

Generation of Nitrogen-Vacancy Centers in Diamond with Ion Implantation *

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Nitrogen-vacancy defect color centers are created in a high purity single crystal diamond by nitrogen-ion implantation. Both optical spectrum and optically detected magnetic resonance are measured for these artificial quantum emitters. Moreover, with a suitable mask, a lattice composed of nitrogen-vacancy centers is fabricated. Rabi oscillation driven by micro-waves is carried out to show the quality of the ion implantation and potential in quantum manipulation. Along with compatible standard lithography, such an implantation technique shows high potential in future to make structures with nitrogen-vacancy centers for diamond photonics and integrated photonic quantum chip.

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Diamond is becoming an ideal platform for quantum-age technologies,^[1] especially when the electron spin operation in nitrogen-vacancy (NV) defect color center can be realized in room temperature.^[2] Recently NV center becomes a leading candidate for a number of applications such as quantum state engineering^[3,4] and computation,^[5,6] quantum communication,^[7] magnetic sensors,^[8–10] and coupling them to a wide variety of interesting systems to achieve scalability and single shot readout.^[11–13] In order to enhance the rate of single photon emission and the coupling strength with photons, there have been lots of approaches to make external optical structures around NV centers,^[14–16] especially with the diamond material itself.^[12,17] More importantly, the recent realization of optical diamond micro-cavity provides a way to obtain a single photon source on chips and to reach a strong coupling regime of cavity quantum electrodynamics (QED) for future quantum networks.^[17–19]

However, natural NV centers distribute randomly in diamond, which induces great difficulties to make photon-NV center coupling on demand. Therefore, it is necessary to produce NV centers in diamond artificially.^[20,21] Especially, to create NV centers at fixed positions is highly required for diamond based nano-photonics and quantum information techniques. In this study, we create NV color centers in a high purity single crystal diamond by implanting nitrogen ions. Optical and microwave properties are measured for these artificial NV centers. With a suitable optical mask, a lattice with NV centers is also fabricated and shows the quality of spin control with the demonstra-

tion of Rabi oscillation driven by microwaves. Because of the implantation process's compatibility with standard lithography, optical structures with NV centers in diamond materials for cavity QED and quantum manipulation can be realized in the future.

In the NV center creation process, a high-quality electronic grade CVD diamond sample ($[N] < 5$ ppb) from element 6 with low background was used to generate NV centers by implanting nitrogen ions with an IBBe device (maximum intensity: 15 mA, maximum energy: 30 keV). Before the irradiation with nitrogen ions, half of the diamond sample was masked by a tape. The diamond sample was radiated with nitrogen ions at an energy of 20 keV and a dosage of 10^{16} cm^{-2} . To mobilize vacancies and generate a shallow layer of NV centers, the diamond sample was annealed at high vacuum ($8 \times 10^{-6} \text{ Pa}$) for two hours at 750°C after the irradiation. Finally the sample was placed in a 1:1:1 boiling mixture of sulfuric, nitric, and perchloric acid for about one hour to remove the non-diamond carbon admixtures.

After the production process, the sample was measured with a home-built confocal microscopy system which was integrated with an optically detected magnetic resonance (ODMR) system.^[22] The schematic illustration was shown in Fig.1. A green continuous laser (wavelength at 532 nm) was used to excite NV centers. Fluorescent photons from NV centers were collected by an objective lens with 0.9N.A. and transmitted through a dichroic mirror (D). A 550 nm long pass filter (LPF) was used to filter out the green laser. Finally the photons were coupled by a collimator to a multi-mode fiber (MF). The multi-mode

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fiber can be connected to a single photon counting mode (SPCM) to obtain fluorescence intensity, or connected to a spectrometer (SPM) to obtain fluorescence spectrum. Utilizing a closed-loop piezoelectric transition stage (PZT), the sample can be scanned in a $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ area with 10 nm resolution. During the confocal scanning measurement, a pinhole with proper diameter was used at the focus of lens (L3) to reach a resolution below $1\text{ }\mu\text{m}$. A microwave source was applied in magnetic resonance experiments, which can scan from 9 kHz to 3 GHz and the maximal output power can reach 1 W . If higher rf power is needed, the source can be amplified up to 40 W by a radio-frequency amplifier. To effectively apply strong microwaves to NV centers, a microwave antenna made by a $10\text{-}\mu\text{m}$ -diameter copper wire was adjusted close to the sample surface. An acoustic optical modulator (AOM) was used to switch the exciting light on or off and the modulation of AOM frequency can reach 200 MHz .

