New Generation of Synthetic Diamonds Reaches the Market

Part B: Identification of treated CVD-grown Pink Diamonds from Orion (PDC)

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Introduction

Natural pink diamonds, particularly those over 0.5ct and intense color are very rare, what makes them both highly precious and in great demand in the diamond market. Today, natural pink diamonds for the most part come from Australia, from the Argyle mine [1,2]. However, only 10% of all pink diamonds coming from that mine are larger than 0.2ct, so screening pink small and melee diamonds for treated and synthetic origin is a very important task of gem laboratories. One of the biggest challenges today in gem industry is to quickly identify the origin of color of pink diamonds - natural, treated or synthetic.

Nowadays the color enhancement is widespread and the aim of the color treatment is to provide stable changes in internal defect structure and produce pink color. The main technologies used for color enhancement of pink diamond include processing at high pressure and high temperature (HPHT), irradiation and subsequent annealing [3]. In the last decade we documented increased use of a new multistep method utilizing these three treatment techniques to produce rare pink colors and even large stones over 10ct were enhanced with this method [4]. Major gem laboratories have identified color surface enhancement processes (plasma deposition of hard ceramic coatings) with limited color stability that is observed primarily in pink diamonds in 2006 [5,6]. Laboratory grown yellow diamonds produced by HPHT process and brownish diamonds produced by CVD process are post-treat-ed with irradiation/annealing to make pink color that became very popular and fashionable [7, 8]. Synthetic diamond producers like AOTC Canada and Scio Diamonds USA increased their production of pink lab-grown diamonds by 5-10 percent over the last 5 years to meet higher demand for more affordable but still stable color. As a consequence a new generation of pink CVD-grown diamonds, produced by “Orion PDC” and “Scio Diamond” were brought onto the market. They are of much more “natural looking” fancy colors (orangy pink and purplish pink) and higher clarity (VVS - VS); they are available in all sizes and harder to identify than HPHT-grown pink diamonds with standard instruments. The most widely used methods for separation of natural, treated and synthetic pink diamonds are optical methods (absorption and photoluminescence) that are used in our study as well to identify these stones as CVD-grown pink diamonds.

We concluded that it is possible to separate pink CVD-grown Orion (PDC) diamonds from natural pink diamonds (Argyle), from multistep treated pink and HPHT-grown pink diamonds by use of a combination of standard and advanced gemological instruments described in detail below.

Keywords: Synthetic, CVD-grown, pink diamond, type IIa, irradiation
Materials & Methods

GRS and CGL-GRS labs acquired 4 pink CVD-grown diamonds from a new producer Orion (PDC) in Hong Kong (see article on “Blue CVD-grown diamond”, Part A, [9]), and compared them to pink diamonds of different origin from our research collection:

• 4 Natural pink diamonds, natural color from Argyle
• 2 Natural pink diamonds, natural color of unknown origin
• 1 Natural pink diamond, multistep treated (HPHT, irradiation and subsequent annealing) by Suncrest Diamonds, USA
• 2 CVD-grown, HPHT enhanced, irradiated and annealed diamonds by Scio Diamond, USA,
• 3 HPHT-grown and irradiated diamonds by Chatham, USA
• 1 HPHT-grown and irradiated diamond by Russian producer, USA
• 1 HPHT-grown and irradiated diamond by AOTC, Canada

The same methods were used as described in part A [9] and an additional luminescence microscope. A Zeiss Axioplan microscope with an external Mercury Short Arc HBO100 W/2 light source (excitation range: 395 – 440 nm) was used to produce luminescence images by UV Luminescence Microscopy.

Fig. 1: A series of CVD pink diamonds from PDC Orion as offered on the market in September 2013 in Hong Kong. The CVD-grown diamonds are 1.2ct each.

Fig. 2a: This HPHT-diamond laboratory of Ziemer Swiss Diamond Art AG (Port, Switzerland) shows a recent example of an upcoming factory producing lab-grown diamonds by BARS split sphere technology. Compare with CVD-diamond factory (Part A, Fig. 1[12])

Fig. 2b: The expert group during the inspection of the HPHT laboratory in Switzerland from left to right: R.E. Chodelka (CEO and Chief Technical Officer of Ziemer Swiss Diamond Art AG, former technician at Gemesis Diamond Company, California), K. Ziemer (founder of the Ziemer Group AG) with GRS gemologists W. Bieri and F. Peretti.
Fig. 3a-b: These 2 pictures were taken in the fluorescence microscope. A HPHT diamond of 0.70ct of the GRS collection showed a very characteristic geometric cubo-octahedral pattern under SW UV fluorescence and medium yellowish green reaction (right side). In contrast, the CVD synthetic pink diamond (left side) that was measured together with this sample in the same run showed strong pinkish orange uniform fluorescence reaction with no other structures than trails of black inclusions. (Photos WB).

