Benchmark for Synthesized Diamond Sensors Based on Isotopically Engineered Nitrogen-Vacancy Spin Ensembles for Magnetometry Applications

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Nitrogen-vacancy (NV) center ensemble in synthetic diamond is a promising and emerging platform for quantum sensing technologies. Realization of such a solid-state based quantum sensor is widely studied and requires reproducible manufacturing of NV centers with controlled spin properties, including the spin bath environment within the diamond crystal. Here, a non-invasive method is reported to benchmark NV ensembles regarding their suitability as ultra-sensitive magnetic field sensors. Imaging and electron spin resonance techniques are presented to determine operating figures and precisely define the optimal material for NV-driven diamond engineering. The functionality of the methods is manifested on examples of chemical vapor deposition synthesized diamond layers containing preferentially aligned, isotopically controlled $^{15}$NV center ensembles. Quantification of the limiting $^{15}$N P1 spin bath, in an otherwise $^{12}$C enriched environment, and the reduction of its influence by applying dynamical decoupling protocols, complete the suggested set of criteria for the analysis of NV ensemble with potential use as magnetometers.

An essential task toward the implementation of scalable quantum technology is to bridge the gap between quantum physics on the sub nanoscale and material science engineering capabilities on the macroscale. Quantum-enhanced sensing based on nitrogen-vacancy (NV) centers is a novel ultra-sensitive methodology for nanoscale detection of magnetic[1] and electric fields,[2] temperature,[3] pressure, and force.[4,5] However, these sensing methods need to be matched with diamond engineering in order to create the NV atomic defect sensors reliably in synthetic diamond. NV center based sensors have been extensively studied in the past, where long coherence times, optical accessibility of spin states, and ambient working conditions were demonstrated.[6] Furthermore, nanoscale magnetic resonance imaging with NV centers shows potential applications toward investigating more complex biological systems like neural networks,[7] living cells,[8] and single proteins.[9] Transferring these sensors to state-of-the-art quantum technology requires the reproducible fabrication of NV centers with high spatial precision and reliable spin coherence properties.[10,11] Nitrogen doping during chemical vapor deposition (CVD) diamond growth is one of the facile means of fabricating thin layers of shallow NV ensembles.[12]

It is essential for ultra-sensitive nanoscale magnetometry that shallow NV centers are engineered to be placed in a close proximity to the sensing target. Furthermore, the CVD growth method offers a crucial advantage in producing different orientations of diamond layers and for the [111] orientation, NV ensembles are preferentially aligned with the ⟨111⟩ direction. Studies show up to 99% orientational polarization of NVs in samples grown along

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the ⟨111⟩ crystal direction.\textsuperscript{[13–15]} For quantum sensing applications, such engineered diamond samples inherently improve the sensor sensitivity by a factor of four while retaining the high SNR. Furthermore, usage of oriented NV samples are particularly beneficial for zero-field applications which extend the dynamic range of the magnetometer.\textsuperscript{[16,17]} Compared to the low-energy ion implantation technique, nitrogen incorporation (e.g., N doping) during diamond growth avoids the collateral damage of the crystal lattice, thus improving the spin environment of individual NV centers. Although some demonstration of enhanced magnetometry with preferentially aligned ensembles has been achieved,\textsuperscript{[18,19]} the coherence time and the ensembles' density remain as critical limitations toward realistic applications.

One of the primary reasons is the low N to NV creation efficiency in these samples. Figure 1a compares the NV to \(N_D\) (nitrogen content in diamond solid phase) ratio for different CVD growth processes from this work, related work,\textsuperscript{[13–15,18]} and work covering electron irradiated and annealed (100) samples.\textsuperscript{[30,31]} b) SIMS measurement showing the depth profile of the carbon (\(^{12}\text{C}\)) and nitrogen (\(^{15}\text{N}\)) content in samples A and B. The pale-colored area indicates the diamond substrate, the intermediate color the buffer layer, and the dark color the nitrogen-doped layer. c) Schematic drawing of the wide-field-set-up used to perform sample analysis. d) Confocal image showing the cross-section of the CVD grown layer on top of the ⟨111⟩ substrate. e) ODMR spectrum showing the characteristic splitting of 3.03 MHz due to the hyperfine interaction with the intrinsic \(^{15}\text{N}\).

