



Application Note:

Large amount of pink and blue CVD-grown synthetic diamonds on the market

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Large parcels of CVD-grown fancy blue and pink diamonds has appeared on the market. New generation of type IIa blue stones are even more difficult to detect without adequate spectroscopic instrumentation. In this application note we discuss about their identification with standard and more advanced gemological instruments.

An US-based diamond dealer presented to the authors large parcels (several hundreds of carats) of relatively uniformly colored fancy to fancy deep brownish pink and blue CVD-grown diamonds at AGTA Tucson 2015 show. Initial tests conducted on random samples indicated that both color variations were Type IIa; no nitrogen (or boron for blue stones) was detected in GemmoFTIR™ analysis. Photoluminescence (PL) studies with GemmoRaman-532SG™ (532 nm excitation) at room temperature confirmed the color origin of both variations was related to irradiation. Pink diamonds exhibited very strong nitrogen-vacancy centers (NV^0 at 575 nm & NV^- at 638 nm) and the spectra of blue stones were dominated by a strong PL-peak of general radiation defect (GR1) at 741 nm. These preliminary results turned to be an alert to conduct more tests in order to confirm the origin of the stones. It is a very rare situation to encounter a blue irradiated natural type IIa diamond, as most of these stones are colorless or can be HPHT-treated to colorless or pink by removing the brown component. Artificial irradiation producing blue color could be only expected for some rare type IIa stones which have not responded favorably to the HPHT-treatment.

*Deljanin et al.*¹ described new pink CVD-grown diamonds manufactured by Orion PDC and Scio Diamond companies. These type IIa stones have been multistep-treated with consecutive irradiation and annealing steps for producing their pink color.

Three versions of blue CVD-grown diamonds exist on the market; Firstly, type IIb boron doped CVD-diamonds were reported already more than a decade ago (*Martineau*).² *Peretti et al.*⁽³⁾ characterized a product which color is most probably related to using excess silicon during the growth process.

The grayish blue to blue color of these stones is proposed to be assigned to strong silicon-vacancy (SiV) center absorbing visible light at red wavelengths. The first occurrence of type IIa CVD diamond which has been heavily irradiated in order to create strong GR1- absorption band responsible for blue color was reported fall 2014 (*Ardon & Wang*)⁴.

The blue stones presented to us belong to this latest generation, and it is worth to note that only four months after the first published find of single stone by a major gemological laboratory these stones are available in large quantities.

Blue irradiated CVD diamond

The color of irradiated CVD-grown diamonds submitted to the authors varied from fancy to fancy deep blue, with no gray secondary hue. The size of the round brilliant cut stones varied between 0.10 and 0.35ct, and the stones were relatively free of inclusions (VVS-VS).

Blue stones were inert to both short-wave and long-wave 6W gemological ultraviolet light. When ex-



Fig 1. Blue post-growth irradiated type IIa CVD diamond.

posed to the strong short-wave UV radiation of MAGI in-house built xenon flash based fluorescence microscope they revealed a weak bluish green luminescence. No phosphorescence was detected. Microscope examination between crossed polarization filters exhibited a combination of natural looking tatami- patterns typical for IIa stones, and columnar extinction patterns typical for CVD- grown diamonds.

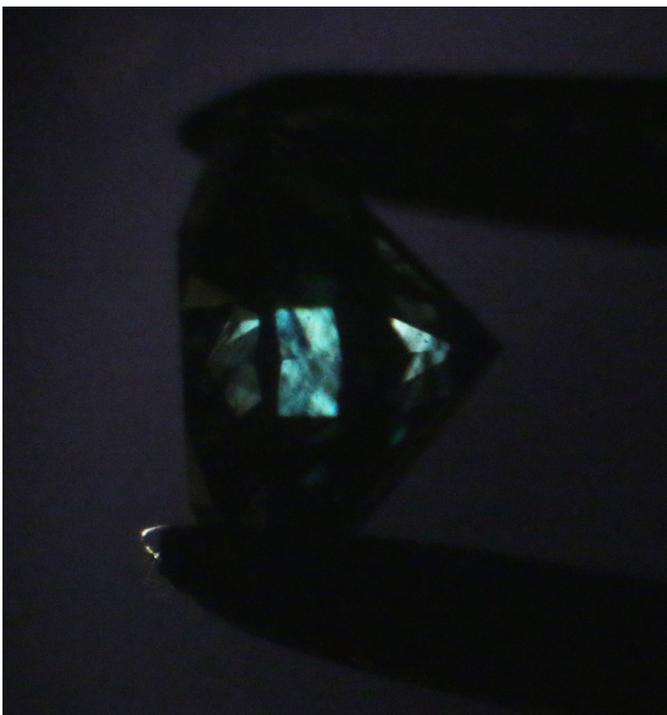


Fig 2. Interference patterns of blue CVD diamond.

