

Enhanced concentrations of nitrogen-vacancy centers in diamond through TEM irradiation

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One of the challenges in spin ensemble-based magnetometry and many-body spin physics in solid state systems is to enhance the spin concentration while maintaining long coherence times. In particular, for an ensemble of nitrogen-vacancy (NV) centers in diamond, high conversion efficiencies between nitrogen (P1) defects and NV centers are essential for quantum information and sensing applications. In this work, we study the effect of electron irradiation on the conversion efficiency of various types of HPHT and CVD diamond samples with different initial nitrogen concentrations. The samples were irradiated using a 200 keV transmission electron microscope (TEM). We observe an order of magnitude improvement in the NV concentration (up to $\sim 10^{11}$ NV/cm²), without any degradation in their coherence properties. We find that the efficiency of NV creation strongly depends on the initial conversion efficiency as well as on the initial nitrogen concentration. The achieved $\sim 10\%$ conversion efficiency from N defects to NV centers in the diamond suggests that such irradiation processes can improve the sensitivity of DC and AC magnetometry, and pave the way toward the study of many-body physics of ensembles of NV spins.

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The unique spin and optical properties of the negatively charged nitrogen-vacancy (NV) centers in diamond make them useful for magnetic [1–11] and electric [12] sensing applications. Moreover, based on their milliseconds coherence times at room temperature [13–16], ensembles of NV centers can act as resources for quantum information processing, quantum simulation and the study of quantum many-body dynamics of interacting spins [17–19]. The sensitivity of magnetic sensing grows as the square-root of the number of spin sensors [1, 5, 6], thus enhanced NV concentration could significantly improve magnetometric sensitivities. Furthermore, enhanced NV concentration could lead to strong NV-NV couplings, which together with long coherence times, achieved using a proper dynamical decoupling protocol [20], could pave the way toward the study of many-body dynamics in the NV-NV interaction-dominated regime [17–19]. However, nitrogen defects not associated with vacancies (P1 centers) create randomly fluctuating magnetic fields that cause decoherence of the quantum state of the NV ensemble [21, 22]. As a result, in most cases it would be beneficial to increase the concentration of NV centers while keeping the nitrogen concentration constant, i.e. improve the N to NV conversion efficiency.

One of the common techniques for improving the conversion efficiency is electron irradiation, which creates vacancies in the lattice. Additional annealing mobilizes the vacancies, thus increasing their probability of occupying lattice sites adjacent to isolated nitrogens and forming stable NV centers. Recently, improved conversion efficiency through irradiation at ~ 200 keV was

demonstrated using a transmission electron microscope (TEM) in high-pressure-high-temperature (HPHT) [23] and delta doped [24] diamond samples.

In this work, we extend these previous results by performing a systematic study of the effect of electron irradiation on various types of diamond samples, which are more relevant to ongoing research (chemical vapor deposition, with as grown and implanted NVs). We achieve an order of magnitude improvement in conversion efficiencies, and examined its resulting contribution to magnetometry and the study of many-body spin physics.

We study the effect of electron irradiation on four different samples (element six). The first sample was produced by a standard HPHT technique, with an initial nitrogen concentration of ~ 200 PPM and poor conversion efficiency ($< 10^{-5}\%$). The second sample was produced by a standard chemical vapor deposition (CVD) synthesis procedure, having a ~ 1 PPM initial nitrogen concentration and initial conversion efficiency of $\sim 0.04\%$ (hereafter - standard grade CVD). The last two samples were produced by a high purity CVD procedure with an initial nitrogen concentration of ~ 1 PPB and an NV concentration that was too low to detect. These two samples then underwent a nitrogen implantation process (in-novion), at an energy of 20 keV and doses of 2×10^{11} and 2×10^{12} N/cm², followed by standard annealing (Across International TF1400, 8 hours, temperature 800°C, vacuum $\sim 7.5 \times 10^{-7}$ Torr), which resulted in different NV concentrations with conversion efficiencies of $\sim 1.2\%$ and 0.77% respectively (hereafter - we refer to these two samples as 2D nitrogen-implanted CVD). All samples were

