Lab Update CVD Synthetic Diamond Identified in the GIT-GTL

Supparat Promwongnan, Thanong Leelawatanasuk, Thanapong Lhuaamporn of the GIT-Gem Testing Laboratory

Keywords: CVD, HPHT, Synthetic, Diamond, Color enhancement, spectroscopy, treatment

Figure 1. A total of 27 faceted slightly tinted yellow CVD-grown synthetic diamonds were sent to the GIT-GTL for diamond grading reports, as of natural origin. The samples selected have an average weight of 0.40 ct. Photo by S. Promwongnan.

Introduction

During the past decade, a large number of gem-quality synthetic diamonds have entered the diamond industry with a wide range of quality in terms of size, colour and clarity. Consequently, there have been reports of cases of fraud in the diamond business, for example: intentionally selling synthetic diamond as natural diamond or intentionally mixing a natural diamond parcel with a synthetic one. Further, a significant number of melee sized synthetic diamonds have flooded the market-place raising concern in the diamond sector at both domestic and international levels. These unethical trade practices have brought a negative impact to consumer confidence in the diamond industry as a whole.

In November 2015, a parcel of slightly tinted yellow diamonds was submitted to the Gem and Jewelry Institute of Thailand's Gem Testing Laboratory (GIT-GTL) for a diamond grading report. What was somewhat surprising was that twenty-seven samples in this suite proved to be Chemical Vapour Deposition (CVD-grown) synthetic diamonds (Figure 1).

These samples exhibit the typical characteristics of the CVD-grown synthetic diamond exhibiting:

- small concentrations of isolated nitrogen (N) impurities;
- infrared absorption spectra showing the presence of trace amounts of nitrogen defect at 1344 cm^{-1};
- photoluminescence spectra showing strong emissions from N-V centres and distinct doublet peaks at 736.6 nm and 736.9 nm, related to the Si-related defect;
- the lamellar growth patterns seen with the DiamondView imaging system.

All these characteristics can be used to sepa-rate the CVD-grown synthetic diamonds from natural diamonds. Moreover, we also observed features indicative of high temperature-high pressure treatment (HPHT) for CVD-grown synthetic diamonds such as the lack of H-related peaks at 3123 cm^{-1} and 3323 cm^{-1} in the mid-IR range and the photoluminescence emission peak at 596.5/597.0 nm doublet, as commonly observed in post-grown CVD synthetic diamonds.

Samples and Procedures

The 27 round brilliant cut CVD-grown synthetic diamonds shown in Figure 1, were sent to the GIT-GTL for diamond grading reports as being of natural origin. They ranged in size from 0.39 to 0.44 ct with approximately 4.6–4.9 mm in diameter. The clarity grade of these samples ranged from VVS2 to SI1. The colour grade of the diamonds is slightly tinted yellow. All samples were further tested with the D-Screen which is a portable diamond screening device. The internal features were observed under a gemmologi-cal microscope. Furthermore between crossed polarizers, strain patterns and interference colours could be seen. All photomicrographs were collected by a Canon EOS 7D Photo-microscope. Fluorescence reactions were observed using a gemmological UV lamp in both long-wave (365 nm) and short-wave (254 nm) ultraviolet light. More observation of growth patterns – photoluminescence images were investigated using the DTC Diamond.

View instrument (wavelength <230 nm). A Thermo Nicolet 6700 Fourier-transform in-frared (FTIR) spectrometer was used to record IR transmittance spectra in the mid-IR range (6000–400 cm^{-1}) with a resolution of 2.0 cm^{-1} and 250 scans to determine the diamond type. Photoluminescence (PL) spectroscopy was performed on all samples while they were immersed in liquid nitrogen using a Renishaw inVia Raman micro-spectrometer with the He-Cd laser (325 nm) and Nd:YAG laser (532 nm).

Results

Gemmological Observation

Based on the observed gemmological properties, these samples were consistent with being diamond with confirmation provided by the diamond tester. And to make sure of this outcome a D-screen device was used to verify the result. However, surprisingly all the samples examined in the study received a "Passed" (green indicators) tag which suggested that they were all natural diamond.

