



Efficient phosphorescence from synthetic diamonds

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ABSTRACT

Synthetic diamonds have inspired much interest for their unique photophysical properties and versatile potential applications, but their phosphorescent phenomenon and mechanism have been paid much less attention. Here, phosphorescent diamonds with a lifetime of 5.4 s were synthesized by high-pressure and high-temperature method, and the diamonds exhibit an emission band at around 468 nm under the excitation wavelength of 230 nm. The quantum yield of the phosphorescent diamonds is about 4.7% at ambient temperature and atmosphere, which is the first report on the quantum yield of diamonds. The unique phosphorescence emission can be attributed to the radiative recombination from iron related donors and boron related acceptors.

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1. Introduction

Besides high hardness diamond possesses several unique properties including high thermal conductivity, high carrier mobility, high breakdown field, various color centers, and good chemical stability, which make it a promising candidate in semiconductor devices, solar cells and single-photon sources [1–6]. Compared with the extensive research on photoluminescence, reports on the phosphorescence in diamond are relatively limited. In 1952, Custers et al. used “phosphorescence” to report the luminescent emission phenomenon in natural diamonds with relatively long lifetimes (several seconds) for the purpose of classification on diamonds [7]. In their report, the phosphorescence emission wavelengths centered at 4665, 5310, and 5720 Å (Å maybe mean Å) were found in a natural diamond. Although the phosphorescence phenomenon is confirmed, the details and mechanism of the phosphorescence are lacking and ambiguous. Subsequently, phosphorescence emission was also found in high-pressure and high-temperature (HPHT) treated diamonds and HPHT synthetic type IIb diamonds [8]. Walsh et al. found the phosphorescence centered at 590 nm with lifetimes of several milliseconds in boron doped diamonds [9]. Later, Eaton-Magaña et al. reported

phosphorescence at 500 nm and 580 nm in HPHT-synthetic diamonds with lifetimes of several seconds [10]. They also reported that all the phosphorescent diamonds, no matter natural or synthetic type IIb diamonds, showed the identical 500 nm band, however, the 660 nm band was only observed in natural diamonds [11]. These two bands (500 and 660 nm) have received the most investigation and attention [10,11]. However, the novel and efficient diamond-based phosphorescence is still scarce for synthetic diamonds, and the related phosphorescence mechanism is far from distinct and clear. Therefore, developing efficient phosphorescence and understanding the phosphorescence mechanism in diamonds are urgently needed.

In this paper, efficient phosphorescence has been observed from HPHT synthetic diamonds. The synthetic diamond crystals exhibit unique phosphorescence centered at 468 nm under 230 nm excitation, and the quantum yield (QY) of the phosphorescence is 4.7% at ambient temperature and atmosphere. Experimental and theoretical calculation results illustrate that boron impurity as the shallow acceptors and iron impurity as deep donors jointly form the donor-acceptor pairs, whose radiative recombination induces the phosphorescence emission in the diamonds.

2. Experimental

2.1. Synthesis of diamond

For this study, the diamonds were fabricated by HPHT method following our previous report with some modification [12].

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Graphite (99.99% purity) powder and Fe₇₀Ni₃₀ alloy were chosen as carbon source and solvent catalyst, respectively. Ti was used as the nitrogen-getter during the growth process. In order to avoid the effect of the adsorbed water on the formation of diamond, the precursors were dried by annealing at 120 °C for 2 h before being transferred into the high pressure apparatus. After the experiment, the collected samples were cracked and treated in the mixture of H₂SO₄ and HNO₃ to remove remaining graphitic components and metal catalysts.

2.2. Characterization

The synthesized diamonds were observed by optical microscope (Olympus SZ61) with a 266 nm laser. The structural properties of the diamonds were characterized using a micro-Raman spectroscope (Renishaw RM 2000). The infrared spectra (IR) of the diamonds were obtained on a Vertex80V Fourier transform infrared (FTIR) spectrometer in the spectral range between 800 and 3000 cm⁻¹ in the transmittance mode. X-ray photoelectron spectroscopy (XPS) data were acquired using a Kratos AXIS HIS 165 spectrometer with a monochromatized Al KR X-ray source (1486.71 eV photons).

The phosphorescence spectra and the phosphorescence time-resolved decay spectra of the diamonds were measured on a Hitachi F-7000 spectrophotometer with an excitation wavelength of 230 nm. The temperature-resolved phosphorescence spectra of the diamonds were measured by using a Horiba FL-322 spectrophotometer with a closed-cycle nitrogen cryostat (Jannis CCS-100) and a digital temperature controller (LakeShore-325) to provide continuous temperature variation from 77 K to 517 K, and a 150 W xenon lamp was employed as the excitation source. The QY of the diamonds was determined using an absolute fluorescence quantum yield measurement system (C9920-02, Hamamatsu Photonics, Shizuoka, Japan).

