Fabrication of nitrogen vacancy color centers by femtosecond pulse laser illumination

Yan Liu,[1] Gengxu Chen,[1] Min Song,[1] Xueting Ci,[1] Botao Wu,[1] E Wu,[1,3] and Heping Zeng[1,2,*]

[1]*State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, China*
[2]*Shanghai Key Laboratory of Modern Optical System, Engineering Research Center of Optical Instrument and System, Ministry of Education, School of Optical-Electrical and Computer Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China*
[3]*ewu@phy.ecnu.edu.cn*
[*]*hpzeng@phy.ecnu.edu.cn*

Abstract: We report on a novel method to fabricate single, multiple and large-area high-density ensembles of nitrogen vacancy (NV) color centers in synthetic type Ib bulk diamond by femtosecond laser illumination. Electron beams generated in propagation of intense infrared laser pulses in air sputtered on a diamond sample under high temperature aroused by the laser illumination, creating NV color centers. Typical photoluminescence (PL) spectra of NV centers could be observed on the illuminated spots. Photon streams from individual photoluminescent points exhibited anti-bunching effect by the second-order correlation measurement, evidencing single and multiple photon-emitters around the laser illuminated spots.

OCIS codes: (160.2220) Defect-center materials; (320.2250) Femtosecond phenomena; (160.2540) Fluorescent and luminescent materials.

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1. Introduction

Various defects in diamond are considered to be prospective single-photon sources (SPSs) due to their remarkable properties [1–5]. Of all the optically active defects, the negatively charged NV center (NV^-) in diamond has been very well studied and used as single-photon emitters in a variety of applications, such as quantum key distribution in free space, experimental demonstration of wave-particle duality of photons [6,7]. Moreover, the NV^- in a diamond carries an electron spin-1, which could serve as a promising candidate of quantum bit to realize solid-state quantum computer [8,9]. In addition, the spin coherence of NV centers in diamond could last for several milliseconds and the spin-triplet ground state of a NV center is quite suitable for sensitive magnetic field measurement. Single NV centers were already used for nanometer-scale magnetometry and high-density ensembles of NV centers have been studied in recent years, also showing possibilities for applications in magnetometry [10–13].

Methods to generate NV centers in diamond are well developed and new methods appear to improve their physical properties. Notably ion-implantation is considered to be an efficient and accurate method [14,15], and other methods like electron irradiation and chemical vapor deposition are also widely adopted [16,17]. Recently, a new ion-implantation method to

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generate NV centers with spatial accuracy below 20 nm was accomplished to achieve millisecond decoherence times, indicating strong coupling for advanced quantum protocol application [18].

In this paper, we demonstrate that femtosecond pulse laser illumination also opens a gate for NV generation. This method is simple and timesaving with a spatial resolution for a few microns with good efficiency, avoiding vacuum or high temperature operation. The single NV centers, multiple NV centers, or even large-area high density NV ensembles could be fabricated with this method for various applications. By means of convenient femtosecond pulse laser illumination, we avoided any complicated vacuum or high-temperature procedures.

Usually electron beam irradiation requires an accelerator and ion-implantation requires an ion planter to produce ion beams with appropriate velocities and particle numbers. And a vacuum chamber is always needed. However, electron beams could also generate by highly intense ultra-short laser beam filamentation in the air, which could be observed as white light [19]. Intense ultra-short pulses propagating in air, induced ionization of O_2 and N_2 molecules, generating free electrons [20–22] that might be captured by the strong electromagnetic waves of the highly focused intense beam. Namely, the electrons were violently accelerated by the subsequent pulses, producing electron beams of varying velocities as a result of the asymmetric electromagnetic fields [23–26]. The electron beams sputtered on diamond sample would knock diamond carbon atoms out of their normal lattice positions, creating vacancies. The vacancies could be driven under high temperature towards immobile nitrogen atoms, forming NV centers. The highly intense pulses would arouse relatively high temperature that might consume a bit sample and even forming some other carbon impurities.