Microscopic Features

The clarity grade of this suite ranged from VVS2 to SI1. Observation with a gemmological microscope showed several samples contained very small, opaque, dark crystals (Figure 2a) and some samples had a number of tiny pinpoint-like inclusions (Figure 2b). Many samples had a small, frosted cavity reaching to the surface on the pavilion (Figure 2c-d) with a few diamonds containing parallel internal growth lines (Figure 2e-f). Observation of such internal graining could be considered an indication of the CVD-grown synthetic diamond. Moreover nicks, cavities, extra facets and scratches were observed as the external inclusions.

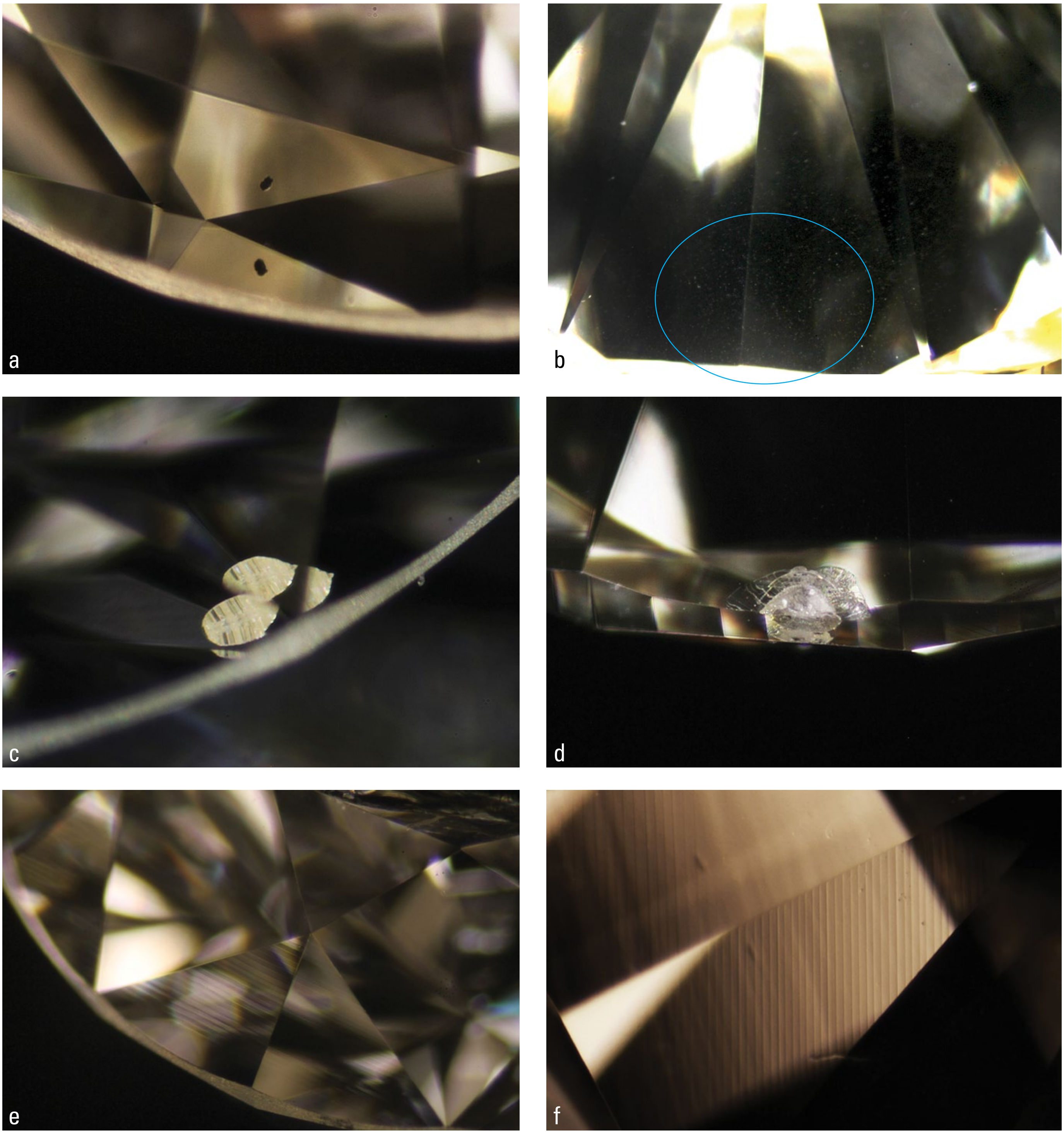


Figure 2. Examined under the microscope: a (No. 152210), the internal inclusion features consist of very small dark crystals. b (No. 152234), Fibre optic light illumination revealed a number of very fine pinpoint-like inclusions. c (No. 152223), Note, frosted cavity reaching to the surface on the pavilion side and d (No. 152234) the girdle of the diamond visible through the crown side. In e & f (No. 152223 internal graining is exhibited. Photomicrographs by S. Promwongnan; field of view 1.4, 2.5, 1.2, 1.5, 2.3 and 1.8 mm for photos a–f, respectively.

Further examination with a microscope with cross-polarized light revealed internal features like the cross-hatched bands (tatami) with irregular bands of interference colours in some areas of all samples (Figure 3a-c). These results are consistent with the presence of very low nitrogen concentration in type Ib diamonds.

Fluorescence & DiamondView

The reactions to ultraviolet radiation were checked in both long-wave and short-wave ultraviolet light. All samples were inert to long-wave UV radiation but fluoresced very weak colour to short-wave UV:

- thirteen samples fluoresced very weak orange;
- six samples fluoresced very weak reddish orange;
- three samples fluoresced very weak red; and,
- five samples fluoresced very weak chalky yellowish green.

None of the samples exhibited any phosphorescence to standard UV lamps.

After exposure to the deep ultraviolet wavelengths under the DiamondView, fluorescence imaging of all the samples revealed uneven blue fluorescence patterns on a background of yellowish green. Twenty-three of the samples tested show distinctive lamellar growth patterns that are features typical for CVD synthetic diamond (Figure 4a-c). Phosphorescence was also seen under the DiamondView instrument; weak to strong greenish blue coloured phosphorescence was also observed in twenty-four samples, weak yellowish green colored phosphorescence in one sample and no phosphorescence in two samples.