Figure 1. a) Overview of created NV centers in comparison to the nitrogen present in the diamond layer \(N_D/N_{NV}\) for different CVD growth processes from this work, related work,\textsuperscript{[13–15,18]} and work covering electron irradiated and annealed (100) samples.\textsuperscript{[30,31]} b) SIMS measurement showing the depth profile of the carbon (\(^{12}\text{C}\)) and nitrogen (\(^{15}\text{N}\)) content in samples A and B. The pale-colored area indicates the diamond substrate, the intermediate color the buffer layer, and the dark color the nitrogen-doped layer. c) Schematic drawing of the wide-field-set-up used to perform sample analysis. d) Confocal image showing the cross-section of the CVD grown layer on top of the ⟨111⟩ substrate. e) ODMR spectrum showing the characteristic splitting of 3.03 MHz due to the hyperfine interaction with the intrinsic \(^{15}\text{N}\).
and the single NV (preferably in a sample A) is estimated to be around 464 ppb. Note that a reliable procedure is shown in Figure 1d. Using this method, NV density in cross-sectional confocal image used for this normalization process and the signal is normalized with the countrate of a single NV. A diamond layer is illuminated with a widened, collimated laser beam, in order to excite the NVs. The density of the P1 spin bath.

The measured data is fit with a mono-exponential function of the form $\exp\left[\frac{t}{\tau}\right]$, and the results for sample D are shown in Figure 2b. The bath pulse sequence depicted in Figure 2b. The bath $\pi$ pulse on the bath spins reintroduces the static dipolar interaction with the NVs, thus causing an observable decrease in the echo amplitude. Figure 2a shows the measured P1 spectrum at an external magnetic field $B_0 \approx 330$ G, aligned parallel to the (111) axis. The observed spectrum matches the characteristic $^{15}$N nitrogen P1 transition frequencies, where the two outer lines (groups I and IV) correspond to the hyperfine transitions of P1 spins parallel to $B_0$. The prominent inner lines (groups II and III) correspond to the hyperfine transition of the other three magnetically equivalent P1 orientations. The weak central peak is due to the dipole forbidden transitions of the $^{15}$N nitrogen electron spins. We emphasize that the observed spectrum does not show any spectral features corresponding to $g = 2$ or NVH spin transitions. Further analysis of the P1 bath spectrum is discussed in Supporting Information.

In order to determine the P1 spin bath density, we use the pulse sequence depicted in Figure 2b. The bath $\pi$ pulse addressing one of the P1 transitions is swept during the second free precession time of the NV echo sequence. This time-swept sequence controls the degree to which the P1 dipolar interactions are reintroduced. These static dipolar interactions lead to a mono-exponential decay of NV coherence, which depends on the density of the inverted bath spins and their decoupling time $T$. The DEER experiment is repeated for each P1 transition and the results for sample D are shown in Figure 2b. The measured data is fit with a mono-exponential function of the form $\exp\left[\frac{-t}{\gamma_{\text{NV}}\gamma_{\text{bath}}T}\right]$, where $\gamma_{\text{NV}}, \gamma_{\text{bath}} \approx 292$ kHz ppm$^{-1}$.[26] The results show that the density of P1 groups I–IV are $4.9 \pm 0.15, 10.9 \pm 0.25, 11.6 \pm 0.19, 5.0 \pm 0.15$ ppm, respectively.
Figure 2. a) Measured $^{15}\text{N}$ nitrogen P1 bath spectrum with the corresponding pulse sequence. The spectrum is obtained at $B_0 \approx 330\text{G}$ aligned parallel to $\langle 111 \rangle$ direction. The solid line corresponds to the simulated P1 spectrum with a common linewidth and amplitude matching their spectral abundance. b) Estimation of P1 bath density. The solid line corresponds to the mono-exponential fit function of the form $\exp[-A_{\text{NV}}/\gamma_{\text{NV}} \cdot T_{\text{bath}}]$, where $A_{\text{NV}}/\gamma_{\text{NV}} \approx 292\text{kHzppm}^{-1}$. c) Estimated NV/P1 ratio received for the samples A–F of this study in relation to the maximum available number of $^{15}\text{N}$ atoms in the growth chamber.

