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Engineered arrays of nitrogen-vacancy color centers in diamond based on implantation of CN^- molecules through nanoapertures

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Abstract. We report a versatile method for engineering arrays of nitrogen-vacancy (NV) color centers in diamond at the nanoscale. The defects were produced in parallel by ion implantation through 80 nm diameter apertures patterned using electron beam lithography in a polymethyl methacrylate (PMMA) layer deposited on a diamond surface. The implantation was performed with CN^- molecules that increased the NV defect-formation yield. This method could enable the realization of a solid-state coupled-spin array and could be used for positioning an optically active NV center on a photonic microstructure.

The nitrogen-vacancy (NV) color center in diamond, consisting of a substitutional nitrogen atom (N) associated with a vacancy (V) in an adjacent lattice site of the crystalline matrix, has found a wide range of applications in quantum information processing. It is a robust luminescent center that, once isolated at the individual level [1], can be used to implement efficient single-photon quantum key distribution protocols [2]. Moreover, the association of a spin structure

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in the ground level having a long coherence time at room temperature with spin-dependent optical transitions allows for quantum-state preparation by optical pumping and single-spin quantum state readout [3]. However, to develop most of the envisioned applications requires one to position the NV center with nanometer-scale accuracy. This spatial control could be the basic technology for building a scalable quantum simulator based on spins associated with an array of NV defects with magnetic dipolar coupling [4]. The control of the position of an NV defect could also help one to enhance the photon out-coupling by channeling its luminescence toward a photonic structure, like a dielectric nanowire [5], a metallic antenna [6] or a photonic crystal microcavity [7, 8].

A practical solution can consist in addressing NV centers in diamond nanocrystals [9]. By manipulating the nanoparticle with a tip-based system [10, 11], it is then possible to place a hosted NV defect at a controlled location. This technique was used to couple the luminescence of a single NV center to a photonic waveguide [12] and could be scaled up to build arrays of NV defects. However, the dipolar magnetic coupling between two NV centers is limited to a distance of a few tens of nanometers in the case of millisecond spin coherence time reached in ultrapure single-crystal diamond grown using the chemical vapor deposition (CVD) method [13]. Due to an uncontrolled level of impurities and to parasitic surface effects, the spin coherence of NV centers in nanodiamonds is up to now limited to much smaller values and this bottom-up approach cannot be realistically envisioned, even with touching state-of-the-art luminescent nanodiamonds [14].

Ion-beam nitrogen implantation is a flexible technique for creating individual NV centers in a diamond sample [15, 16], and two-qubit coupling was obtained between implanted nitrogen atoms coming from the dissociation of a nitrogen molecule impinging on a diamond surface [4, 17]. However, the resolution of a nitrogen ion beam is limited to a few hundreds of nanometers even with ion optics correction [18], thus preventing the scale-up of this clever recipe. Alternative techniques enabling the reliable placement of nitrogen impurities into a diamond substrate have therefore to be developed. Spatially resolved ion implantation with nanometer resolution can be achieved by limiting the aperture of a low-energy ion beam with a hole made in a scanning probe, which will then define the implantation spot [19, 20], or by the release from a Paul-like ion trap in which the ions were captured and cooled [21]. In this paper, we report a versatile technique consisting in ion implantation through an array of apertures that was patterned in a PMMA layer initially deposited on top of the diamond substrate. Our results demonstrate that this technique is well adapted to the parallel implantation of any impurity inside a large number of targeted spots, with a resolution defined by the diameter of the aperture.

We used an ultra-pure CVD-grown single-crystal diamond with an intrinsic nitrogen content much below 1 ppb [22], ensuring that each detected NV center can be faithfully attributed to an implanted nitrogen impurity [23]. After acid cleaning of the sample, a 200-nm-thick layer of PMMA A4 was deposited on the diamond surface by spin-coating. Arrays of 80 nm diameter apertures were then patterned on the PMMA layer using a 80 kV–2.3 nA electron beam lithography equipment (Nanobeam Ltd). The apertures were regularly spaced with a 2 μ m pitch array. After electron beam lithography, the mask was finally developed using methyl isobutyl ketone/isopropyl alcohol (MIBK/IPA). It resulted in an array of apertures with controlled spacing and diameter, as shown in figures 1(a) and (b). This process, which simply relies on the deposition of a PMMA resist and patterning using electron beam lithography, prevents any damage of the diamond substrate, as compared to other methods like plasma etching or carving with a focused ion beam.

