The First Undisclosed Colourless CVD Synthetic Diamond Discovered in a Parcel of Natural Melee-Sized Diamonds

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During the March 2015 Diamond Show in Basel, Switzerland, a parcel of 6,000 melee-sized colourless diamonds was analysed using the GGTL Diamond Fluorescence Imaging (DFI) Laser+ fluorescence imaging and spectroscopy system. From the entire parcel, one sample stood out clearly with unusual fluorescence colours and distribution, combined with a photoluminescence spectrum that clearly indicated it was a synthetic diamond grown by chemical vapour deposition (CVD).

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Introduction

With the introduction of near-colourless, single-crystal, gem-quality CVD synthetic diamond into the market in recent years, and the enormous progress made in the growth of near-colourless synthetic diamond produced by high-pressure, high-temperature (HPHT) synthesis in the past two years, the gem industry has been very concerned about these synthetics being sold without proper disclosure. One of the main concerns is the mixing of near-colourless melee-sized synthetics into parcels of natural diamond, but so far this has not been confirmed despite many rumours within the trade. The only scientific reports of undeclared melee-sized synthetics detected in parcels of natural diamonds have been HPHT-grown yellow samples (Kitawaki et al., 2008; Hainschwang and Notari, 2012), and recently a single CVD-grown yellow synthetic diamond (Hainschwang, 2014). Until now, near-colourless CVD synthetic diamonds submitted to laboratories were in larger sizes. Since they are straightforward to identify by a well-equipped lab, they have not caused major concern within the trade.

The efficient testing of melee-sized diamonds is a highly specialized task and requires a lot of expertise and specially adapted analytical methods, particularly for fancy-colour diamonds. GGTL Laboratories is one of the few facilities with the expertise and equipment to test large amounts of colourless and fancy-colour melee diamonds for the watch and jewellery industry. After several years of testing such parcels (with several million pieces analysed), GGTL Laboratories recently found the first undisclosed melee-sized colourless CVD synthetic diamond in a parcel of natural diamonds (Hainschwang and Notari, 2015). This article describes the properties of this specimen.

Materials and Methods

A parcel of 6,000 diamonds, each measuring 1.6 mm in diameter, was analysed by GGTL Laboratories during the Diamond Show in Basel in March 2015. The parcel had been purchased

Figure 1: This 1.6-mm-diameter, F-colour, IF-clarity CVD synthetic diamond was found in a parcel of natural melee (left; photo by T. Hainschwang). Its lamellar appearance between crossed polarizing filters (here, shown immersed in methylene iodide) is typical of CVD synthetic diamond (right; photo by F. Notari).

in Mumbai, India, and consisted of high-quality melee (mainly E-F-G colour and IF to VS clarity).

The distinction of natural and synthetic diamonds and imitations with the GGTL DFI Laser+ system is non-automated but very efficient, based on the observation of luminescence colour, distribution and intensity under various excitations, combined with the simultaneous analysis of the photoluminescence (PL) and Raman spectra of the diamonds. The GGTL DFI system uses a suitably filtered 300 W full-spectrum xenon lamp to give six different broadband excitations in the range of 230–420 nm, plus a 250 mW 405 nm laser. Room-temperature PL spectra are collected during luminescence imaging by a single-channel spectrometer (1.5 nm resolution) using a thermoelectrically cooled CCD detector.

The internal features and strain pattern in the synthetic diamond were visualized using a Leica M165C trinocular microscope, equipped with a Leica DFC420 CCD camera with a resolution of 5 megapixels; the strain pattern was observed with the sample immersed in methylene iodide between crossed polarizing filters. Luminescence was observed under 254 nm short-wave (SW) and 365 nm long-wave (LW) UV radiation from a 6 W lamp (model UVP UVSL-26P), and also under broadband UV from the GGTL DFI system using the three different excitations that made the sample luminesce distinctly: 250–350 nm (SW/LW band), 300–410 nm (LW band 1) and 355–375 nm (LW band 2). Luminescence images were acquired with a Leica DFC450 C CCD camera with a resolution of 5 megapixels and the CCD sensor thermoelectrically cooled with a delta of −20°C compared to the surrounding temperature.

