively both experimentally and theoretically in recent years with a view to understanding the fundamental cause of brown colour. Useful summaries of current experimental and theoretical understanding can be found in [10] and [11] respectively. Such diamonds are known to be plastically deformed with the brown colour tending to be concentrated along slip bands (i.e. giving strong brown colour in {111} planes) [2, 3]. The link with plastic deformation suggests dislocations as

the defect responsible for the absorption, but extensive TEM analysis of brown and colourless diamonds [12, 13] and comparison with absorption strengths associated with different dislocation structures [14] has indicated that the concentrations of potentially active sites are not sufficient to give the strength of absorption observed. Vacancies are a potential by-product of plastic deformation as interaction between the dislocations generated can produce jogged dislocation segments that can only move via non-conservation motion. Such motion requires the generation of trails of vacancies (or interstitials) and these can coalesce to form stable clusters in a process know as Ostwald ripening [15, 16]. Theoretical calculations indicate that sites at the surface of such clusters are capable of generating electronic states in the band gap of diamond that could generate optical absorption with a wavelength dependence consistent with that observed in brown diamond [17, 18]. Such open volumes within crystals can be probed experimentally using positron annihilation [19] and vacancy clusters consistent with the absence of around 60 carbon atoms have been observed in type IIa brown diamonds [20]. HPHT treatment to remove the brown colour has been shown to remove the signal associated with these vacancy clusters suggesting strongly that these are indeed the defects responsible for the colour.

1.2. Type IIa pink diamonds

Pink coloration in natural diamond, like brown, is usually associated with plastic deformation with the colour again concentrated in {111} planes (see for example [2]). The colour arises due to the presence of two broad absorption bands centred at about 390 and 550 nm [1, 21]. They can occur in both type I and type IIa diamonds with the colour tending to be weaker in type IIa stones. Whilst these bands usually occur together, examples have been found in Siberian diamonds [22] where only the 550 nm band is present and work in our own laboratory has found examples of South African pink diamonds also showing only this longer wavelength absorption band. The common association with plastic deformation for brown and pink means that absorption related to both can be found in the same stone, so samples with the pink absorption bands will often show an underlying continuously rising absorption. Brownish-pink and pinkish-brown colour grades are often encountered in certificates issued by gemmological laboratories, reflecting this overlap in the absorption characteristics. Pink diamonds are extremely rare naturally with occurrences tending to be confined to particular localities. The Argyle mine in Australia is a major producer of type I pink diamonds along with mines in South Africa and Siberia. The Williamson Mine in Tanzania has produced a number of type IIa pink diamonds. Good gemstone examples can command extremely high prices. Early studies to determine the origin of pink colour suggested the presence of unusual impurity atoms [23], but convincing evidence for this is lacking. The link with plastic deformation suggests the possibility that defects similar to those in brown diamond may be involved or that the modification of a pre-existing defect by the passage of a dislocation could be involved.

Pink diamonds show thermochromic (enhanced pink colour on heating) and photochromic behaviour, the latter leading to considerable distress on occasion when the colour of a pink stone is temporarily bleached by exposure to ultraviolet light. This study will provide some quantitative data on such photochromic effects.

1.3. Type IIb diamonds

One rare form of nitrogen-free (or more accurately low nitrogen) diamond is type IIb diamond. In addition to the absence of nitrogen, such stones contain small concentrations of substitutional boron. This boron generates an acceptor state 0.38 eV above the valence band and bound hole transitions at the centre produce a number of characteristic absorption bands in the mid-infrared region, the strongest of which is centred at 2802 cm^{-1}. The high energy tail of this absorption feature extends throughout the mid-infrared to near-infrared and visible regions of the spectrum, decreasing in strength with decreasing wavelength. The resultant enhanced absorption in the red region of the visible spectrum imparts a blue colour to such diamonds. Such diamonds are again extremely rare in nature with the Cullinan mine in South Africa (formally called Premier mine) being one of the world's main producers. The characteristic infrared absorption can be used to provide quantification of the concentration of uncompensated boron centres [24] and in natural type IIb stones this concentration is typically up to about one atomic part per million. It is well known from work on synthetic diamond that charge transfer can take place between the donor state of single-substitutional nitrogen (about 1.7 eV below the conduction band) and the boron acceptor state, thus compensating the latter defect and removing the absorption associated with the neutral charge state (see for example [25]). The wide band gap and the relative shallowness of the boron acceptor state make it a potential candidate for compensation by other deep donor states. Boron may therefore be present as a substitutional defect in diamonds of other types, but only be detectable in infrared absorption in samples identified as type IIb because of the absence of other defects that could cause compensation. High sensitivity photoluminescence measurements of type IIb diamonds in our own laboratory indicate that, in comparison with other diamond types, pure type IIb diamonds tend to show much lower levels of luminescence from impurity related defects. Type IIb diamonds can come in a range of colours varying from very pure blue through to more grey. This is almost certainly as a consequence of the same process as generates brown colour in type IIa diamonds. Plastic deformation produces vacancy clusters which on their own would produce a brown colour, but which in combination with the blue colour from the boron results in a grey colour.