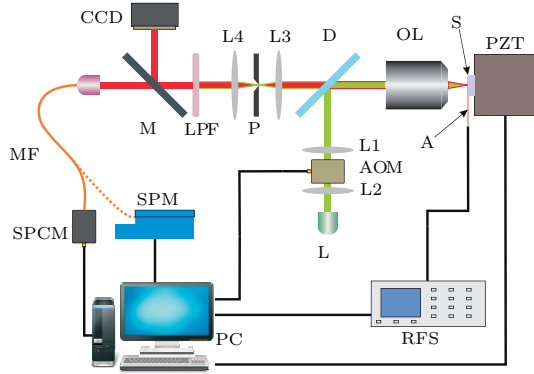


Fig. 1. Confocal microscope-ODMR system. RFS: microwave source; A: antenna; S: sample; PZT: piezoelectric transition stage; OL: objective lens; D: dichroic mirror; L1, L2, L3, L4: optical lens; P: pin hole; LPF: long wavelength pass filter; MF: multimode fiber; SPCM: single photon counting module; SPM: spectrometer; M: flipable reflect mirror; AOM: acoustic optical modulator; L: excitation laser.

The scanning confocal microscopy image of NV fluorescence was measured around the mask edge. Signals from SPCM were counted by a counting board (NI6602) plugged in a personal computer (PC). By program controlling, the PZT movement and counting can be synchronized to obtain a scanning fluorescence image. Figure 2(a) shows the scanning fluorescence image of the sample with the scanning step of 100 nm and confocal resolution about 500 nm . The brightness contrast of masked and unmasked areas was obvious: counts from the masked area were about 1.5 kcps/s while the unmasked area with NV fluorescence were about 400 kcps/s . The confocal focus was then fixed at point A or point B to measure the fluorescence spectrum under the same excitation condition. A strong NV fluorescence spectrum can be observed at point B from Fig. 2(b), while the spectrum at point A was

mainly the noise. The zero phonon line (ZPL) of implanted NV centers at 637 nm was also obvious in Fig. 2(b).

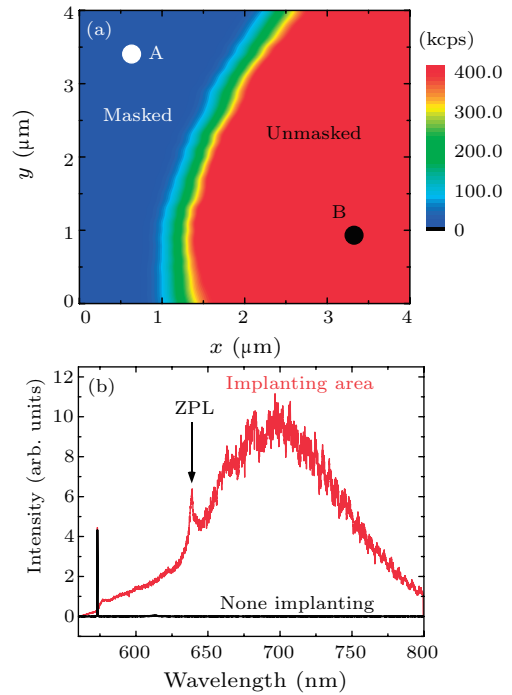


Fig. 2. Confocal microscope image and fluorescence spectrum. (a) Scanning confocal image of NV fluorescence around the edge of masked area. (b) The spectrum of point A in masked area and point B in unmasked area. Two points were measured under the same condition with the same diamond Raman signal. Point A has no NV fluorescence while point B has strong NV fluorescence with clear NV ZPL at 637 nm .

