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Effective production of fluorescent nanodiamonds containing negatively-charged nitrogen-vacancy centers by ion irradiation

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ABSTRACT

Fluorescence from negatively-charged nitrogen-vacancy centers (NV^-s) in diamonds has unique optical properties with none of the undesirable effects such as photo-bleaching and photo-blinking. In addition, the spin-dependent fluorescence intensity of NV^-s allows us to perform optically detected magnetic resonance (ODMR) investigation for evaluating the presence of NV^-s and for the electronic local environment. In this work, we irradiated H^+, He^+, Li^+ and N^+ ions to nanodiamonds with a median size of 26 nm at various irradiation energies and doses for improving the NV^- concentration. ODMR observations of the nanodiamonds showed that ion irradiation increased the number of nanodiamonds containing NV^-s up to 200 ppm, whereas without ion irradiation, only few NV^-s were found. The number of nanodiamonds containing NV^-s at various ion irradiation doses was not monotonous, but had maxima at certain irradiation doses. These results suggest a competition in two opponent roles of vacancies, effective for pairing with nitrogen atoms and as defects for developing damage in crystalline. We also found that sharp and strong ODMR signals were obtained from nanodiamonds irradiated at the optimal condition for the highest yield of NV^-s. We concluded that He^+ ion irradiations with 60 or 80 keV at a dose of 1×10^{13} ions cm^{-2} are the conditions required for the most efficient production of a high quantity of nanodiamonds containing NV^-s.

1. Introduction

Fluorescent nanodiamonds (FNDs) have been attracting much attention as new bio-imaging probes due to their unique optical properties. The negatively-charged nitrogen-vacancy color center (NV^-) in FNDs, which is formed by a substitutional nitrogen atom combining with an adjacent vacancy, is responsible for fluorescence that is emitted in the near-infrared region (600–800 nm) with a high quantum yield of ~0.7 [1,2]. Its well-known photo-stability of displaying neither photo-blinking nor photo-bleaching enables long-term *in vivo* and *in vitro* imaging, which is not readily achieved by commonly used fluorescent agents such as organic dyes and fluorescent proteins [3–5]. It has also been reported that FNDs are highly bio-compatible and non-toxic to various kinds of cell types, and are thus superior to quantum dots which often show cyto-toxicity [6,7]. These advantages of FNDs over conventional fluorescent dyes could make them a potential candidate for optical bio-imaging probes [5,8,9].

Optically detected magnetic resonance (ODMR) has been demonstrated for detection of a single NV^- at ambient conditions [10], and significant attention has been paid in the field of quantum information [11], magnetic sensing [12,13] and bio-application [14,15]. In particular, advanced applications in the nano-scale sensing of magnetic [16,17] and electric fields [18] and temperature [19] require a long-time coherence of spin state, which strongly depends on the quality of the diamond matrix. For this reason, methods for synthesizing high quality nanodiamonds and the efficient production of NV^-s are highly desired. Here, we report the effects of ion irradiation on the production of NV^-s in nanodiamonds.

There are two types of nitrogen-vacancy centers (NVCs), each with a different charged state [20,21]. One is a neutral NVC (NV^0, electron spin: $S = 1/2$), while the other is a negatively-charged NVC (NV^-, electron spin: $S = 1$), represented by zero-phonon lines at 575 nm and 637 nm respectively [22,23]. Both NVCs emit fluorescence, but only the NV^- allows for measurement by ODMR. The ground state of NV^- is a spin-triplet, and the spin sublevels, $m_s = 0$ and $m_s = \pm 1$ are split by 2.87 GHz. The spin sublevels $m_s = \pm 1$ are degenerated in the

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absence of an external magnetic field. Microwave (MW) irradiation at this frequency induces electron spin magnetic resonance between $m_s = 0$ and degenerated $m_s = \pm 1$ spin levels, which results in a reduction of the fluorescence intensity from NV^- due to spin-dependent intersystem crossing [10]. On the other hand, NV^0 is insensitive to MW irradiation. By comparing the fluorescence intensity upon MW irradiation, we can distinguish the two types of NVCs, as shown later.

In general, the concentration of NVCs in diamond is on the order of sub ppm [16]. The existence probability of NVCs contained in nanodiamonds is lower than that in bulk diamonds, because vacancies are annihilated at the surface [24]. In order to increase the concentration of NVCs in nanodiamonds, the method of ion irradiation is commonly used for creating carbon vacancies [3,25]. In this technique, ionized atoms are accelerated and are allowed to penetrate into nanodiamonds, where collisions of the ions with atoms force the carbon atoms to be expelled, resulting in the creation of vacancies. Subsequent thermal annealing at 800 °C leads to trapping of moving vacancies by nitrogen atoms which pre-exist in the diamond lattice, thereby forming an NVC [26]. Although this method is quite effective, optimal conditions for producing a high quantity of NV^-s in nanodiamonds are still unknown. In this study, we also investigated how ion irradiation affects the production of nanodiamonds containing NV^-s, and their ODMR spectra when irradiated by H^+, He^+, Li^+ and N^+ ions. Furthermore, we elucidated the optimal irradiation condition.