3. Results and discussion

3.1. Experimental data analysis

The optical properties and morphology of the HPHT synthetic diamonds are displayed in Fig. 1. The diameter of the diamond is about 2 mm. The synthesized diamond crystal is colorless under bright-field microscope, as shown in Fig. 1a. From the optical images, the diamond crystal shows some pits and other defects. The phosphorescence images were collected at 1 s interval time after the illumination for 20 s using a 266 nm laser, as shown in Fig. 1b–d, respectively. From these images, one can see that the intensity of the phosphorescence of the diamond decreases gradually with time. The QY of the single crystal diamonds is about 4.7%, this is the first report on phosphorescence quantum yield of diamond to the best of our knowledge.

In order to further elucidate the phosphorescence properties, the phosphorescence and excitation spectra of the diamond crystals are shown in Fig. 2a. A broad emission appears at around 468 nm (~2.65 eV) and the excitation maximum is at around 230 nm for the diamonds. The phosphorescence spectra were collected at 0.5 s after 20 s of excitation, as showed in Fig. 2b. The lifetime of the phosphorescence was measured from the time-resolved phosphorescence spectrum of the diamond, as depicted in Fig. 2c. The experimental data can be well fitted with a hyperbolic function [10,11,13], and the average lifetime of the emission is about 5.4 s. We note that the optical properties of several HPHT diamonds synthesized under similar conditions have been measured, as shown in Figs. S1–4 and Table S1 (Supplementary information). The results reveal that the diamonds have very

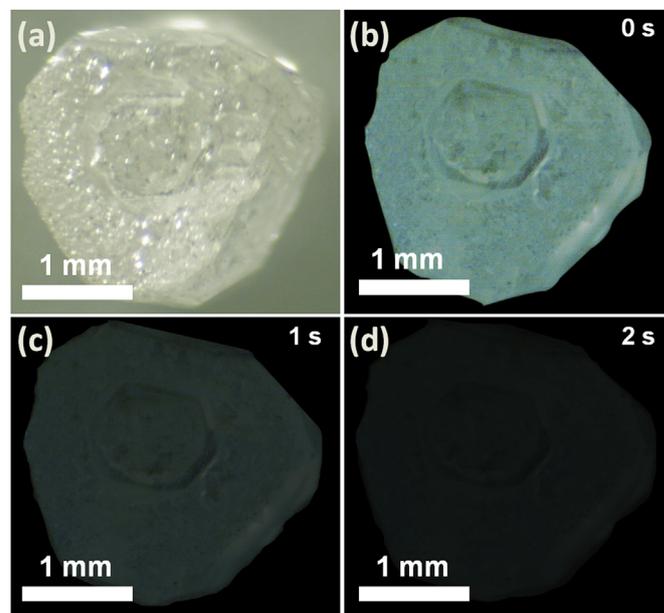


Fig. 1. Optical images of the diamond under bright field (a); (b)–(d) The phosphorescence images of the diamond collected at 1 s interval after the illumination using a 266 nm laser for 20 s. (A colour version of this figure can be viewed online.)

similar phosphorescence spectra and lifetimes, revealing the good reproducibility of the phosphorescence.

Eaton-Magaña et al. suggested that the relatively long delay time for the emission suggests that the radiative recombination probably happens between donor-acceptor pairs (DAP), retrapped at neutral donors and acceptors or a low percentage of ionized acceptors [10]. An explanation for this mechanism of DAP recombination will be provided below. In order to explore the donor and the acceptor, the confirmation of the impurity elements in this diamond is needed.

To understand the phosphorescence properties of the diamond better, the structural characteristics of the diamond were studied. The typical Raman spectrum of the diamond is shown in Fig. 3a. There is only one peak loaded at 1332 cm⁻¹ in the spectrum, which can be ascribed to the first-order zone-center modes of diamond [14]. The full width at half maximum (FWHM) of the peak is about 4 cm⁻¹.

To identify the impurities and defect species that are responsible for the phosphorescence in diamond further, FTIR absorption spectra of the diamond were measured, as presented in Fig. 3b. The absorption bands centered at 2160 cm⁻¹, 2028 cm⁻¹ and 1972 cm⁻¹ are due to multiphonon absorption, which are intrinsic vibration mode of diamond [15,16]. We note that the spectra exhibit two weak absorption peaks located at around 2852 and 2927 cm⁻¹, which are the characteristic stretching vibrations in hydrocarbons in the form of sp³-CH₂ [17–20]. The peak at 1458 cm⁻¹ can be assigned to the bending mode of C-H and the 1050 cm⁻¹ band to -OH [19,21]. The above results indicate that oxygen and hydrogen have been simultaneously incorporated into the diamond.

In order to explore the impurity elements incorporated into the diamonds further, XPS analysis was performed, and the results are shown in Fig. 3c–f. Obviously, the peaks of C, N and O present in the XPS survey spectrum of diamond (Fig. 3c). Meanwhile, the magnesium (Mg), boron (B), iron (Fe) and nickel (Ni) are also confirmed in the diamonds via the high-resolution XPS spectra, as shown in Fig. 3d–g, respectively. XPS results prove that N, O, Mg, B, Fe and Ni exist in the diamond.

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