1.4. HPHT treatment of type IIa and type IIb diamonds

The commercial application of HPHT treatment to diamonds is aimed at enhancing their value, so relatively low value stones with a brown colour component are chosen as starting material. Colour changes produced by HPHT treatment of type II diamonds generally involve the removal of the brown

**Table 1.** Colour changes on HPHT treatment of diamonds of different types.

	Diamond type			
	Type IIa	Type IIb	Type IaAB	Type IaB
Starting colour	Brown	Brown/grey	Brown	Brown
Colour after HPHT treatment at intermediate temperature	Pale brown or pink		Yellow/green	Near-colourless
Colour after HPHT treatment at high temperature	Colourless	Blue	Yellow/orange	Yellow

component and the resulting colours are dependent on the starting material and the treatment conditions employed. A summary of the colour changes is given in table 1. Brown type IIa diamonds will turn colourless after treatment at high temperatures (typically around 2500 °C) whilst at intermediate temperatures a reduction in brown and, in a small proportion of cases, an increase in pink is produced. Grey or brown type IIb diamonds, on removal of their brown component, are turned blue.

The experimental investigation presented in the following sections was aimed at determining the activation energy associated with the removal of the brown colour and the interaction of the defects responsible for the brown colour with those responsible for pink colour and with substitutional boron.

2. Experimental techniques

All the samples used in these experiments were natural diamonds and these were polished in the conventional manner to produce windows through which reliable absorption spectra could be acquired. A Perkin Elmer Lambda 9 UV/visible/NIR spectrophotometer was used to acquire absorption spectra from the near-infrared (typically around 1000 nm) through to the valence band to conduction band transition at 225 nm. The beam from the spectrometer is monochromated prior to interaction with the sample so this reduces any effects from the spectrometer light source when carrying out experiments on light induced changes. Only broad absorption features were under investigation so a relatively low resolution of 2 nm was used with a data spacing of 1 nm. Spectra were acquired with the sample at room temperature and mounted on an aperture (circular, 2 mm diameter) to define the sampling region. Photochromic changes were induced by exposing samples to light from a 100 W mercury arc lamp with the short wavelength cut-off being provided by a series of Schott glass filters. Short wavelength ultraviolet excitation (filtered 225 nm light) was provided by exposure in the DTC DiamondView instrument. Consistent positioning of the sample was ensured by keeping the sample on the mounting aperture throughout and samples were kept in the dark during transfer between the spectrometer and the excitation set-up. Infrared absorption spectra were acquired using a Nicolet Magna 750 FTIR spectrometer. Again samples were mounted on apertures to define the sampling region and for individual samples this was matched as closely as possible to the sampling region used for the UV/visible/NIR absorption spectroscopy. HPHT treatment of samples was carried out using high pressure presses belonging to Element Six Technologies.
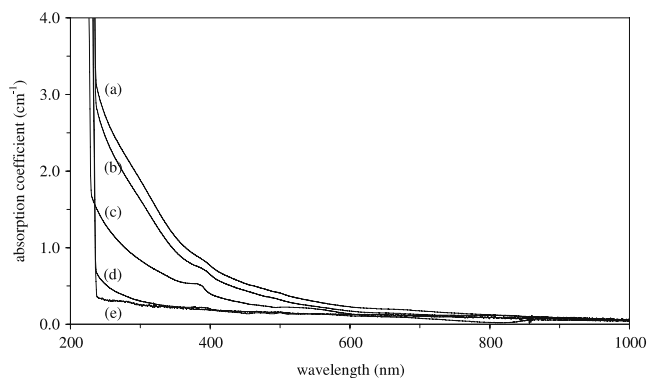

Figure 1. Room temperature UV/visible/NIR absorption spectra from a type IIa brown diamond (a) untreated and after HPHT treatment for 1 h at (b) 1858 °C, (c) 2082 °C, (d) 2300 °C and (e) 2500 °C.

3. Results

3.1. Isochronal annealing of type IIa brown diamond

Brown colour in type IIa diamonds is due to a continuously rising absorption extending from the near-infrared region to the indirect band gap at 225 nm. In order to accurately track the removal of such a broad absorption feature on HPHT treatment, various steps were taken to minimize effects that could introduce inaccuracies. Large samples were used to give as strong an absorption signal as is practically possible for such an experiment. These were also of benefit in reducing the relative effect of reflection losses compared with genuine absorption; all the spectra were corrected for reflection loss. Ideally identical regions of the sample would be analysed at each stage as brown diamonds are known to show inhomogeneous colour distribution. However, surface damage during HPHT treatment required re-polishing at each stage and this study also formed part of a joint investigation using positron annihilation that required two 0.5 mm thick plates to be removed after each anneal. These requirements were accommodated by starting with a particularly large sample (26 carats weight prior to polishing, largest linear dimension around 20 mm) and making the absorption measurements on the remaining block after removal of the plates. Reflection losses were corrected for and any effect from scattering losses at the surfaces was minimized by careful polishing of surfaces. The use of absorption coefficient values took account of the reduction in size of the sample during the course of the experiment.

Figure 1 shows the absorption spectra for the type IIa brown diamond after consecutive HPHT treatments for
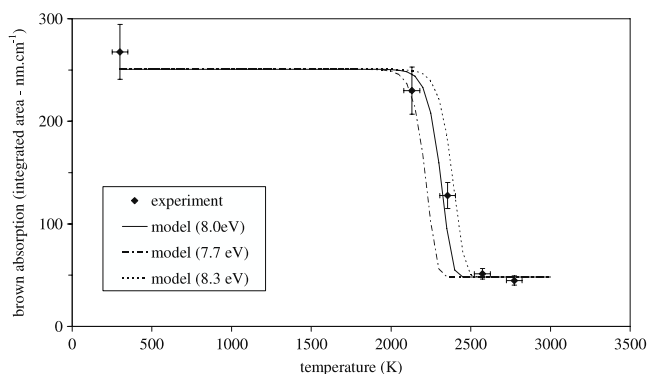
Figure 2. Integrated absorption associated with brown colour as a function of HPHT treatment temperature—experimental and modelled data for different activation energies.