FTIR analysis confirmed the stones as type IIa with no significant nitrogen, hydrogen or boron related absorptions.

Only minor unknown features were detected at 1115 cm^{-1} and 1258 cm^{-1} . We did not detect any irradiation related defects in FTIR spectra, which can be explained by low concentration of nitrogen.

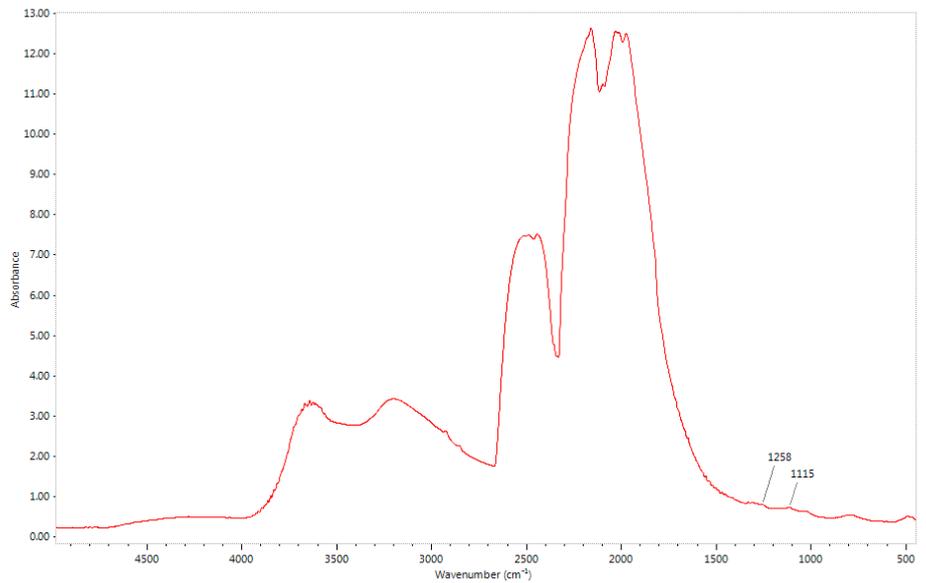


Fig 3. FTIR spectrum of blue irradiated type IIa CVD diamond.

UV-Vis-NIR absorption spectra were acquired with MAGI GemmoUV-Vis-NIR™ spectrometer in both room temperature (RT) and with samples cooled down to liquid nitrogen temperature (LNT). Absorption features recorded in room temperature resembled the typical spectra of blue irradiated natural diamonds to the extent that no conclusive identification was possible.

