



The Study on CVD Synthetic Diamond from Various Producers

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In the past decade, the diamond industry has been facing a new challenge as synthetic diamond (i.e., LGD or Laboratory-grown Diamond) become commercially available as gem grade and present a new natural diamond alternative besides diamond simulants that had already been available in the trade for several decades. While the emergence of the synthetic diamond market is not a concern itself, the mixing of synthetic diamonds and natural diamonds in the same batch can have a negative impact on the confidence of the entire supply chains in the jewelry industry.

Currently, there are two main crystal growth processes of the gem-quality synthetic diamond, namely the High Pressure and High Temperature or HPHT-grown and the Chemical Vapor Deposition or CVD-growth diamonds. In the last several years, the CVD synthetic diamonds have been gaining popularity in the market, especially in the melee-size diamond market and has often been found mixed with natural diamond parcels sold in the market. In 2021, the CVD production rose to 8 million carats of gem-quality material and there are expectations that the trend would move upwards continuously. China, India, and the United States are currently the world's largest producers of CVD-grown diamonds. The most common CVD method used is Microwave Plasma Chemical Vapor Deposition (MPCVD) for growing single-crystal synthetic diamonds. Therefore, the current situation regarding CVD-grown diamonds raises concern over their identifiability, especially with those of the melee size.

In this research, the gemological and spectroscopic properties of CVD synthetic diamond samples produced from China, India, and the United States were examined to search for a suitable detection technique. The basic gemological analysis such as internal features analysis by gem-microscope, UV-fluorescence tester, and cross polar filter (CPF) was conducted on all samples. Advanced instruments such as DiamondView™ Laser Raman spectrometer, EXA™ diamond tester and, FTIR spectrometer has also been used for the analysis. In conclusion, it is found that luminescence imaging and the PL spectrum are crucial in separating the CVD synthetic diamonds from their natural diamond counterparts.

1. Introduction

Screening the CVD synthetic diamonds is quite a challenge in the laboratory due to the current synthesis technology. There are various techniques and constantly evolving. Unfortunately, basic instruments commonly used in jewelry stores are not effective enough since most detect the sample by fluorescence/phosphorescence under ultraviolet light or detect only certain properties. In many cases, if the sample does not show those properties, this tool will reach its limitation to separate the synthetic diamonds from the natural diamonds.



This is why systematic testing with various techniques of synthetic diamond is significant. In this study, the CVD synthetic diamonds from major producers such as China, India, and the United States of America have been collected and analyzed by standard and advanced gemological methods to manage and expand the database and develop the appropriate method in effectively identified CVD synthetic diamonds from HPHT synthetic diamonds and natural diamonds.

2. Materials and Methods

Forty-six samples were collected in this investigation, including type Ia natural diamonds as reference stones from GIT and CVD synthetic diamonds from three major sources : India, China, and the USA. All CVD samples are produced by an ionization process, using electromagnetic waves or microwave waves (Microwave plasma CVD, MPCVD). It is the most popular CVD diamond synthesis technique in the jewelry industry. The CVD synthetic diamond samples are shown in Figure 1. In addition, this research studied the identification technique for melee-size synthetic diamonds (less than 0.2 ct). A total of 37 melee samples ranging from 0.005 - 0.02 ct were purchased from an Indian trading company and claimed to be CVD synthetic diamond.



Figure 1 : These colorless samples are representative of CVD-grown diamonds from India, China, and the United State examined by GIT. They range from 0.3 to 0.1 ct.
photo by M. Seneewong-Na-Ayutthaya

This study conducted the physical properties measured with basic gem testing tools: specific gravity, inclusion, UV fluorescence under short-wavelength (254 nm) and long-wavelength (365 nm), and birefringence pattern through cross polarized filter (CPF). In addition, spectroscopic characterization was studied with advanced instruments focused on fluorescence and phosphorescence. Fourier-transform infrared spectroscopy (FTIR) was carried out using Thermo Scientific FTIR microscope Nicolet iS50 (mid-IR spectra, 4500–400 cm^{-1}) in absorbance mode at 4 cm^{-1} resolution and 64 scans. The fluorescence image and crystal growth pattern were obtained using DiamondView™ with short wave (~230 nm) UV radiation. To investigate the photoluminescence (PL) spectra were collected with EXA™ and Laser Raman spectroscopy and these were performed under the cryogenic condition with liquid nitrogen. PL spectra were measured by EXA™ using UV radiation at an approximate wavelength of 410 nm. The further PL spectra excited with a 532 nm laser using Raman spectroscopy were measured in the 535-850 nm range.

3. Result and Discussion

3.1 Gemological properties

The physical properties of diamond samples were summarized in Table 1. Their SGs ranged from 3.49–3.55 and RIs were over the limit (OTL). The fluorescence using a standard UV lamp was inert to short-wave and long-wave UV in natural diamonds. Whereas CVD samples reacted weak to strong level with yellowish-green fluorescence under short-wave UV and inert to long-wave UV.