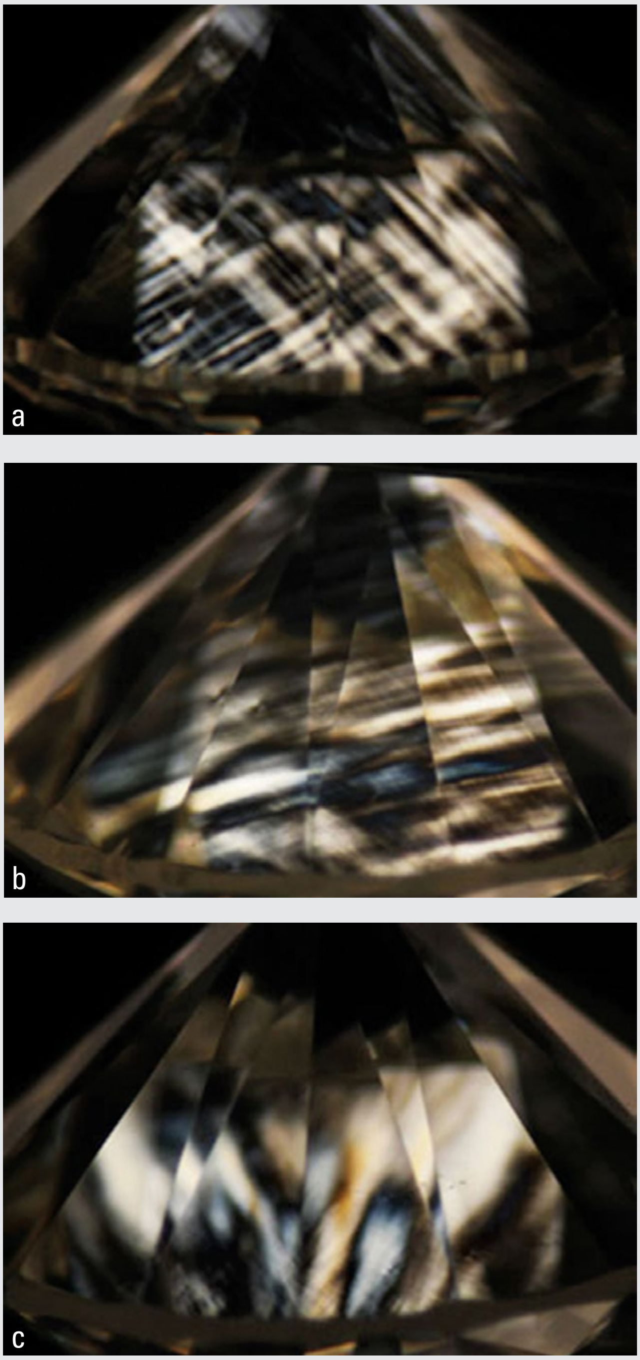


Figure 3. The cross-hatched bands (tatami) with irregular bands of interference colours seen with crossed polarizers on all samples investigated. Photomicrographs