

IDENTIFICATION OF CVD SYNTHETIC GEM DIAMONDS USING RAMAN SPECTROSCOPY

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Gem quality single-crystal diamonds can be produced using chemical vapor deposition (CVD) technology. Significant progresses have been achieved in last decade in improving diamond quality and sizes. Nowadays, CVD synthetic gem diamonds are comparable to top-quality natural diamonds up to 2 carats, including colorless, near-colorless to fancy colors. It is critically important for the jewelry industry that these synthetic diamonds can be confidently separated from natural ones. However, these stones are visually identical to natural diamonds, and the conventional gemological tests are not reliable for a confident separation. Spectroscopy analysis is getting more and more important for gem diamond identification, in particular for those with post-growth treatment applied. In this study, we will review the major Raman photoluminescence features of CVD synthetic diamonds.

Growth with starting materials of CH₄ and H₂ gases at very low pressures, CVD diamonds are usually very pure in chemistry. They contain normally very low concentration of nitrogen and are comparable with natural type IIa diamonds. In this study, we systematically analyzed many thousands of natural type IIa diamonds and several hundreds of CVD synthetic diamonds with infrared absorption spectroscopy, Raman photoluminescence spectroscopy with varying laser excitations from UV to IR region at liquid nitrogen temperatures, and UV fluorescence image analysis, in order to identify their differences in optical centers and their distribution. The CVD samples include both as-grown crystals and some with post-growth annealing under high-pressure and high-temperature (HPHT).

For as-grown CVD diamonds, analysis revealed a few CVD-specific spectral features, including a sharp absorption peak at 3123 cm⁻¹ in the infrared region which is attributed to defect [NVH]⁻ and emissions at 596/597 nm with undecided assignment. Also revealed in as-grown CVD diamonds are emissions at 736.6/736.9 nm from [Si-V]⁻, and at 945 nm from [Si-V]⁰ when the concentration of Si impurity is relatively high. In addition, relatively high concentrations of NV centers were detected in all samples, showing strong emissions with zero-phonon lines at 575.0 and 637.0 nm. Occurrence of NV centers is common in natural type IIa diamonds. With all of these features, as-grown CVD diamonds can be easily separated from natural type IIa diamonds since some of these defects will not occur in natural ones.

However, many CVD diamonds in the market were annealed under HPHT, to remove some brownish hue in the as-grown stones and to improve their transparency. After HPHT annealing, the CVD-specific spectral features such as 3123 cm⁻¹ absorption and 596/597 nm emissions were entirely destroyed. Instead a hydrogen-related absorption at 3107 cm⁻¹ is created. Absorption at 3107 cm⁻¹ is very common in natural diamonds. With Si-related defects and a large part of NV centers surviving the process of HPHT annealing, CVD diamonds will only show very natural-looking absorption spectrum in infrared region and emissions from NV centers and Si-related defects in Raman photoluminescence spectroscopy. This study discovered only very few natural type IIa diamonds show spectral features of Si-related emissions at 736.6 and 736.9 nm. As a result, occurrence of this emission doublet has become an important indication of possible CVD synthetic. It is interesting to note that natural diamonds with detectable [Si-V]⁻ defects usually contain olivine inclusions which showed very high Mg# number (>94), indicating they are formed in a very depleted mantle environment.

With foreseeable advances in technology, separation of CVD synthetic diamonds from natural ones could be facing more challenges. Raman photoluminescence spectroscopy with higher sensitivities and spatial resolutions will be pursued as a possible solution.