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Brown diamonds and HPHT treatment

David Fisher

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

A significant proportion of gem quality natural diamonds have a brown component to their colour. Whilst a number of different defect centres can give rise to a brown hue, the main process associated with the generation of brown colour is plastic deformation. Not all plastically deformed diamonds are brown, however, and, in spite of many years of speculation about and investigation into this problem, the specific defects associated with the brown colour have until recently remained a mystery.

The need to gain better understanding of this phenomenon has been given added impetus by the discovery that high pressure high tempertaure (HPHT) treatment can be applied to remove the brown colour in diamonds. In addition to the scientific understanding systematic studies of such treatment can provide, there is also a strong commercial incentive to carry out such treatment on relatively low value brown stones to improve their colour and increase their value. Work in this area at the DTC Research Centre forms part of the Consumer Confidence Technical Research programme. This aims to provide reliable techniques for the identification of such treatments that can be used in gemmological laboratories as a means of maintaining consumer confidence in natural diamonds.

This presentation will review the progress made in gaining a fundamental understanding of the cause of brown colour and how this knowledge is being applied to the identification of HPHT treated stones in gemmological laboratories.

Origin of brown colour



Figure 1 Type I brown diamond (a) transmission and (b) between crossed polarisers.

Brown colour can be present in both type II and type I diamonds. Its presence in type II diamonds indicates that nitrogen is unlikely to be a major component in the defect responsible for the absorption. As Figure 1



illustrates, if viewed in the correct orientation, the brown colour can be seen to be concentrated in socalled slip-bands and a clear link with plastic deformation is evident.

Whilst plastic deformation is necessary to produce such brown colouration, not all plastically deformed diamonds are brown. The DiamondView image (short wave uv excited luminescence) of a colorless type IIa diamond (Figure 2) shows blue luminescing dislocations in polygonised networks, indicative of plastic deformation at some point in the diamond's history followed by a period of annealing during which dislocations have undergone glide and climb to arrange into a lower energy network configuration.



Figure 2 DiamondView image of a type IIa colourless diamond.

Dislocations

Such observations on brown diamonds led to the suggestion that dislocations may be directly responsible for the absorption states associated with brown colour. TEM imaging of the dislocation arrangements in brown and colourless type IIa diamonds showed significant differences which suggested that different dislocation configurations could give rise to brown colour. However, imaging of an originally brown diamond after HPHT treatment to turn it colourless showed similar configurations to the original brown diamond (Willems, 2006). Any effect associated with the absorption could therefore only be on a smaller scale, i.e. associated with the bonding configuration at the dislocation core. Electron energy loss spectroscopy (EELS) was also used to try to probe gap states specific to individual dislocations (Kolodzie, 2003), but proved inconclusive. Theoretical calculations of the electronic states associated with different dislocation core structures showed that it is possible to produce absorption at dislocations, but that limited specific core structures were required (Fall et al., 2002) and that the dislocation concentrations typical of natural diamond are not high enough to account for the strength of the observed absorption.

Vacancy clusters

A clue as to the defect responsible for brown colour is provided by results on HPHT treatment of type I diamonds. Figure 3 shows such a diamond before and after HPHT treament. It can be seen that the distribution of the final yellow colour follows closely that of the original brown colour. The yellow colour is due to absorption at the H3 centre, associated with a nitrogen-vacancy-nitrogen defect. This defect has been formed via the combination of a vacancy with an Acentre (substitutional nitrogen pair) and the distribution of the H3 absorption suggests that significant numbers of vacancies have been generated in the brown areas on Dislocation motion can, under HPHT treatment. certain circumstances, result in the release of vacancies, but an alternative is that vacancy clusters are present in the brown regions and these break up at higher temperatures to release individual vacancies.



Figure 3 Type Ia diamond (a) before and (b) after HPHT treatment.

Such vacancy clusters could therefore be responsible for the brown colour and the link with plastic deformation is retained as, during deformation dislocation interactions can generate vacancies which would then form clusters via the process of Oswald ripening. Theoretical calculations support the idea that such vacancy clusters could be responsible for the brown colour as the bonding configurations at the surface of the cluster give rise to suitable electronic states in the band gap (Hounsome et al., 2006).

Such clusters are, however, difficult to analyse experimentally, being too small to be routinely imaged in TEM. Positron annihilation can be used to investigate such defects via the increase in the positron lifetime when open volumes are present in the sample. This technique has been used to investigate individual vacancies and larger vacancy clusters in diamond and results suggest that brown type IIa diamonds do have clusters equivalent to a few tens of vacancies in them and that these are absent in colourless diamonds (Avalos and Dannefaer, 2003). We have been working on an experiment attempting to link the clusters detected via positron annihilation and the gradual remdyal of brown colour on HPHT treatment.