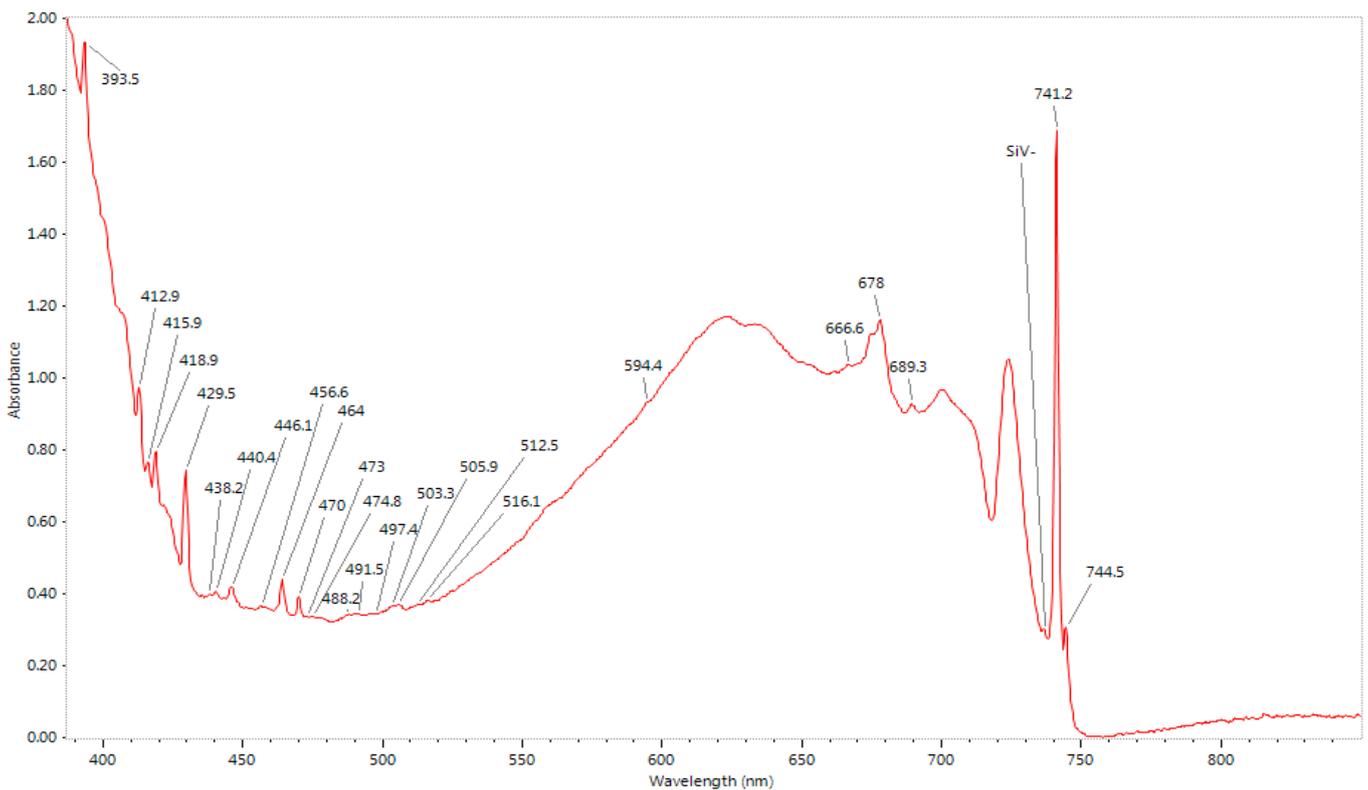


Fig 4. UV-Vis-NIR spectrum of blue irradiated type IIa CVD diamond acquired in liquid nitrogen temperature.

Only cooling the sample to LNT revealed very tiny SiV^- peak at 737 nm, a feature assigned to CVD-diamonds and only very rarely seen in natural stones. The feature is very weak, and there is a risk of confusing it to small side band of GR1 often visible in natural irradiated diamonds. Therefore, even more sensitive photoluminescence spectroscopy is required for making the final conclusions.

Photoluminescence spectra (PL) were recorded in room temperature and in LNT using excitation wavelength of 532 nm. In room temperature a strong broad PL feature of irradiation related GR1 band was detected at 741 nm.

A very careful observation of room temperature PL spectrum (532nm excitation) may reveal a tiny SiV⁻ - shoulder on the side of the GR1-band, but more samples would be needed to verify the existence of this band in all CVD stones of this type.

