Diamond & Related Materials 58 (2015) 94–102

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Comparison of luminescence lifetimes from natural and laboratory irradiated diamonds

Sally Eaton-Magaña

Gemological Institute of America, Carlsbad, CA, United States

ARTICLE INFO

Article history:
Received 7 August 2014
Received in revised form 8 June 2015
Accepted 9 June 2015
Available online 14 June 2015

Keywords:
Luminescence lifetime
Natural diamond
Optical centers

ABSTRACT

Among gem diamonds, one of the most challenging identifications is distinguishing naturally irradiated diamond from laboratory irradiated diamond. In both cases, the GR1 optical center is created, which in high concentrations imparts a greenish color to the diamond. This research attempted to identify if time-resolved spectroscopy at the nanosecond scale would demonstrate substantive differences between the lifetime behavior of the GR1, in addition to the H3 and NV^0 centers due to the type of irradiation. All three centers showed nominally similar behavior and decay times; however, the luminescence decay of treated diamonds showed more complex behavior with additional exponential decay components able to be resolved. To our knowledge, this is the first study directly comparing data derived from natural and laboratory irradiated diamonds, specifically here, the H3, NV^0, and GR1 optical centers.

1. Introduction

Natural-color diamonds are among the most valuable gemstones, and can reach per-carat prices of US$100,000 or more. This high value, combined with their rarity, has created a demand for less expensive color-treated diamonds for commercial jewelry applications. A diamond's history—whether it came from a lab, from the earth, or subsequently treated—can be the largest factor affecting value. One such challenge for decades has been determining if radiation-related features were derived from natural or laboratory sources. Radiation exposure produces vacant carbon-atom positions in the diamond lattice and creates the GR1 optical center with a zero-phonon line (ZPL) at 741.2 nm. Its absorption within the red region of the visible spectrum creates the blue-to-green coloration of the diamond.

Photoluminescence (PL) and UV–Vis-NIR absorption spectroscopy have proven very useful tools to distinguish between natural diamond and other forms of treatment such as detecting the presence of coatings, high-pressure, high-temperature (HPHT) annealing [1], and a combination of treatments [2]. However, these methods have not shown any reliable differences between the GR1 centers regardless of the method of creation or the radiation type. Therefore, despite extensive study over the past five decades, reliably distinguishing natural and laboratory irradiation remains a challenge within gemological laboratories.

1.1. Natural and laboratory irradiation of diamonds

The vast majority of naturally irradiated diamonds normally exhibit a shallow green coloration in an irregular patchy pattern at or just beneath their crystal surfaces. The shallow color is generally attributed to exposure to alpha particles given off by radioactive minerals in direct contact with the diamond over long periods of geologic time near the Earth's surface (typically attributed to uranium-238 and thorium-232 bearing minerals) [3]. Radiation exposure also results from diamond being in contact with radioactive aqueous solutions. This is particularly true when the green coloration occurs along surface-reaching cleavages. Due to the very shallow penetration of alpha particles (generally less than 1 mm) [4], that greenish color is polished away in most gem diamonds leaving only a weak GR1 center as the sole evidence of radiation exposure.

Rarely, diamonds will have greenish color that appears at depth within the diamond and is still present after polishing. This would require exposure to beta or gamma radiation which have a greater penetration depth into diamond than alpha particles. Potassium-40 is an abundant isotope in the crust, and it undergoes radioactive decay by emitting beta particles and less commonly gamma rays. Large diamonds with a green body color are more likely to have been exposed to these types of radiation.

The radiation-related blue-to-green color in diamonds changes to an orangey brown color when a diamond is heated to 550–600 °C [5]. Therefore, the green coloration does not occur deep within the Earth and the diamond was not subsequently exposed to high temperatures after the radiation exposure.

In the past decades, researchers have examined green diamonds with known historical provenance, such as the 41 carat Dresden Green [6] to compare with their laboratory-irradiated counterparts. Additionally, there is surficial damage on rough diamonds, generally called radiation stains, that can assist to confirm natural origin. Unfortunately those features are not always available on polished gems. Oftentimes, this necessitates a polisher to submit the diamond as a rough gem to

E-mail address: sally.magana@gia.edu.

http://dx.doi.org/10.1016/j.diamond.2015.06.007
0925-9635/

have the natural origin verified and then to submit several times throughout the polishing process.

Laboratory-irradiated diamonds are believed to have been first produced in 1904 when Sir William Crookes surrounded a diamond with radium salts for 78 days. The experiment greatly intensified the GR1 center, changed its color to bluish green, and it became strongly radioactive [7].

Today gem diamonds are irradiated by several safer methods so the diamond does not have measurable radioactivity, but also they do not show visible indicators of laboratory irradiation such as color zoning, which is caused by the direction of radiation exposure. Instead, they are typically exposed to a beam of electrons in a linear accelerator or neutron bombardment using energies less than 10 MeV which creates a more uniform coloration [8]. Gamma rays are occasionally used but are not common due to the time requirement to create a color change in diamond.

1.2. Time-resolved luminescence

Over the last few decades, optical centers in diamond have been studied by time-resolved luminescence (TRL). This prior research has identified the intrinsic lifetime for many optical centers and has shown that several factors such as the presence of other impurities can create a range of measured lifetimes.