1 h at the temperatures shown. Little change in the absorption spectrum is observed at 1858 °C but changes become significant at 2082 °C and the brown colour is completely removed at 2300–2500 °C. The shape of the absorption remains fairly consistent although a few subtle changes are evident. Between 1858 and 2082 °C there appears to be the removal of a relatively weak absorption band at around 300 nm resulting in a slight change in shape of the spectrum in this region. As the brown colour starts to anneal out, the two broad absorption bands associated with pink colour (390 and 550 nm) anneal in.

Quantification of the strength of the absorption was carried out by determining the integrated absorption between 250 and 450 nm, well away from any spectrometer induced artefacts. Any absorption from the 390 nm band was adjusted for by determining its integrated area (via the fitting of a quadratic baseline to the underlying absorption and an asymmetric function to the band) and subtracting it from the total integrated area. The data points so determined are plotted in figure 2.

This behaviour has then been modelled assuming a first-order decay process. Such first-order removal is frequently observed for the annealing out of defects in diamond, although the data obtained in this experiment, whilst entirely consistent with a first-order process, do not unambiguously show the process to be first order. The behaviour has been modelled

using the following dependence:

$$[X_n] = [X_{n-1}] \exp(-K_T t)$$

where $[X_n]$ and $[X_{n-1}]$ are the strengths of the brown absorption after the nth and $(n-1)$th anneals, t is the anneal time and K_T the rate constant, which is given by

$$K_T = A_0 \exp\left(-\frac{E_A}{k_B T}\right).$$

A_0 is the 'attempt to escape' frequency and is assumed to be the Raman frequency of diamond (=4 × 10^{13} Hz), k_B is Boltzmann's constant and E_A the activation energy associated with the removal of the brown colour. The data do not decrease to a zero value so a suitable offset has been incorporated into the model to allow for this. The solid line in figure 2 represents the best fit to the data and the two dashed lines show what the model data would look like 0.3 eV above and below this value. From this we derive an activation energy for the removal of the brown colour of 8.0 ± 0.3 eV.

### 3.2. Photochromic behaviour in pink diamonds

The data in figure 1 show the production of the broad absorption bands at 390 and 550 nm associated with pink colour in natural diamonds on HPHT treatment of a type IIa brown diamond. This effect is not universal, with only a small proportion of type IIa brown stones turning pink at these intermediate temperatures. This suggests that there are differences in the starting material presumably requiring some precursor of the defect giving the pink colour to be present for the bands to be generated. The bands are relatively weak in type IIa stones, so a systematic study of their behaviour was carried out on a type IaAB pink stone where they were strong and the key results checked for consistency with suitable type IIa stones.

Absorption spectra from the type IaAB pink diamond are shown in figure 3. The concentrations of aggregated nitrogen in the sample were determined from the infrared absorption spectrum by fitting the relevant absorption components in the single-phonon region (1500–800 cm^{-1}) and using the conversion factors given in the literature [26, 27]: $[N_A]$ = 7 ppm
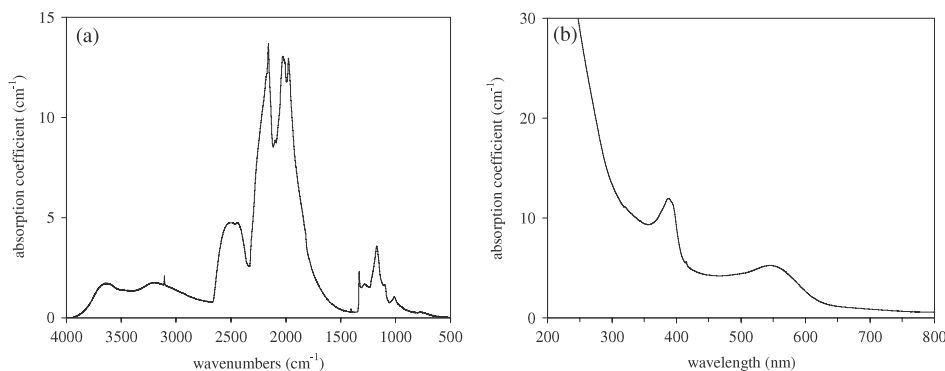

Figure 3. Absorption spectra from the type IaAB pink diamond used in the study of photochromic effects: (a) infrared region showing the nitrogen related absorption and absence of a platelet peak, (b) UV/visible/NIR region showing the dominant absorption bands typical of natural pink diamonds centred at 390 and 550 nm.
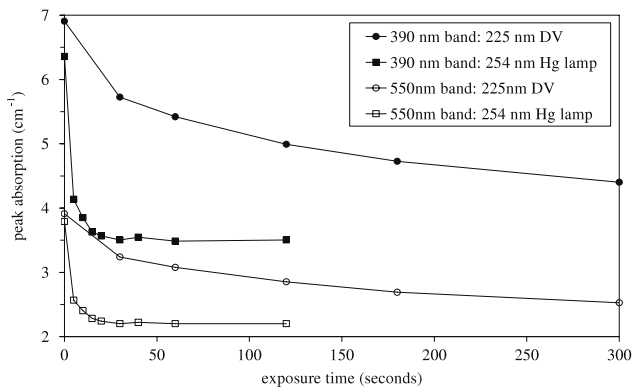
Figure 4. Peak intensity of the two absorption bands at 390 and 550 nm as a function of exposure to ultraviolet light from two different sources.
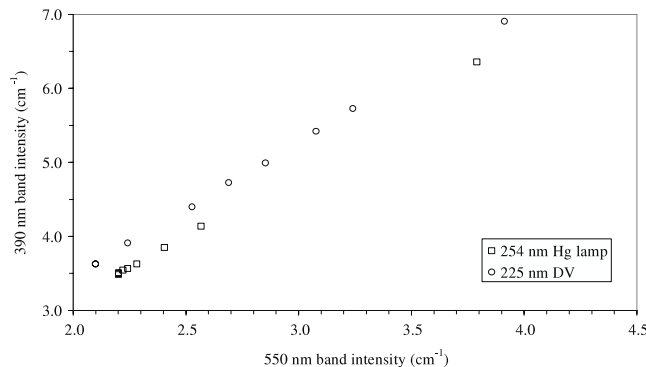