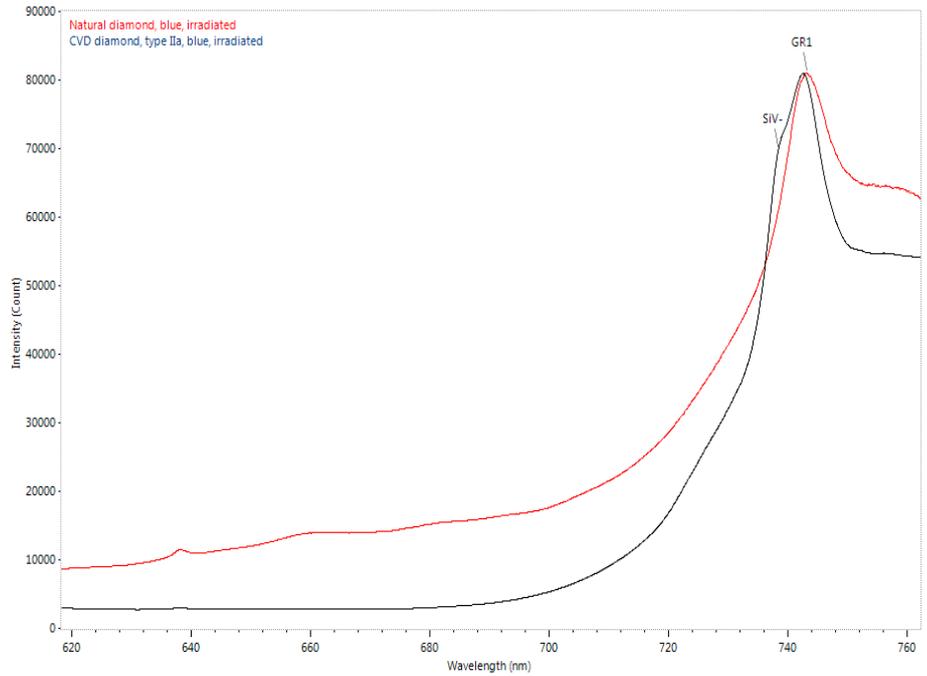


Fig 5. Comparison of room temperature PL₅₃₂ reactions of natural blue irradiated and CVD-grown blue irradiated diamonds.

