Luminescence study of defects in synthetic as-grown and HPHT diamonds compared to natural diamonds

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ABSTRACT

The optically active defects in as-grown, high-pressure high-temperature-treated (HPHT), boron-doped, and synthetic diamonds (SD) grown with a nitrogen-getter, as well as of natural diamonds (ND), were characterized by absorption and luminescence spectroscopies using different excitation sources. The laser-excited photoluminescence (PL) spectra of SDs show numerous sharp lines characteristic for nickel-related centers, whereas NDs yield mainly broad PL bands. The emission from the nickel-related defects in NIR range increases and the maxima of the bands shift to lower energies with increasing temperature. Under UV and electron beam excitation, the yellow synthetic diamonds display green luminescence patterns along octahedral directions. The UV-excited PL spectra of the yellow SDs show a green band associated with nickel-related optical species. NDs display broad bands centered at ca. 450 nm that are related to complex nitrogen-related aggregates formed in the mantle in a long period of geological time. The cathodoluminescence (CL) spectra of SDs reveal many nickel-related and simple nitrogen-vacancy defects. Differences among as-grown, HPHT, and boron-doped diamonds can be observed. The CL bands of NDs are partly formed or caused by complicated nitrogen aggregates, like N3 and N4 centers. The CL band of NDs shifted from blue to green with increasing irradiation time. The deep-UV (DUV) excited time resolved PL spectra of NDs showed fast-decaying donor-acceptor pair recombination (DAPR) bands at around 410 nm. With longer delay and gate times, the broad band shifted to ca. 435 nm. All synthetic diamonds display luminescence from nickel-related defects centered at ca. 480 and 530 nm at room temperature (RT) and 77 K, respectively, and all SDs had a sharp luminescence band at 694 nm due to a Cr³⁺ impurity in corundum inclusions.

INTRODUCTION

Superior mechanical properties, beneficial optical features, high thermal conductivity, unique electronic characteristics, high chemical resistance, and bio-compatibility of diamond materials can be explained mainly by the tetrahedrally oriented sp³-hybrid orbitals of the carbon atom. The physical properties related to the covalent bonding between carbon atoms make the diamond structures, high pressures and temperatures are essential to produce SDs. The synthetic as-grown diamonds typically display a brownish color due to a high content of nitrogen N1 (or C) centers, which are isolated substitutional lattice defects (Collins 2000). The term “as-grown” refers to synthetic diamonds that have not experienced any treatment. The as-grown diamonds can be annealed at high temperatures to refine the color. Above 2000 K, the C centers become mobile and form energetically more stable defect centers, like substitutional nitrogen pairs, N2 aggregates (or A centers). Further annealing may produce complexes composed of three nitrogen atoms and a vacancy, an N3 aggregate. Four nitrogen atoms symmetrically surrounding a vacancy form an N4 aggregate (or B center) (Collins 2000, Iakoubovskii and Adriaenssens 2002b) under extreme annealing conditions (ca. 2700 K). The typical greenish-yellow color of the synthetic HPHT diamonds is due to the absorption of visible light by the N2 aggregates. Boron doping produces SDs with a blue color. The synthesis of colorless diamond material requires a decrease in the nitrogen concentration, which is possible by using the melt an element with a high affinity to nitrogen, a getter, such as aluminum, titanium, or zirconium (Burns et al. 1999). The syntheses of gem-quality diamonds require high-technological solutions and a great deal of research as well as financial investments, indicating the enormous economic significance of