2. Illumination process

The sample used in this work was a $3\times3\times1$ mm^3 synthetic type Ib bulk diamond that contained quantities of nitrogen atoms. Before femtosecond laser pulse illumination, fluorescence was scarcely detected on the bulk diamond. The illumination was performed with a visualized microscope system with an objective lens of 50× (NA=0.5) and a 800-nm Ti:sapphire pulsed laser of 250 kHz repetition rate and 80 fs pulse duration as shown in Fig. 1(a). In this experiment, with an average power of 1 W, each fs laser pulse carried 4 μJ energy, the peak intensity reached 2.8×10^{13} W/cm^2 near the focus point, inciting both multi-photon ionization ($I<10^{12}$ W/cm^2) and tunneling ionization ($I>10^{14}$ W/cm^2) of oxygen and nitrogen molecules in air to a relatively high ionization rate [20,21]. The femtosecond laser was focused 1 or 2 μm above the diamond sample in the air to form the filament and the distance between sample surface and the laser focus was very close for the electrons to fall on the diamond. If the laser spot was deeply focused inside the diamond, since no electrons were generated, vacancies could not be produced by electron irradiation. Only damage of the diamond sample was found. Figure 1(b) and 1(c) was taken by a microscope camera with objective lens of 10×. Figure 1(b) shows 10 spots induced by different illumination time of 1/125, 1/64, 1/32, 1/16, 1/8, 1/4, 1/2, 1, 2 and 4 seconds with almost the same diameter around 15 μm. Theoretically, higher focusing should be carried out with laser pulses of lower energy to avoid objective lens damage and sample consumption. However, when a higher NA objective (NA=0.95, 100×) was employed in the illumination experiment while keeping all the other sets unchanged, it turned out that the focusing angle of the laser was too large that that the filaments were hard to form. The illuminated spots were separated by 50 μm and a line marker burnt on the surface of the diamond. The femtosecond laser illumination created pores with the typical diameters around 10 μm, while as measured by using an atomic force microscope, the pore depths varied from 1 μm to several μm under different illumination times.

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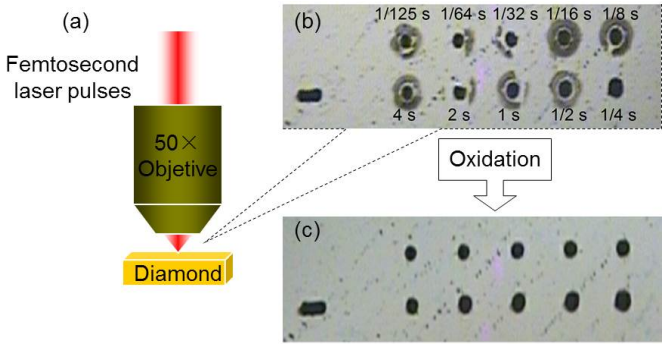

Fig. 1. (a) Experimental setup for the femtosecond laser illumination on a diamond sample. (b) Illuminated diamond sample by fs pulsed laser with different illumination time. (c) Same diamond sample after slow oxidation.

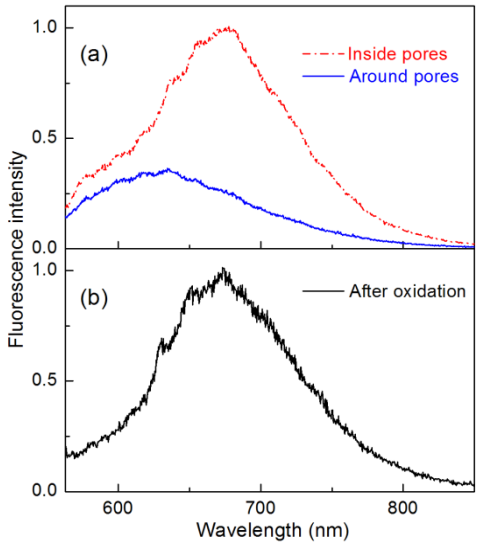

Fig. 2. Typical PL spectra acquired under continuous-wave excitation at 532 nm at large area of strong fluorescence inside and outside the pores before (a) and after (b) oxidation.