Table 1 : Gemological properties of 46 diamond samples

Sample	Source	Pieces	Color	Clarity	Refractive Index (RIs)	Specific gravity (SGs)	Fluorescence	
							SWUV	LWUV
Natural	-	3	E-G	VVS-VS	OTL	3.52 - 3.54	Inert	Inert
CVD Diamond	India	26	G-I	VVS-SI	OTL	3.49 – 3.54	Wk to Md yG	Inert
CVD Diamond	China	8	F-K	VS-SI	OTL	3.52 – 3.55	Md to Str yG	Inert
CVD Diamond	USA	10	G-H	VVS2-VS1	OTL	3.49 – 3.52	Wk. to Md. yG	Inert

Abbreviations: Str. = strong fluorescence Md. = moderate fluorescence
Wk. = weak fluorescence yG. = yellowish green

3.2 Microscopic Features

3.2.1 Internal Features

The internal features were recorded under trinocular gemological microscopic. Mineral inclusions were contained within natural diamonds. They appeared large to small crystals, the group of tiny crystals with spherical shape, called pinpoint and a long thin needle-shaped inclusion that is the most common inclusions found in natural diamond. Moreover, natural diamond also found an indented nature at the girdle. For CVD diamonds, dark crystals or black inclusions (Figure 2A, 2B, 2C, 2D) were composed of non-carbon diamonds (graphite), which are also common features in CVD-grown diamonds. Black inclusions can be seen in a cloud of small dark particles with shapeless (Figure 2E). Moreover, feather-like and blade-like inclusions (Figure 2F, 2G, 2H) were found in CVD samples too.

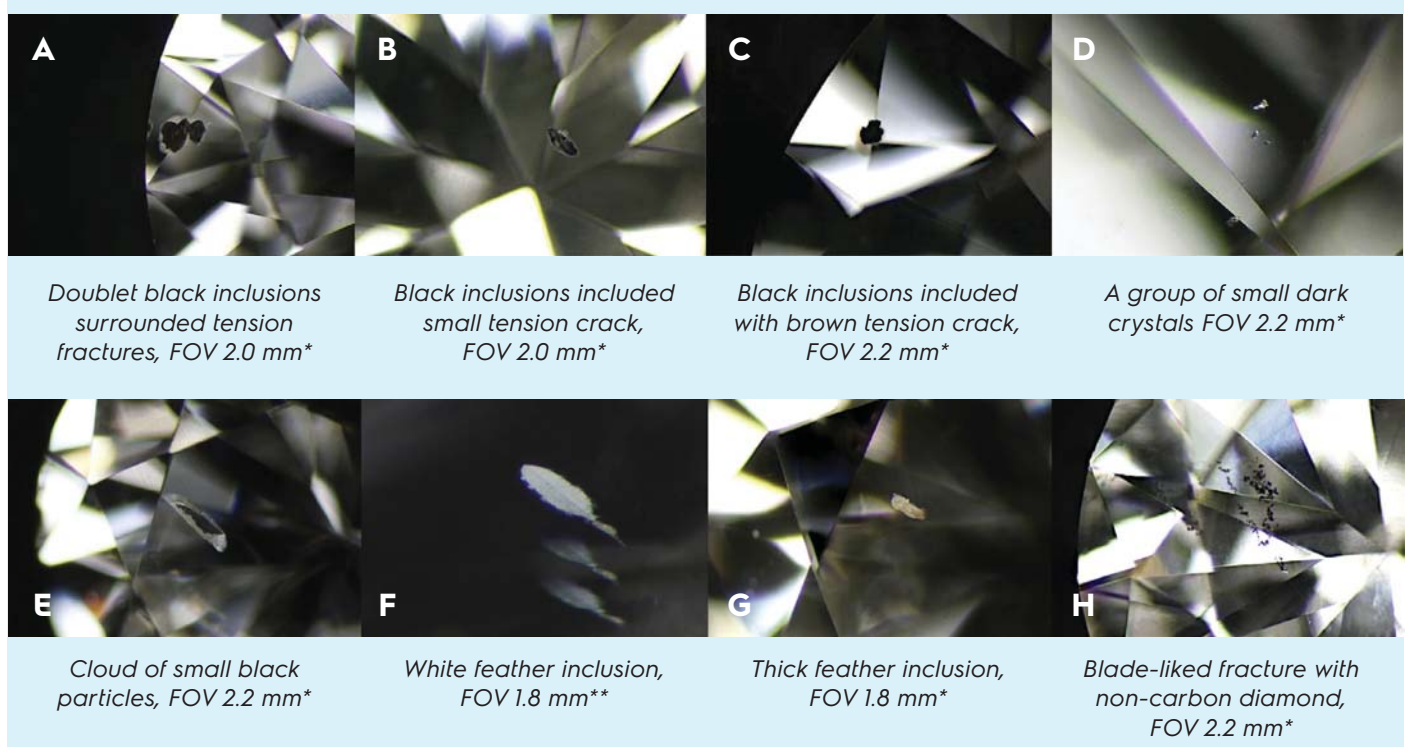


Figure 2 : Internal features of CVD synthetic diamonds from (A, B, F, H) India, (C, E, G) China, and (D) the United States
photomicrographs by : M. Seneewong-Na-Ayutthaya and W. Suwanmanee