Figure 3. a) Hahn Echomeasurements performed on sample B with the wide-field setup. The illustrated area is subdivided into 64 x 64 pixels, where each pixel represents the fitted decay time of a Hahn echo measurement. The image indicates a rather uniform distribution among coherence times of the created ensembles. b) A Hahn Echo measurement performed on an ensemble of sample B with the confocal microscope setup. Additional dynamical decoupling protocols are applied to prolong the coherence time from initial $T^2_{\text{Hahn}} = 1.2\text{µs}$ up to $T^2_{\text{XY8-32}} = 23\text{µs}$. c) Saturation behavior of the $\text{XY8}$ dynamical decoupling protocols applied to samples A–F. Solid lines represent fit functions (fit errors are illustrated as colored area) based on a power scaling law ($T^2 \propto N^\kappa$) with a free parameter $\kappa$. Remarkable is that all samples show similar values ($\kappa_A = 0.59, \kappa_B = 0.59, \kappa_C = 0.60, \kappa_D = 0.58, \kappa_E = 0.66, \kappa_F = 0.59$) suggesting a Lorentzian distributed spin bath, where the decoherence originates from one spin type.[28,29]

Hence the total measured $^{15}\text{N}$ substitutional nitrogen density is $\approx 32\text{ppm}$. Since the main interest of the study is the optimization of NV density during CVD growth, we compare the NV/P1 ratios in the prepared samples A–F. Estimation of NV center density is a difficult task, and proper estimation methods are still under investigations.[19,26] The technique used to perform the NV density estimation is, similar to the one presented in ref. [19]. In Figure 2c, we show the NV/P1 ratio as a function of gas-phase nitrogen concentration inside the PECVD growth chamber. Clearly visible is that sample A shows the best NV/P1 ratio of approximately 1.2%, which is of the same order of magnitude as previously reported values for nitrogen-doped CVD layers.[25] The low N/C ratio of the source gases, in combination with the intermediate growth temperature of 1005 °C promotes the formation of NV centers while keeping a high conversion rate from P1 to NV. A possible explanation is that the NV formation kinetics is slower than the nitrogen incorporation (P1 formation), which is supported by the reported NV/P1 ratios in bulk diamond samples.[24] A low N concentration though, decelerates the diamond growth and gives NV defects sufficient time for the formation. A further hint supporting this hypothesis is that the variation of growth temperature shifts the NV/P1 ratio in disadvantage of NV creation (samples E and F). An increased and decreased temperature leads to an elevated growth rate (see Supporting Information) but a decreased NV/P1 ratio. Obviously, this has to be studied in more detail in the future, but the temperature dependence on NV creation is in agreement with results of other groups.[21]

Another relevant parameter for the realistic application of NV magnetometry is the uniformity of sensor spin coherence across the sample volume. Figure 3a shows this circumstance, where the Hahn echo coherence time is measured over a large area using the wide-field setup.

The coherence times measured among sample B are on the order of $1\text{µs}$, which is limited by the electronic spin bath. Decoherence from an electronic spin bath can be effectively mitigated through quantum control of the spin bath or through dynamical decoupling sequences. The latter is known to artificially prolong the coherence time since only the influence and not the spin bath itself is reduced, which is desired from a material scientist’s point of view. The XY8 sequence is chosen
Using the proposed standard of comparison, it is possible to find the best growth strategy for the fabrication of NV center ensembles, with respect to the primary decoherence source, which we identify as P1 centers. Clearly, the growth procedure for sample A is the most promising one, with superior magnetic field sensitivity, since not only the measured interaction times are among the longest but also the absolute NV concentration is the highest, at a moderate background level of P1 centers. Note that in this work a subset of all possible NV fabrication parameters are discussed, namely nitrogen gas concentration and growth temperature. Many more have to be optimized in order to push the sensitivity to its limit. Hints for this are the different NV/P1 ratios of samples A and D, which were created under the same plasma conditions. This can probably be related to different influences in the diamond substrates provided by different suppliers. Besides the crystalinity and the surface roughness, the surface miscut-angle is probably the most influencing parameter. The influence of these substrate related parameters on the NV creation, though, was not studied during this work.