Figure 5. Correlation between the absorption intensities of the 390 and 550 nm bands under bleaching with ultraviolet light.

Figure 6. Effect of minimum excitation wavelength on the bleaching of the two absorption bands associated with pink colour (exposure time at each stage: 5 min).

and $[N_B] = 100$ ppm. No platelet peak is observed, so this diamond would be classified as irregular [28]. The 390 and 550 nm absorption bands are shown in figure 3(b).

3.2.1. Bleaching of pink colour—wavelength and time dependence.   It is possible to decrease the strength of the pink colour via exposure to ultraviolet light, although references to this effect in the literature are rare (see [21, p 141]). In the present study a comparison has been made between the time dependence of two readily available sources of ultraviolet light: 254 nm light from a 100 W mercury lamp (filtered) and 225 nm light from a DTC DiamondView™ instrument. The wavelength of the latter source corresponds to excitation from the valence to the conduction band so was thought to have the potential to produce different effects. The two absorption bands are not symmetric so they were fitted to an asymmetric function that best represented their shape without any consideration for the significance of the function chosen. Figure 4 shows the reduction of the two bands with increasing exposure time. The 254 nm excitation is shown to produce more rapid bleaching and this is likely to be due to the higher intensity of this source. The ultimate degrees of bleaching achieved are similar in the two cases. The two bands bleach out together and the plots of their intensities in figure 5 show that they are very well correlated. The offset in the values for the two different excitations is due either to a small error in the determination of the absorption values or to slightly different sampling positions in the two experiments.

The wavelength dependence of the bleaching was determined by exposing the sample for 5 min to the light from a 150 W xenon lamp and using a selection of Schott glass long pass filters to progressively decrease the short wavelength limit of the exciting light. The pink absorption bands were maximized at the start of the experiment by heating the sample to 800 °C for 4 h. Figure 6 shows the intensities of the pink bands as a function of the wavelength cut-off value. Significant bleaching of the bands is only observed once the excitation wavelength is reduced to between 475 and 420 nm. This corresponds reasonably well with the onset of absorption in the 390 nm band.
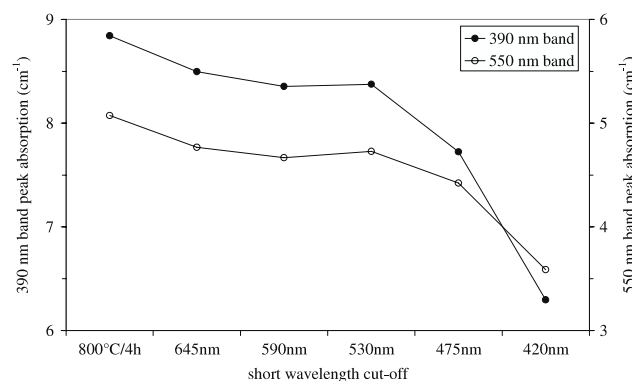
3.2.2. Restoration and enhancement of pink colour.   The restoration of the pink colour after bleaching was studied at room temperature with the sample kept in the dark. In reality the sample was kept mounted in the sample compartment of the spectrometer, so was constantly illuminated by light at the long wavelength limit of the scan used (in this case 1600 nm). Spectra were taken over the range 1600–200 nm every hour for the duration of the experiment, so the sample will have been briefly illuminated with light over this range during the scan (scan rate 120 nm min^{-1}). The spectra shown in figure 7 show the absorption of the sample initially, after bleaching with UV light and after 20 h in the dark. The bleached and dark restored spectra are virtually identical, with any change being indistinguishable from spectrometer drift. A similar experiment was then carried out but exposing the sample to the ambient lighting conditions in the laboratory (fluorescence tube lighting) between scans. Restoration of the pink bands under these conditions was much more rapid. Figure 8 shows the strength of the 550 nm absorption band as a function of time—the lifetime for the restoration determined from a single-component exponential fit was 95 min.