3.2.2 Cross polarized filter (CPF)

Birefringence via the CPF technique of all diamond samples was evidently observed on a side view of the pavilion. The natural diamond showed interference color called “patchy strain pattern, caused by stress in the growth process of natural diamond crystals under high temperature and high pressure. The appearance of a patchy strain is an irregular blue patch included with brown and grey color (Figure 3A). The birefringence of all CVD diamonds from three countries exhibited interference color characterized by frequent thick black lines arranged in rows (columnar pattern) combined with the blue patch, brown, and gray stripes (Figure 3B). Some CVD samples displayed strong interference color (Figure 3C), distributing orange, brown and blue patch with black rim and showed frequent black lines intersecting (cross-hatched bands) also known as “tatami strain” (Figure 3D)

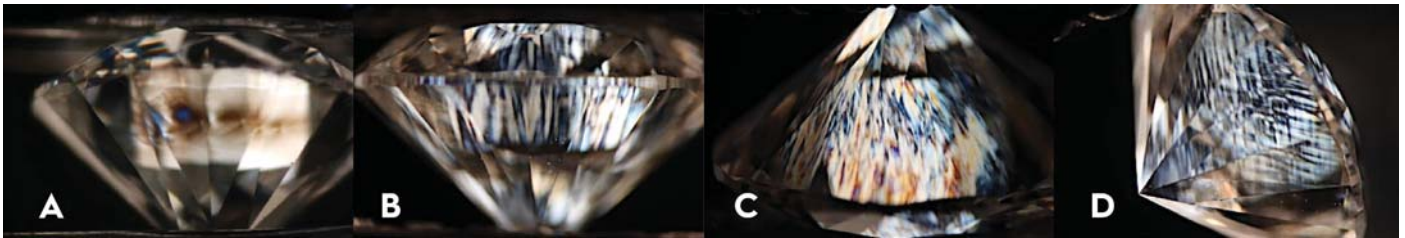


Figure 3 : Birefringence pattern images, viewing under gemological microscope with cross polarized filter of diamond samples;
(A) natural diamond, FOV 7.2 mm. and CVD synthetic diamonds from
(B) India, FOV 7.2 mm. (C) China, FOV 6.4 mm. and
(D) the United States, FOV 7.2 mm.; photomicrographs by W. Suwanmanee

3.3 DiamondView™

The fluorescence and phosphorescence images under short-wave ultraviolet light (~230 nm) for all diamond samples were shown in Figure 4. The natural diamonds displayed deep blue fluorescence without phosphorescence. The CVD diamonds exhibited several colors of fluorescence. The distinctive bluish-green fluorescence mostly reacted in CVD synthetic diamonds from India and China and illustrated greenish-blue phosphorescence with weak to moderate reactions. By contrast, the CVD samples from the USA mainly displayed red and reddish-orange fluorescence. They also showed weak greenish-blue phosphorescence reactions. In addition, the fluorescence features of CVD synthetic diamonds were found fine, straight and curve growth lines or the multiple striations of the fluorescence (Figure 5A-5C). The red fluorescence in CVD samples from the USA showed the layered growth structure included with the blue patch (Figure 4D-4E), indicating a stage for start-stop synthetic diamond growth (Dieck et al., 2015) as well as the structural distortion of synthetic diamonds in area of blue distribution (Figure 5F).

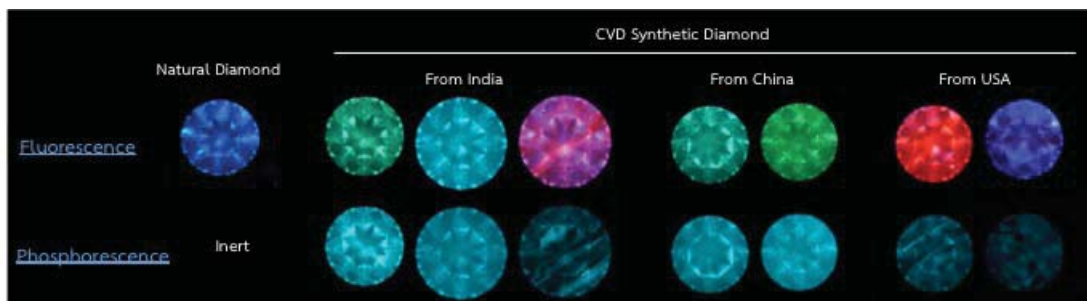


Figure 4 : The fluorescence and phosphorescence images reacted under DiamondView™ that compared between natural and CVD synthetic diamonds;
photos by K. Yadawadee

