

# Gemmological studies of “Hybrid Diamond” (Natural + CVD synthetics)

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## Introduction

Size and quality of CVD synthetic diamonds for jewelry market have been improved over the years, and various fancy colour CVD diamonds have also been produced. In addition, overgrowth of type IIb blue CVD synthetic diamond on colourless natural diamond has been made, aiming at fancy colouration (Moe et al., 2017, Ardon et al., 2019), and colourless natural diamond on which CVD diamond layer has been overgrown with the aim of increasing its weight has been reported (Serov et al., 2017., Tan et al., 2018). Appearance of these natural diamonds with CVD overgrowth layer, so called “hybrid diamonds” constitute a new challenge for diamond identification. For this report, we have overgrown a CVD diamond layer on a natural diamond substrate with a target thickness of 2000  $\mu\text{m}$ , and performed gemmological observations after cutting and polishing in order to investigate possibilities of commercial benefits and gemmological detection of such “hybrid” diamonds.

## 2. Materials and Methods

The CVD overgrowth and cutting/polishing process were performed at Diamond Elements Pvt. Ltd. India, and gemmological observations were performed at Central Gem Laboratory (CGL), Japan. Two apparently colourless octahedral type Ia natural rough diamonds (1.570ct and 1.049ct) were divided by center sawing to obtain four substrates. The CVD overgrowth was performed using a MP-CVD system (Seki Technotron Corp., SDS6K) at temperatures of 1050-1100  $^{\circ}\text{C}$ , a pressure of 150 Torr, and a growth rate of 12  $\mu\text{m}/\text{hour}$ . In order to grow the colourless layer so that the layer is not discerned from the natural diamond substrates, strict temperature control around the substrates was required. A special holder was designed to grow the diamond layer with the same quality on each of the four substrates in a single step. After growing the layer of a target thickness of 2000  $\mu\text{m}$ , 3 of the 4 grown stones were cut and polished to

square modified brilliant cut (Fig.1). These faceted stones were subjected to standard gemmological examinations: UV-Vis Absorption Spectroscopy, FTIR Spectroscopy, DiamondView<sup>TM</sup> observation, Photoluminescence Spectroscopy and SYNTHdetect.

## 3. Results

Sample 1 was 0.494 ct, G colour, SI1 clarity, and the CVD layer thickness was 1100-1200  $\mu\text{m}$ . Sample 2 was 0.391 ct, H colour, I2 clarity, and the CVD layer thickness was 660-910  $\mu\text{m}$ . The natural parts of Sample 1 and Sample 2 are cut from the same rough crystal. Sample 3 was 0.329 ct, H colour, I2 clarity, and the CVD layer thickness was 880-940  $\mu\text{m}$ .

## Standard Gemmological Observation

Observation using a gemmological microscope showed black inclusions in all three samples, and these were the main sources affecting clarity grade. It was confirmed that these black inclusions are located near the boundary between the CVD growth layer and the natural seed crystal used as the substrate. In addition, pinpoint-like inclusions were distributed at the boundary. Under cross-polarized light, strain birefringence parallel to the octahedral plane was observed in the natural seed crystal, and brush-like strain birefringence was observed in the CVD growth layer. In samples 1 and 2, a boundary between the seed crystal and the CVD growth layer was observed on the girdle (Fig.2).



Figure 1: "hybrid diamonds" (from left 0.494ct, 0.391ct, 0.607ct (as grown), 0.329ct)



Figure 2: A boundary between natural seed crystal and the CVD growth layer was seen on the girdle.

### UV-Vis Absorption Spectra

The N3 absorption system (415.2, 403.2, 394.4, 384 nm), N4 (344.2 nm), N5 (329.6 nm) and N6 (315 nm) were detected in all three samples in the ultraviolet-visible absorption spectrum at a liquid nitrogen temperature. All of these absorption peaks are all believed to be located in the natural diamond substrates. The Si-V (737 nm doublet) peak shown by Tang et al. (2018) was not detected.

### FTIR Spectra

Absorption spectra from a whole body were measured by bringing the table facet into contact with the diffuse reflector. All three samples showed a type Ia character consisting of A center, B center, platelet and hydrogen-related peaks.

### DiamondView™

When observed from the table side, the samples 1 and 2 showed dark blue and reddish fluorescence, which probably originate from band A and NV center, respectively. Dark blue with yellow-green fluorescence was observed from sample 3. The yellow-green fluorescence is thought to be due to the H3 from the natural site protruded to the crown region. Observation from the pavilion side showed blue fluorescence, which is thought to be due to N3, in all three samples. When observed from the girdle direction, it was difficult to find a difference in fluorescence colour between the natural crystal substrate and the CVD layer, but a clear bluish-white phosphorescence was observed at the boundary between the CVD layer and the natural diamond substrate.

### Photoluminescence Spectra

Photoluminescence measurement was performed at a liquid nitrogen temperature using 457, 488, 514, 633 and 830 nm lasers. The measurements were performed at a number of points on the table side (CVD layer) and the pavilion side (natural substrate) as well, but no clear difference was observed in the spectra. They exhibited the same peaks with the same intensity at each point. The peaks were N3 (415 nm), H4 (496 nm), H3 (503 nm), Si-V (737 nm doublet), 596 nm, 597 nm doublets, NV0 (575 nm) and NV- (637 nm). The former three peaks may be from the natural substrate and the latter from the CVD growth layer.

### SYNTHdetect

The table side (CVD layer), the pavilion side (natural substrate) were inspected with SYNTHdetect. All three samples were judged as "refer" from the table side, but sample 1 was "natural" from the pavilion side although the others were "refer".

#### 4. Conclusions

CVD synthetic diamonds were overgrown on type Ia natural diamond. In order to grow CVD synthetic diamonds with the same colour as natural diamonds, growth temperature was precisely controlled around the natural diamonds used as substrates.

In general, overgrowth on small stones would have little commercial benefit, but large crystals may give some profit. Since the diamonds contain type Ia natural diamonds, they may be misidentified as natural by rough sorting methods such as UV transparency, N3 defect detection, and bulk FTIR measurement. But SYNTHdetect judges as refer, when inspected from the table side (CVD part). The presence of black inclusions and minute inclusions distributed on the plane and characteristic strain birefringence are clues for detecting the CVD overgrowth. Concludingly, our study shows that it is possible to identify “hybrid diamonds” by combining data obtained from advanced identification techniques such as DiamondView and PL spectroscopy as well as standard methods.

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