After laser illumination, a scanning confocal microscopy was used to check the fluorescence of the spots under excitation of a continuous-wave laser at 532 nm [27]. The laser beam was focused on the diamond sample by a high numerical aperture microscope objective (NA = 0.95, ×100). The PL from the diamond sample was collected by the same microscope objective, sent to the detector after spatial and spectral filtering, and then detected by a silicon avalanche photodiode single-photon detector. All the illuminated spots emitted strong fluorescence. The observed fluorescence area on each spot shaped like a ring with 1~5 μm width. It was reported that fs laser pulse irradiation not only induced pores in diamond, but also generated other carbon materials such as graphite or diamond nanobumps in the pores, which may have equivalent properties to diamond nanocrystals [28]. Figure 2(a) shows the typical PL spectra acquired inside and around the pores. The major band of PL spectra acquired inside the pores varied from 560 nm to 800 nm, of which the spectrum lineshape was very similar to that of NV centers. And that also might be the spectrum of some graphite. Moreover, a spectral peak could be observed around 637 nm, corresponding to the zero-phonon line of NV centers. However, the spectral band acquired around the pores showed a spectral peak at different wavelengths, similar to the PL spectra of NV centers in diamond nanocrystals [29]. The irradiation intensity of the laser is important to the experiment. We

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believe that the irradiation intensity of the laser should be about ~10^{13} W/cm^2, which is a threshold for effective air filament. With higher intensity, the laser could be too violent that it would damage much more diamond sample and even NV centers. Different from Ref [30,31]. which showed the multiphoton ionization of carbon atoms in the diamond, here it was the air that was multiphoton-ionized to provide the electrons. It is true that the pore on the sample was created by femtosecond laser-induced multi-photon ionization of the carbon atoms in the diamond as in the Ref [31]. However, the NV color centers were created out of the burning spot, showing that they were created by the electrons in the laser filament instead of multi-photon ionization.

3. Slow oxidation

The illuminated diamond sample was put into a ceramic stove at 300 °C and started heating to 680 °C and maintained for 5 minutes, so that the oxygen in air oxidized the impurities on diamond surface and possibly a small amount of diamond surface itself. The high temperature could also enhance vacancies moving towards nitrogen atoms. Time of the whole oxidation procedure including annealing to room temperature was about 15 minutes. Shallow rings around the pores in Fig. 1(b) vanished in oxidation, as shown in Fig. 1(c). The former carbon impurities on the spots might be entirely oxidized in air. Hence the deeper illuminated spots could be observed. Under high temperature, the vibration of carbon atoms in diamond lattice could be enhanced and the diamond lattice would be re-constructed. Thus, the vacancies could be moved and "trapped" by close nitrogen atoms. On one hand, high temperature achieved in laser focal point could drive vacancies towards immobile nitrogen atoms. On the other hand, oxidation procedure also has a relevant part as it was carried out under 680 °C. The main idea of oxidation procedure is also to reduce fluorescence-unstable carbon impurities (could be graphite) which were formed in illumination procedure. After the oxidation, spectra acquired inside and outside the pores became consistent, and a representative PL spectrum is shown in Fig. 2(b), which certificated the fabrication of NV centers transparently and also indicated the nanobumps deduction. As the NV centers generated by femtosecond laser illumination were close to the surface. The surface of the diamond could influence the charge state of the subsurface-laying NV centers. And oxidation in air treatment also resulted in high generation of NV^- other than NV^0 [32].