2. Experimental section

2.1. Sample preparation

In our experiments, we used synthetic type Ib nanodiamonds which contain typically 100 ppm nitrogen atoms (Micron + MDA Element Six). A suspension of nanodiamonds in Milli-Q water was centrifuged at 15,000 rpm for 20 min, and the supernatant was freeze-dried. The median size of the nanodiamond particles was determined by dynamic light scattering (DLS) to be 25.9 nm (Fig. 1). 2 μl of a nanodiamond suspension in Milli-Q water at a concentration of 2 mg/ml was dropped on the surface of a silicon wafer measuring 1 cm^2, and subsequently spin-coated at 7000 rpm for 20 s. To estimate the number of nanodiamonds on the silicon wafer, we carried out atomic force microscope (AFM) measurements and obtained the images of prepared samples (Fig. S1), from which we directly counted the number of nanodiamonds which cover an area of 1 mm^2 on a wafer to be 1.6×10^6 particles.

2.2. Ion irradiation

The samples were irradiated by H^+, He^+, Li^+ and N^+ ions in vacuum at ~10^{-5} Pa under various energy and dose conditions at Takasaki Advanced Radiation Research Institute, JAEA. The ion penetration depth and the number of vacancies created per incident ion at a given irradiation energy were evaluated in advance by SRIM (http://www.srim.org/) (Table 1). For obtaining desired dosages, ion beam currents in the range of ~0.1 nA to ~300 nA and the exposure times were adjusted. Under the conditions employed in this experiment, most ions passed through the nanodiamond arrays. After the irradiation, the samples were thermally annealed at 800 °C under a reduced pressure of ~1 Pa for 2 h, for the purpose of pairing nitrogen atoms and vacancies. Since the graphite layer on the surfaces of nanodiamonds interferes with fluorescence emission from NV^-s, the layer was removed by oxidizing at 500 °C under atmospheric conditions for 2 h.

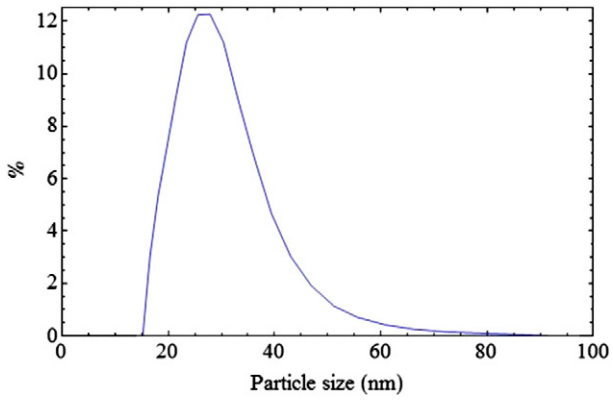

Fig. 1. Particle-size distribution of nanodiamonds as measured by dynamic light scattering (DLS).

2.3. Count of nanodiamonds containing NV^-s and measurement of its ODMR spectra

The number of nanodiamonds containing NV^-s generated by ion irradiation was counted by the following method using a home-built fluorescence microscope. In our experimental set-up, the field of view was illuminated with a 532-nm Nd:YAG laser at 7 mW, and fluorescence images (40 μm × 40 μm) were measured by an electron multiplying charge coupled device (EMCCD) camera. The emitted light was collected by an oil immersion 60× objective lens (NA = 1.49) and passed through a dichroic mirror centered at 575 nm and a long (short)-wave pass filter longer than 590 nm (shorter than 842 nm) to detect the intrinsic signal. The microscope was equipped with a computer-controlled moving stage. Firstly, the sample was roughly scanned in a broad range of areas in steps of 50 μm. At each position, fluorescence images were measured while MW was swept point-by-point across the resonant frequency from 2.865 to 2.875 GHz. The intrinsic fluorescence from NV^-s was deduced by the selective imaging protocol reported by Igarashi et al. [15]. This procedure provides a conventional fluorescence image as well as a selective one, the latter displaying only a signal arising from NV^- fluorescence. Typical obtained images are shown in Fig. 2. After the pre-scanning, the allocation numbers of images which contained the fluorescence from NV^-s were listed and stored. In order to precisely measure the entire ODMR spectrum for each nanodiamond containing NV^-s in the allocated field, a second run

Table 1
Mean penetration depths and the distribution widths of stopped ions implanted into a diamond crystal of sufficient thickness. The calculation was made by SRIM. (a) H^+, (b) He^+, (c) Li^+ and (d) N^+ ion irradiations.

Energy	Range	Straggle	Vacancy
keV	Å	Å	/ion
(a)			
20	1281	229	4.7
40	2135	248	5.4
60	2903	258	5.7
80	3647	298	6.2
(b)			
20	936	220	37
40	1594	287	44
60	2157	321	49
80	2671	357	51
(c)			
25	879	222	59
50	1607	320	76
75	2225	359	85
100	2773	406	91
(d)			
100	1150	218	190
150	1650	271	224
200	2126	293	245
250	2565	335	265