Fig. 4: These faceted synthetic pink diamonds were tested for this report: four CVD diamonds grown by Orion PDC (on top), one CVD diamond grown by Scio Diamond, four synthetic HPHT-grown diamonds from Chatham, AOTC and Tairus (Russia). Color and carat weights of these stones range from Fancy light pink to Fancy intense pink, and from 0.05 to 0.60 carats respectively.
Results & Discussion

Visual characteristics
Visually, pink CVD-grown diamonds grown by Orion PDC Diamond companies look very similar to natural diamonds or Scio pink CVD-grown diamonds, mostly in Fancy color grade with orange or purple modifiers. HPHT-grown pink diamonds tend to have more nitrogen than CVD-grown diamonds and colors are usually darker, more intense and more purplish, and it’s the similar case with natural diamonds that are multistep treated to make pink colors.

As in case with blue CVD-grown diamonds, most pink Orion PDC CVD-grown diamonds exhibit high clarity (VVS2-VS2). Based on this clarity it’s not possible to distinguish them from pink natural diamonds just by using a loupe or a microscope. Yet, in some CVD stones, black inclusions (assumed to be non-diamond carbon) are visible and when located in one plane perpendicular to the direction of growth, they are a reliable indicator of the diamond’s CVD origin.

Fig. 5a: Blackish irregular clouds are found in this CVD-grown pink diamond from PDC (HRef-0161-2)

Fig. 5b: Blackish irregular clouds are found in this CVD-grown pink diamond from PDC (HRef-0172, 0.50ct, 80x, fiberoptic, L.H.)

Fig. 6a-b: Black inclusion in a CVD synthetic diamond from Scio Diamond is assumed to be non-diamond carbon.

Fig. 5c: A blackish layer in a PDC CVD-grown pink diamond is accompanied by whitish particles and transparent crystals (HRef-0172, 0.50ct, 100x, fiberoptic, L.H.)
Examination in polarized light

The birefringence patterns of natural pink diamonds vary from type I (more intense interference colors) to type II (displaying a subtle ‘tatami’ pattern). The birefringence of synthetic pink HPHT-grown diamonds is not present and that assists with identification of these diamonds. All new-generation pink CVD samples are type IIa diamonds, low nitrogen diamonds. Observed between cross-polarized filters, they produce two general patterns:

- A natural-looking pattern similar to ‘tatami pattern’ of type IIa natural diamonds and
- Columnar pattern” typical for CVD–grown diamonds [10], see Fig. 7.

UV-Fluorescence

A quick screening of loose and mounted pink diamonds is possible by using strong UV illumination in a dark room. Natural Argyle diamonds studied for this project and by one of the authors (BD) in 2007 [5] are showing strong (LW) and weak (SW) blue florescence caused by N3 centre. On the contrary multistep treated natural [23] and irradiated and annealed HPHT-grown and CVD–grown samples from different producers are displaying characteristic medium to strong orange florescence in LW/SW light caused by dominant N·V0 centre (575nm). The fluorescence test indicated that the new CVD material show similar reaction to UV light as Scio CVD–grown and HPHT–grown synthetic diamonds (Fig. 8) and it is not possible or very difficult to separate these 2 categories of synthetic diamonds based on the fluorescence test only. A weak orange phosphorescence was observed in one of the CVD–grown pink diamonds (see Table 1).
Contributions to Gemology
Part B - CVD-grown Pink Diamonds

Box: Natural Pink and Red Diamonds from the Argyle Mine in Australia

The most prominent occurrence of pink and red diamonds are known from the Argyle mine in Western Australia and a few examples of the color varieties, rough shapes are described below:

Fig. 10: Aerial view of Argyle mine, major source of pink diamonds since 1980’s. The Argyle mine located in the remote northwest of Australia first started producing diamonds 30 years ago and at its peak output produced 42 million carats from the lamproite pipe in 1994. Since then the output has dwindled to a recent low of 10 million carats, but with the current underground operation the annual output is expected to increase beyond 20 million carats. Argyle is the largest mine in the world by production, but produced mostly brown diamonds. Less than 0.1% of the production is pink diamonds, whereas almost three-quarters are brown hues popularly referred to as ‘champagne’, ‘cognac’ and ‘chocolate’ colors. Of its total output, only a total of a few kilos of pinks are produced per year. These are mostly small diamonds and of that, only approximately 50 stones over 1 ct are found. These stones gain a lot of attention when sold in specially organized auctions (see Fig. 13a-d and Fig. 13a-b) / Fig. 10 - 14 Copyright Argyle Diamonds.