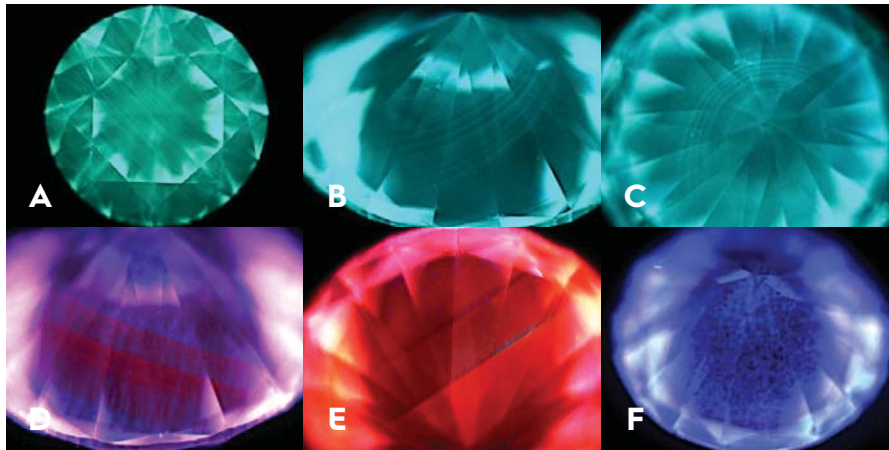


Figure 5 : DiamondView™ images of CVD synthetic diamonds show distinctive straight and curve growth striations (A-C), layered growth structure (D-E) and blue patch distribution (F) ; photos by W. Suwanmanee

3.4 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of diamonds are shown in Figure 6. For natural diamond, the sharp absorption band observed at 1405 and 3107 cm^{-1} represent the hydrogen content (Fritsch *et al.*, 2007), whereas the spectral region between the 482 and 1500 cm^{-1} includes the absorption from the nitrogen (Scarani *et al.*, 2015; Breeding & Shigley, 2020). Therefore, natural diamond samples were classified as type Ia (diamond with aggregated nitrogen). In contrast, all CVD diamonds showed no nitrogen and boron related absorption band in IR spectra typical for type IIa diamond characteristics.

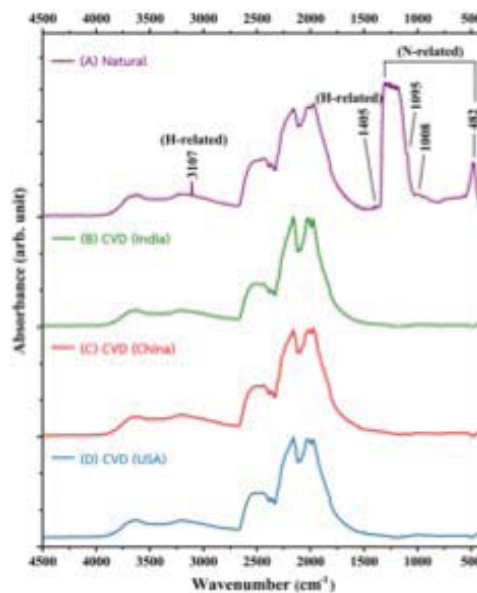


Figure 6 : FTIR spectra of (A) natural diamond and (B) CVD synthetic diamond



3.5 Photoluminescence spectroscopy

3.5.1 EXA™ – The natural diamond detector

The photoluminescence (PL) spectra were measured by EXA™. The representative PL spectrum for natural diamond and CVD samples is shown in Figure 7. The PL spectrum of natural diamonds presented a narrow peak at 415 nm that are N3 center defect (Tang *et al.*, 2018). All CVD samples displayed a significant peak at 737 nm, indicating [Si-V] center (Eaton-Magana & Shigley, 2016). Additionally, PL spectrum pattern of CVD samples from different sources related to the luminescence color under DiamondView™ equipment. Most CVD diamonds from India and China, having green and greenish-blue fluorescence, appeared fluorescence bands at around 480-550 nm are probably related to Ni-related defect from using the HPHT grown diamond as a seed crystal for the CVD synthesis (Zaitsev *et al.*, 2016). The one CVD diamond from India and most of the United States CVDs, having red fluorescence with blue pattern and reddish-orange, displayed a sharp peak at 575 nm and the fluorescence bands at around 585-620 nm that responsible for [N-V] center (Schreyvogel *et al.*, 2015)