4. Results and discussion

Surface fluorescence images of spots after illumination and oxidation were acquired with a scanning confocal fluorescence microscopy with an objective lens with numerical aperture of 0.95, as shown in Figs. 3(a)-3(c). All fluorescent areas in the three images were induced by the 800-nm fs laser illumination of 1/125, 1/64 and 1/8 s, corresponding to 2.0×10^3, 3.9×10^3, and 3.1×10^4 pulses, respectively. The excitation power of the green laser at 532 nm was about 60 μW. Large-area highlights on the ring were high-density ensembles of NV centers. Individual photoluminescent points could also be observed. Multiple NV centers and large-area NV center ensembles could be found on all illuminated spots. The large and strong fluorescent area formed a ring around the beam focus. By focusing deep in the sample, fluorescence was detected inside the craters. However, NV centers fabricated inside the craters contained large-area high-density ensembles even with the shortest illumination time of 1/125 s. Individual NV centers were located around the craters. Fluorescence features in these spots revealed a trend that larger area and higher density of NV centers were generated with longer illumination time. A careful comparison on the created NV center distribution under various experimental situations showed that individual NV centers could be fabricated with laser illumination duration of ~1/64 s. According the PL intensity distribution, we evaluated the density of NV center to be around 20~30/μm^2 at the bright zone, and 0.4/μm^2 for isolated emitters.

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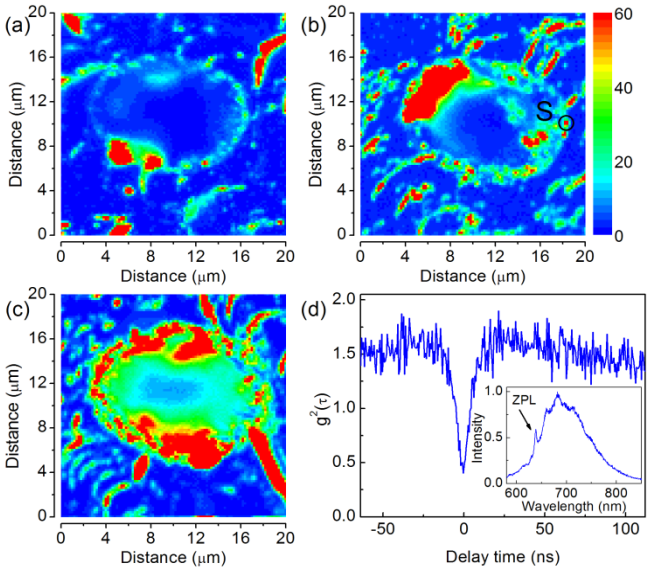

Fig. 3. Fluorescence scanning images of three spots after respective 1/125 s (a), 1/64 s (b) and 1/8 s (c) fs pulse laser illumination and 15-minute oxidation. (d) Anti-bunching effect of a single NV center marked with S in (b). Inset: PL spectrum of the single NV center showing sharp zero-phonon line at 637 nm.

We set up a Hanbury Brown and Twiss (HBT) interferometer for the photon second-order correlation function measurement to check the unity of the photon-emitters. Of all the illuminated spots, most individual fluorescence emitters on the fluorescence rings, more than a dozen, were confirmed to be multiple NV centers. But single-photon emitters could also be found. Point S in Fig. 3(b) was a single NV center. The counting rates were 75×10^3 and 60×10^3 counts per second for each single photon detector in the HBT interferometer. The dip in the second-order correlation function curve showing anti-bunching effect of the single NV center was plotted in Fig. 3(d). The corresponding PL spectrum with a sharp zero-phonon line at 637 nm is shown in the inset. All the identified NV centers showed good photostability. No blinking or blanch was observed during the experiment.

5. Conclusion

In summary, fabrication of NV centers was accomplished with fs pulse laser illumination on synthetic bulk diamond of high nitrogen content followed by appropriate oxidation procedure. It facilitates controllable generation of single NV centers, multiple NV centers, or even large-area high-density NV ensembles for various applications. Quantities of individual multiple NV centers were produced, providing interest in studying the performance of advanced quantum protocols which demand strong coupling. High-density NV ensembles generated by this technique may find applications in magnetic, electronic field and temperature sensing. We are considering further experiment with this technique by decreasing the repetition rate of the laser pulse, as the energy of the laser pulse could not be change for the formation of filament. Using nano/micro-structured masks and purer diamond samples with lower concentration of N atoms are also taken into consideration.

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