Luminescence occurs when light from an energy source (laser, UV lamp, etc.) excites an electron out of its ground state. As the electron returns to its normal ground state, energy is released, usually in the form of visible light. The emission lifetime provides an indication of the amount of time in which the electron resides in its excited state. The emission lifetime is defined as the time necessary for the luminescence to drop to 1/e of its initial intensity. If several factors influence the observed lifetime then the decay can be described not by a single exponential representing its intrinsic lifetime, but split apart into a series of exponentials.

Several factors influence the observed luminescence including valence state, position, structure, charge compensation, and other elements [9]. Prior research of optical centers in diamond demonstrated that observed lifetimes are often shortened due to quenching, in which energy transfers to other impurities and can create several distinct observed lifetimes for an optical center.

The intrinsic lifetime for NV^0 (ZPL at 575.0 nm) based on high-purity, low-nitrogen samples was recently confirmed as 19 ± 2 ns [10]; however, quenching caused by single, substitutional nitrogen [N_S^0] can reduce the lifetime. Additionally, they showed that treatment can directly affect the lifetime of optical centers. HPHT annealing shortens the decay time of the NV^0 center by increasing the concentration of N_S^0.

The intrinsic lifetime of the H3 center (503.2 nm) was determined as 16.7 ± 0.5 ns [11], the N3 center (415.2 nm) as 41 ± 1 ns [12], and the H4 center (495.9 nm) as 19 ± 1 ns when measured with 488 nm excitation [11]. Quenching mechanisms shorten the N3 and H3 lifetimes by the presence of A aggregates of nitrogen (i.e., pairs of substitutional nitrogen atoms in the diamond lattice).

The decay time for the GR1 is given as 2.55 ± 0.1 ns [13,14], but can vary from 0.4 to 3.1 ns depending on the excitation source and sample temperature. The lifetime for Si-V (737 nm) was determined as 1.20 ± 0.04 ns [15]. The interstitial-related TR12 (470.5 nm) has a measured lifetime of 3.6 ns [16]. These non-nitrogen related optical centers that have been determined thus far (GR1, TR12 and Si-V) have the shortest recorded lifetimes in diamond. There was no data available on the 3H defect, centered at 503.5 nm [17].

Additionally, most vacancy-related lifetimes chronicled thus far (N3, NV^0, NV^-, GR1, Si-V) demonstrate a linear relationship between the intrinsic lifetime and zero-phonon line wavelength. H3 and H4 do not conform to that relation; however H4 has the additional complication that its intrinsic lifetime shifts with excitation energy [11].

In this study, naturally irradiated and laboratory irradiated diamonds were tested by time-resolved luminescence to gauge if the dimension of time would yield differences between these ostensibly identical centers through their decay characteristics. Investigations of the decay curves of diamond defects may reveal important differences between these natural and treated diamonds that could aid in their identification (Fig. 1).

2. Techniques and materials

A suite of 26 naturally irradiated samples and 20 naturally sourced diamonds that were subsequently laboratory irradiated were examined in this study. The rough natural diamonds had extensive radiation staining and each weighing ~0.03 carats. The treated diamonds were blue or green in color, polished as round brilliants, and weighed ~0.06 carats each. They were procured through a diamond dealer and their color origin confirmed through microscopic examination and photoluminescence (PL) spectroscopy.

FTIR absorption spectra were collected from 6000 to 400 cm^{-1} range using a Thermo Nicolet Nexus 6700 spectrometer furnished with KBr and quartz beam splitters and a DRIFT (diffuse-reflectance infrared Fourier transform) accessory. Nitrogen A and B aggregates and single substitutional nitrogen concentrations were determined using a customized computer algorithm derived from a spreadsheet provided by Dr. David Fisher (DTC Research Center, Maidenhead); [18–21].

Photoluminescence data using a Renishaw inVia Raman microscope with 457 and 488 nm laser excitation, at liquid nitrogen temperature, were collected on all samples. These PL spectra confirmed the presence of each center in each sample and determined if any other optical

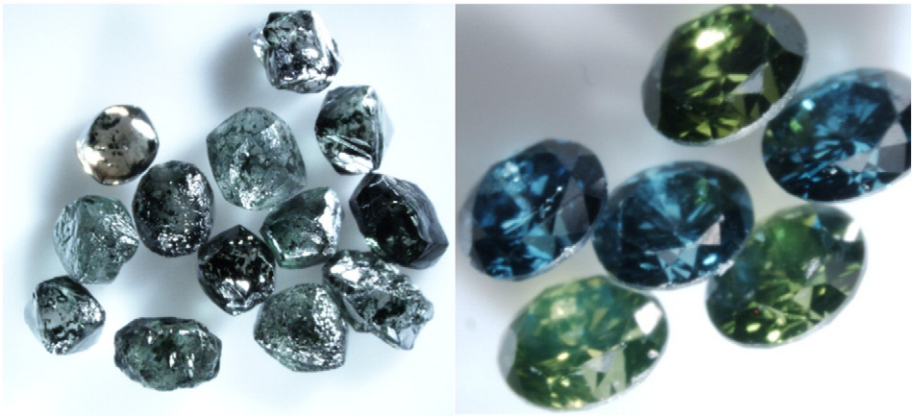

Fig. 1. A partial sample of the naturally irradiated diamonds (left) and the laboratory irradiated diamonds (right).