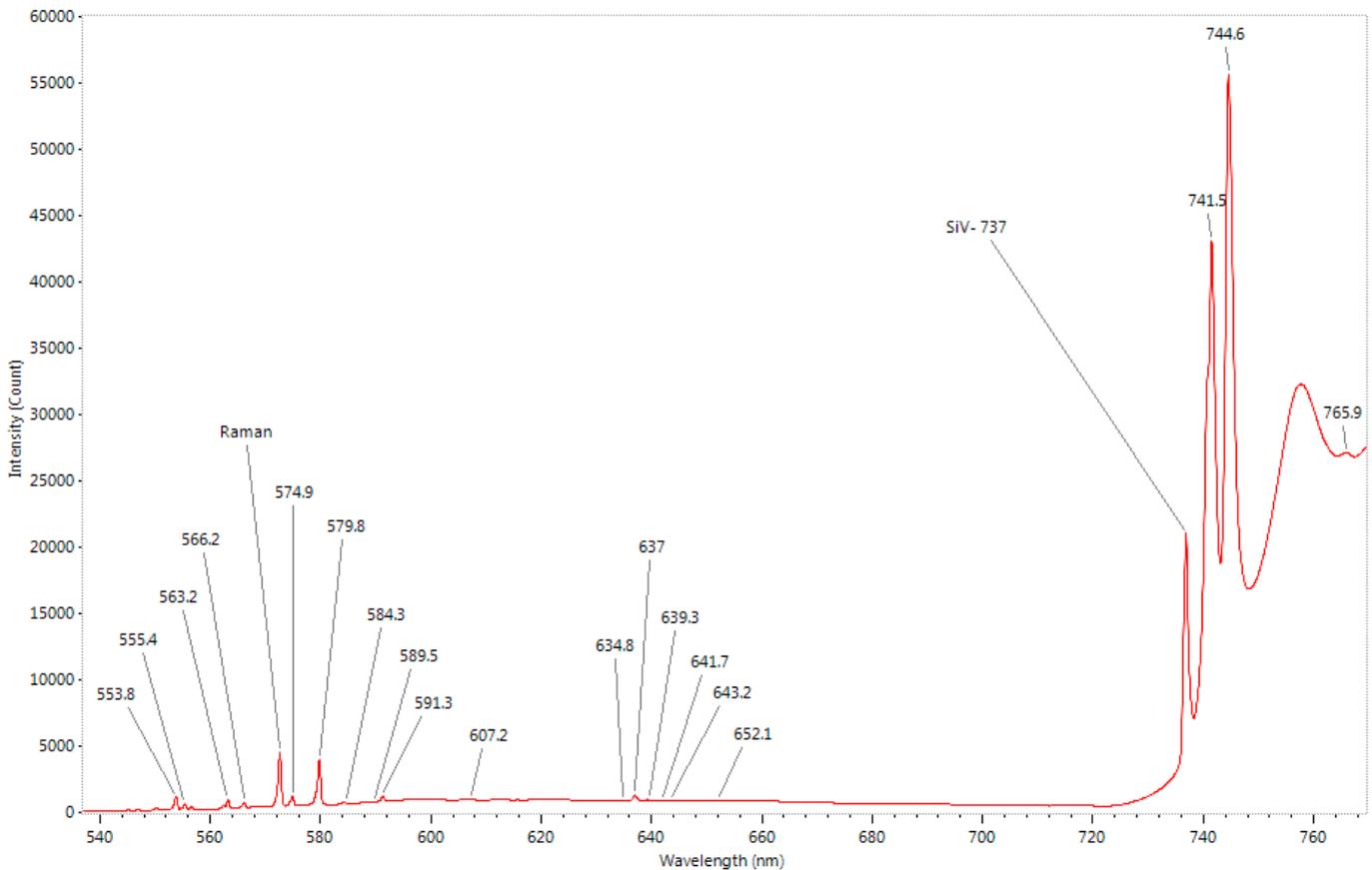


Fig 6. Photoluminescence spectrum (532 nm excitation) of blue irradiated type IIa CVD diamond acquired in LNT.

Cooling the diamond to LNT revealed distinct SiV⁻ doublet at 737 nm, and numerous other irradiation-related PL peaks.

Pink multi-treated CVD-diamonds

Pink color of CVD diamonds is always a result of post-growth treatments. Small amount of single nitrogen must be present in the stone. Irradiation and low temperature annealing processes are used to create high concentration of negatively charged nitrogen-vacancy defects for achieving the desired color.

The color of studied pink CVD- diamonds had relatively strong brown secondary hue. The color was shifted to orange brown under fluorescent diamond grading lamp, which suggests that fluorescence excited by the shortest wavelengths of daylight contributes to their perceived pink coloration. Examination in microscope between the crossed polarization filters revealed columnar interference patterns typical for CVD diamonds.

Pink stones fluoresced orange under 6W gemological short-wave and long-wave ultraviolet lamp. This fluorescence reaction serves as an good indicator, as virtually all intensively colored natural pink diamonds with natural origin of color fluoresces blue due to N3 center and relatively low A-type nitrogen content. Natural multistep-treated pink diamonds usually exhibit mixed fluorescence patterns of orange (NV⁻), green (H3) and blue (N3) colors.



Fig 7. Pink irradiated and annealed type IIa (+Ib) CVD diamond.

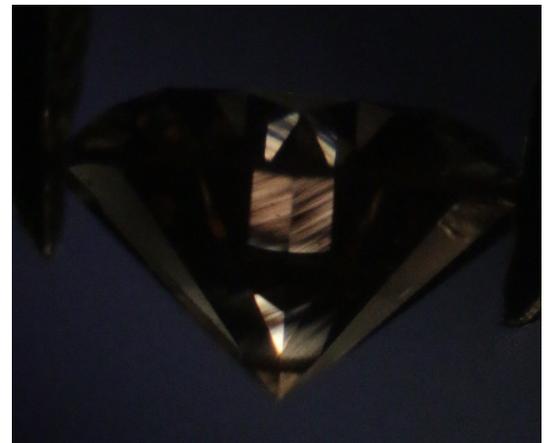


Fig 8. Columnar interference patterns typically seen in CVD diamonds.

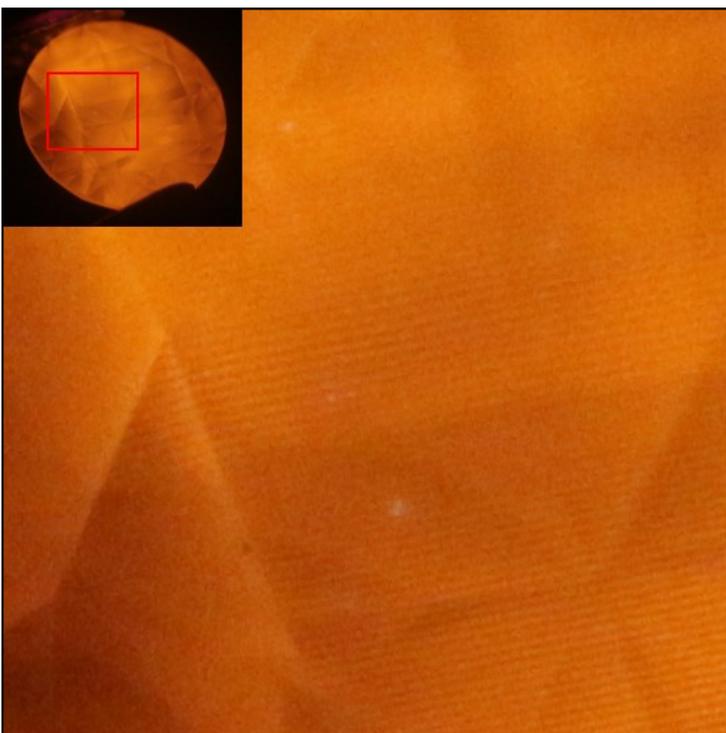


Fig 9. Parallel growth striations are diagnostic for CVD-diamonds.