Fig. 11: The Argyle Mine is the world’s only consistent source of Vivid Purplish Pink diamonds sold at breaking record prices at special tenders around the world, such as the one pictured.

Fig. 12: Variety of brown color crystals with one intense purple-pink crystal.
Box: Color Varieties of Natural Fancy Diamonds from the Argyle Mine, Australia

Fig. 13a: Variety of PURPLE colors.

Fig. 13b: Variety of Pinkish BROWN colors.

Fig. 13c: Variety of PINK colors.

Fig. 13d: Variety of Brownish PINK colors.

The Pink Diamond Tender 2000
Tokyo, Honk Kong, Sydney, New York, Geneva

Fig. 14a: 1.14ct GIA Fancy Deep PINK I1
HRD Fancy Intense Brownish PINK P1.

Fig. 14b: 1.66ct GIA Fancy Vivid Purplish PINK SI1
HRD Fancy Intense Purplish PINK SI2.

Fig. 14a-b: Same pink diamonds could receive different color and clarity grades from different gem laboratories, because grading of colored diamond is subjective and depends on color masters and grading standards used in various laboratories.
Fig. 15a: UV-VIS-near IR absorption of synthetic and natural pink diamonds as indicated. Spectra registered at Liquid nitrogen temperatures. For more details see the Fig 15b-d.

UV-VIS-NIR spectroscopy

The common dominating features of UV-VIS absorption spectra of the studied CVD pink diamonds are a broad band with maximum at about 520 nm, NV<sup>0</sup> (ZPL at 575 nm) and NV<sup>-</sup> (ZPL at 637 nm) centres (Fig. 15b). Two diamonds also reveal strong presence of the silicon-related SiV<sup>-</sup> centre with ZPL at 737 nm. The NV<sup>0</sup> centre is observed in the regime of luminescence suggesting its low efficiency in absorption, but high efficiency in luminescence.

Many weak absorption features have been found through the whole UV-VIS spectral range. In the spectral range of 380 to 460 nm, the studied pink CVD diamonds reveal numerous absorption features, the most common and obvious of which are lines at wavelengths 424.7, 436.4 and 441.9 nm. Traces of the 388 nm centre (a defect containing single nitrogen atom) and the ND1 centre (ZPL at a wavelength of 393.5 nm, negatively charged single vacancy) can be found in most Orion (PDC) too.

The main absorption feature distinguishing the studied natural pink diamonds from their CVD-grown and treated HPHT-grown counterparts is a pronounced N3 centre, which together with the 550 nm band (“Natural Pink Band) and the 380 nm band are the dominating color centres (Fig. 15c). These two bands are among the most important optical centres. Indeed they come
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Part B - CVD-grown Pink Diamonds

![UV-VIS, CVD](image1)

**Fig. 15b**

![UV-VIS, HPHT](image2)

**Fig. 15c**

![UV-VIS, natural](image3)

**Fig. 15d**

usually together in natural pinks, not in synthetic (both HPHT and CVD) pinks. Although their intensities do not correlate well, there is a tendency of stronger 380 nm bands in diamonds with a strong 550 nm band. Both bands are usually stronger in type I diamonds than in type IIa.

Thus it is quite possible that they originate from nitrogen-related defects. When the spectra of these bands are compared with the absorption spectra of nitrogen-related centres, it is seen that the spectral range of the 550 nm band coincides with that of the phonon sidebands of the NV centre, while the spectral range of the 380 nm band is almost the same as that of the N3 centre. Based on this match, one may come to an assumption that the 550 and 380 nm bands originate from defects similar to NV and N3 defects. The N3 centre is almost never seen in spectra of as-grown CVD diamonds. However traces of this centre can be detected in CVD diamond after HPHT treatment performed at temperatures high enough to cause aggregation of dispersed nitrogen atoms [12]. Very weak N3 centre has been found in absorption spectra of some studied CVD diamonds what suggests that these diamonds were subjected to high temperature annealing in their post-growth processing (Fig. 15b).