The infrared spectra of the sample were recorded with a resolution of 4 cm^{-1} on a PerkinElmer Spectrum 100S Fourier-transform infrared (FTIR) spectrometer equipped with a thermoelectrically cooled DTGS detector. The beam was transmitted through the diamond using a diffuse reflectance accessory as a beam condenser, over a range of 8500–400 cm^{-1}, with 500 scans.

PL spectra were recorded with the GGTL PL-7 system using 405, 473, 532, 635 and 785 nm laser excitations, and a high-resolution echelle spectrograph by Catalina Scientific equipped with an Andor Neo sCMOS camera (resolution of 5 megapixels) that was thermoelectrically cooled to −30°C. The system was set up to record spectra in the range of 350–1150 nm with an average resolution of 0.04 nm. All of these PL spectra were recorded with the sample cooled to 77 K by direct immersion in liquid nitrogen.

Results and Discussion

Gemmological Properties and Initial Detection

The CVD synthetic diamond (Figure 1, left) was detected by its uncommon 'greenish' orange to pink to purple luminescence under the intense broadband UV excitations of the fluorescence imaging system (Figure 2) combined with relatively strong emission from the Si centre, together with distinct luminescence from the NV^0 and 467.7 nm centres (Figure 3). The sample showed no visible luminescence under the standard LW and SW UV lamp.

This CVD synthetic diamond weighed 0.015 ct and was graded F colour and IF clarity (Figure 1, left). Between crossed polarizing filters, in certain orientations it exhibited distinct grey-to-black lamellar extinction, typical for CVD synthetic diamond (Figure 1, right). However, in some orientations the appearance could be confused

Figure 2: The luminescence exhibited by the 1.6-mm-diameter sample under three different broadband UV excitations is highly unusual for a colourless diamond. The 'greenish' orange (under 250–350 nm excitation), pink (355–375 nm excitation) and purple (300–410 nm excitation) luminescence with a slight streakiness are very good indicators of its CVD synthetic origin. Photos by F. Notari (left) and T. Hainschwang (centre and right).

with the so-called tatami strain pattern that is so typical of natural (and HPHT-treated natural) type IIa and low-nitrogen type Ia diamonds.

IR Spectroscopy

To characterize this small CVD synthetic diamond in detail, it was analysed by several spectroscopic techniques. FTIR spectroscopy showed that it was type IIa with no detectable nitrogen, and the spectrum did not exhibit any additional features indicative of a natural vs. synthetic origin: none of the small absorption lines characteristic of CVD synthetic diamond in the near-infrared range were observed (e.g. 7353, 6425 and 5562 cm^{-1}; see, e.g., Wang et al., 2007). Since 'pure' type IIa diamonds in such small sizes are extremely rare (and even far rarer than larger type IIa diamonds), a melee-sized sample that is truly type IIa is very suspect of synthetic origin.

Although this sample showed the expected SW UV transparency for type IIa diamond, in the experience of the authors, the vast majority of SW UV–transparent melee-sized natural diamonds are low-nitrogen type Ia. SW UV transparency is not—as believed by many—a property that changes abruptly from nitrogen-containing to nitrogen-free diamond. Therefore, stones that are low in aggregated nitrogen (easily identified by IR spectroscopy) are SW UV transparent, just like type IIa diamonds. As a result, such low-nitrogen type Ia diamonds are usually erroneously identified as type IIa by SW UV transparency–based methods.