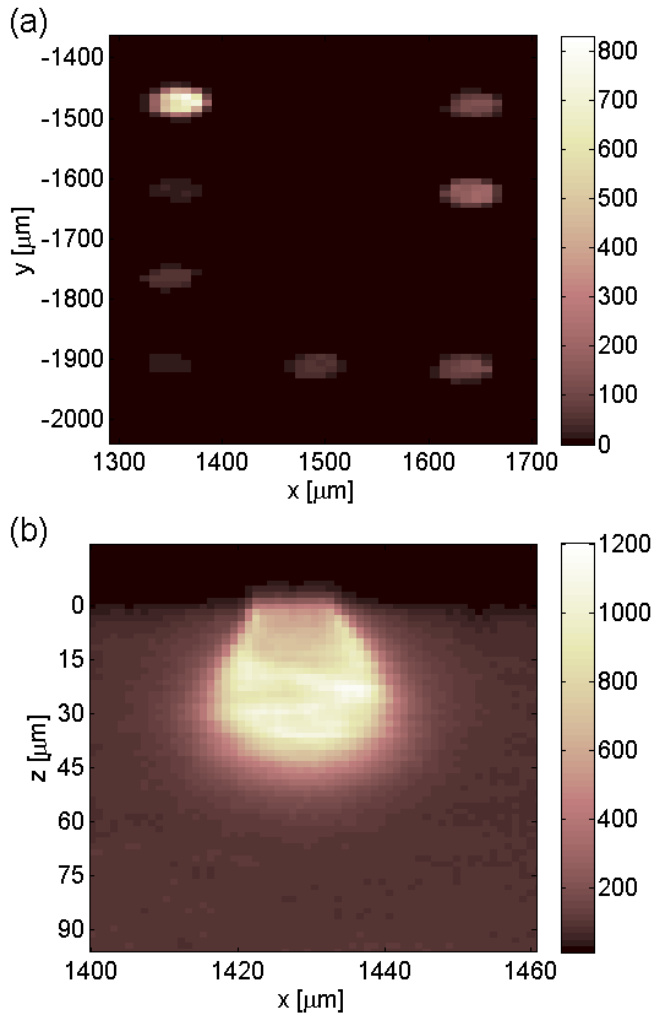


Figure 1. (Color online) (a) Two dimensional (X-Y) scan of the surface of the HPHT sample, brightness level represents fluorescence produced by the NV centers in kilocounts per seconds. (b) Two dimensional (X-Z) scan of the fluorescence as a function of depth for a standard grade CVD sample, demonstrating the electron penetration, where $z = 0$ represents the surface plane.

then irradiated using a 200 keV TEM (FEI Tecnai G2 T20 S-Twin) with various doses ranging from 7.0×10^{17} to 1.3×10^{20} e/cm^2 , and experienced the same standard annealing. The diameter of the irradiated regions was 20 μm for the HPHT sample and 10 μm for the CVD samples.

We used a 532 nm off-resonant laser to induce fluorescence from NV centers in the sample. We located the electron-irradiated regions by performing a two dimensional (X - Y) scan using precision piezoelectric translation stages (PI Micos LPS65) (Fig. 1(a)). Typically, the electrons penetrate and create NV centers within dozens of microns inside the diamond (Fig. 1(b)), as the exact penetration depth depends on the irradiation dose [23]. In order to estimate the NV concentration, we