Fig. 15b-d: UV-VIS-near IR absorption spectra recorded at liquid nitrogen temperature (LNT) for the respective groups: CVD-grown, HPHT-grown and natural diamonds. Important features are highlighted. The synthetic (CVD, HPHT) diamonds were all irradiated. Apart from Ref20031 (natural, multistep treated) the natural diamonds show their natural (original) color. The ordinate shows the absorbance in arbitrary units. For better presentation the different spectra have been moved relatively to each other.
The well-known line at wavelength 594.4 nm (the 595 nm centre) has been found in all pink CVD diamonds. This centre is evidenced as an evidence of irradiation followed by low temperature treatment [13]. In case of CVD diamonds, the generation of the 595 nm centre does not require the step of irradiation for they always possess high concentration of vacancies, which are required for the building of the defects responsible for the 595 nm centre. The presence of this centre is evidence that the studied CVD diamonds were not heated at temperatures over 1000°C at the last stage of treatment.

A weak GR1 centre is seen in absorption spectra of most CVD- and HPHT-grown pink diamonds (Fig. 15b-c). Conversely, GR1 centre has not been detected in spectra of natural pinks. GR1 centre together with ND1 centre strongly suggest that these diamonds were treated using irradiation followed by low temperature annealing. A multistep treatment HPHT + irradiation + annealing would be a possible procedure. In case of HPHT-grown diamonds, the standard procedure to achieve pink color via generation of high concentration of negatively charged NV defects is irradiation and low temperature annealing (Fig. 15c). In these diamonds, the NV centre band can be so strong that it is seen even with portable OPL spectroscope. In case of CVD-grown diamonds, which do not have the 520 nm absorption band strong enough to induce pink color, the generation of NV defects by multistep treatment is a reliable way to achieve the desired pink color.

The ND1 centre is almost always observed in absorption spectra of CVD-grown diamonds and treated HPHT-grown diamonds processed at low temperature. This centre, however, is rarely seen in spectra of natural diamonds (Fig. 15a). The ND1 centre is a negatively charged vacancy and its presence is an indication of an enhanced concentration of nitrogen C-defects, which are a common result of CVD growth and/or HPHT-growth. The broad band with maximum at about 520 nm present in absorption spectra of all studied pink CVD-grown and treated HPHT-grown diamonds deserves special attention (Fig. 15b,c). This band is most pronounced in synthetic and treated diamonds with pink-red color component and its spectral parameters differ from those of well known “Natural” Pink Band observed in natural pink diamonds at a wavelength of 550 nm (Fig. 15a,d). The spectral shape of the 520 nm band may vary from diamond to diamond and it can be considerably modified via interference with photo-
FTIR spectroscopy

All Orion PDC pink CVD-grown diamonds are of type Ila with negligible absorption in the range 1000 to 1500 cm\(^{-1}\). Yet small peaks at 1503, 1450 (H1a centre), 1340 and 1332 (N+ centre) can be recognized. Two out of 4 stones display the peak at 3107 cm\(^{-1}\) related to hydrogen (Fig. 16a) [14]. Scio pink CVD-grown diamonds are also type Ila with FTIR spectra similar to those of Orion (PDC) pink CVD-grown samples (Fig. 16a). Type Ila natural pink diamonds are quite rare in nature (less than 2% of all natural pinks). Most natural pink diamonds come from Argyle mine and they are typically type IaAB with moderate to high nitrogen content and display the hydrogen-related peak at 3107 cm\(^{-1}\) (Fig. 16c). One of the characteristic “fingerprints” of Argyle natural pinks, as compared to non-Argyle” pinks, is that B aggregate concentration is higher than that of A aggregates [18, 19].

In case of HPHT-treated pink diamonds, Suncrest company uses low nitrogen type Ia diamonds and processes them by multistep treatment in order to get “natural looking” pink colors [11]. Producers of treated pink HPHT-grown diamonds from Russia, Chatham and AOTC also try to use type Ila or low nitrogen type Ib diamonds to obtain fancy pink diamond colors [17] (Fig. 16b). FTIR spectroscopy could be used as a preliminary screening technique for separation of treated pink diamonds based on their type, however further VIS absorption and PL spectroscopy is necessary to reliably identify them (Fig. 16a-c, Fig. 17a-c and Fig. 18a-d).