The excitation wavelength dependence for the restoration was determined using filtered excitation from a 100 W mercury lamp. Long pass Schott glass filters were used to set the short wavelength limit of the excitation and progressively shorter limits were selected. The changes to the 390 and 550 nm
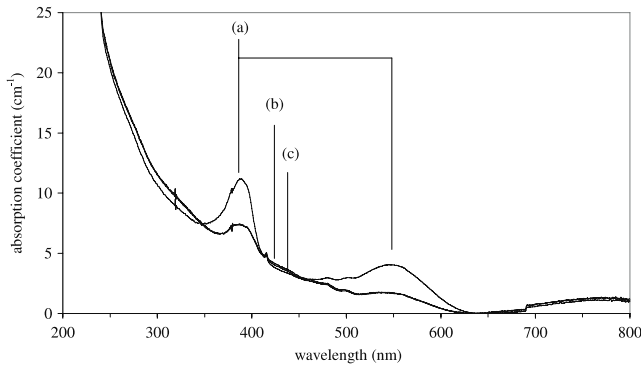
Figure 7. Room temperature UV/visible/NIR absorption spectra of a pink diamond (a) initially, (b) after bleaching with ultraviolet light and (c) after 20 h in the dark. Spectra (b) and (c) are indistinguishable from each other within the limits of the measurement.
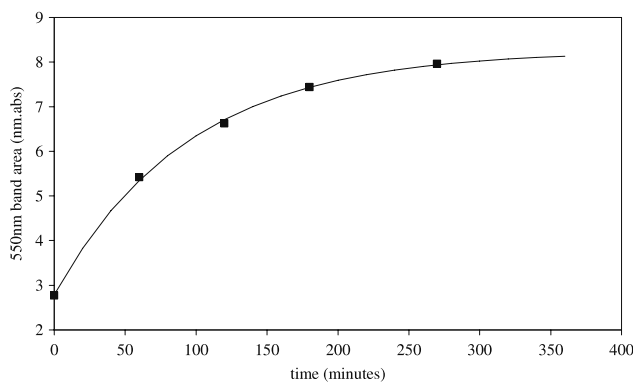

Figure 8. Increase in the area of the 550 nm band as a function of exposure time to ambient fluorescent room lighting. The line shows a single-component exponential fit corresponding to a lifetime of 95 min.
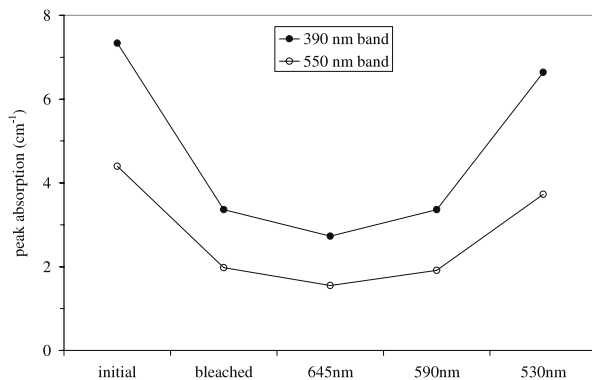

Figure 9. Wavelength dependence of the restoration of the two absorption bands at 390 and 550 nm. The wavelengths shown are the short wavelength limit of the filter used.

bands are shown in figure 9 after bleaching for 15 min with 254 nm light and successive 5 min exposures with the cut-off wavelengths shown. Increases in the pink bands only start to be observed for excitation wavelengths of around 590 nm and this increase becomes significant with the 530 nm cut-off filter with the bands almost being restored to their original values.
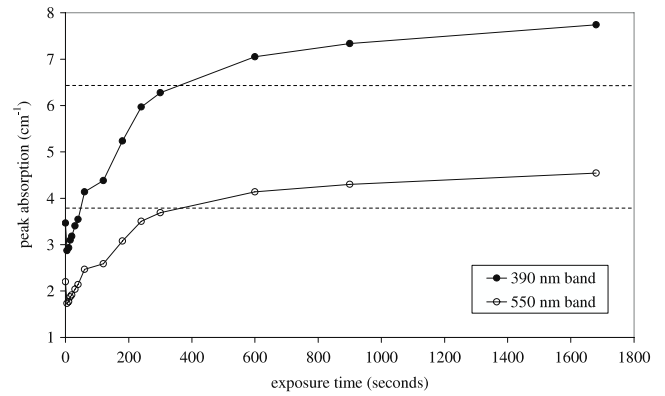

Figure 10. Time dependence of the restoration of the 390 and 550 nm bands for exposure to light of wavelength greater than or equal to 530 nm. The dashed and chain lines show the initial unbleached values of the absorption of the 390 and 550 nm bands, respectively.
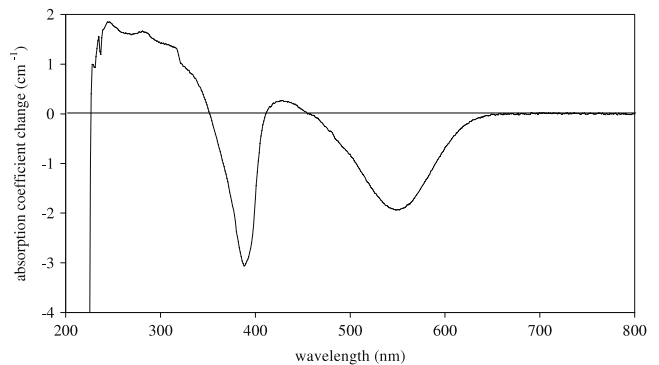
Figure 11. Change in absorption of a type IaAB pink diamond on exposure to 225 nm ultraviolet light for 20 min. The dominant change is a decrease in the broad bands at 390 and 550 nm and an increase in the underlying absorption associated with brown colour.

The time dependence for restoration under these excitation conditions (i.e. $\lambda \geqslant 530$ nm) is shown in figure 10. In general there is a steady increase in the absorption with increasing exposure time with the absorption strengths returning to their original values after about 5 min. Two features are worth noting. The first is the initial decrease in absorption beyond the saturation values obtained with 254 nm excitation after an exposure of 10 s. The second is the potential for enhancing the strength of the pink colour beyond the ambient level for exposures of more than 5 min. The values tend towards saturation, but are still slowly increasing after 28 minutes' exposure.

