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# Charge Stability of Shallow Nitrogen Vacancy Center in Diamond with Radical Exposure Nitridation Surface for DNA Detection

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**Abstract**

**We investigated the charge state stability of shallow nitrogen vacancy center created by nitrogen ion implantation in $^{12}C$ enriched diamond. We found that its negatively charged state was stabilized by nitrogen radical exposure.**

## 1. Introduction

Negatively charged Nitrogen Vacancy (NV) center in diamond has excellent properties such as, manipulation and readout of spin state and long coherence time $T_2$ (~2 ms [1]) even at room temperature. For these reasons, NV center is expected for many applications (e.g. quantum information processing, sensing of magnetic and electric field and biological sensing). NV center has two charge states, which are neutral state ($NV^0$) and negatively charged state ($NV^-$). Only $NV^-$ contributes to above-mentioned applications. Detection of nuclear spin was reported in Ref. [2] as a kind of magnetic field sensing. Magnitude of magnetic dipole-dipole interaction is inversely proportional to third power of the distance between NV center and nuclear spins. Hence, it is hoped that NV center is created as shallow as possible for high resolution nuclear spin detection. However, NV centers in shallow region can be easily affected by surface and external environment and thus show instability of negatively charged state as compared to these in bulk. Therefore, it is necessary for detection of nuclear spin to improve the charge stability of shallow NV center. Oxygen terminated diamond shows positive electron affinity (PEA) which suppresses upward band bending and stabilizes negatively charged state of shallow NV center. Previous work revealed that UV/ozone exposure [3] and annealing in dry oxygen atmosphere at 465°C [4] can stabilize its negatively charged state [5]. Both of these processes create oxygen terminated surface. It is also reported that nitrogen terminated surface has positive electron affinity (PEA) [6] and shows characteristic that it is possible to directly fix biomolecule to the surface by using $NH_2$ functional group [7]. However, there are few reports to investigate properties of NV center in nitrogen terminated diamond. Here, we performed nitrogen radical exposure as process to terminate diamond by nitrogen and achieved to improve the charge stability of shallow NV center.

## 2. Experimental Details

$^{12}C$ enriched high purity diamond films were homoepitaxially grown on (001) diamond substrate [8]. Nitrogen atoms accelerated by low energy (2.5 keV; the average ion depth calculated by SRIM [9] is 4.6 nm) was implanted to the substrate with the fluence of $10^{12}$ $cm^{-2}$ through the nano-hole resist mask fabricated by EB lithography for creating arrays and addresses of NV centers (shown in Figure 1). Combination of the fluenece of $10^{12}$ $cm^{-2}$ and the mask could induce single NV center into an each hole of arrays. Then the substrate was annealed at 1000 °C for 2 hours [1] for diffusing vacancy and forming NV centers. Hot acid mixture treatment was carried out for cleaning the surface before the following measurements. To improving the properties of shallow NV centers, first we carried out vacuum ultra violet (VUV) ozone treatment for 15 minutes. Hot acid mixture treatment and VUV/ozone treatment form oxygen termination. In addition, we also carried out radical exposure nitridation using RF radical beam source with $N_2$+$H_2$ (4%) forming gas for 20 minutes [10]. Our group reported the result of X-ray Photoelectron Spectroscopy (XPS) before and after nitrogen radical exposure [10]. There was no N1s peak before nitridation. On the other hand, N1s peak was clearly observed after nitrogen radical exposure. Thus, it is considered that surface was terminated by nitrogen after that treatment. Our previous result suggested that the diamond surface was mainly covered with N-dimer or N-C-H and a few $NH_2$ existed [10].

Laser scanning confocal fluorescence microscope was used for observation of NV center. We observed single NV centers selectively because there were also ensemble NV centers in some fluorescence spots. The charge stability was evaluated by the contrast of Rabi oscillations (Figure 2(a) is an example) and spin coherence time $T_2$ was estimated by Hahn echo. Figure 2 (a) is the result after ~$10^5$ times integration of Rabi sequence which is shown in Figure 2 (b). The contrast $C$ of Rabi oscillations is defined as $C = 2A/y_0$, where $A$ represents amplitude and $y_0$ represents zero level of Rabi oscillations. Each Rabi oscillation contrast shows barometer of the charge stability of an individual NV center. For example, Rabi oscillation contrast of a deep NV center in 10 MeV region was 0.46.