Fig. 16a-c: FTIR absorption spectra of pink diamonds for the respective groups: CVD-grown, HPHT-grown and natural diamonds. The spectra were taken at room temperature (RT). The synthetic diamonds (Fig 21a,b), which were all irradiated, are type Ila diamonds whereas the natural diamonds (Fig. 21c) are type Ia diamonds. The sample Ref20031 is a natural, multi-step treated diamond. The ordinate shows the absorbance in arbitrary units. For better presentation the different spectra have been moved relatively to each other.
Other FTIR absorption features found in spectra of all studied pink CVD diamonds are peaks at 1292 and 1130 cm\textsuperscript{-1} (single nitrogen), which have been already reported for pink diamonds of CVD origin (synthetic) [18]. The 1292 cm\textsuperscript{-1} band is the main feature of the spectra of all but one CVD diamond (Fig. 17a). The origin of this band is unknown. However, since it is present in spectra of many synthetic pink diamonds, it is possible that the 1292 cm\textsuperscript{-1} band originates from defects common for these diamonds. Comparing the FTIR and VIS absorption spectra reveals some correlation of the 1292 cm\textsuperscript{-1} band intensity with the intensity of the short wavelength wing of the 520 nm CVD Pink Band, which probably originates from a broad band component with maximum at a wavelength of 480 nm.
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**Fig. 18a:** PL spectra of synthetic and natural pink diamonds as indicated. Spectra registered at Liquid nitrogen temperatures. For more details see the Fig. 18b-d.

**PL spectroscopy**

PL spectra of all studied diamonds are very complex revealing a few major centres and numerous week features over the whole visible spectral range (Fig. 18a). The most general feature distinguishing the natural pink diamonds from the CVD-grown, HPHT-grown and multistep treated pink diamonds is the different sets of dominating centres: the N3 and H3 centres in natural diamonds [19] and NV centres in synthetic and treated diamonds. This observation presents clear evidence that the aggregation of nitrogen even in type IIa diamonds from the CVD-grown, HPHT-grown and multistep treated pink diamonds is the different sets of dominating centres: the N3 and H3 centres in natural diamonds [19] and NV centres in synthetic and treated diamonds. This observation presents clear evidence that the aggregation of nitrogen even in type IIa diamonds from the CVD-grown, HPHT-grown and multistep treated pink diamonds is different. The aggregation of nitrogen is almost always close to completion, whereas it is not at all in any laboratory-grown diamond even if it has been HPHT treated (Fig. 18b-c).

The behaviour of the NV centres in PL spectra depends considerably on the excitation wavelength. When excited with a wavelength of 405 nm, which does not fit into the excitation spectral range of the NV centre, the NV$^0$ centre always dominates and the NV$^-$ centre is seen in the regime of absorption (negative luminescence) only (Fig. 18a-d). With excitation at a wavelength of 532 nm, both centres are excited in the regime of luminescence with comparable intensities (Fig. 19a-d). However, when the concentration of negatively charged NV defects is high, ZPL of the NV$^-$ centre shows simultaneously luminescence and absorption resulting sometimes in a “doublet” line.

The SiV centre with ZPL at 737 nm [20], a feature manifesting the growth in a standard CVD reactor, has been found in some CVD diamonds only (Fig. 18a, b and Fig. 19a). None of the HPHT-grown and natural diamonds studied in this research have revealed even traces of this centre (Fig. 18b,c and Fig. 19b,c).

In PL spectra excited with a 532 nm laser, most of CVD
and HPHT-treated diamonds, as well as some of natural diamonds reveal the presence of weak GR1 centre (Fig. 19b-c). An unusual behavior of this centre is that in natural diamonds its ZPL is detected in the regime of luminescence only. All CVD and HPHT diamonds studied in this research exhibited the GR1 centre in the regime of absorption. Most of pink CVD-grown diamonds reveal in PL spectra (excitation at 405 nm) the narrow lines at wavelengths 503.2 nm (H3 centre), 496.1 nm (possibly H4 centre) and 498.5 nm. Interestingly that in spectra of CVD diamond these lines are always accompanied by the lines at 505.2, 498.1 and 492 nm (Fig. 18b). In one HPHT diamond, the H3 and H4 centre are also accompanied by the lines 505.2 and 498.1 nm (Fig. 18c). The 505 and 498 nm centres were already reported [24, 13] and they were tentatively ascribed to H3 and H4 defects trapped into brown lamellae of natural diamonds. Both centres do not survive HPHT treatment. However, they can be well restored by following irradiation and conventional low temperature treatment [25, 17]. The present research reveals that these centres can be seen in pink synthetic diamonds (Fig. 18b,c).