by S. Promwongnan; field of view 3.6 mm for photos a–c (No. 152201, 152205, 152224), respectively.

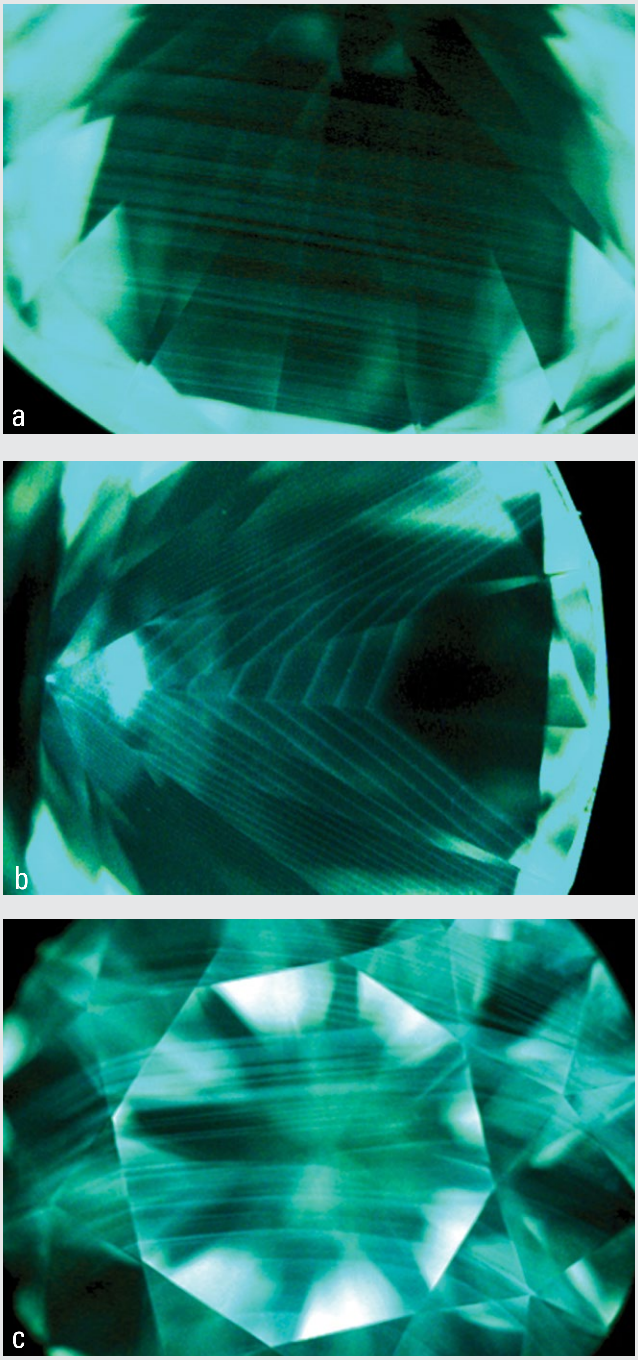
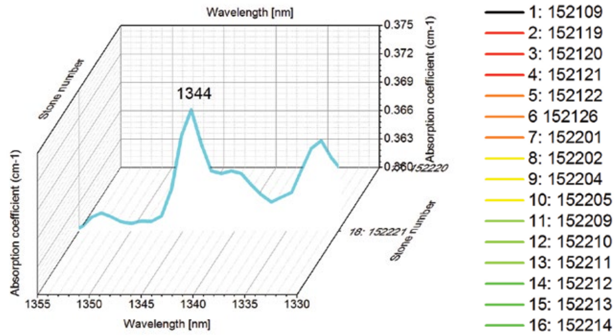