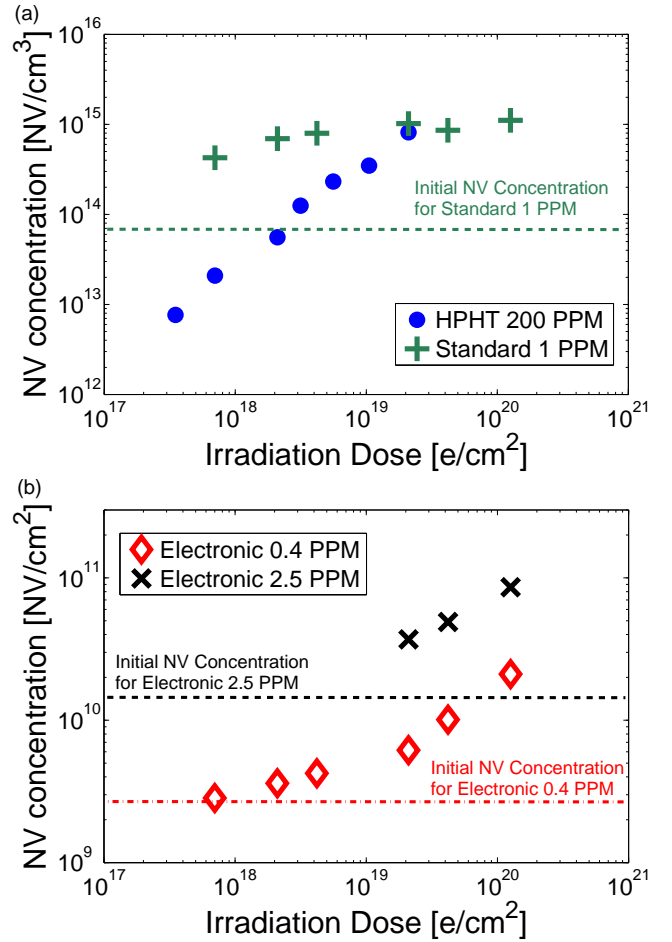


Figure 2. (Color online) NV concentration as a function of the irradiation dose. (a) 3D samples - HPHT and standard grade CVD. (b) 2D samples - nitrogen implanted CVD.

used relatively low laser powers (~ 10 μW), for which the fluorescence signal is linearly proportional to the NV concentration, and compared the signal to the fluorescence measured from a reference sample with a known NV concentration. We plot the results as a function of the irradiation dose for the 3D bulk (Fig. 2(a)), and 2D implanted (Fig. 2(b)) samples. Electron irradiation at doses up to 10^{20} e/cm^2 enhances the NV concentration by more than an order of magnitude, up to $\sim 10^{15}$ NV/cm^3 for the 3D samples, and up to $\sim 10^{11}$ NV/cm^2 for the nitrogen implanted samples. The typical conversion efficiencies achieved by this technique are close to 10% for the nitrogen implanted samples (Fig. 3(a)). However, for most samples the NV concentration does not reach saturation, thus higher irradiation doses could lead to further enhancement of the conversion efficiency.

In Fig. 3 we analyze the data in terms of conversion efficiencies and their improvement following irradiation. First, for a sample with a lower initial conversion efficiency, the resulting enhancement is more significant. Assuming that a particular irradiation dose creates a given