All studied synthetic diamonds revealed in PL spectra “negative” luminescence (absorption) of a line at wavelength 594.4 nm, which originates from the well-known 595 nm centre (Fig. 18b,c).

Fig. 18b-d: PL spectra (excitation 405nm) of pink diamonds recorded at liquid nitrogen temperature (LNT) for the respective groups: CVD-grown, HPHT-grown and natural diamonds. The synthetic (CVD, HPHT) diamonds were all irradiated. The sample Ref20031 is a natural, multi-step treated diamond. The ordinate shows the intensity (counts) in arbitrary units; for better presentation the different spectra have been moved relatively to each other.
A remarkable feature of the studied natural pink diamonds, like of almost any natural diamond of a color with the pink-brown component, is the presence in PL spectra excited with 532 nm laser at least traces of the 576 nm centre (Fig. 19c). The 576 nm centre is an evidence of plastic deformation and it is a very characteristic feature of natural untreated pink-brown diamonds. The 576 nm centre always anneals after HPHT treatment performed at temperatures over 1800°C. Thus, with rare exception of low temperature HPHT treatment, the presence of the 576 nm centre is a reliable proof that diamond has not been HPHT processed [23]. Some other observations, which could be useful for separation of natural pink diamonds from their synthetic and treated counterparts, are the following:

(i) In PL spectra, natural pink diamonds frequently show a weak line at a wavelength of 444.6 nm, which is not seen in HPHT-grown and CVD-grown diamonds (Fig. 18d).

(ii) The spectra of natural pink diamonds do not show variety of many optical centres of measurable intensity over the whole visible spectra range like all studied pink CVD diamonds do (Fig. 15d).

(iii) In PL spectra, many natural pink diamonds reveal a centre with ZPL at 669 nm (Fig. 18d). Its position may vary from 669.0 to 668.6 nm [24]. Notwithstanding this variation, the 669 nm centre can be well recognized by its phonon replica at 690 nm. This centre is not the feature of pink CVD diamonds and HPHT-treated pink stones (Fig. 18b-c).

(iv) All pink CVD-grown (as well as most HPHT-grown) show the 1042 nm centre, which is another optical transition at NV defects [25]. This centre is always very weak and its presence is a proof of an enhanced concentration of the NV defects. Thus a clearly seen 1042 centre is a feature of lab-grown and treated diamonds (Fig. 19a-c).

Fig. 19a-c: PL spectra (excitation 532nm) of pink diamonds recorded at liquid nitrogen temperature (LNT) for the respective groups: CVD-grown, HPHT-grown and Natural diamonds. The synthetic (CVD, HPHT) diamonds were all irradiated. The sample Ref20031 is a natural, multi-step treated diamond. The ordinate shows the intensity (counts) in arbitrary units; for better presentation the different spectra have been moved relatively to each other.
Conclusion

We studied Orion PDC pink CVD–grown diamonds and compared them to natural, natural multistep treated, HPHT-grown and CVD-grown diamonds from other producers and similar pink colors (Appendix - Box 1). We found that screening with UV lamp is a useful test, especially convenient for melee and mounted pink diamonds. For pink diamonds a medium to strong orange fluorescence resulting from excitation by LW and SW-UV-light is a clear evidence, that this particular stone is NOT a Natural pink diamond with Natural color. The 520 nm absorption band is obviously the main reason of pink color of pink CVD-grown diamonds. The NV centres may also contribute to pink coloration, but their presence as the color centres in pink CVD-grown diamonds is not required. In this respect, pink CVD-grown diamonds resemble natural pink diamonds. Yet the spectral shapes of the Pink Bands in CVD-grown and natural diamonds are sufficiently different and their differentiation does not cause a problem.

PL spectroscopy is the most powerful technique in separation of natural untreated, natural treated and lab-grown pink diamonds. The major feature of PL spectra of natural untreated pink diamonds is the dominating N3 and H3 centres, whereas NV and NV\(^0\) centres dominate PL spectra of treated and synthetic diamonds. Many other features uniquely present in spectra of either natural untreated, or natural HPHT-treated, or HPHT/CVD-grown diamonds also contribute to the reliable identification of color origin of pink diamonds.