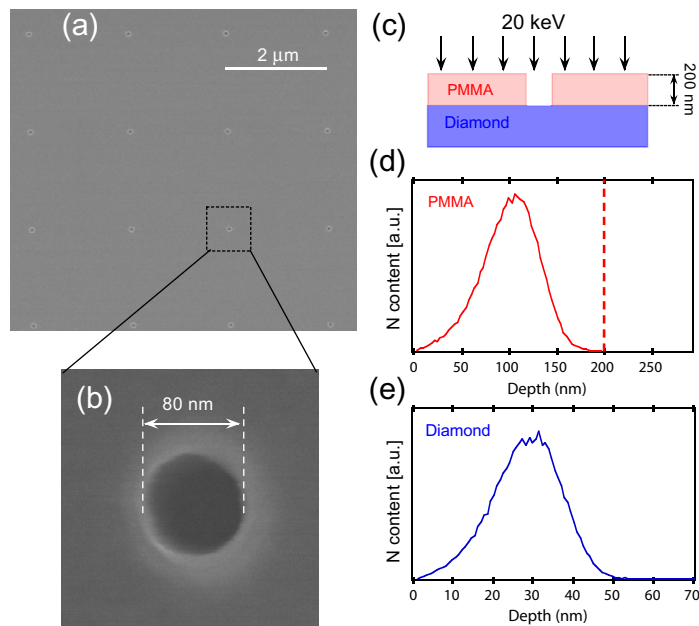


Figure 1. (a) Scanning electron microscope image of the surface of the PMMA layer, displaying the array of apertures drilled using electron beam lithography. (b) Enlarged image of the PMMA layer surface zooming a single aperture. (c–e) Implantation scheme, with SRIM simulations corresponding to the 20 keV nitrogen irradiation of the PMMA layer and the unmasked diamond surface. According to the simulation shown in (d), the ions are fully stopped by the 200 nm thickness of the PMMA layer.

Nitrogen was then implanted from a CN^- molecular ion beam with 40 keV kinetic energy. When a CN^- molecule hit the surface, it broke into two parts. Taking into account the mass selection in the ion beam, it then became equivalent to a joint implantation of nitrogen ^{14}N and carbon ^{12}C with respective energies of about 20 and 18 keV. As shown in figures 1(d) and (e), a stopping and range of ions in matter (SRIM) simulation [24] indicates that the nitrogen atoms will stop at an approximate depth of 30 ± 10 nm below the diamond surface, whereas they are stopped by the PMMA layer in the masked parts of the sample (see figure 1(c)). The evaluated straggling was about 9 nm, much smaller than the diameter of the aperture. Note that the simultaneous breaking of the nitrogen and carbon atoms as they penetrate into the diamond will increase the number of vacancies created close to the implanted nitrogen atoms, thus helping in the formation of the NV centers [23].

The toxic CN^- molecules were *in situ* produced with a negative sputter ion source. Cs ions were used to sputter a target consisting of a mixture of BN and graphite powders and reaction in the plasma generated above the target led to the creation of CN^- molecules, among other species. In this ion source, which was initially developed for the tandem accelerator, the negatively charged ions were only produced in their single charged state. This effect decreased the number of possible ions corresponding to a given energy–mass product, providing an easy identification of a given ion, whose selection was realized by a double focused 90° magnet. The sorted ions were then accelerated to an adjustable kinetic energy ranging from a few keV to hundreds of keV. The output of the accelerator is equipped with an implantation setup consisting