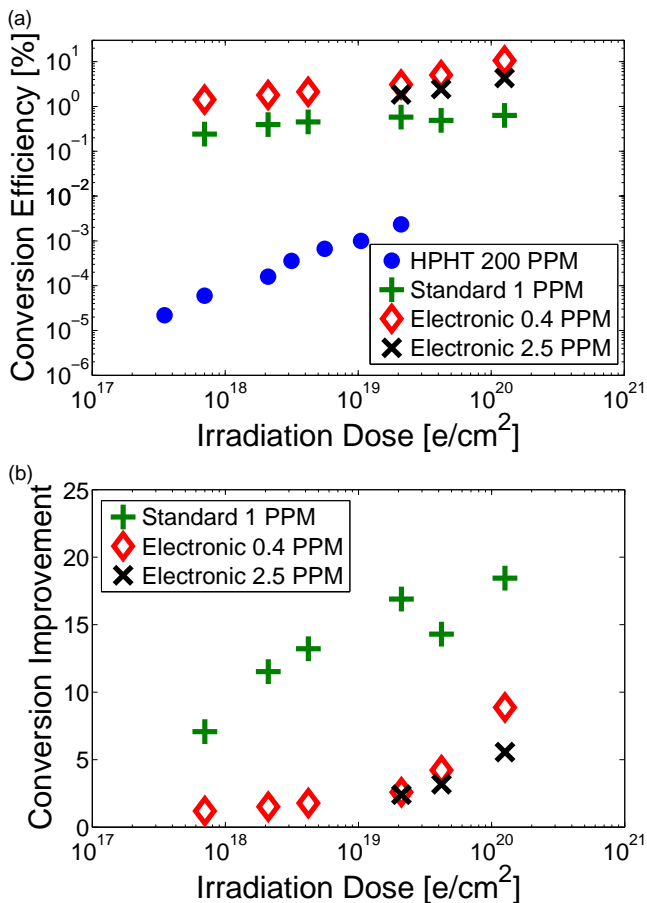


Figure 3. (Color online) (a) Conversion efficiency between nitrogen spins and NV centers as a function of the irradiation dose. (b) Improvement factor of the NV concentration over a non-irradiated region. The data for the HPHT sample is not shown since the initial NV concentration is negligible.

number of vacancies in the lattice, and the initial conversion efficiency is low, more isolated nitrogens are available for binding with the vacancies, thus forming NV centers. Since HPHT samples have a poor initial conversion efficiency, the irradiation process improves the NV concentration by more than two orders of magnitude. Moreover, due to its lower initial conversion efficiency, the standard grade CVD sample exhibits a higher improvement than the 2D implanted compared to the non-irradiated case (Fig. 3(b)). Second, for a given high initial conversion efficiency, the improvement factor depends on the initial nitrogen concentration: for the first 2D implanted sample having 0.4 PPM nitrogen, the NV concentration was improved by a larger factor (≈ 9) than the second 2D sample, having an initial 2.5 PPM nitrogen concentration, improvement factor of ≈ 5.5 , even though its initial conversion efficiency was lower (0.77% versus 1.2%). We explain these results in the following way: assuming that a particular irradiation process creates a given number of vacancies, and the vacancy concentration is the limit-

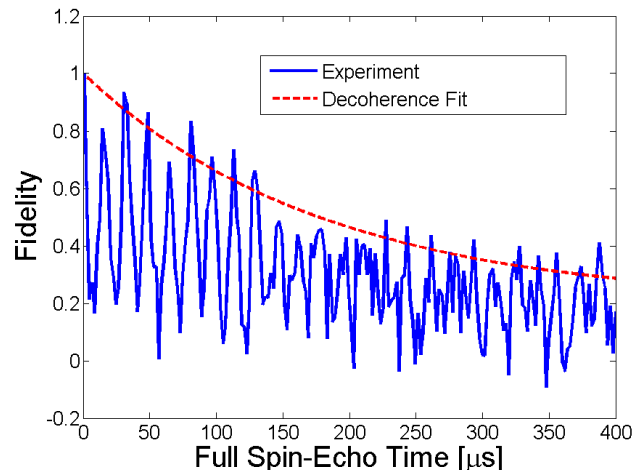


Figure 4. (Color online) Hahn-Echo decoherence curve of an NV spin ensemble's quantum state in a standard grade CVD diamond sample, at an irradiation dose of $\sim 7 \times 10^{17} \text{ e/cm}^2$. The decoherence time is $T_2 \approx 180 \text{ } \mu\text{s}$. Revivals are caused by interactions with ^{13}C nuclear spins at a constant static magnetic field of $\sim 115 \text{ Gauss}$ [27]. The results for other irradiation doses are similar [26].

ing factor in the binding process with nitrogens to form NVs, the resulting conversion efficiency will be higher for a smaller initial nitrogen concentration.

In order to take advantage of the sensing capabilities of the NV ensemble after irradiation, any arbitrarily initialized quantum state has to be preserved for a long coherence time. In Fig. 4 we plot the decay of coherence versus time, for a Hahn-Echo experiment [25] performed on the standard grade CVD sample at a representative irradiation dose of $\sim 7 \times 10^{17} \text{ e/cm}^2$. Within the accuracy of our measurement of the coherence time, its value of $\sim 180 \text{ } \mu\text{s}$ does not exhibit dependence on the irradiation dose [26]. The absolute measured fluorescence contrast level drops with the irradiation dose, probably due to a simultaneous creation of NV0 defects, which do not contribute to magnetic sensing [23]. Nevertheless - the sensitivity of magnetic sensing grows with the irradiation [26].