The number of pink CVD-grown diamonds grows on the market in Asia, however their identification does not cause problems to the gem laboratories equipped with good VIS absorption and PL spectrometers. Nevertheless it is necessary to screen and test “natural looking” pink diamonds of different sizes in parcels of small and melee diamonds for their color origin: natural, treated or synthetic (HPHT-grown or CVD grown).

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Perfect CVD diamonds, like perfect type IIa natural diamonds, are colorless. Introduction of certain impurities during growth and/or activation of them by post-growth treatment produces color. Two colors characteristic of Orion colored CVD diamonds are pink and blue.

Pink color is produced by two color centres: a broad band centred at a wavelength of 520 nm and the nitrogen-related NV centre. Both centres absorb in the green spectral range making these diamonds to transmit preferentially red and blue colors. A combination of these colors is seen as purple to pink. The 520 nm band and NV centre can be well induced in CVD diamond by doping with nitrogen, irradiation and annealing (e.g. HPHT treatment) and pink CVD-grown diamonds are becoming a pervasive synthetic gem material on the diamond market.

Blue color of CVD diamonds can be induced by doping with boron and, more recently, with silicon. Both impurities form optical centres absorbing preferentially the red and partially in green spectral ranges. Thus the boron- and silicon-doped diamonds have maximum transparency for blue light. The boron doped HPHT-grown diamonds are a perfect imitation of natural blue diamonds since the latter also owe their blue color to boron impurity. The blue color of the silicon-doped diamonds differs from that of the boron-doped ones. The reason is some additional absorption in a wide spectral range produced by silicon impurity. This absorption adds a grey-“steel” color modifier to the blue color of silicon-doped CVD diamonds. In contrast to pink CVD diamonds, blue CVD-grown diamonds are still relatively rare on the diamond market.
Table 1: Summary of tested natural and synthetic pink diamonds of different producers and synthesis methods and results of examinations