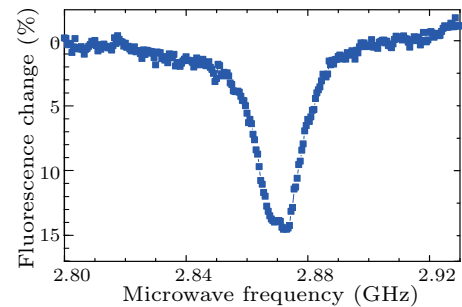


Fig. 3. ODMR spectrum of the artificial NV centers.

NV centers have spin triplet ground state with $S = 1$. The sublevels $m_s = 0$ and $m_s = \pm 1$ are split by about 2.87 GHz without external field, which can be detected by the ODMR.^[22] The green continuous laser beam can polarize the NV center into the $|m_s = 0\rangle$ state. It will be pumped into $|m_s = \pm 1\rangle$ when the applied microwave is resonant with the split between the ground state sublevels. Consequently, fluorescence intensity will decrease. In the ODMR measurement, microwave and optical excitation were applied at constant power to the NV centers. We scanned

the microwave frequency from 2.84 GHz to 2.9 GHz and detected the fluorescence variations. The ODMR spectrum is illustrated in Fig. 3, showing the resonant frequency at about 2.873 GHz at room temperature. However, it has been shown that the resonant frequency changes a lot with temperature variation.^[23]

From the characteristic optical and microwave resonant properties, we can confirm that NV centers have been created in diamond with the nitrogen-ion implantation. However, it is highly demanded to produce the NV centers at fixed positions for the coupling with other structures, such as optical waveguides and microcavities. To this aim, here we coated another diamond sample by poly-(methyl methacrylate) (PMMA) with the thickness of 300 nm. In the coating of PMMA, a square lattice of holes was fabricated by electron-beam lithography, as shown in Fig. 4(a). The diameter of each hole was 50 nm or 100 nm and the separation distance (lattice constant) was 5 μm . Then the diamond sample with this structured coating was radiated with nitrogen ions of the energy of 15 keV and the dosage of 10^{13} cm^{-2} . Here low energy and dosage can reduce the production of NV centers. After annealing and the removal of non-diamond carbon admixtures, the sample was scanned in the confocal microscopy system. From the fluorescent emission, as shown in Figs. 4(c) and 4(d), a lattice with NV centers was clearly presented. The emission in Fig. 4(c) was stronger than that in Fig. 4(d) since the diameter of holes in PMMA coating was 100 nm, while the diameter was 50 nm in the latter. Also, in each point of Fig. 4(d), there were about ten NV centers.

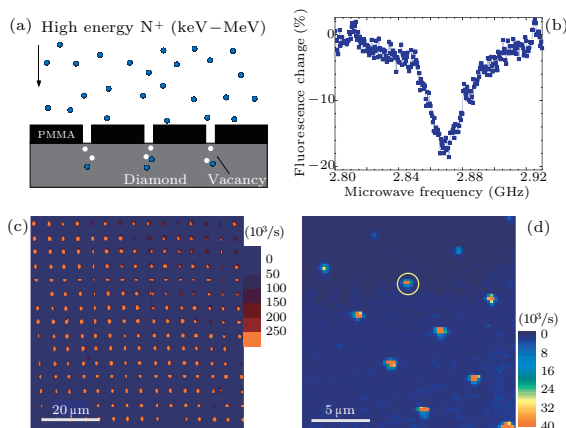


Fig. 4. Fabrication and measurement of NV centers lattice. (a) Illustration of nitrogen-ion implantation with PMMA coating. (b) ODMR spectrum of NV centers in the lattice. (c) and (d) Fluorescent emission from confocal scanning with the diameters of the holes in PMMA coating of 100 nm and 50 nm, respectively. In (d), the point in the circle was used in the measurement of ODMR and Rabi oscillation.

The measurement of ODMR (shown in Fig. 4(b)) was performed on one of these points (circled in Fig. 4(d)), showing the micro-wave resonance fre-

quency at about 2.87 GHz. Based on ODMR, Rabi oscillation of implanted NV centers was further tested.^[24] In this experiment, optical excitation was modulated into pulses for initialing or reading out the spin state. A high speed programmable pulse generator board was used to generate pulse sequences to control microwaves, AOM, and counter gate. It can output four-channel signals synchronously, and the timing sequence of pulses is shown in Fig. 5(a). We used two counters to record the ODMR signal. One was for counting signal while the other was for reference at the end of measurement cycle to reduce the pump noise. This method was realized by applying two gating signals to control two counters, as shown Fig. 5(a). To observe Rabi oscillations, we drove the transition with a resonant microwave pulse of varying duration t and then measured the population remaining in $|m_s = 0\rangle$. Figure 5(b) shows the experimental result of Rabi oscillations at the 2.87 GHz resonance. An oscillation is obvious with 36.5 ns period and about 10% fluorescence change. The coherent time from the Rabi nutation was less than 1 μs .