Finally, we compare the conversion efficiencies achieved using the above-mentioned TEM irradiation, to those obtained by a commercially available high energy irradiation process (Golan plastic, energy $\sim 2.8 \text{ MeV}$, dose $\sim 8 \times 10^{17} \text{ e/cm}^2$) on samples with similar properties (summarized in Table I). The resulting NV concentrations using the high energy irradiation are $\sim 4.3 \times 10^{16} \text{ NV/cm}^3$ (conversion efficiency of $\sim 0.12\%$) for an HPHT sample, $\sim 8.1 \times 10^{14} \text{ NV/cm}^3$ (conversion efficiency of $\sim 0.4\%$) for a standard CVD sample, and $\sim 5.7 \times 10^{10} \text{ NV/cm}^2$ (conversion efficiency of $\sim 2.9\%$)

Sample Type	Init. N conc. [PPM]	Init. conv. eff. [%]	TEM fin. NV conc.	TEM fin. conv. eff. [%]	2.8 MeV irradi. fin. NV conc.	2.8 MeV irradi. fin. conv. eff. [%]
HPHT	200	$< 10^{-5}$	8.2×10^{14} [/cm ³]	0.0023	4.3×10^{16} [/cm ³]	0.12
CVD	1	0.04	1.1×10^{15} [/cm ³]	0.63	8.1×10^{14} [/cm ³]	0.4
2D imp.	0.4	1.2	2.1×10^{10} [/cm ²]	10.6	—	—
2D imp.	2.5	0.77	8.6×10^{10} [/cm ²]	4.3	5.7×10^{10} [/cm ²]	2.9

Table I. NV concentrations and N-to-NV conversion efficiencies for various samples, before and after electron irradiation. The presented results are for the highest examined dose for the 200 keV TEM irradiation, and commercial irradiation process at an energy of ~ 2.8 MeV and dose of $\sim 8 \times 10^{17}$ e/cm²

for a 2D nitrogen-implanted sample. Since the high energy irradiation is applied on a much larger area, small irradiation doses were available ($\sim 8 \times 10^{17}$ e/cm², two orders of magnitude smaller than the doses of the TEM). It is thus clearly seen (Table I) that except for the HPHT sample (with a low initial conversion efficiency), the resulting conversion efficiencies using the TEM irradiation are slightly higher than those achieved by the commercial high energy and low dose process. As TEMs are available in many in-house nanotechnology facilities, they can be used as quick and efficient tools for the enhancement of NV concentration in high-quality diamond samples.

To summarize, we have shown that 200 keV electron irradiation with doses up to 10^{20} e/cm² can enhance the NV concentration by an order of magnitude, and reach conversion efficiencies of up to 10% for nitrogen-implanted diamond samples, with no degradation in their coherence properties. Since the NV concentration did not reach saturation in our experiments, higher irradiation doses could lead to even further enhancement. The TEM irradiation could significantly improve the sensitivity of NV magnetometry, which grows as the square-root of the number of spins [1, 5, 6]. For example, a magnetometric sensitivity of $\sim 7 \frac{nT}{\sqrt{Hz}}$ was demonstrated using an ensemble of NV centers in a sample with 1 PPM nitrogen and 0.06% conversion efficiency, for measuring a 220 KHz oscillating AC field [6]. As demonstrated in Fig. 3(a), even at doses as low as 10^{18} e/cm², the NV concentration in a similar sample increased by a factor of ~ 10 , which can result in an improved sensitivity of $\sim 7/\sqrt{10} = 2.2 \frac{nT}{\sqrt{Hz}}$. Furthermore, applying a similar irradiation process on deeply implanted and isotopically pure ¹²C samples with several millisecond long coherence times for NV ensembles, and with the use of optimized dynamical decoupling sequences to decouple the spin-bath environment [20], the NV-NV interaction dominated regime could be reached, opening an avenue for the study of many-body spin dynamics [17–19].

