SYNTHETICS AND SIMULANTS

CVD Synthetic Diamonds Identified in a Parcel of Light Brown Melee



Figure 17: These six 2.5-mm-diameter CVD synthetic diamonds were found in a parcel of more than 1,000 light brown diamonds. Photo by T. Hainschwang.

The Liechtenstein branch of GGTL Laboratories received a parcel of more than 1,000 melee-sized (1.2–3 mm diameter) light brown diamonds for authenticity and treatment identification (part of the lab's fancy-colour diamond screening services). Their depth of colour was below that required to be called 'Fancy'.

As per the lab's common procedure, the parcel was tested with the prototype of GGTL's Mega-DFI fluorescence microscopy and spectroscopy system. The vast majority of the samples showed the expected luminescence reactions, with the exception of seven diamonds (2.5 mm diameter) that showed distinct orange fluorescence. The PL spectra of these samples, which the DFI system records simultaneously during visual observation, revealed that six of the seven were synthetic diamonds grown by chemical vapour deposition (CVD; Figure 17). Between crossed polarisers the synthetics showed obvious brush-like extinction (e.g. Figure 18), which is characteristic for CVD products but sometimes resembles the extinction patterns seen in natural type IIa brown diamonds.

The room-temperature UV-excited PL spectra recorded with the DFI system for all seven samples revealed the presence of the NV⁰ centre, which is characterised by a zero-phonon line at 575 nm and vibronic sidebands extending into the red part of the spectrum, which causes orange to reddish orange fluorescence (Figure 19a). Such UV-excited PL dominated by the NV⁰ centre is very rare in natural brown diamonds since it is only found in type Ib samples. Brown does occur in type Ib diamonds, although it is the rarest colour for this type (Hainschwang *et al.* 2013).

Using the seven different fluorescence excitations of the DFI system for visual and spectral analysis, we confirmed that the six samples were as-grown CVD synthetic diamonds and the one additional diamond was a natural type Ib stone. The fluorescence pattern of the synthetics revealed the characteristic CVD layer-by-layer growth and associated dislocations, while the natural diamond exhibited deformation-related green PL from the H3 centre together with the orange NV⁰ luminescence.

When excited by the 405 nm laser, the luminescence of all seven samples was a distinct green (e.g. Figure 19b), a phenomenon known in both natural type Ib and CVD synthetic diamonds. In natural diamonds the 405 nm laser excites the H3 centre more strongly than the NV⁰ centre, while in as-grown CVD synthetics the laser excites the 467.6 nm centre more strongly than the NV⁰ centre; both the H3 and the 467.6 nm centres result in green fluorescence. The room-temperature PL spectra recorded for the seven diamonds confirmed these respective centres were responsible for the green luminescence.

Infrared spectroscopy identified the six CVD synthetic diamonds as type IIa and the natural diamond as pure type Ib. The latter displayed a very distinct 'amber centre' absorption at 4110 cm⁻¹. The IR spectra of the other samples exhibited several features characteristic for CVD synthetic diamonds, such as lines at 7362, 6856, 6424, 5566 and 3123 cm⁻¹.

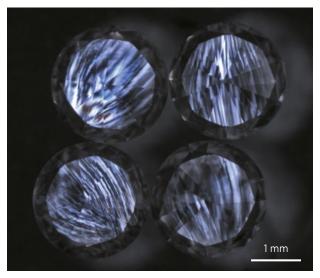
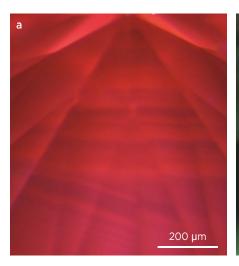


Figure 18: Some of the CVD synthetics are shown here between crossed polarising filters (and immersed in alcohol) to reveal their distinct brush-like extinction patterns. Photo by T. Hainschwang.



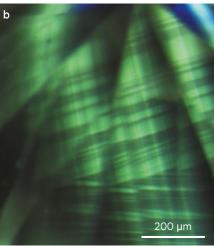


Figure 19: (a) Under all of the UV excitations of GGTL's DFI system, the CVD synthetic diamonds generally fluoresce a distinct orange due to the presence of the NV⁰ centre, while also revealing their growth layers under some specific excitations of shorter wavelength. (b) Under 405 nm (in the visible range) laser excitation, the CVD synthetic diamonds fluoresce green from the 467.6 nm centre and show even more distinct growth layers. Both images were taken from the same sample. Photomicrographs by T. Hainschwang.

High-resolution, low-temperature PL spectroscopy using 360, 402, 473 and 532 nm laser excitations on a GGTL Photoluminator research PL system confirmed the findings made by DFI testing. The CVD samples all exhibited very similar spectra, with a series of defects characteristic for CVD synthetic diamonds, such as the 388.8 nm, 467.6 nm, NV⁰ and Si-V⁻ centres. In addition to these, numerous sharp PL peaks were measured, particularly in the spectra recorded using the 360 nm laser (Figure 20). The vast majority of those are, in the author's experience, unique to CVD synthetic diamond, even though their causes are generally unknown.

The evaluation of melee-sized fancy-colour diamonds for their authenticity and colour origin is a specialised task that requires a combination of extensive diamond-testing experience and instrumentation created specifically for this type of screening. Until now, the mixing of synthetics (and colour-treated diamonds) into melee-sized parcels has almost exclusively been restricted to yellow to orange diamonds. However, the present case confirms rumours that untreated brownish CVD synthetics are now being mixed into parcels of natural brown diamonds, thereby eliminating the need for HPHT treatment of as-grown CVD material to render it near-colourless to colourless.

After preparing the first draft of this article, we received several parcels of brown and pinkish brown diamonds from various sources totalling more than 20,000 pieces,

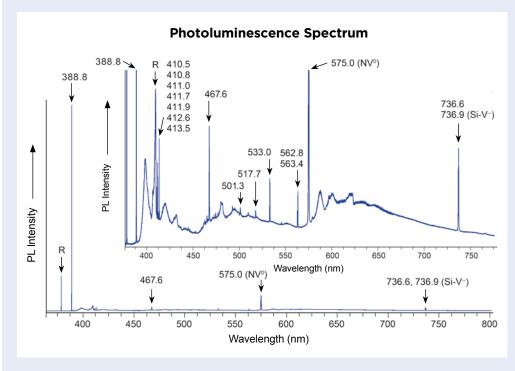


Figure 20: This PL spectrum, recorded for one of the CVD samples using 360 nm laser excitation, shows characteristic features for as-grown (that is, untreated) CVD synthetic diamond The spectrum displays numerous very sharp peaks, and the most intense ones include the 388.8 nm, 467.6 nm, NV⁰ and Si-V⁻ centres. The inset includes all spectral details, while the general spectral view shows the dominance of the very narrow 388.8 nm peak compared to the other PL emissions. R = Raman line.

and in these we detected more than 200 CVD synthetic diamonds, all with properties very similar to the ones described here. This provides further evidence that the contamination of brown melee parcels with CVD synthetics seems to have become a significant problem.

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Reference

Hainschwang, T., Fritsch, E., Notari, F., Rondeau, B. & Katrusha, A. 2013. The origin of color in natural C center bearing diamonds. *Diamond and Related Materials*, **39**, 27–40, https://doi.org/10.1016/j. diamond.2013.07.007.