Figure 4. With a DiamondView, distinctive straight-to wavy lamellar growth striations were seen in most samples.
*Photos by S. Promwongnan; Image width **4.0**, **3.3**, and **4.5 mm** for photos a–c (No. 152204, 152223, 152220), respectively.*

Advanced Instrument Analysis

Spectra

FTIR analysis identified absorption in the mid-IR region of all samples as type Ib diamond exhibiting absorption due to isolated nitrogen impurities, and characterized by a feature at 1344 cm^{-1} (Figure 5). The Hydrogen-related absorption features at 3107 cm^{-1} were also detected in fifteen samples. There was no H-related evidence of 3123 cm^{-1} and 3323 cm^{-1} in all samples examined.



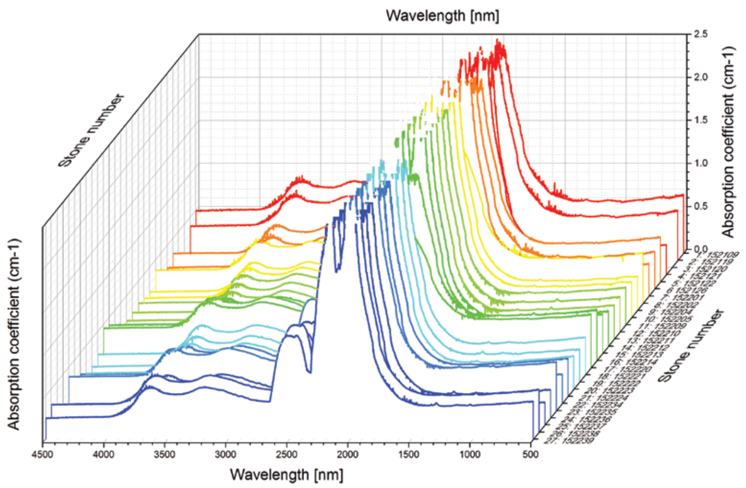


Figure 5. FTIR transmittance spectra from most samples showing an absorption of isolated N defects at 1344 cm^{-1} which were classified as type Ib diamonds.

On the top-right, absorption transmittance spectrum of sample No. 152221 represented clearly a N-related defect.