<table>
<thead>
<tr>
<th>Producer</th>
<th>CVD-grown irradiated Orion PDC 4 samples</th>
<th>CVD-grown, irradiated Scio 2 samples</th>
<th>HPHT synthetic, irradiated Chatham 4 samples</th>
<th>HPHT synthetic, irradiated Russia 1 sample</th>
<th>HPHT synthetic, irradiated AOTC 1 sample</th>
<th>Natural, multistep 1 sample</th>
<th>Natural, natural color 2 samples</th>
<th>Natural, natural color Argyle 4 samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>fancy pink, fancy brownish orange pink (&quot;peach&quot;); fancy intense purplish pink</td>
<td>fancy orange pink to fancy intense purplish pink</td>
<td>fancy intense pink to fancy intense purplish pink</td>
<td>fancy pink</td>
<td>fancy intense purple pink</td>
<td>fancy purplish pink</td>
<td>fancy light orange pink</td>
<td>fancy light pink</td>
</tr>
<tr>
<td>Clarity</td>
<td></td>
<td></td>
<td>black metallic inclusions, small crystals forming a cloud</td>
<td>big crystal with associated feather</td>
<td>none</td>
<td>small feathers</td>
<td>feathers</td>
<td>rVA (fragments)</td>
</tr>
<tr>
<td>Solid Inclusions (at 60x magnification)</td>
<td>dark cloud, crystals, feathers around girdle, dark blue staining</td>
<td>graphitization of fracture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorescence SWUV (254nm)</td>
<td>medium to strong orange, weak orange phosphorescence</td>
<td>strong orange</td>
<td>medium orange</td>
<td>medium orange</td>
<td>medium orange</td>
<td>inert to weak blue</td>
<td>weak blue, none to weak blue phosphorescence</td>
<td></td>
</tr>
<tr>
<td>Fluorescence LWUV (365nm)</td>
<td>medium to strong orange, weak orange phosphorescence</td>
<td>strong orange</td>
<td>medium to strong orange</td>
<td>medium orange</td>
<td>strong orange</td>
<td>inert to strong blue</td>
<td>strong blue, none to weak blue phosphorescence</td>
<td></td>
</tr>
<tr>
<td>Cross Polarized Filters (CPF)</td>
<td>&quot;Tatami&quot; pattern</td>
<td>no pattern</td>
<td>no pattern</td>
<td>no pattern</td>
<td>patchy pattern</td>
<td>rVA (fragments)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FTIR spectroscopy (absoption, cn-1)</td>
<td>type IIa spectrum, small peaks at 1504, 1540 (H1a), 1340, 1332 (N+), 1296, 1263. Peak at 2107 (H-center).</td>
<td>type IIa spectrum, sample 1: small peak at 1340 and 1406, sample 2: 1450 (H1a), 1342, 1331 (N+), 1298 (C-center), peak at 3107(H)</td>
<td>type IIa spectrum, small H1a (1450) and N’ (1332) peaks. Peak at 1560, sample 4: peaks at 1560, 1545, 1537, 1504, 1451 (with side band at 1470) 1344 and 1129 (C-center), 1332 (N+), broad peak at 766.4</td>
<td>type IIb with indications of C-centers (1344, 1332), peaks at 1560, 1502, 1450 and 1332.</td>
<td>type Ib of low nitrogen. H1a-center at 1450 and N’ at 1331. A-aggregate at 1284, no signs of single nitrogen or B-aggregates. H-center related peaks at 3107 and 1405.</td>
<td>type IaAB, B=A, with a plateau peak at 1365, H-center related peaks at 4949, 3107 and 1405</td>
<td>type IaAB, B=A, plateau peak at 1362 (three samples only), H-related peak at 3108 and 1405; sample 4 shows no plateau but peaks at 1378 and 1359</td>
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<tr>
<td>UV-VIS-NIR spectroscopy at LNT (absorption):</td>
<td>small peaks at 415.8 (N3), 424.2, 436.8, 442.0 (radiation damage center), valley at 575 (NV3), peaks at 594.4, 637.1 (NV1), 737 (Si-center), sample 2: no 415 sample 2 and 4: small peak at 741 (GR1)</td>
<td>small peaks at 385.8, 387.9, 389.3, 416.2 424.7 436, 441.9, 506.2, 516.5, 535, peaks at 575, 637 and 594.2. Small peaks at 724.8, 732.6 and 764.6 sample 1 with doublet at 883.2-894.8, sample 4 with 741 (GR1)</td>
<td>small peaks at 385.4, 387.9, 415.8, 424.7, 436.4 and 441.8 , peaks at 637, 575 and 594</td>
<td>small peaks at 385.8, 387.9, 389.3, 416.2 424.7 436, 441.9, 506.2, 516.5, 535, peaks at 575, 637 and 594.2</td>
<td>small peaks at 385.4, 387.9, 415.8, 424.9, dip at 575.5, small peak at 741</td>
<td>peaks at 393.8, 415.4, 424.9, dip at 575.5, small peak at 741</td>
<td>peaks at 315.6 (N6), 317.8, 320.1, 338.2, 344.8 (N4). Clear 415 (N3-center &quot;Cape&quot;-line), small peaks at 477 (N2), 533.4 (H3), 763 and at 823.5 (very small)</td>
<td>small peak at 435 and clear N3-center at 415, peak at 450</td>
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<tr>
<td>PL-spectroscopy at LNT - 450nm</td>
<td>peaks at 453.7, 462.3, 468.0, 496.1, 503.3, 503.8, 515.1, 517.8, small peaks at 533.1, 540.7, 575, 637.4, 658.2, 736.8 (Si), 767.5, 820.0, 823.0, sample 2 with small 441.9 and 594.4 peaks but no 737; sample 4 peak at 594.4</td>
<td>peaks at 496.0, 498.2 and 503.2, 505.1, peak at 575, small peak at 637, valley at 575(NV3), peaks at 594, 637.1 (NV1), 741 (GR1)</td>
<td>peaks at 494.8, 498.4, 498.3, 499.1, 503.5, 572, 637.3, small doublet at 882.9 and 884.6; sample 4 with peaks at 394 and 415</td>
<td>peaks at 498.4, 503.5, 572.5, 637.3</td>
<td>peaks at 491.5 (N3), very small peak at 470.1. Peaks at 490.2 and 496.1, strong H3-peak at 503.3. Strong peaks at 575 and 637.3</td>
<td>peaks at 415.3 (N3) with side bands at 421, 439, 452 and 463. H-center at 503.2 with phonon side bands at 512 and 520. Small peaks at 657.4 and 668.9</td>
<td>peaks at 415, 499, 496, 503.3, 575, 654.5, 657.9, 669.0, 679.6, 711.2, 802.5</td>
<td>peaks at 388.2 and (NV)-center related peaks at 575 and 637, small peaks at 658.2, 669.2, Sample 2 with a small 741 (GR1)</td>
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References