## 3. Results and Discussion

Figure 3 shows the distribution of the Rabi oscillation contrast $C$ of single NV centers in 2.5 keV ion implanted region after VUV/ozone treatment and nitrogen radical exposure. First, we measured Rabi oscillations after hot acid mixture treatment as a reference and the average contrast was 0.22. The average contrast after VUV/ozone treatment was 0.25 and the one after nitrogen radical exposure was 0.38. Figure 4 is the schematic picture of Rabi oscillation measurement. The two fluorescence "$F_{\text{actual top}}$" and "$F_{\text{actual bottom}}$" in Figure 4, which are actually plotted at Rabi oscillation measurement, are defined as

$$F_{actual\ top} = P_{NV^-} \cdot F_{top} + P_{NV^0} \cdot F_{NV^0} \quad (1)$$

$$F_{actual\ bottom} = P_{NV^-} \cdot F_{bottom} + P_{NV^0} \cdot F_{bottom} \quad (2)$$

, where $F_{\text{top}}$ and $F_{\text{bottom}}$ are ideal fluorescence in the case that the population of $NV^-$ is 100 percent and $F_{NV^0}$ is the fluorescence of $NV^0$. $P_{NV^-}$ and $P_{NV^0}$ is the population of each charge state, and has a relation: $P_{NV^-} = 1 - P_{NV^0}$. Using this model, the image of Rabi oscillations by actual measurement is depicted in the middle of Figure 4. Negatively charged state of NV center is unstable in case $P_{NV^-}$ is low. Decrease of $P_{NV^-}$ induces shrink of Rabi oscillation amplitude and results in low contrast. Thus, it is suggested that negatively charged state of NV center which has high Rabi oscillation contrast is stable.

After VUV/ozone treatment, improvement of Rabi oscillation contrast cannot be observed compared to hot acid mixture afterwards because 15 minutes was insufficient to change the surface (c.f. UV/ozone exposure, our previous work, was carried out for 3 hours). On the other hand, improvement of the contrast was observed after nitrogen radical exposure and the charge stabilization of shallow NV center by nitrogen radical exposure was confirmed. It is suggested that nitrogen terminated diamond suppresses surface upward band bending. $T_2$ was estimated to be 3.9 µs after nitrogen radical exposure. 3.9 µs is shorter $T_2$ than other reports about single NV centers placed at almost same depth as 2.5 keV ion implantation because ion implantation dose was 3 orders of magnitude higher as compared with some reports. We need to optimize both conditions of VUV/ozone treatment and nitrogen radical exposure for further improvement of negatively charged state and coherence property of shallow NV center.

## 4. Conclusions

We achieved to stabilize the charge state of shallow NV center by nitrogen radical exposure in 2.5keV nitrogen ion implanted region. However, $T_2$ estimated by Hahn echo was still short. We will carry out dynamical decoupling [11] that can cancel out the noises perturb the NV electron spin and improve coherence property. Then we will try to detect DNA on nitrogen terminated diamond. For DNA detection, it is also needed to investigate the influence of fixing DNA to shallow NV center.


## Acknowledgements

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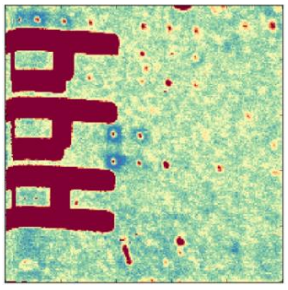

Fig.1 Confocal mapping of 20 µm square.

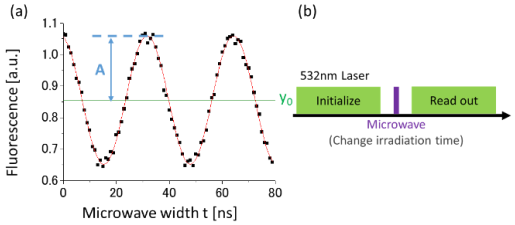


Fig. 2 (a) Example of Rabi oscillations. (b) Pulse sequence of Rabi oscillations.

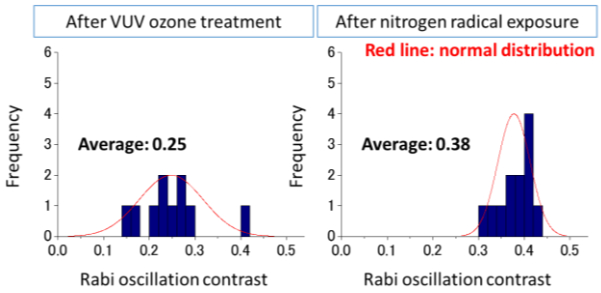


Fig. 3 The comparison of Rabi oscillation contrast after VUV/ozone treatment (left) and nitrogen radical exposure (right). The average contrast after hot acid mixture (before VUV/ozone treatment) was 0.22.

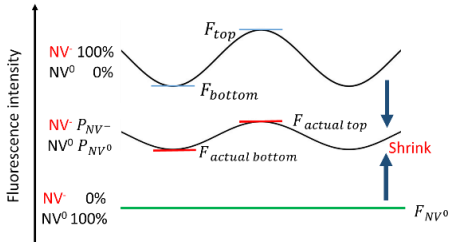


Fig. 4 Schematic picture of Rabi oscillations. The contrast depends on the population of negatively charged state.