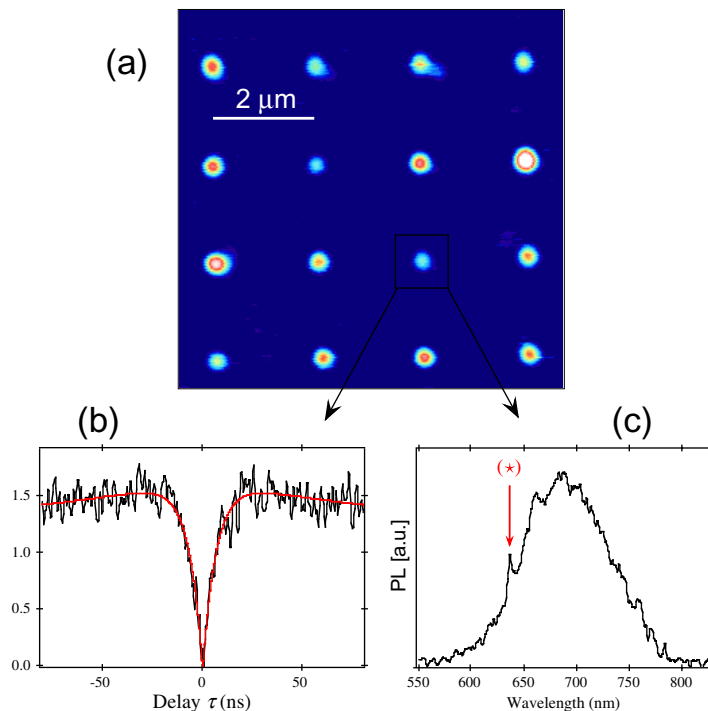


Figure 2. (a) PL raster scan of the sample, displaying an emission pattern matching the array of holes drilled in the PMMA layer. (b, c) Analysis realized for each spot, corresponding to the determination of the second-order autocorrelation function associated with the time delay τ between consecutive photon detections, and to the record of the luminescence spectrum. The zero-phonon line (\star symbol) at 637 nm identified the center as negatively charged NV^- . The signal over background associated with a single emitter, as observed in the circled spot, was nearly 4.

of an electrostatic scanning system and a specifically designed chamber with secondary electron suppression⁶.

After the implantation run corresponding to an applied dose of 10^{12} ions cm^{-2} with a current of 600 nA, the PMMA layer was removed by acid treatment. The sample was then annealed at 800 °C for 2 h to induce vacancy diffusion leading to the conversion of the implanted nitrogen atoms into luminescent NV color centers.

The photoluminescence (PL) properties of the implanted and annealed sample were then studied using a home-made scanning confocal microscope. A laser operating at 532 nm wavelength was focused onto the sample through an oil immersion microscope objective. The PL was collected by the same objective, spectrally filtered from the remaining excitation laser light, and focused onto a 50 μm diameter pinhole. The PL was finally directed to avalanche photodiodes working in the photon counting regime. A typical PL raster scan of the sample is shown in figure 2(a), displaying an array of photoluminescent spots that matches the PMMA

⁶ The implantation chamber was tilted at 7° to avoid ion beam channeling that could induce an increase in the ion penetration depth compared to the SRIM prediction. The efficiency of the design was controlled by an independent SIMS measurement, which gave a derivation below 5% in dose and depth for a silicon sample implanted with 60 keV B^+ ions.

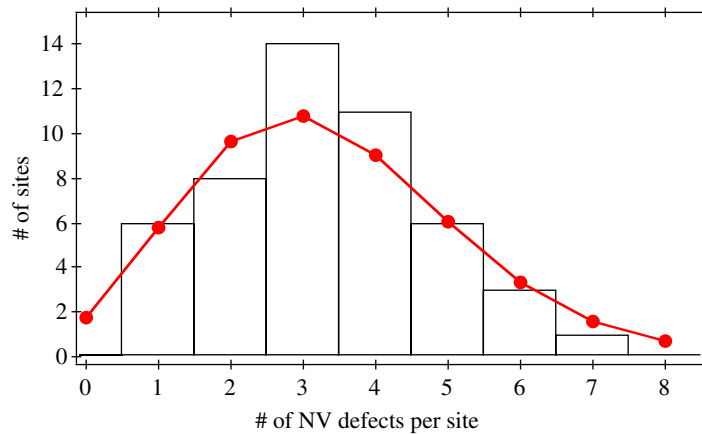


Figure 3. Statistics evaluated on 49 sites of the number of NV defects per implanted spot, and fitted by a Poisson distribution.

mask with its period of drilled holes. This observation clearly demonstrates the efficiency of the implantation technique.