In conclusion, we have presented a new benchmark for NV center ensembles in a thin layer of diamond produced during a PECVD growth process. The characterization techniques exploit the core feature of the NV center itself, namely its sensing capability. This feature can be used to isolate main driving parameters influencing the NV/P1 ratio and to improve PECVD diamond growth processes with the distinct goal to fabricate NV center ensembles for magnetometry applications. Furthermore, by applying the presented benchmark criteria, NV rich diamond samples can be analyzed and, more importantly, ranked for an unbiased potential synergistic effects that accelerate the development of optimized diamond samples, which are indispensable toward real-life quantum technology applications.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
CVD diamond growth, nitrogen-vacancy centers, preferential alignment, quantum sensing

Table 1. Summary of the results for the six diamond samples investigated in this work.

| Sample | Temp | N/H | d_{buffer} | d_{NV} | T_{1} | T_{2}^{P1} | T_{2}^{NV} | n_{NV} | n_{P1} | n_{ND} | T_{2}^{ac} | T_{2}^{ac}^{P1} | T_{2}^{ac}^{NV} |
|--------|------|-----|------------|--------|------|----------|----------|--------|-------|-------|---------|---------|---------|----------|
|        | [°C] | [%] | [nm]       | [nm]   | [ns]  | [ns]     | [ns]     | [mm]   | [mm]  | [mm]  | [ps]    | [ps]    | [ps]    |
| A      | 1005 | 0.1 | 50         | 190    | 3.2   | 44       | 464      | 40     | 41    | 0.26  | 137     | 137     | 137     |
| B      | 1005 | 1.0 | 155        | 875    | 1.0   | 15       | 109      | 100    | 222   | 0.95  | 20.6    | 20.6    | 20.6    |
| C      | 1005 | 0.5 | 25         | 66     | 4.3   | 13.5     | 447      | 100    | 432   | 0.41  | 18.4    | 18.4    | 18.4    |
| D      | 1005 | 0.1 | 500        | 190    | 3.1   | 2.6      | 38.7     | 290    | 32    | 4.1   | 12.1    | 12.1    | 12.1    |
| E      | 965  | 0.1 | 66          | 235    | 2.4   | 26.1     | 181      | 50(3)  | 73    | 0.47  | 9.1     | 9.1     | 9.1     |
| F      | 1035 | 0.1 | 78          | 320    | 5.7   | 31.1     | 69       | 42    | 77    | 0.75  | 11.9    | 11.9    | 11.9    |

The growth temperature is labeled as Temp, the nitrogen gas concentration during the growth in respect to hydrogen as N/H, the thickness of the buffer layer as d_{buffer}, the one of the NV rich layer as d_{NV}, the dephasing time measured by Ramsey sequence as T_{1}, the coherence time measured by Hahn echo as T_{2}, the artificially prolonged coherence time by X8Y sequence with 128 π-pulses as T_{2}^{8Y16}, the NV density as n_{NV}, the P1 density as n_{P1}, the overall nitrogen density measured by SIMS n_{ND}, and the estimated volume normalized ac magnetic field sensitivity as \eta_{ac}. The latter's estimation was performed using a pulse detection scheme with a readout laser pulse of t_{l} = 300 ns, full spin contrast, and a count rate of a single NV center c_{P1} = 200 kcts s^{-1} as reported in ref. [3,18,32]. Conditions of the growth processes are microwave (MW) frequency f = 2.46 GHz, MW power P = 1.92 kW, pressure p = 52.5 mbar, methane concentration c_{CH_{4}} = 0.1 % with respect to hydrogen which was applied with a flow of 400 sccm. Estimated from SIMS results of sample A, which was grown under identical conditions.

to perform this task[27] and therefore increase the sensitivity of a quantum sensor. The results of an ensemble from sample B, which is dynamically decoupled with different orders of the XY8-N sequence, where N denotes the number of repetitions of 8 π-pulses, is shown in Figure 3b. The saturation behavior of this decoupling allows a conclusion on the underlying decoherence causing spin bath. For this purpose, all samples are investigated with the XY8 technique and the measured coherence times scale equally for samples A–F (see Figure 3c). The data points of each sample are fitted with a power-law of the form (T_{2} \propto \tau^{n})

where \tau_{l}, \tau_{P1}, \tau_{ac}, and \tau_{NC} are the magnetic field sensitivities of the core feature of the NV center itself, namely its sensing capability. This feature can be used to isolate main driving parameters influencing the NV/P1 ratio and to improve PECVD diamond growth processes with the distinct goal to fabricate NV center ensembles for magnetometry applications. Furthermore, by applying the presented benchmark criteria, NV rich diamond samples can be analyzed and, more importantly, ranked for an unbiased potential synergistic effects that accelerate the development of optimized diamond samples, which are indispensable toward real-life quantum technology applications.

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