3.2.3. Spectral changes. Figure 7 showed the changes in the absorption spectrum on bleaching with ultraviolet light. In addition to the reduction in the broad bands at 390 and 550 nm there are changes elsewhere in the spectral range studied. Such relatively small changes are best illustrated using a difference spectrum. Figure 11 shows the absorption coefficient change over the range 800–200 nm when the sample was bleached using a 20 min exposure to 225 nm ultraviolet
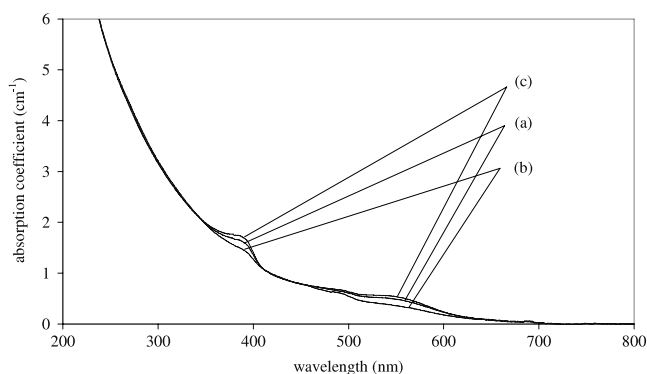
Figure 12. Absorption spectra of a type IIa pink/brown sample (a) initially, (b) after bleaching with 254 nm ultraviolet light and (c) after subsequent restoration with light of wavelength $\lambda \geqslant 530$ nm.

Figure 13. Changes in absorption from the spectra in figure 12; (a) bleached minus initial and (b) restored minus bleached.

light. The strong decreases in the 390 and 550 nm bands are the dominant features, but there is also an increase in the underlying absorption with the degree of change increasing to shorter wavelength. This underlying absorption is consistent with that associated with brown colour and suggests that as the absorption from the defects responsible for pink colour decreases there is a corresponding increase in absorption from defects responsible for brown colour. A decrease is also detected in two relatively sharp absorption lines at 236 and 230 nm. These two lines are the N9 centre whose strength correlates with the concentration of B centres [29]. The excitation used to bleach the pink bands appears to have an effect on the charge state of the defect responsible for the N9 absorption centre. It was noted in figure 3 that there was weak absorption from the N3 centre present in this sample. The N3 feature is not detected in the difference spectrum in figure 11 and appears unaffected by charge state changes induced by the ultraviolet light excitation used in this experiment.

3.2.4. Photochromic changes in pink type IIa diamonds. The results presented above are for a type IaAB diamond as this stone had particularly strong absorption features allowing a detailed systematic study of light induced changes. The two broad absorption bands are similar in terms of their positions and widths in type IIa pink stones. Bleaching and restoration conditions have been established for the type IaAB diamond and these were applied to a type IIa diamond to check consistency of behaviour. Figure 12 shows spectra for a type IIa diamond with the 390 and 550 nm absorption bands initially, after 5 min bleaching using 254 nm emission from a 100 W mercury lamp and after subsequent restoration and enhancement for 5 min using emission from a 100 W mercury lamp filtered to pass wavelengths longer than 530 nm.

The spectral changes are weak compared to those of the type IaAB diamond, but are more clearly illustrated in the difference spectra shown in figure 13. The changes are consistent with the type IaAB stone in that there is an anti-correlation between the strength of the pink bands and the underlying absorption associated with brown colour. The exact shape of the spectrum near the band edge deviates from
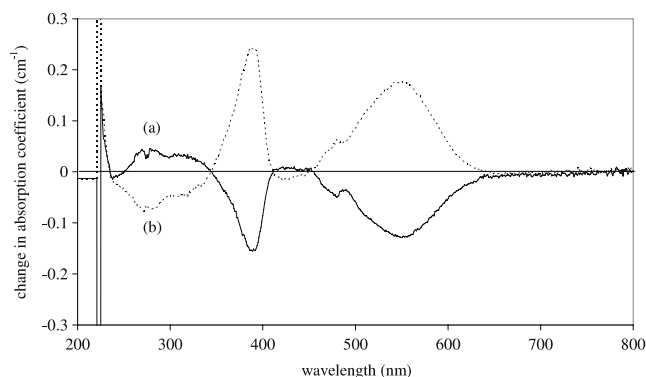
that associated with brown colour. This may be due to the presence of other defects whose charge states are varying, which are detected in this case due to the relative weakness of the pink and brown absorption features. This consistency between type IaAB and type IIa diamonds suggests that the same electronic states are involved in the transitions associated with the photochromic changes.

*3.3. HPHT treatment induced changes in type IIb diamonds*

HPHT treatment was carried out on type IIb diamonds with a variety of starting colours from brown to grey due to different proportions of boron related absorption and brown colour. Treatment conditions consistent with significant reduction in the brown colour in type IIa diamonds were used. Examples of the changes in room temperature absorption in the UV/visible/NIR and mid-infrared region are shown in figure 14 where the general changes on HPHT treatment are shown.