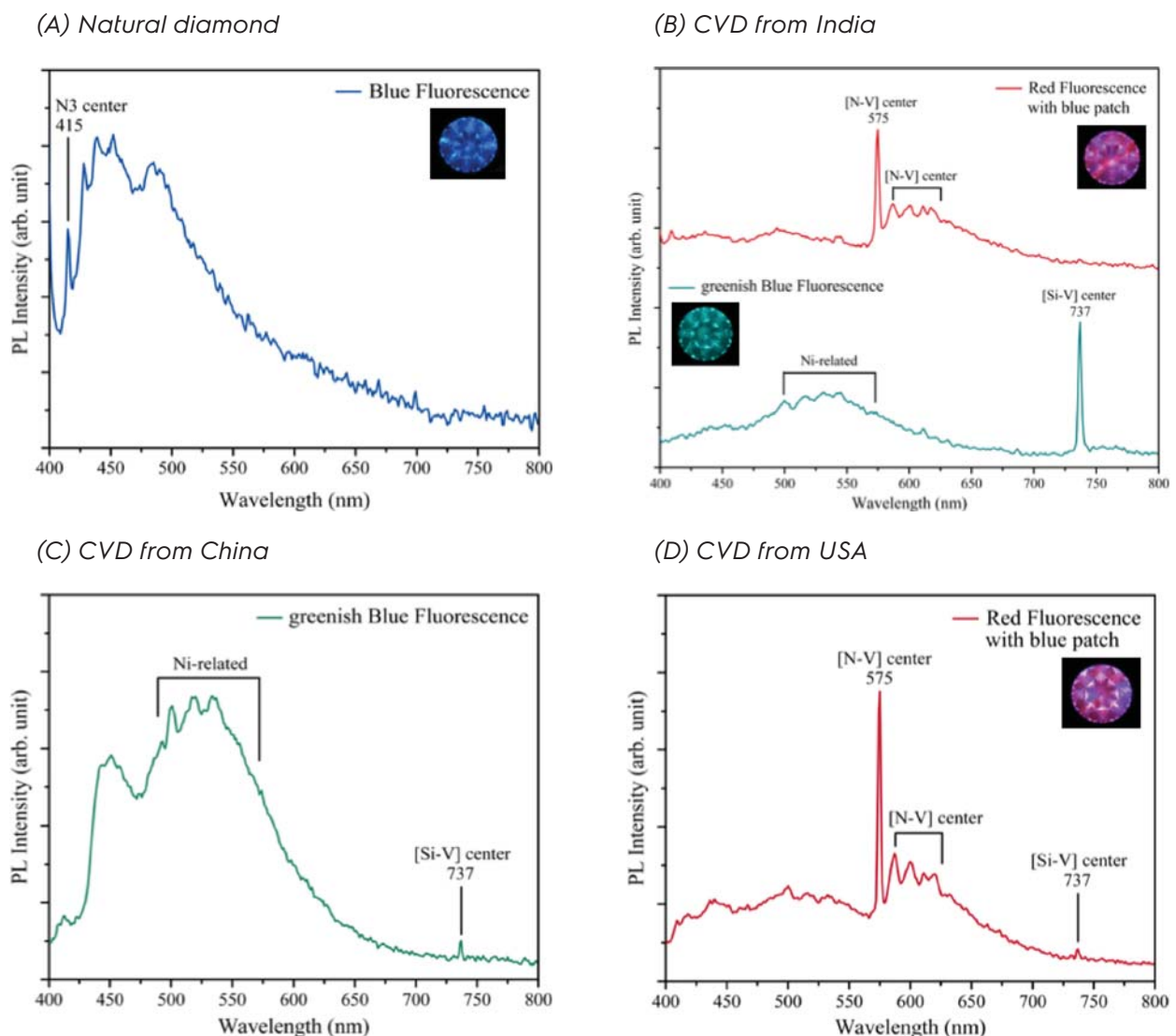


Figure 7 : Photoluminescence spectra by EXA™ of a natural diamond (A) and CVD synthetic diamonds from India(B), China(C), and the United States (D).



3.5.2 Laser Raman spectroscopy

The photoluminescence spectra induced by 532 nm excitation laser (PL532) by Laser Raman spectroscopy are shown in Figure 8. Both natural and CVD diamonds exhibited a sharp peak at 572.6 nm (= 1332 cm⁻¹ Raman shift mode) associated with Diamond Raman (Forneris *et al.*, 2016). Furthermore, CVD synthetic diamonds appeared doublet peaks at 736.3 and 736.7 nm related to [Si-V]⁻ center (Eaton-Magaña & Shigley, 2016). This emission can be helpful as a significant indicator of CVD synthetic diamonds because these peaks have never been reported found in HPHT synthetic diamond. The [N-V]⁰ and [N-V]⁻ center peaks at 574.6 and 636.6 nm also appeared in CVD samples. (Schreyvogel *et al.*, 2015).