The analysis carried out to date suggests strongly that brown colour in diamonds is associated with absorption from vacancy clusters.

HPHT treatment

It is possible to remove the brown component of a diamond's colour by annealing at high temperatures under a stabilising pressure to prevent graphitisation. Commercial exploitation of this technique first emerged in 1999 with the activities of General Electric and a number of companies now offer HPHT treated stones or a service to carry out the treatment on clients' stones.

contains nitrogen	no (or v. low)		yes
diamond type	lla	llb	la
starting colour	brown	brown/grey	brown
final colour	colourless	blue	yellow/green
	pink		fancy yellow

Figure 4 Table of colour changes induced by HPHT treament.

The colour of diamond produced at the end of such treatment is dependent on diamond type and treatment condition as summarised in Figure 4. Type IIa diamonds can be turned colourless or in some cases pink, whilst the boron in type IIb diamonds allows blue stones to be produced after removal of the brown component. Colour changes in type I diamonds are dominated by nitrogen-containing defects, with yellow colours being produced: yellow-green from H3 absorption at intermediate conditions, yellow to yellow-orange at higher temperatures from generation of N3 centres and single nitrogen. Type IaB stones represent an exception to this general trend for nitrogen containing diamonds, where it has been possible to produce near-colourless stones via HPHT treatment due to the enhanced thermal stability of the B-centre over the A-centre.

HPHT treatment - detection

Detection of HPHT treatment relies upon a careful comparison of the characteristics of HPHT treated stones with those of untreated natural diamonds of similar colour and type. The research at the DTC has provided vital input to the establishment of reliable detection techniques via the analysis of known natural benchmark samples from the DTC intake and systematic treatment experiments exploring the range of possible treatment conditions and starting material.

Detection in the case of type I stones is generally carried out using absorption spectroscopy. The combination of nitrogen-related absorption centres present in HPHT treated stones is unlike that usually encountered in untreated stones and, in cases where these characteristics prove inconclusive, it is possible to combine these observations with characteristics not directly influencing the colour in order to arrive at a reliable decision.

One useful characteristic is the platelet related infrared absorption peak. Platelets are layers of interstitial carbon atoms generated as a biproduct of nitrogen aggregation (Woods, 1986). The peak is generally asymmetric and its position has been found to be related to the size of the platelets (Clackson et al., 1990). Figure 5 shows the results of a comparison of the fit parameters for platelet peaks from untreated and HPHT treated type I yellow-green samples. It can be seen that for a given peak centre position the width of the platelet peak is broader for the HPHT treated samples, indicative of a wider distribution of platelet sizes. Such analysis can provide a useful indication as to whether a stone has been treated, although some care must be exercised as cases of untreated stones have been found that lie in the *treated* region. Generally a number of techniques must be combined to provide reliable identification of a stone.



Figure 5 Plot of platelet peak width as a function of position for untreated and HPHT treated type I yellow/green diamonds.

In the case of type II stones, detection is complicated by the fact that such stones are inherently low in impurities and therefore requires more sensitive techniques. Laser excited photoluminescence spectroscopy is a vital tool in the identification of such treatment and is used to analyse impurities at the parts per billion level in order to assess subtle differences that exist between the impurity contents of untreated and HPHT treated type II stones. Such analysis was, until recently, beyond the scope of most gemmological laboratories, but in response to this challenge a number of the major laboratories now have the capability to apply this technique to the reliable identification of HPHT treated stones. A number of criteria are in use and often a combination of features is used to arrive at a decision on a particular stone. In some cases it is not simply the presence or absence of a feature that determines whether the stone has been treated, but the charge state of the defect as indicated in work on the nitrogen-vacancy centre (Fisher and Spits, 2000).

Conclusions

This review highlights the important role that a good understanding of the fundamental properties of diamond plays in assisting in the development of reliable identification criteria for treated stones. Whilst much can be achieved using a purely empirical



approach, the fundamental understanding allows detection criteria to be assessed for robustness to future developments. Maintenance of consumer confidence in the area of HPHT treatment of type II diamonds has been extremely important. The proportion of type II stones increases with both the size and the colour of the diamond and so the reputation of some of the world's most value diamonds could be called into question without the robust and reliable means of identification that are now in place.

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