In order to infer the number of emitters associated with each luminescent spot, we performed a photon correlation measurement using a Hanbury Brown and Twiss interferometer. Following the procedure of [25] for background correction and normalization to shotnoise level, the histogram of the time delays τ between two consecutive photon detections is equivalent to the second-order autocorrelation function $g^{(2)}(\tau)$ of the luminescence intensity emitted by the analyzed spot. Figures 2(b) and (c), respectively, show the photon correlation measurement and the spectral analysis associated with the circled spot in figure 2(a). The dip observed at zero delay in the $g^{(2)}(\tau)$ function is the signature of a single emitter located in the corresponding implanted area. Complementary spectral analysis showed that most of the observed emitters were of the negatively charged state NV^- . Note that in our case of shallow implantation, the remaining defects of neutral charge state NV^0 could be efficiently transformed into their counterpart NV^- by surface oxidation, as shown in [26, 27].

The number of emitting NV defects in the implanted spots was finally determined from combined measurements of the depth of the zero-delay dip in the $g^{(2)}(\tau)$ function, and of the luminescence intensity compared to the mean level corresponding to a single NV emitter. The corresponding histogram is shown in figure 3. Since the number of implanted ions is random, we obtained a broad distribution, which can be fitted by a Poissonian distribution with a mean value equal to 3.5. Since the irradiation dose corresponds to approximately 50 nitrogen atoms per spot, the conversion yield of implanted nitrogen ions into NV defects is near 0.07. As expected from the higher ion energy and from the joint implantation of carbon atoms associated with the CN^- molecular beam that leads to an increased number of vacancies created around the implanted atom, this value is more than two times higher than the reported ones for low-energy nitrogen implantation [16, 28].

In conclusion, we have shown that arrays of NV color centers can be reliably produced by implanting CN^- molecules through the 80 nm diameter holes in a PMMA mask of 200 nm thickness, which was deposited on top of a single-crystal diamond sample. The joint implantation of carbon increased the conversion of the implanted nitrogen atoms into NV centers. The apertures and the thickness of the PMMA layer have to be optimized in order

to improve the resolution of the implanted impurities but fabrication of patterns below 10 nm have already been reported in thinner PMMA layers [29]. This flexible technique therefore holds strong promise for building scalable quantum registers based on coupled spins. More generally, ion implantation is a standard tool for the semiconductor industry, and the spatial control of impurities at the nanoscale is now required as transistor size shrinks to this length scale. Following our procedure, implanted NV centers, which can be directly imaged with below nanoscale precision using the optical stimulated emission depletion microscopy technique [30], could then be used as a near perfect test bed for evaluating efficiency and resolution of novel implantation techniques.