Low-Temperature PL Spectroscopy

The PL spectra recorded with all five laser excitations at 77 K confirmed what was clearly indicated by the GGTL DFI system: that the sample

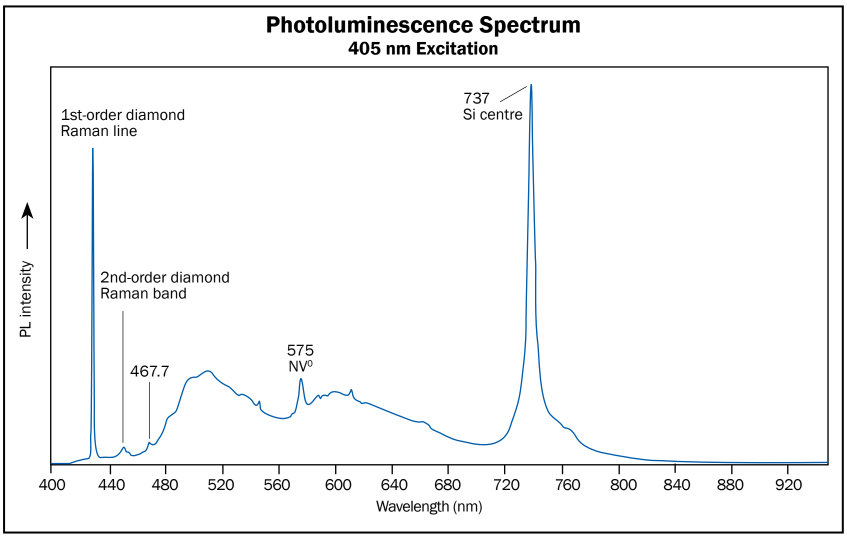

Figure 3: The room-temperature PL spectrum of the sample recorded with the GGTL DFI system shows features characteristic of untreated CVD synthetic diamond, with a strong Raman line diagnostic for diamond and bands from the 467.7 nm centre, the NV^0 centre and the Si centre (which identify it as a CVD synthetic).