MAGI high intensity Xenon flash based fluorescence microscope equipped with broadband (260-390 nm) UV-filtering revealed sharp linear growth striations on the surface of the stones. These striations are unique feature of CVD diamonds.

A relatively large magnification is required for observing the growth structure. The stone must be examined from all directions while adjusting the focus of the microscope on its surface.

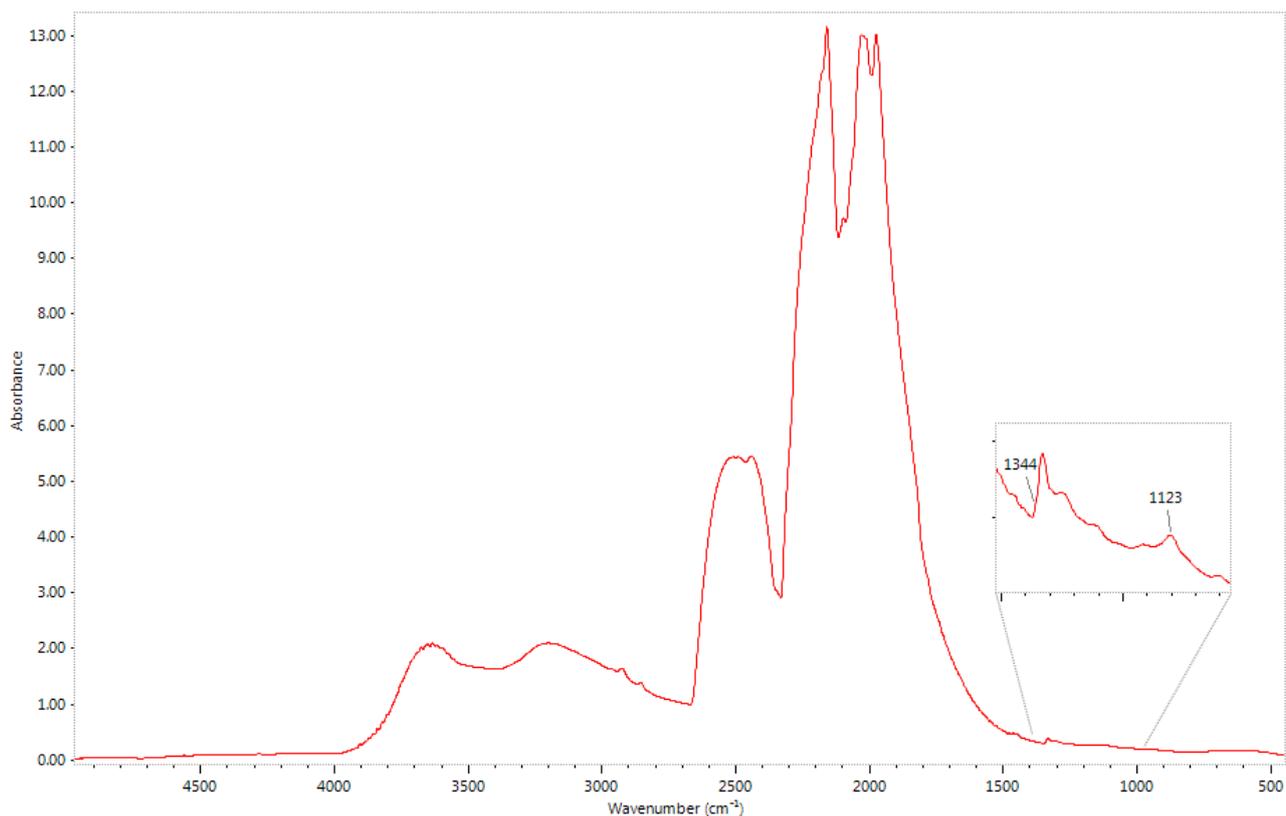


Fig 10. FTIR spectrum of multistep-treated type IIa pink CVD diamond with minor type Ib character (C-defect).