As for type IIa diamonds, there is a decrease in the continuously rising absorption associated with brown colour, with the strongest effects being at shorter wavelengths. There is also an increase in the absorption associated with neutral boron as shown by the increase in the absorption band at 2802 cm^{-1} and other related features. The concentration of neutral boron ([B$_0$]) can be determined from the integrated area of the 2802 cm^{-1} band (I_{2802}) using the relationship given in [24], i.e.

$$[B_0] \text{ (ppm)} = (5.53 \times 10^{-4}) \times I_{2802} \text{ (cm}^{-2}\text{)}.$$

The strength of the absorption related to the brown colour was estimated from the absorption coefficient value at the intersection of the continuously rising absorption with the indirect band gap at 225 nm. These values will be influenced by the tail of the absorption from the neutral boron, but this will be relatively weak at 225 nm. A plot of the change in neutral boron concentration as a function of brown reduction is given in figure 15. It can be seen that there is a correlation between the increase in neutral boron concentration and the decrease in the absorption related to brown colour. There is significant scatter in the data, the most likely cause being errors in determination of the reduction in the brown absorption,
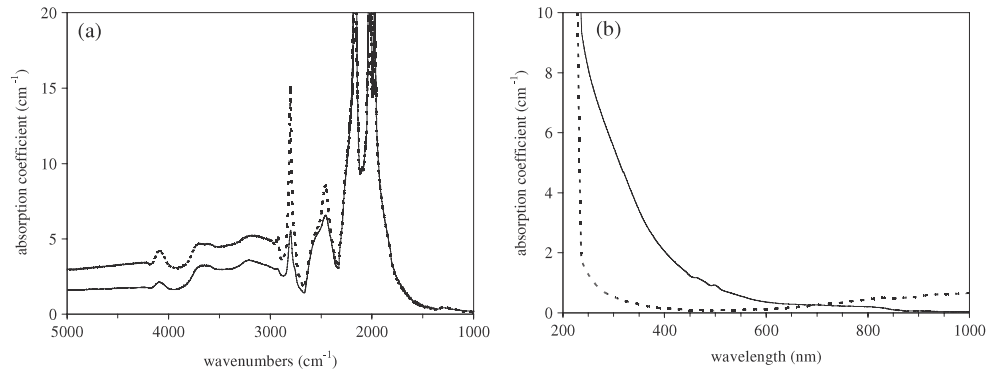
Figure 14. Room temperature absorption spectra of a type IIb diamond before (solid line) and after (dashed line) HPHT treatment at 2500 °C for 1 h; (a) infrared region and (b) UV/visible/NIR region.
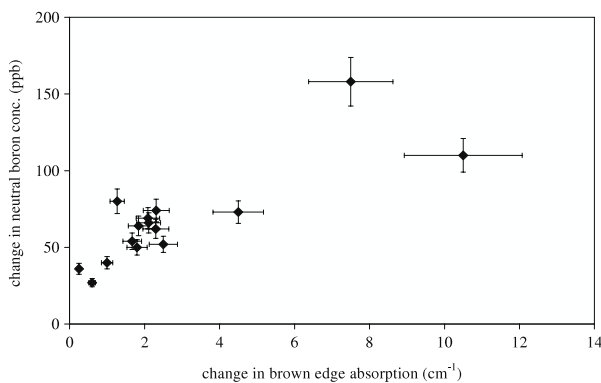

Figure 15. Plot to show the correlation between the change in the neutral boron concentration and the reduction in the edge absorption associated with brown colour.

but the general trend is visible. It therefore appears that a proportion of the substitutional boron present initially in brown and grey type IIb diamonds is converted into its negative charge state via electron transfer from the defect producing the brown colour. On HPHT treatment the reduction in the number of defects causing brown colour leads to less charge transfer and a corresponding increase in the concentration of neutral substitutional boron defects. It can also be seen that the data points in figure 15 suggest a trend that intercepts the ordinate axis at a non-zero value, indicating an increase in the neutral boron concentration not related to the reduction in brown colour. This highlights one of the significant difficulties associated with working with natural diamond. Whilst ideally for this analysis one would work with a simple two-component system (substitutional boron and the defect causing brown colour), natural diamonds typically contain many other defect centres, the influence of which can become significant when the defects of interest are only present at very low concentrations. Neutral boron produces a relatively shallow acceptor level and could thus be compensated by a wide range of defects and if the latter are removed or modified on HPHT treatment this would also give an increase in the neutral boron concentration. Variation between samples in the concentration of these additional defects would have the effect of introducing the non-zero intercept observed but also

the effect of producing additional scatter in the data. If the additional centres are less thermally stable than the defects causing the brown colour, then their effect could be removed by a relatively low temperature anneal and the resultant sample then used as the starting point for the HPHT treatment, but such pre-annealing was not carried out in this case. We also cannot rule out the possibility that boron exists initially in a complex with other intrinsic or extrinsic impurities and the complex is broken down by the HPHT treatment to yield single-substitutional boron and that any correlation with the brown colour removal is accidental. Allowing for these difficulties, the data still suggest that the proposed electronic donor states associated with the brown colour are consistent with these experimental observations in that the neutral boron shows an increase as the absorption causing the brown colour decreases and that a proportion of this change could be related to charge transfer between the electronic states of these defects.

