New Generation of Synthetic Diamonds Reaches the Market (Part A): CVD-grown Blue Diamonds

Peretti A. 1*, Herzog F. 2, Bieri W. 2, Alessandri M. 3, Günther D. 4, Frick D.A. 4, Cleveland, E. 5, Zaitsev A.M. 6, Deljanin B. 7

1 DR Peretti Co LTD, Thailand and GRS Laboratories
2 GRS Gemresearch Swisslab AG, Switzerland
3 GRS Lab (Hong Kong) Ltd, Hong Kong, China
4 Laboratory for Inorganic Chemistry, ETH Zurich, Switzerland
5 Delaware, USA
6 The City University of New York, USA
7 CGL-GRS Swiss Canadian Gemlab Inc., Canada
*Corresponding author: adolf@peretti.ch

Abstract
A new type of synthetic blue diamonds appeared on the market. These diamonds were identified as CVD-grown. Optical spectroscopy revealed that they are of type Ila and their colour is caused by strong absorption of very intense silicon-related SiV\(^+\) center (negatively charged Silicon and Vacancy centre). A structural and chemical layering was identified by SEM-CC analyses. Enhanced concentration of Bi and Pb elements was found by LA-ICP-MS method. Reliable identification of silicon-doped blue CVD diamonds can be performed in different ways and these diamonds can be unambiguously distinguished from their blue natural and HPHT-grown synthetic counterparts. The most effective identification methods are absorption and photoluminescence spectroscopy in the visible spectral range, which reveal extremely intense SiV\(^+\) (737 nm) center. The silicon-doped blue CVD diamonds are not conductive. Thus the electrical conductance test is a method contributing to the recognition of these diamonds.

Keywords: Synthetic, CVD-grown, blue diamond, type Ila, SiV colour centres

Introduction
On October 18, 2013 Rapaport Diamond Report issued a trade alert warning “Buyers beware; Persistent reports indicate that large amounts of synthetic lab-grown diamonds are being mixed with natural diamonds in parcels of melee and pointers. Know your supplier and insist the phrase ‘natural, untreated diamonds’ to be included on all invoices”. More than 600 undisclosed CVD-grown diamonds of less than 0.70 carats came through major laboratories in both Antwerp and Hong Kong for certification in 2012 [1]. As prices for natural diamonds in India rise, synthetic diamonds are also gaining attraction [2]. “The synthetic diamond market in India has captured around 1% of the overall diamond jewellery market,” said Vipul Shah, chairman of the Gems and Jewellery Export Promotion Council (GJEPC). Therefore, disclosure of these new synthetic diamonds is also a matter of concern.

Orion PDC Diamonds, a company producing CVD diamonds, asserts in their marketing brochure entitled PDC Company that both genuine earth-mined and synthetic diamonds are ‘real diamonds’. Although theoretically correct in that they both share the same physical and chemical properties, this statement, when used within the gem-diamond market, is very misleading. It implies that these lab grown diamonds are ‘natural’, which is certainly not the case.

Synthetic diamonds are indeed an important part of today’s commercial gemstone industry and are being created by a variety of companies, like AOTC, Chatham, Scio Diamond, Gemesis, Washington Diamonds, and Orion PDC, all using various production methods (Fig. 1). To create different colours, a variety of treatments are applied to either natural or synthetic diamonds. Diamonds of practically any colour including colourless, yellow, blue, green, orange, and pink and their countless variations may result from the
controlled application of different combinations of irradiation, heat and high pressure. Commercial production of blue diamonds relies upon one of three methods:

1. **electron irradiation with energy of a few MeV at moderate doses applied to practically any diamond (common treatment)**

2. **high-pressure / high-temperature (HPHT) annealing of initially natural grey-colour (very rare) type IIb diamonds**

3. **HPHT growth of synthetic boron-doped diamonds**

No other technique, including that of chemical vapour deposition (CVD) growth, has reportedly been used for commercial production of gem-grade diamonds with blue body colour. Of late, synthetic gem diamonds produced by CVD method could appear as brown, pink (post grown irradiated), yellow or colourless. But quite recently, CVD-grown diamonds of a greyish-blue colour have entered the marketplace (Fig. 2). The first characterisation and identification of these diamonds is the aim of this present publication.