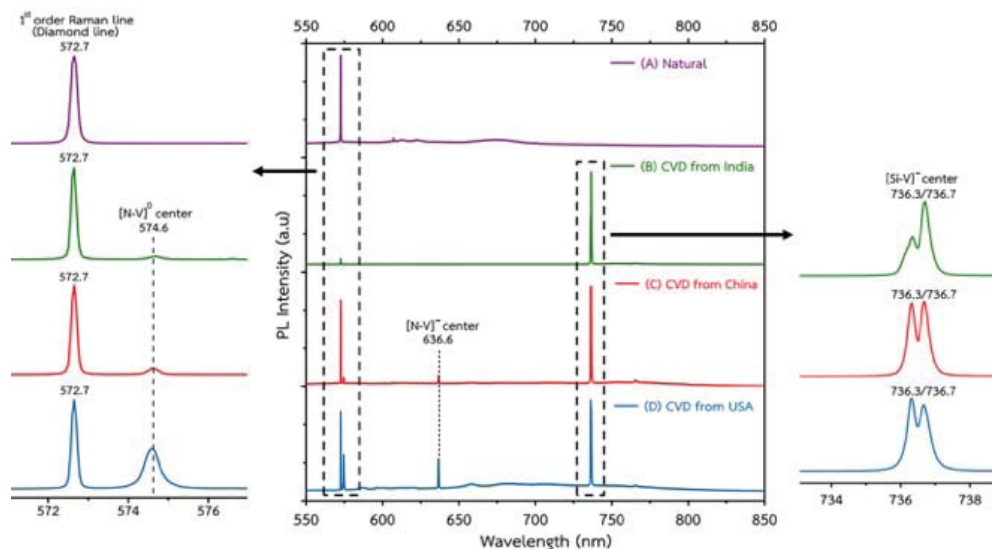


Figure 8 : Photoluminescence spectra by Laser Raman spectroscopy of natural diamond (A) and CVD synthetic diamond from India (B), China (C), and United states (D).

The PL spectra of CVD synthetic diamonds from each source are shown in Figure 10. The PL spectra features can be correlated with the distinctive fluorescence reactions under the DiamondView™ due to the structural defects of the CVD diamond. Indian and Chinese CVDs that have green and greenish-blue fluorescence show variously absorption peaks such as [N-V]⁰ (574.6-607.2 nm), [N-V]⁻ (636.7 nm), Si-Ni (765.5 nm) and Ni-N (795.6 nm) (Rabeau *et al.*, 2005; Khomich *et al.*, 2012). Orangy-red and red fluorescence with blue patches that appear in the Indian and US CVDs, presenting absorption peaks related to [N-V]⁰ (574.6 nm) and [N-V]⁻ (636.7 nm).

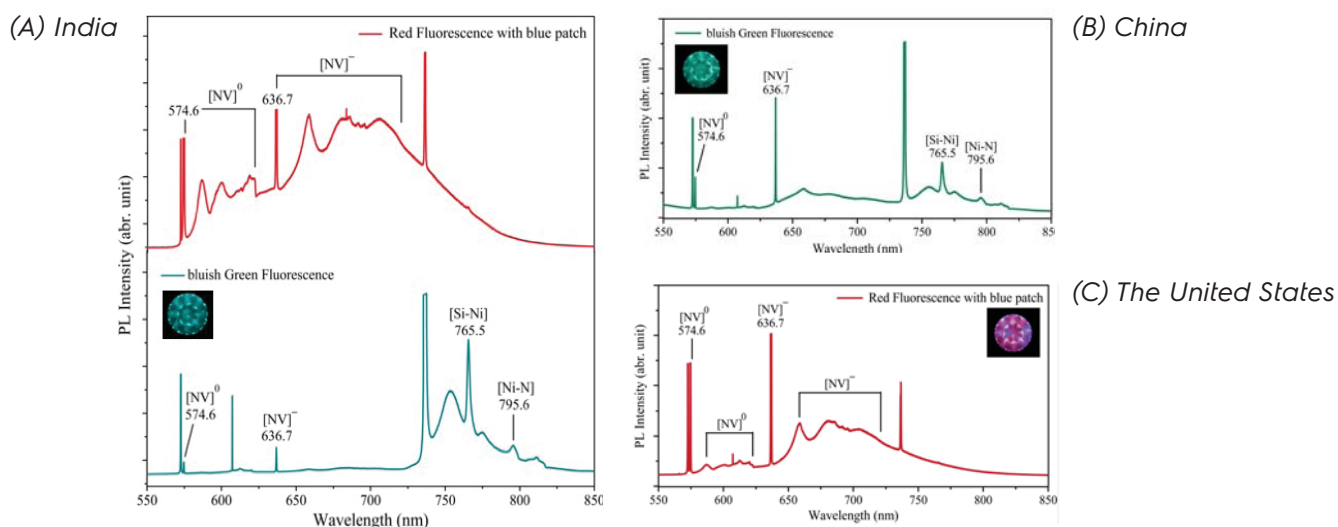


Figure 9 : Photoluminescence spectra related to the defect in diamond structure by Laser Raman spectroscopy of CVD synthetic diamond from India (A), China (B), and the United States (C)