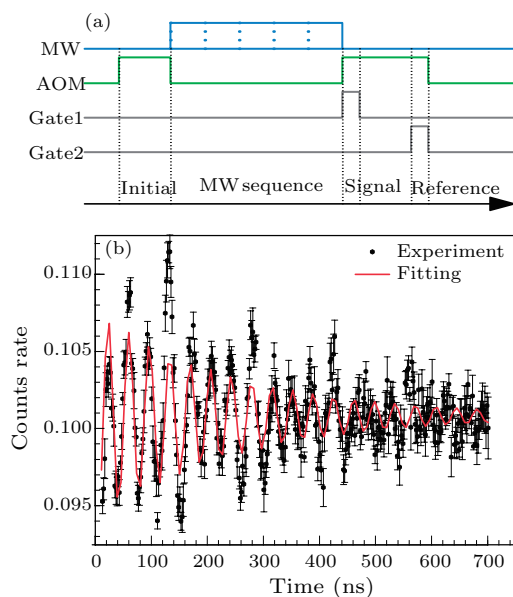


Fig. 5. Rabi oscillation measurement on the point in the lattice. (a) Control sequence of spin operation. The microwave (MW) sequence is a pulse varying duration time to realize Rabi oscillation. (b) Experimental result of Rabi oscillation.

The oscillation signal was noisy and damped quickly in the artificial sample. Long coherent time is needed in quantum manipulation to have enough operation cycles, and improvement of the properties is very important in future fabrication process. There are several possible reasons for the present spin properties. Firstly, the implanting process makes too many vacancy defects in diamond. One 15 keV nitrogen ion can create 70 vacancies simulated by SRIM.^[25] Secondly, nitrogen ions in the diamond did not fully yield

NV centers. Only about 2% nitrogen can form NV centers in the ion implantation,^[21] and other 98% nitrogen ions just exist in diamond as other defects and impurity. In order to improve implanted NV spin properties, decreasing defects around NV centers is necessary. Some following conditions can be considered: (1) Decreasing the implanting dose to create less NV centers, even a single NV center. It is more promising for quantum information technique. (2) Using suitable implanting voltage. High voltage can improve the yield efficiency,^[21] whereas it also makes more vacancy defects and larger straggling. Thus there should be an optimal voltage and dose to satisfy conditions 1 and 2 to make the minimal undemanded defects to NV center ratio. (3) Annealing in higher temperature. Annealing conditions can impact the NV yield efficiency and reduce the overall crystal damage. Proper annealing temperature is needed to reduce damage defects for achieving a good NV yield efficiency. Since NV centers are stable below 1600 °C, we can try to take the temperature higher more than 1000 °C to reduce defects more efficiently.

In conclusion, we have created NV centers in high purity bulk diamond by nitrogen-ion implantation. Scanning fluorescence image, optical spectrum and microwave resonance spectrum for spin levels with ODMR are measured to reveal the typical properties of NV centers. Moreover, with the structured mask, a lattice of NV centers is also created. Based on ODMR, Rabi oscillations is achieved in the artificial NV centers. These results have demonstrated that implanted NV centers can be used in quantum operations. By controlling ions dosage and energy, it is possible to obtain NV centers with the density down to $1/\mu\text{m}^3$, which will be essential to realize single photon source and other quantum manipulation in future. Furthermore, because the ion implantation process can be integrated with lithography, it will be realizable to implant a single NV center or NV centers in designed form with other structures such as micro-cavities, nano-photonics and micro-circuits on a chip.