Although published research does exist on CVD technique producing boron-doped blue colour diamond coatings, blue diamonds created by this method have not previously been seen as faceted stones in the marketplace. Synthetic blue diamonds appearing closest to their natural counterparts are usually produced by HPHT growth [5].

In September 2013, one of the authors (AP) conducted a survey at the Bangkok Gems & Jewelry Fair and discovered that synthetic blue diamonds over 1 carat in size (See Fig. 2b) appeared in the market along with a variety of other colours (See Fig. 2a). Later on, in Hong Kong, we were able to acquire a few reference samples of the blue diamonds from the producer, along with other samples for this study (see Tab.1).

In this effort, we express our discovery of a new type of synthetic blue diamond which had not been previously identified in scientific literature. This is a key finding for the gem trade especially in light of recent developments in CVD technology which turns out higher quality, greater colour range, and larger carat size synthetic diamonds.
**Conclusion**

A new type of CVD-grown synthetic blue diamond has been discovered. We discovered that some of these CVD-grown diamonds can be identified by their characteristic strain-pattern under cross-polarized light conditions. These diamonds are inert to SWUV and LWUV illumination and reveal no specific phosphorescence characteristic of HPHT-grown and natural blue diamonds. Comparative analysis of new blue CVD diamonds with their HPHT-grown and natural counterparts using FTIR, UV-VIS and PL spectroscopy has revealed that these diamonds are of type IIa. They do not owe their blue colour to boron impurity.

Because they are not doped with boron, the new blue CVD diamonds are not electrically conductive. Thus, the new CVD blue diamonds can be identified with the use of an electric conductivity tester for natural blue and HPHT synthetic blue diamonds which is available in the marketplace. This tester is useful for identification of irradiated blue natural diamonds which are of type Ia or Iia, and act as electric insulators.

The diamonds’ blue colour is attributed to a high intensity of the silicon-related SiV\(^+\) centre, which produces preferential absorption in red spectral range. The SiV\(^+\) centre is so strong that it is the sole feature present in absorption and luminescence spectra taken in visible spectral range. By analysing the assembled data, we concluded that co-doping with silicon and some other impurity might be performed during the growth phase of blue CVD diamonds in order to stimulate efficiency of the SiV\(^+\) centre.

Chemical analysis performed on the blue CVD diamond has identified the elements Pb and Bi as the major contributing impurities. Pb and Bi are heretofore unknown impurities in diamonds, so their influence on optical properties of diamonds has not been studied. Therefore at this stage, we cannot presume that these impurities were intentionally introduced in diamonds for the purpose of stimulating the SiV\(^+\) centre. There is clearly more need for further research by LA-ICP-MS and alternative methods before every aspect of the new material is understood. Nevertheless, it is important to note that a new type of synthetic blue diamond has been discovered and identified (see also alert in “news section” at www.gemresearch.ch).

The trade and the public need to be made keenly aware of this discovery, particularly in light of the fact that the seller promotes this material as real diamonds in the marketplace [16]. Other types of synthetic blue diamonds (HPHT) are doped with boron corresponding to the trace elements found in nature. But they must be clearly described as lab-grown, and truthfully labelled as synthetic diamonds. This new generation of synthetic diamonds is different in that the origin of colour is related to Si and possibly a dopant. Therefore, these new synthetic blue diamonds origin of colour is not the same as is found in natural diamonds. Furthermore, they are synthetic and should not bear the conflicting misnomer of real diamonds. They may accurately be described as “CVD-grown blue diamonds”, however.

Major lab-created diamond manufacturers such as AOTC, Chatham, Gemesis, and Scio Diamond are transparent in their disclosure and cooperative within our trade. The majority of their diamonds are certified. Still, there are synthetic diamonds that reach laboratories undisclosed, and there are also synthetic diamonds brought in by individuals who bought them believing they are natural diamonds. Today, an increasing number of facilities grow diamonds, especially in Asia due to lower production costs. It appears that the CVD technology is increasingly employed to grow both near-colourless and coloured diamonds. This development makes it imperative to screen melee and small coloured diamonds parcels for determination of synthetic origin as well as for colour origin, especially in the Asian markets.