3.6 Melee-size Synthetic Diamonds

Melee-size synthetic samples are typically in size from 1 mm, 1.5 mm, and 1.7 mm in diameter. Due to the very small size, some instruments have limitations in analysis. The instruments that can be measured are Diamond View™ to analyze the luminescence image and Laser Raman spectroscopy to analyze the photoluminescence spectrum.

3.6.1 DiamondView™

The fluorescence and phosphorescence images for melee samples are shown in Figure 10. The melee samples have mostly resulted in strong greenish-blue fluorescence and strong greenish blue phosphorescence. They also displayed cubo-octahedral growth lines, which were observed. These results were typical features commonly seen in HPHT synthetic diamonds. However, few melee samples showed the medium reaction as greenish-blue in fluorescence and weak phosphorescence that were probably indicated CVD synthetic diamonds.

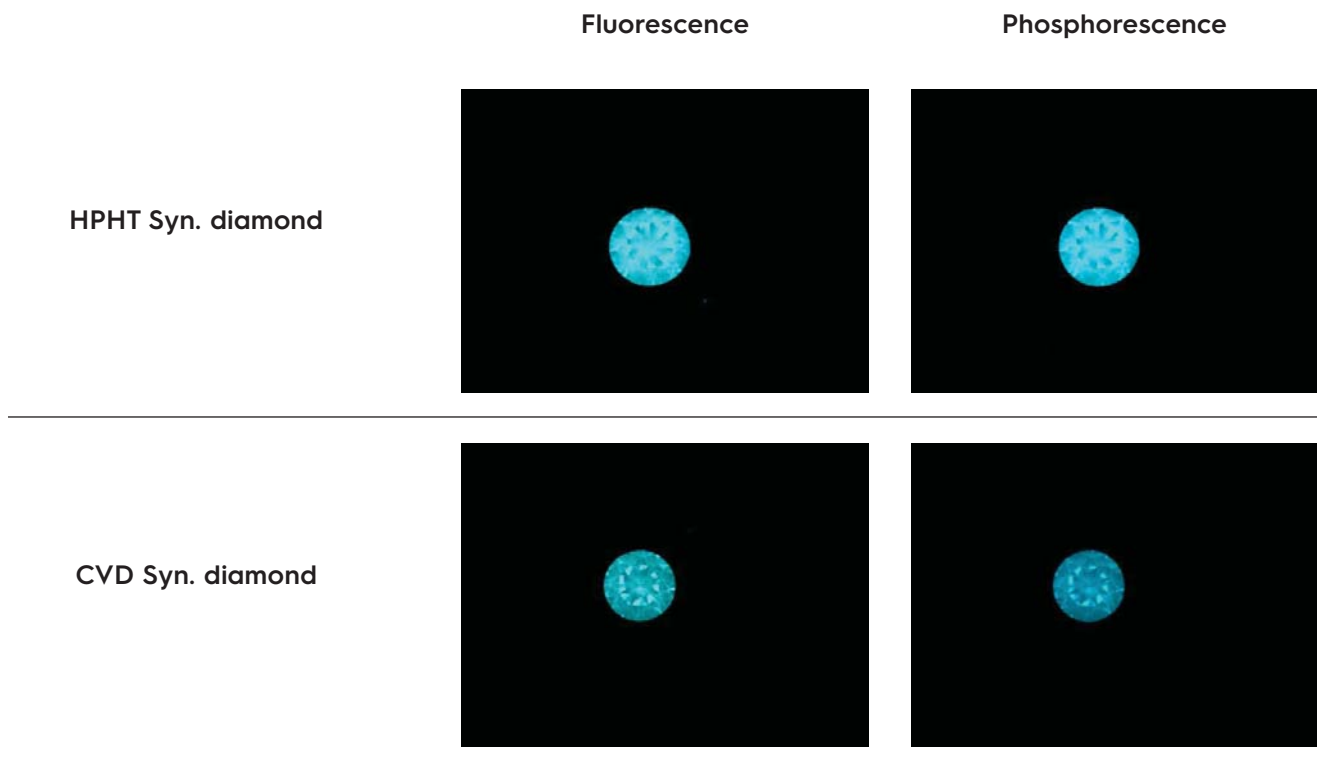


Figure 10 : The fluorescence and phosphorescence images of HPHT synthetic diamond (A) and CVD synthetic diamond samples, melee size (B) under deep ultraviolet wavelengths with DiamondView™