Photoluminescence spectra

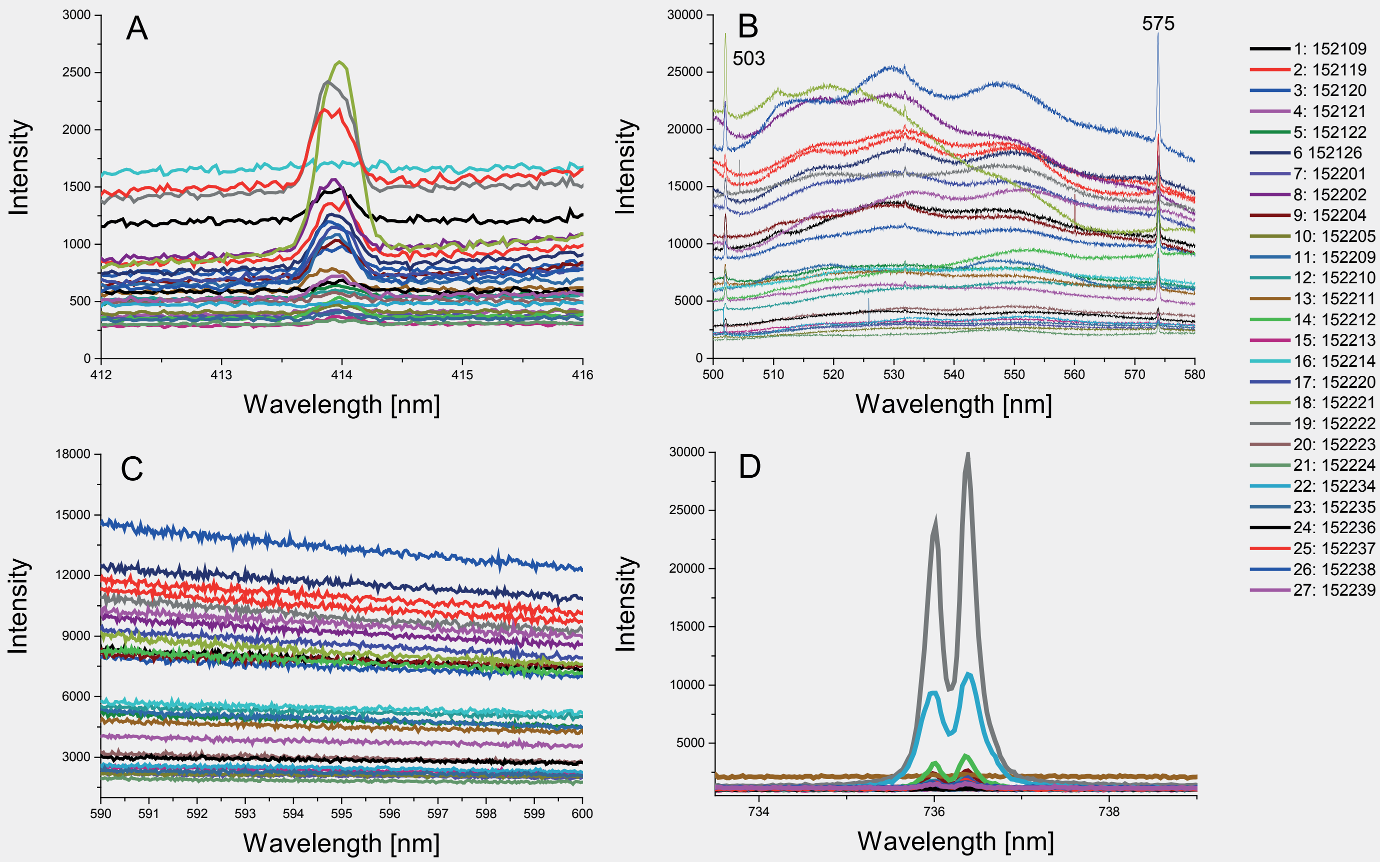


Figure 6. When the photoluminescence spectra were collected with the He-Cd laser (325 nm) in low-temperature, twenty-six samples showed N3 centre at 414 nm (A). The PL spectra for these samples also exhibit N-V centres at 575 nm stronger than H3 luminescence at 503 nm (B) and a lack of a pair of lines at 596.5 and 597.0 nm (C). Most of the samples contained Si-related defects doublet peaks at 736 nm (D).

PL Spectroscopy

For further analysis, the photoluminescence spectrum was collected with a He-Cd laser (325 nm) and Nd:YAG laser (532 nm). When excited by the He-Cd laser (325 nm) in low-temperature photoluminescence spectra were detected. Twenty six samples showed a small peak at 414 nm related to the N3 centre (Figure 6A). The PL spectra for these samples also exhibit N-V centres at 575 nm, and H3 luminescence at 503 nm (Figure 6B) and a lack of a pair of lines at 596.5 and 597.0 nm (Figure 6C). The H3 centre was the source of the yellowish green fluorescence under the DiamondView instrument. Further the photoluminescence spectroscopy revealed that the twenty-six samples contained Si-related defects at the 736 nm doublet (Figure 6D).