**Acknowledgements**

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**Table 1: Summary of tested natural and synthetic blue diamonds of different producers and synthesis methods and results of examinations**

<table>
<thead>
<tr>
<th>Producer</th>
<th>CVD-grown - Orion PDC 4 samples</th>
<th>Natural 1 sample</th>
<th>HPHT synthetic - Chatham 1 sample</th>
<th>HPHT synthetic - Taurus 1 sample</th>
<th>HPHT synthetic 3 samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour</strong></td>
<td>light blue, fancy greyish blue</td>
<td>very light blue</td>
<td>fancy blue</td>
<td>fancy blue</td>
<td>fancy blue</td>
</tr>
<tr>
<td><strong>Clarity</strong></td>
<td>VS1 to VS2</td>
<td>SI2</td>
<td>I1</td>
<td>I1</td>
<td>SI to I</td>
</tr>
<tr>
<td><strong>Solid Inclusions (at 60x magnification)</strong></td>
<td>transparent crystals, clouds and pinpoints</td>
<td>none</td>
<td>black metallic inclusions, feathers</td>
<td>black metallic inclusions</td>
<td>black metallic inclusions, feathers</td>
</tr>
<tr>
<td><strong>ED-XRF</strong></td>
<td>none</td>
<td>none</td>
<td>Fe, Co</td>
<td>Fe, Co</td>
<td>Fe, Co</td>
</tr>
<tr>
<td><strong>SEM-EDS</strong></td>
<td>Pb, Bi</td>
<td>not measured</td>
<td>not measured</td>
<td>not measured</td>
<td>not measured</td>
</tr>
<tr>
<td><strong>Fluorescence SWUV (254nm)</strong></td>
<td>inert</td>
<td>medium to strong milky green; phosphorescence</td>
<td>medium to strong milky yellowish green; phosphorescence</td>
<td>weak chalky green; phosphorescence</td>
<td></td>
</tr>
<tr>
<td><strong>Fluorescence LWUV (365nm)</strong></td>
<td>inert</td>
<td>very weak light orange</td>
<td>inert</td>
<td>inert</td>
<td></td>
</tr>
<tr>
<td><strong>Cross Polarized Filters (CPF)</strong></td>
<td>irregular pattern or “tatami pattern”</td>
<td>weak pattern</td>
<td>no pattern</td>
<td>no pattern (straining around black metallic inclusion)</td>
<td>no pattern</td>
</tr>
<tr>
<td><strong>FTIR spectroscopy (absorption, cm⁻¹)</strong></td>
<td>type Iia, weak bands at 1340 and 1332cm⁻¹</td>
<td>type Iib, Boron related bands at 2455, 2802, 2928, small 1332 and 1303cm⁻¹</td>
<td>type Iib, very strong Boron related bands at 2455, 2802, oversaturated above 2750cm⁻¹</td>
<td>type Iib, very strong Boron related bands at 2455, 2802, oversaturated above 2750, band at 1332 and 1292cm⁻¹</td>
<td></td>
</tr>
<tr>
<td><strong>UV-Vis-NIR spectroscopy at LNT (absorption)</strong></td>
<td>prominent 737 band, peaks at 830, 833, 856, 870 and 946, additional peaks around 530 (523.9, 529.9, 546.6) and at 676.8nm</td>
<td>lack of sharp absorption bands, gradually increasing absorption towards near infrared (500 to 1000nm), slightly increasing towards the UV (420 to 300nm)</td>
<td>lack of sharp absorption bands, gradually increasing absorption towards near infrared (420 to 1000nm), slightly increasing towards the UV (420 to 300nm)</td>
<td>lack of sharp absorption bands, gradually increasing absorption towards near infrared (320 to 1000nm)</td>
<td></td>
</tr>
<tr>
<td><strong>PL spectroscopy at LNT - 405nm</strong></td>
<td>very strong 736 and 766 bands, peaks at 796 and 811; small to pronounced 719 peak; valley at 946nm</td>
<td>weak 741nm (GR1) due to natural irradiation</td>
<td>no PL features</td>
<td>no PL features</td>
<td></td>
</tr>
<tr>
<td><strong>PL spectroscopy at LNT - 532nm</strong></td>
<td>very strong 736 and 766 bands, peaks at 796 and 811; small to pronounced 719nm peak</td>
<td>weak 741nm (GR1) due to natural irradiation</td>
<td>no PL features</td>
<td>no PL features</td>
<td></td>
</tr>
<tr>
<td><strong>Electrical conductivity</strong></td>
<td>non-conductive</td>
<td>conductive</td>
<td>conductive</td>
<td>conductive</td>
<td>conductive</td>
</tr>
</tbody>
</table>
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