4. Discussion

The currently favoured model for the defect associated with brown colour in diamond is the vacancy cluster. Theoretical calculations have shown that this produces an array of partially filled electronic states about 1 eV above the valence band and that transitions between these states and the valence and conduction bands can account for the absorption characteristics observed. Experimental work has been aimed at confirming the structure of the defect. The study presented here has allowed a determination of the activation energy associated with the removal of the absorption causing the brown colour, a value of 8.0 ± 0.3 eV. The value is broadly consistent with expectations for a vacancy cluster. The breakdown of this defect would involve the breaking of carbon bonds at the internal surface of the void in a process similar to graphitization. Activation energies associated with graphitization were determined by Davies and Evans [30] who found that these varied with surface orientation, dependent on the number of carbon–carbon bonds that had to be broken. Activation energies of 7.5 and 11.0 eV for {110} and {111} surfaces respectively were determined and these are similar to the value determined for the brown colour. Work has been carried out correlating the absorption properties with vacancy cluster defects detected using positron
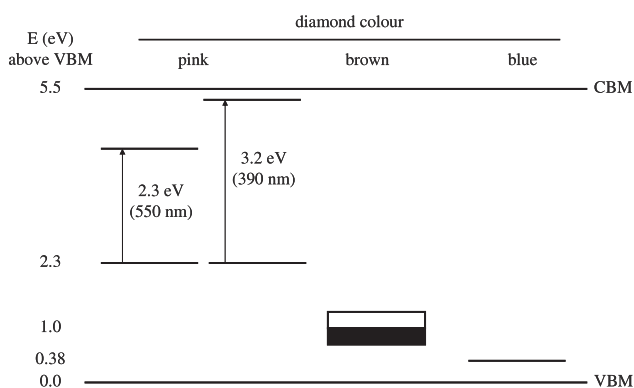
Figure 16. Schematic representation of the electronic states associated with the defects producing pink, brown and blue colours in type II diamonds. VBM: valence band maximum, CBM: conduction band minimum.

annihilation and this will be published elsewhere [31]. The activation energy determined suggests that brown diamonds are likely to have had their colour generated late in their history. Early deformation followed by residence in the Earth's mantle at a temperature of around 1200 °C would result in a 99% reduction in the brown colour in several million years, a time period significantly shorter than typical mantle residence times of 1–3 billion years [32]. Such a process appears to have occurred in type IIa colourless diamonds as these show remnants of the plastic deformation in the form of polygonized networks of dislocations. The observed changes in absorption properties are difficult to relate to the details of the changes in the structures of the defects. Large clusters are likely to anneal out gradually via the release of individual vacancies. In absorption we effectively measure the decrease in the concentration of the active sites for absorption. What we do not know is whether these active sites remain active as the size of the cluster decreases or whether all sites for a particular cluster are removed as the defect decreases below some critical size. An improved understanding of the precise mechanism for the removal of the vacancy clusters would allow a more accurate assessment of the means by which the optical absorption is decreased, but experimentally this would probably involve not just detection of the clusters, but also determination of their surface structures—an analysis beyond current capability.

The work on the behaviour of the pink centres and the type IIb diamonds in combination with the electronic states determined theoretically for the vacancy clusters and the known acceptor state of boron allows an energy level scheme to be proposed that accounts for the observations. This is shown in figure 16.

The two broad bands in pink diamonds at 390 and 550 nm correspond to transition energies of 3.2 and 2.3 eV respectively. Both of these absorption features show correlated behaviour in the photochromic experiments carried out so they either share a common ground state or have ground states that are close to each other. The latter seems more likely as we do see a variation in the relative intensities of the two bands within individual samples and between samples. Both centres are efficiently bleached by excitation with ultraviolet light

of wavelength less than 420 nm. Assuming the bleaching corresponds to excitation of electrons from the ground state to the conduction band, this would place the ground state towards the middle of the band gap around 3 eV below the conduction band. The excited state associated with the 390 nm band must therefore lie very close to the conduction band. For the bleaching to be sustained, the electron excited into the conduction band must be trapped. The state associated with the vacancy clusters 1 eV above the valence band can trap these electrons and this is consistent with the observation that the pink absorption bands decrease as the underlying absorption causing brown increases, and vice versa. The restoration of the pink colour is extremely slow in the dark with no detectable change being observed after 20 h. This process was enhanced by visible light excitation, with changes becoming significant for wavelengths down to 530 nm (2.3 eV). Clearly this energy is insufficient to excite the electron at the state 1 eV above the valence band up to the conduction band. An electron could, however, be excited from the valence band into the ground state levels associated with the pink bands with the hole left in the valence band then being filled by an electron from the 1 eV state. Thus the model can account for the wavelength dependence of the light induced changes in samples containing defects associated with both pink and brown colours. The 'equilibrium' colour of such a diamond will depend on the relative occupancy of the states associated with the two colours and will be dependent upon the ambient lighting conditions. Any significant deviation from white light illumination will affect the observed colour (increased ultraviolet giving weaker pink and stronger brown; increased red light giving the opposite effect) and several minutes under a white light source should be sufficient to return the stone to its ambient condition.

For type IIb diamonds with a brown component to the colour, the presence of a state 1 eV above the valence band provides a suitable donor state for interacting with the boron acceptor state 0.38 eV above the valence band. Removal of the vacancy clusters via HPHT treatment thus gives the observed increase in neutral boron and this combined with the removal of the brown colour results in a colour change from grey or brown to blue. The long-lived photochromic changes observed in pink diamonds are not observed in this case as, at room temperature, the relative shallowness of the boron acceptor state means that any light induced charge redistribution is short-lived.

5. Conclusions

Systematic absorption spectroscopy studies have allowed current models for defects associated with brown and pink colour in diamond to be investigated. An activation energy for the removal of brown of 8.0 ± 0.3 eV has been determined and this is consistent with expectations for the annealing out of vacancy clusters. The theoretically determined electronic states for these clusters fit with observations on diamonds with both brown and pink colour diamonds and a model has been proposed for the states associated with the pink colour that is consistent with light induced absorption changes. Evidence for the compensation of substitutional boron by charge transfer from vacancy clusters has been presented.

Acknowledgments

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