When Nd:YAG laser (532 nm) excitation was operated in the same conditions, photoluminescence spectra were detected at 637 (NV–) nm and 575nm (NVO) with none at the 596.5/597.0 doublet in most samples. PL spectra confirm the presence of the Si-related feature clearly with a doublet peak at 736.6 nm and 736.9 nm in all samples (Figures 7, 8). These spectra identify these diamonds as CVD-growth synthetic diamonds.

Conclusions and Discussions

The gem-quality CVD-grown synthetic diamonds is starting to be well known in the diamond market. A number of previous documents report the development of CVD material. In this report, slightly tinted yellow CVD-grown synthetic diamonds have been examined at the laboratory in GIT-GTL. All samples show yellow tone colouration due to their nitrogen impurity. FTIR transmittance spectra revealed N defects, including strong photoluminescence emissions from N-V centres and the Si-related emissions that confirm all samples are the nitrogen-doped CVD grown material. We also observed features such as no evidence of H-related peaks at 3123 cm^{-1} and 3323 cm^{-1} with a faint defect peak at 3107 cm^{-1} and luminescence features such as H3, N3 but lack of a peak at the 596.5/597.0 nm doublet which indicate that they were treated by HPHT (Martineau *et al.* (2004). The fluorescence patterns under the DiamondView instrument show the character of these CVD-grown diamonds. All features concur with previously CVD-grown synthetic diamonds as examined at the laboratory in Japan (Kitawaki *et al.*, 2015). For this study the D-Screen instrument cannot distinguish samples that are natural from synthetic due to the nitrogen impurity content from the growth process.

Photoluminescence spectra

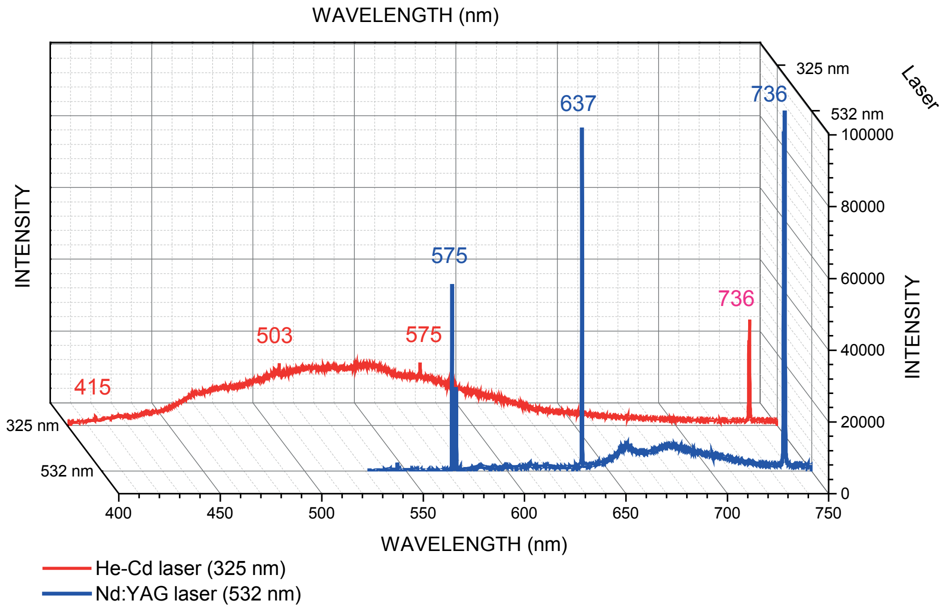


Figure 7. Low-temperature representative photoluminescence spectra (No.152222) collected at liquid-nitrogen temperatures using both excitation 532 nm laser and 325 nm. The Si-related defect that produces a doublet with peaks at 736.6 nm and 736.9 nm was seen clearly when using a 532 nm laser.