FTIR analysis confirmed the stones are type IIa. Only very minor type Ib component (single nitrogen) was detected at 1123 cm^{-1} and as a weak shoulder at 1344 cm^{-1} . No irradiation related defects were found.

The absorption spectrum acquired in RT provides some important information for these stones; the silicon-vacancy defect was readily apparent at 737 nm. Instead of so called “pink band” at about 550 nm seen in natural pink stones, a broad band with maximum at about 520 nm was detected. No N3 center at 415.2 nm typical for natural stones was found. Cooling the samples to LNT revealed many absorption features never seen in natural diamonds having natural origin for their color. The most important clue for CVD-origin

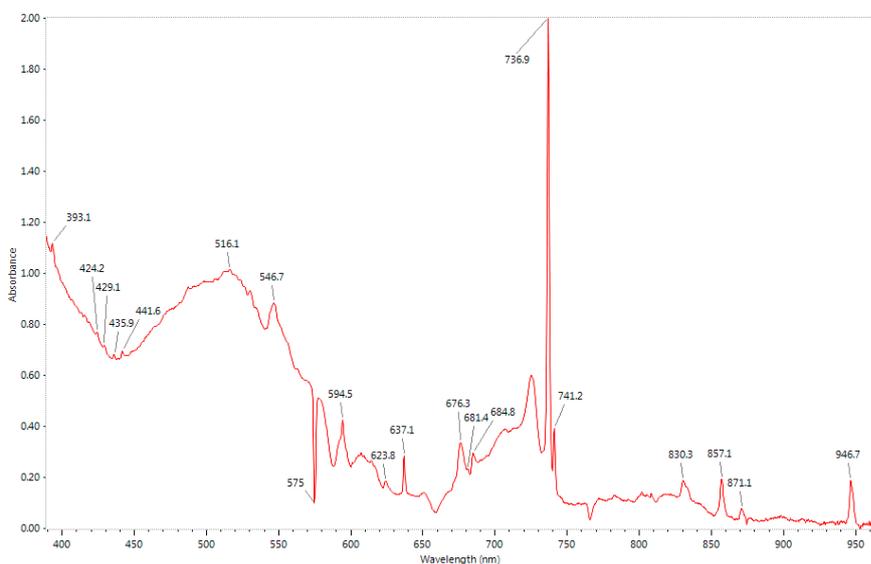


Fig 11. UV-Vis-NIR spectrum of multistep-treated type IIa pink CVD diamond

was again now pronounced SiV⁻ peak at 737 nm and other Si-related absorptions, such as 946.7 nm peak. Neutrally charged nitrogen-vacancy pair (NV⁰) at 575 nm was visible as “negative absorption” due to its strong luminescence under broadband halogen light illumination of the spectrometer. ND1 peak at 393.1 and 594.5 nm peak are evidence of irradiation followed by low temperature (<1000°C) annealing as last step of treatments. GR1 line at 741.2 nm supports this fact as it would not survive any HPHT-treatment.