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- [1] J. M. Taylor, P. Cappellaro, L. Childress, L. Jiang, D. Budker, P. R. Hemmer, A. Yacoby, R. L. Walsworth, and M. D. Lukin, *Nat. Phys.* **4**, 810 (2008).
 - [2] J. R. Maze et al., *Nature (London)* **455**, 644 (2008).
 - [3] G. Balasubramanian et al., *Nature (London)* **455**, 648 (2008).
 - [4] M. S. Grinolds, P. Malentinsky, S. Hong, M. D. Lukin, R. L. Walsworth, and A. Yacoby, *Nat. Phys.* **7**, 687 (2011).
 - [5] L. M. Pham et al., *New J. Phys.* **13**, 045021 (2011).
 - [6] L. M. Pham, N. Bar-Gill, C. Belthangady, D. Le Sage, P. Cappellaro, M. D. Lukin, A. Yacoby, and R. L. Walsworth, *Phys. Rev. B* **86**, 045214 (2012).
 - [7] V. M. Acosta et al., *Phys. Rev. B* **80**, 115202 (2009).
 - [8] V. M. Acosta, E. Bauch, A. Jarmola, L. J. Zipp, M. P. Ledbetter, and D. Budker, *Appl. Phys. Lett.* **97**, 174104 (2010).
 - [9] G. de Lange, D. Ristè, V. V. Dobrovitski, and R. Hanson, *Phys. Rev. Lett.* **106**, 080802 (2011).
 - [10] H. J. Mamin, M. H. Sherwood, M. Kim, C. T. Rettner, K. Ohno, D. D. Awschalom, and D. Rugar, *Phys. Rev. Lett.* **113**, 030803 (2014).
 - [11] N. Alfasi, S. Masis, O. Shtempluck, V. Kochetok, and E. Buks, *AIP advances* **6**, 075311 (2016).
 - [12] F. Dolde et al., *Nat. Phys.* **7**, 459 (2011).
 - [13] C. A. Ryan, J. S. Hodges, and D. G. Cory, *Phys. Rev. Lett.* **105**, 200402 (2010).
 - [14] B. Naydenov, F. Dolde, L. T. Hall, C. Shin, H. Fedder, L. C. Hollenberg, F. Jelezko, and J. Wrachtrup, *Phys. Rev. B* **83**, 081201(R) (2011).
 - [15] J. H. Shim, I. Niemeyer, J. Zhang, and D. Suter, *Europhys. Lett.* **99**, 40004 (2012).
 - [16] D. M. Toyli, C. F. de las Casas, D. J. Christle, V. V. Dobrovitski, and D. D. Awschalom, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 8417 (2013).
 - [17] P. Cappellaro and M. D. Lukin, *Phys. Rev. A* **80**, 032311 (2009).
 - [18] S. D. Bennett, N. Y. Yao, J. Otterbach, P. Zoller, P. Rabl, and M. D. Lukin, *Phys. Rev. Lett.* **110**, 156402 (2013).
 - [19] H. Weimer, N. Y. Yao, and M. D. Lukin, *Phys. Rev. Lett.* **110**, 067601 (2013).

- [20] D. Farfurnik, A. Jarmola, L. Pham, Z. Wang, V. Dobrovitski, R. Walsworth, D. Budker, and N. Bar-Gill, *Phys. Rev. B* **92**, 060301(R) (2015).
- [21] R. de Sousa, in *Electron Spin Resonance and Related Phenomena in Low-Dimensional Structures* (Springer, Berlin, 2009), vol. 115 of *Topics in Applied Physics*, pp. 183–220.
- [22] N. Bar-Gill, L. M. Pham, C. Belthangady, D. Le Sage, P. Cappellaro, J. R. Maze, M. D. Lukin, a. Yacoby, and R. Walsworth, *Nat. Commun.* **3**, 858 (2012).
- [23] E. Kim, V. Acosta, E. Bauch, D. Budker, and P. Hemmer, *Appl. Phys. Lett.* **101**, 082410 (2012).
- [24] C. McLellan, B. Myers, S. Kraemer, K. Ohno, D. Awschalom, and A. Jayich, *Nano Lett.* **16** (4), 2450 (2016).
- [25] E. L. Hahn, *Phys. Rev.* **80**, 580 (1950).
- [26] See Supplemental Material.
- [27] T. Gaebel et al., *Nat. Phys.* **2**, 408 (2006).