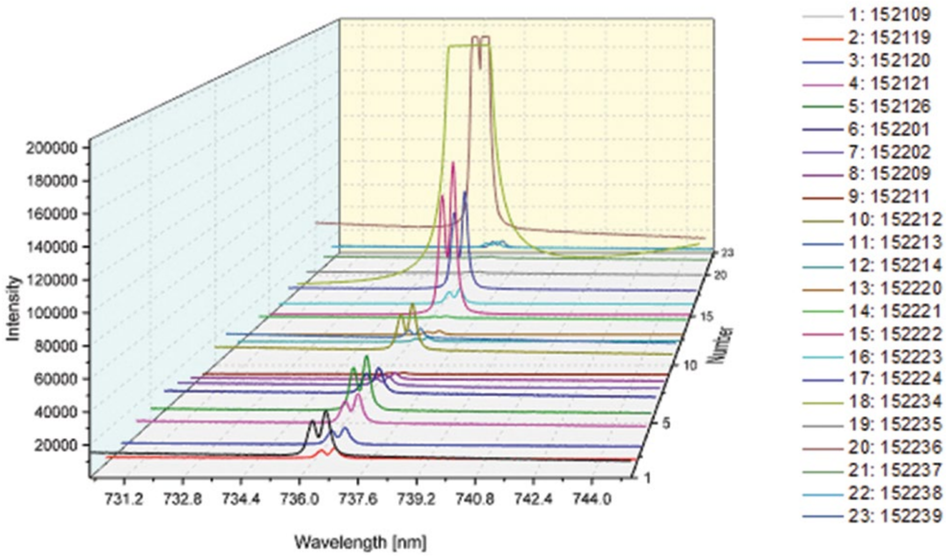


Figure 8. The photoluminescence spectra of all 27 CVD-grown synthetic diamonds revealed sharp Si-related emission peaks at 736.6 nm and 736.9 nm. These features were clearly seen when 532 nm laser excitation was used in low-temperature.

Acknowledgements

We would like to express our profound thanks to Dr. Visut Pisutha-Anond, Ms. Wilawan Atichat and Mr. Boontawee Sriprasert for their valuable suggestions and their kind reviewing and editing of this article.

References

S. R. Boyd, I. Kiflawi and G. S. Woods, 1994. The relationship between infrared absorption and the A defect concentration in diamond. Philosophical magazine B, Vol. 69, No. 6, pp. 1149–1153

Christopher P. Smith, George Bosshart, Johann Ponahlo, Vera M. F. Hammer, Helmut Klapper, and Karl Schmetzer, 2000. GE POL Diamonds: Before and After. Gems & Gemology, Vol. 36, No. 3, pp. 192–215

David Fisher and Raymond A. Spits, 2000. Spectroscopic evidence of GE POL HPHT-treated natural type IIa diamonds. Gems & Gemology, Vol. 36, No. 1, pp. 42–49.

Wuyi Wang, Thomas Moses, Robert C. Linares, James E. Shigley, Matthew Hall, and James E. Butler, 2003. Gem-quality synthetic diamonds grown by a chemical vapor deposition [CVD] method," GEMS & GEMOLOGY, Vol. 39, No. 4, pp. 268–283.

Philip M. Martineau, Simon C. Lawson, Andy J. Taylor, Samantha J. Quinn, David J. F. Evans, and Michael J. Crowder, 2004. Identification of synthetic diamond grown using chemical vapor deposition (CVD). GEMS & GEMOLOGY, Vol. 40, No. 1, pp. 2–25.

Wuyi Wang, Matthew S. Hall, Kyaw Soe Moe, Joshua Tower, and Thomas M. Moses, 2007. Latest-Generation CVD-Grown Synthetic Diamonds. from Apollo Diamond Inc. GEMS & GEMOLOGY, Vol. 43, No. 4, pp. 294–312.

Karen M. Chadwick, 2008. HPHT-Treated CVD Synthetic diamond Submitted for Dossier Grading. Lab notes GEMS & GEMOLOGY, Vol. 44, No. 4, pp. 365–367.

Christopher M. Breeding and James E. Shigley, 2009. The type classification system of diamonds and its importance in gemology. GEMS & GEMOLOGY, Vol. 45, No. 2, pp. 96–111.

Hiroshi Kitawaki, Mio Hisanaga, Masahiro Yamamoto and KentaroEmori, 2015. Type Ib Yellow to Brownish Yellow CVD Synthetic Diamonds Seen at CGL. The Journal of Gemmology, 34(7), pp. 594–604.