3.6.2 Laser Raman spectroscopy

PL spectra of the melee samples are shown in Figure 11. Doublet peaks of [Si-V] (736.3 and 736.7 nm) were presented for CVD samples, while these HPHT samples do not appear this absorbance. The results showed that all melee samples ranging 1.7 mm were HPHT diamonds. For 1.5 mm size, were 10 HPHT diamonds and there was only one sample as CVD diamond. And 1.0 mm size found that 12 samples were HPHT diamonds, and 3 samples were CVD diamonds.

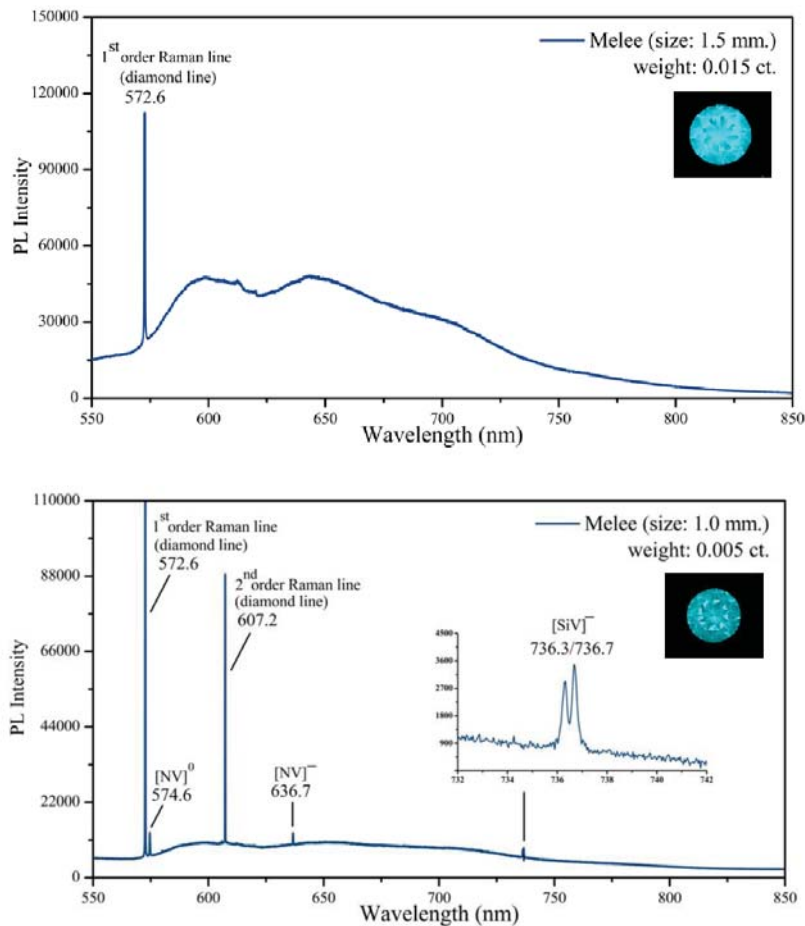


Figure 11 : Photoluminescence spectra by Laser Raman spectroscopy of HPHT synthetic diamond (top) and CVD synthetic diamond (bottom) melee-size

4. Conclusion

According to the obtained data from various techniques, it can be concluded that the analysis of physical properties and simple UV fluorescence could not be clearly separated CVD synthetic diamond from type I natural diamonds. The birefringence patterns through a cross polarized filter (CPF) can be used as a pre-screening method in most cases, except for the tiny melee size diamonds where such interference patterns are hardly seen. It is found that advanced analytical techniques such as the luminescence image by DiamondView™ instrument to observe the crystal growth pattern and photoluminescence techniques (PL) by Raman Spectroscope and EXA™ are crucial for the identification of CVD synthetic diamonds.

This study compares the characteristics of the CVD synthetic diamonds from major producers. It was found that the CVD synthetic diamonds produced from India and China share many similar properties that may indicate their similar crystal growth conditions. In contrast, the CVD synthetic diamonds from the USA show fluorescence that differs from India and China sources, indicating different crystal growth environments. Moreover, this study also found that the PL technique by using EXA™ and Raman spectroscopy accompanied by the database of CVD synthetic diamonds from major sources could be efficiently applied in the screening of natural and CVD synthetic diamonds. For proclaimed melee-size CVD synthetic diamonds purchased on the gem market, it is surprising to find that the majority (up to 90%) of the parcel had proved to be HPHT synthetic rather than CVD synthetic diamonds based on luminescence image and Photoluminescence.



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