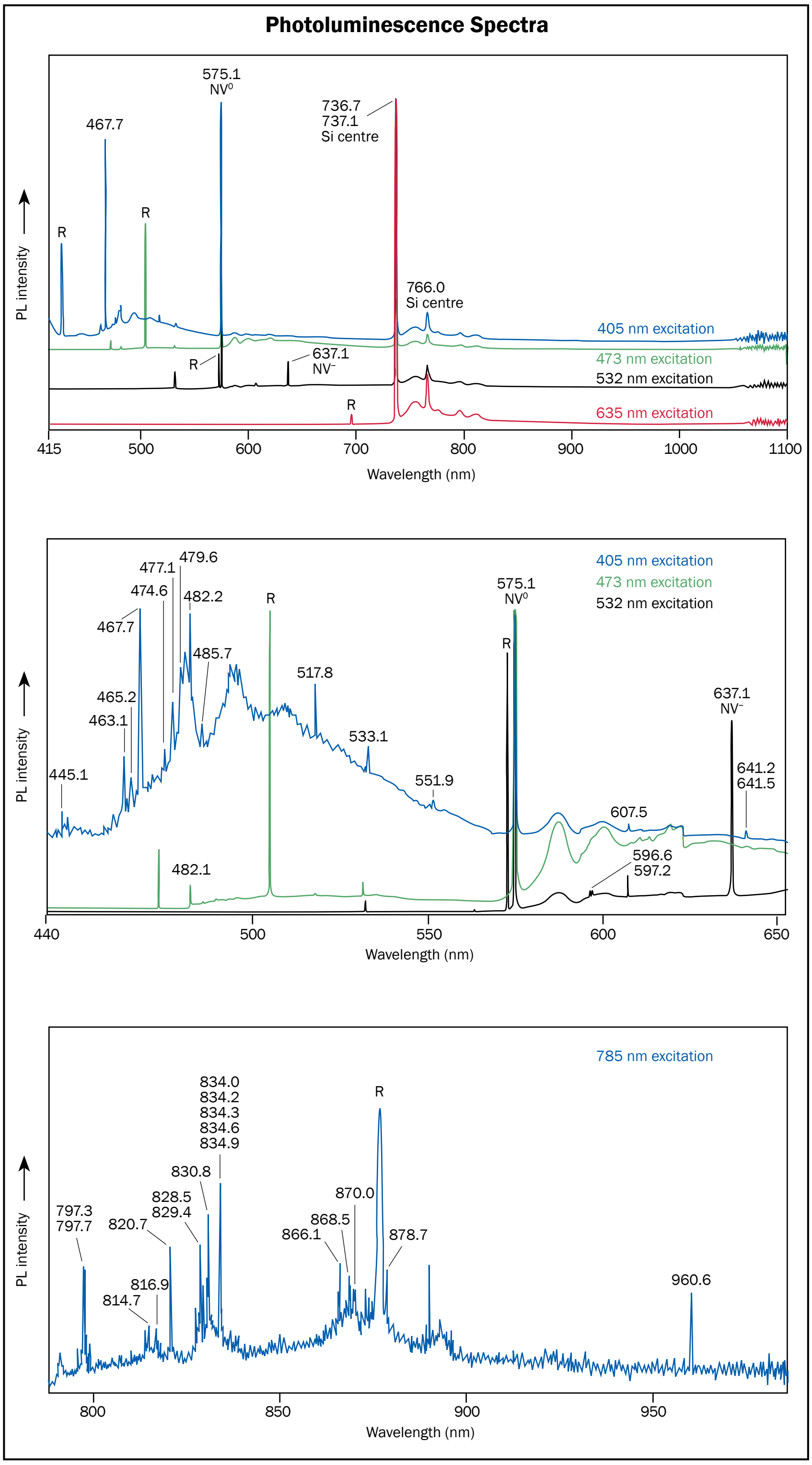

Figure 4: The PL spectra recorded using 405, 473, 532, 635 and 785 nm lasers show many characteristic peaks for CVD synthetic diamond. The well-known doublet at 736.7/737.1 nm is produced by the Si centre, which is the dominant defect recorded with 405, 473, 532 and 635 nm excitations. The 467.7 nm centre is another characteristic feature of CVD synthetic diamond. R = Raman line.

was an as-grown (untreated) CVD synthetic diamond, high in silicon-vacancy defects (Figure 4). The spectra strongly resembled those of violet-grey CVD synthetic diamonds from Orion (PDC) in Hong Kong (Peretti et al., 2013), and also the melee-sized yellow CVD sample recently described by one of the authors (Hainschwang, 2014). Unfortunately the manufacturer of the latter sample is unknown, although the parcel was supplied from Hong Kong, which may point toward the same company mentioned above. The orange/pink/purple luminescence of the sample clearly originates from the NV^0 centre with its zero-phonon line at 575.1 nm, while a green component observed under 405 nm laser excitation originates from the 467.7 nm centre

(Figures 3 and 4). Besides the Si centre—which also can be detected in some HPHT-grown synthetic diamonds (D'Haenens-Johansson et al., 2015) and very rarely in natural type IIa stones (Breeding and Wang, 2008)—the 467.7 nm centre is a characteristic defect in untreated CVD synthetic diamond (Martineau et al., 2004).

In addition to the NV-centre emissions, a large number of very sharp and typically rather weak peaks are evident in the PL spectra, all of which appear to be characteristic of CVD synthetic diamond, and which are—in the experience of the authors—unknown in natural diamond.

Conclusions

This 1.6-mm-diameter sample is the first confirmed melee-sized colourless CVD synthetic diamond discovered by a laboratory in a parcel of natural diamonds submitted by a client for testing and described in a scientific publication. Such CVD synthetics can be identified based on their luminescence under intense UV excitation and their PL spectra.

In the millions of melee-sized diamonds screened by the authors, no other near-colourless synthetic diamonds have been found until now, and therefore the CVD sample described here has the same 'exotic' status as the yellow CVD synthetic diamond discovered in a melee parcel in the latter part of 2014 (Hainschwang, 2014). Until such cases occur repeatedly and in higher percentages than 0.016% (one sample in 6,000), there is no reason to believe that melee-sized colourless CVD synthetic diamonds are currently a major problem in the market.

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