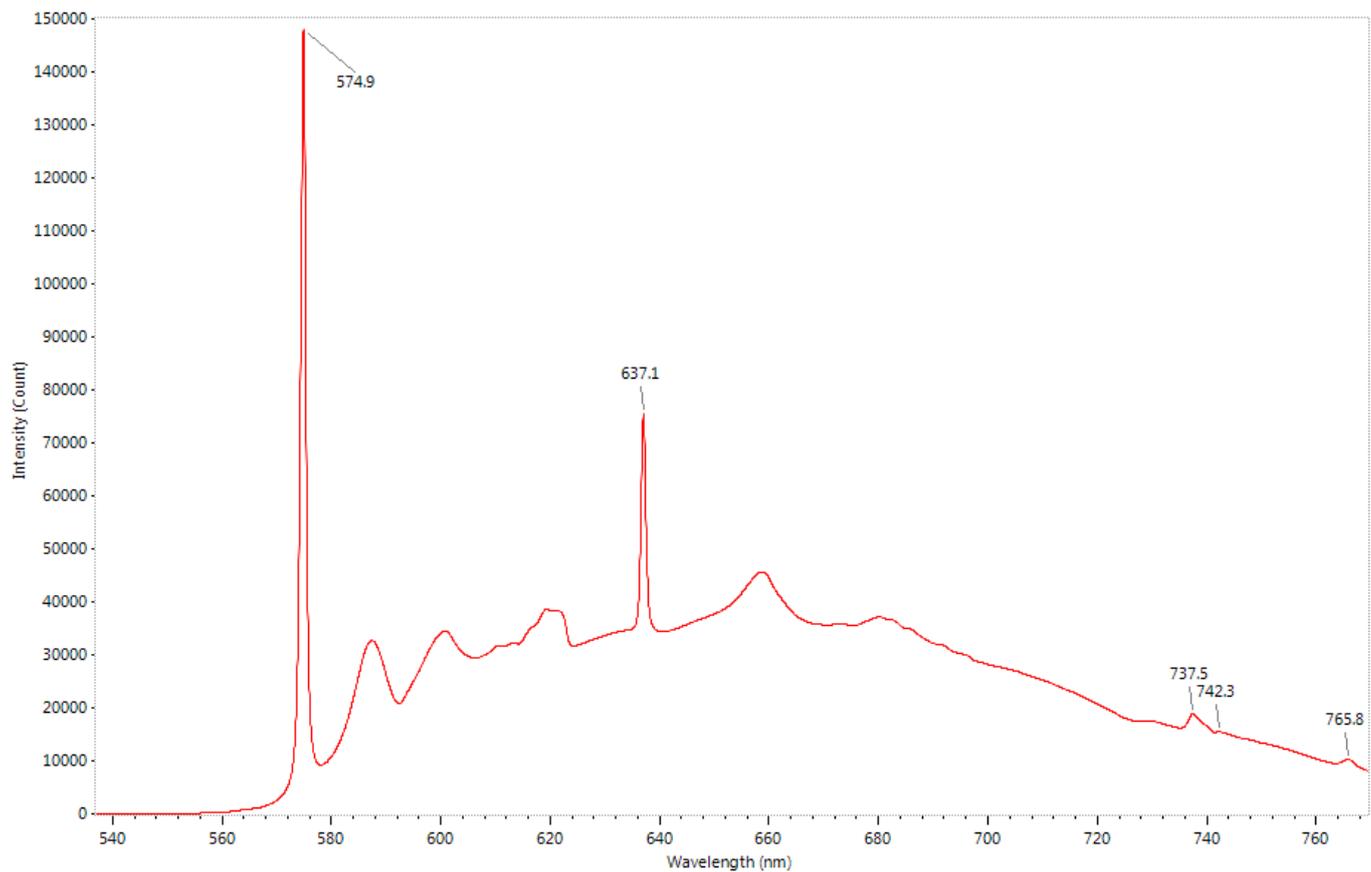


Fig 12. Photoluminescence spectrum (532nm excitation) of pink type IIa post-growth multistep-treated CVD diamond

Photoluminescence spectra of pink CVD-stones recorded in LNT were highly dominated by strong luminescence of nitrogen vacancy centers (NV^0 , ZPL at 575 nm and NV^- , ZPL at 637 nm) and their side bands. This is typical situation for any diamond owing its pink to red coloration to treatments, and completely different to the PL spectra of natural pink diamonds having natural origin of color. SiV^- peak at 737.5 nm was detected also in PL regime, but it is important to note that cooling the sample to LNT was essential in order to make it visible. The peak at 765.8 nm is also related to silicon impurities.

Discussion

Newest generation of fancy colored CVD-grown diamonds has arrived on the marketplace soon after their first occurrence reported by a major gemological laboratory. These stones are more difficult to separate from natural diamonds with standard gemological tools. The orange LWUV-fluorescence of pink stones is the most important single indication of possible CVD- origin, but further optical spectroscopy and luminescence imaging are required for separating them from synthetic HPHT-grown and natural color-treated diamonds. The arrival of new blue type IIa CVD-grown diamonds creates much more severe problem, because their spectroscopic characteristics acquired in room temperature are similar to natural irradiated blue diamonds, and these stones are not electrically conductive. Major problems are to be expected for testing mounted stones if and when immersion in liquid nitrogen is not possible. PL spectroscopy in liquid nitrogen temperature appears to be one of the few reliable spectroscopic methods for detecting this newest generation of blue CVD diamonds. These stones are no longer a gemological curiosity, they are available in large quantities as witnessed by the authors.

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