References

- [1] Aharonovich I, Greentree A D and Prawer S 2011 *Nature Photon.* **5** 397
- [2] Awschalom D D, Epstein R and Hanson R 2007 *Sci. Am.* **297** 84
- [3] Togan E, Chu Y, Trifonov A S, Jiang L, Maze J, Childress L, Dutt M V G, Sørensen A S, Hemmer P R, Zibrov A S and Lukin M D 2010 *Nature* **466** 730
- [4] Pan X Y, Liu G Q, Yang L L and Fan H 2011 *Appl. Phys. Lett.* **99** 051113
- [5] Wrachtrup J and Jelezko F 2006 *J. Phys. Condens. Matter* **18** 807
- [6] Shi F, Rong X, Xu N, Wang Y, Wu J, Chong B, Peng X, Kniepert J, Schoenfeld R, Harneit W, Feng M and Du J F 2010 *Phys. Rev. Lett.* **105** 040504
- [7] Childress L, Taylor J M, Sørensen A S and Lukin M D 2006 *Phys. Rev. Lett.* **96** 070504
- [8] Balasubramanian G, Chan I Y, Kolesov R, Al Hmoud M, Tisler J, Shin C, Kim C, Wojcik A, Hemmer P R, Krueger A, Hanke T, Leitenstorfer A, Bratschitsch R, Jelezko F and Wrachtrup J 2008 *Nature* **455** 648
- [9] Degen C L, 2008 *Appl. Phys. Lett.* **92** 243111
- [10] Maze J R, Stanwix P L, Hodges J S, Hong S, Taylor J M, Cappellaro P, Jiang L, Dutt M V G, Togan E, Zibrov A S, Yacoby A, Walsworth R L and Lukin M D 2008 *Nature* **455** 644
- [11] Schietinger S, Barth M, Aichele T and Benson O 2009 *Nano Lett.* **9** 1694
- [12] Babinec T M, Hausmann B J M, Khan M, Zhang Y, Maze J R, Hemmer P R and Lončar M 2010 *Nature Nanotech.* **5** 195
- [13] Fu K M C, Santori C, Barclay P E, Aharonovich I, Prawer S, Meyer N, Holm A M and Beausoleil R G 2008 *Appl. Phys. Lett.* **93** 234107
- [14] Barclay P E, Fu K M C, Santori C, Faraon A and Beausoleil R G 2011 *Phys. Rev. X* **1** 011007
- [15] Hadden J P, Harrison J P, Stanley Clarke A C, Marseglia L, Ho Y L D, Patton B R, O'Brien J L and Rarity J G 2010 *Appl. Phys. Lett.* **97** 241901
- [16] Steinmetz D, Neu E, Hepp C, Albrecht R, Bolse W, Meijer J, Rogalla D and Becher C 2010 *Proc. SPIE* **7727** 77270P
- [17] Faraon A, Barclay P E, Santori C, Fu K M C and Beausoleil R G 2010 *Nature Photon.* **5** 301
- [18] Stannigel K, Rabl P, Sørensen A S, Zoller P and Lukin M D 2010 *Phys. Rev. Lett.* **105** 220501
- [19] Yang W L, Yin Z Q, Xu Z Y, Feng M and Du J F 2010 *Appl. Phys. Lett.* **96** 241113
- [20] Meijer J, Burchard B, Domhan M, Wittmann C, Gaebel T, Popa I, Jelezko F and Wrachtrup J 2005 *Appl. Phys. Lett.* **87** 261909
- [21] Pezzagna S, Naydenov B, Jelezko F, Wrachtrup J and Meijer J 2010 *New J. Phys.* **12** 065017
- [22] Oort E, Manson N B and Glasbeek M 1988 *J. Phys. C Solid State Phys.* **21** 4385
- [23] Chen X D, Dong C H, Sun F W, Zou C L, Cui J M, Han Z F and Guo G C 2011 *Appl. Phys. Lett.* **99** 161903
- [24] Gaebel T, Domhan M, Popa I, Wittmann C, Neumann P, Jelezko F, Rabeau J R, Stavrias N, Greentree A D, Prawer S, Meijer J, Twamley J, Hemmer P R and Wrachtrup J 2006 *Nature Phys.* **2** 408
- [25] Zeigler J 2008 *The Stopping Range of Ions in Matter* SRIM-2008 <http://srim.org>