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References

- [1] Grüber A, Drabenstedt A, Tietz C, Fleury L, Wrachtrup J and von Borczyskowski C 1997 *Science* **276** 2012–4
- [2] Alleaume R, Treussart F, Messin G, Dumeige Y, Roch J F, Beveratos A, Brouri-Tualle R, Poizat J P and Grangier P 2004 *New J. Phys.* **6** 92
- [3] Jelezko F, Gaebel T, Popa I, Gruber A and Wrachtrup J 2004 *Phys. Rev. Lett.* **92** 1–4
- [4] Neumann P *et al* 2010 *Nat. Phys.* **6** 249–53
- [5] Babinec T M, Hausmann B J M, Khan M, Zhang Y, Maze J R, Hemmer P R and Loncar M 2010 *Nat. Nanotech.* **5** 195–9
- [6] Esteban R, Teperik T V and Greffet J J 2010 *Phys. Rev. Lett.* **104** 026802
- [7] Wolters J, Schell A W, Kewes G, Nusse N, Schoengen M, Doscher H, Hannappel T, Lochel B, Barth M and Benson O 2010 *Appl. Phys. Lett.* **97** 141108
- [8] van der Sar T, Hagemeyer J, Pfaff W, Heeres E C, Oosterkamp T H, Bouwmeester D and Hanson R 2010 arXiv:1008.4097 [quant-ph]
- [9] Treussart F, Jacques V, Wu E, Gacoin T, Grangier P and Roch J F 2006 *Physica B* **376–377** 926–9
- [10] Ampem-Lassen E, Simpson D A, Gibson B C, Trpkovski S, Hossain F M, Huntington S T, Ganesan K, Hollenberg L C and Prawer S 2009 *Opt. Express* **17** 11287
- [11] van der Sar T, Heeres E C, Dmochowski G M, de Lange G, Robledo L, Oosterkamp T H and Hanson R 2009 *Appl. Phys. Lett.* **94** 173104
- [12] Barth M, Nüsse N, Löchel B and Benson O 2009 *Opt. Lett.* **34** 1108–10
- [13] Balasubramanian G *et al* 2009 *Nat. Mater.* **8** 383–7
- [14] Tisler J *et al* 2009 *ACS Nano* **3** 1959–65
- [15] Meijer J, Burchard B, Domhan M, Wittmann C, Gaebel T, Popa I, Jelezko F and Wrachtrup J 2005 *Appl. Phys. Lett.* **87** 261909
- [16] Rabeau J R, Reichart P, Tamanyan G, Jamieson D N, Prawer S, Jelezko F, Gaebel T, Popa I, Domhan M and Wrachtrup J 2006 *Appl. Phys. Lett.* **88** 023113
- [17] Gaebel T *et al* 2006 *Nat. Phys.* **2** 408–13
- [18] Vogel T, Meijer J, Stephan A, Weidenmüller U, Dagkaldiran, Kubsky S, Baving P, Becker H W and Rcken H 2002 *Nucl. Instrum. Methods Phys. Res. B* **188** 174–8

- [19] Pezzagna S, Wildanger D, Mazarov P, Wieck A D, Sarov Y, Rangelow I, Naydenov B, Jelezko F, Hell S W and Meijer J 2010 *Small* **6** 2117–21
- [20] Weis C D *et al* 2008 *J. Vac. Sci. Technol. B* **26** 2596
- [21] Schnitzler W, Linke N, Fickler R, Meijer J, Schmidt-Kaler F and Singer K 2009 *Phys. Rev. Lett.* **102** 1–4
- [22] Tallaire A, Collins A T, Charles D, Achard J, Sussmann R, Gicquel A, Newton M E, Edmonds A M and Cruddace R J 2006 *Diam. Relat. Mater.* **15** 1700–7
- [23] Naydenov B, Richter V, Beck J, Steiner M, Neumann P, Balasubramanian G, Achard J, Jelezko F, Wrachtrup J and Kalish R 2010 *Appl. Phys. Lett.* **96** 163108
- [24] Ziegler J F 2004 *Nucl. Instrum. Methods Phys. Res. B* **219–220** 1027–36
- [25] Brouri R, Beveratos A, Poizat J P and Grangier P 2000 *Opt. Lett.* **25** 1294–6
- [26] Fu K M C, Santori C, Barclay P E and Beausoleil R G 2010 *Appl. Phys. Lett.* **96** 121907
- [27] Rondin L *et al* 2010 *Phys. Rev. B* **82** 15
- [28] Pezzagna S, Naydenov B, Jelezko F, Wrachtrup J and Meijer J 2010 *New J. Phys.* **12** 065017
- [29] Vieu C, Carcenac F, Pépin A, Chen Y, Mejias M, Lebib A, Manin-Ferlazzo L, Couraud L and Launois H 2000 *Appl. Surf. Sci.* **164** 111–7
- [30] Rittweger E, Han K Y, Irvine S E, Eggeling C and Hell S W 2009 *Nat. Photon.* **3** 144–7
- [31] Toyli D M, Weis C D, Fuchs G D, Schenkel T and Awschalom D D 2010 *Nano Lett.* **10** 3168–72