Quantum-assisted Sensing Using Nitrogen-vacancy (NV) Centers in Diamond

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Research efforts towards detection of a single nuclear spin using a single nitrogen-vacancy (NV) center in diamond are introduced. While the current achievement by the present author's group is successful detection of ~6,000 proton nuclear spins, other groups have reported single nuclear spin detection more recently. The basic principle behind using an NV center as a quantum-assisted sensor is described.

Keywords; diamond, NV center, quantum sensor, magnetic resonance, magnetometry

INTRODUCTION

Quantum-assisted sensing has attracted much attention recently.[1, 2] The purpose of the research described in this paper is to achieve the sensitivity defined as the standard quantum limit, which is given by the uncertainty principle and other physical constraints. Breaking the standard quantum limit requires sophisticated quantum control such as the formation of multiple qubit entanglements,[3] and a description of such research is beyond the scope of this article. The present research employs a single electron spin, i. e. a single qubit, in diamond as a quantum-assisted sensor to approach the standard quantum limit with atomic-level (nm-level) spatial resolution.

Let us first introduce a nitrogen-vacancy (NV) center in diamond, whose structure is shown in Fig.1.[4] Compared to a perfect diamond crystal, the number of electrons that do not participate in the formation of covalent bonds is one from a nitrogen atom and four from a vacancy (a carbon-missing site). Therefore, five electrons exist in the vicinity of an electrically neutral NV center (NV^0). However, such an NV center can capture an extra

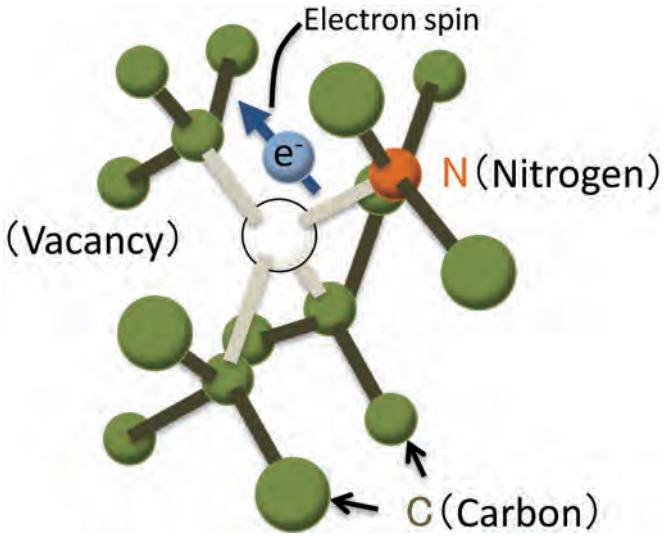

Fig. 1: A nitrogen-vacancy (NV) center in diamond.

electron from somewhere in the lattice and form a singly-negative NV^- center. In this case, two electrons form a spin-triplet state with the magnetic quantum numbers m_s=-1, 0, +1. This single spin state can be regarded as a qubit that can operate at room temperature, and such a qubit can be used as a highly sensitive sensor to detect external perturbations such as magnetic fields, electric fields, strain, etc.

The protocol for using a single NV^- as a sensor works as follows. In the experimental set-up shown in Fig. 2, the blue arrow represents a single electron spin bound to an NV^- center placed near the surface of the diamond. A target molecule is placed on the surface immediately above the center. A static magnetic field is applied externally to induce precession of the NV^- electron spin

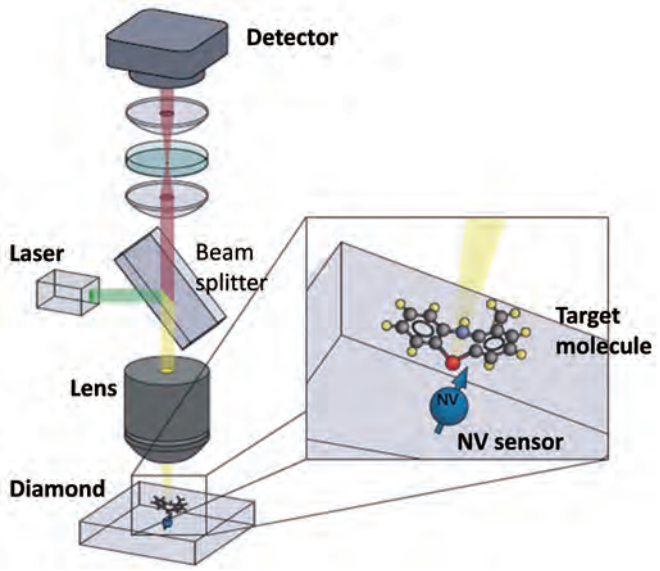

Fig. 2: A diamond megnetometry system.

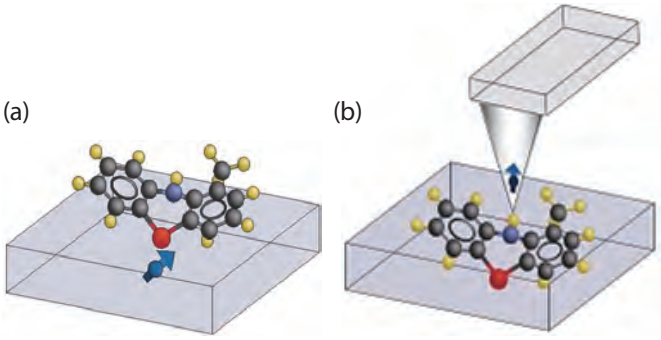

Fig. 3: Two different configurations for the use of a single NV center for nuclear spin field detection. (a) Target nuclear spins are placed on top of the diamond surface near the embedded NV center. (b) The NV center is placed at the tip of the cantilever to approach the target.

around the magnetic field axis. This can be achieved simply by placing a small permanent magnet nearby. The qubit state with $m_s=0$ is the ground state while the states with $m_s=-1$ or $+1$ are regarded as excited states, corresponding to the $|0\rangle$ and $|1\rangle$ states of a qubit, respectively. Initialization, i. e. setting the state to $m_s=0$, is achieved by shining a green laser on the NV^-. Next, programed microwave pulses are applied to induce magnetic resonance of the NV^- electron spin and tilt it in the direction perpendicular to the externally applied magnetic field. In other words, the superposition state $|0\rangle+|1\rangle$ is formed and the spin precesses in the plane perpendicular to the externally applied static field. If our aim is to detect the magnetic field arising from the nuclear spin of a single proton placed on the surface of the diamond, we should note that the proton nuclear spin also precesses around the static field. The magnetic field strength due to the single proton spin at the NV^- sensor decays as r^3, where r is the distance between the proton and NV^-. If r is as small as a few nano meters, it is possible to detect the single nuclear spin.[5] Such detection can be achieved by measuring the change in the precession rate of the NV^- electron spin modulated by the precession of the nearby proton nuclear spin. The change in the precession rate can be measured using a variety of spin-echo methods established in the research community of NMR.[6] Finally, the phase of the precessing spin can be determined from the emission of photons from the NV^- that is induced by the excitation by the green laser. Here, the NV^- emits photons only when it is in the $m_s=0$ state. Therefore, whether or not photons are detected at the detector in Fig. 2 allows us to determine whether the NV^- is in the $m_s=0$ or $m_s=\pm1$ states.

Single proton or molecule NMR using a single NV^- center as a sensor can be performed using one of the two different configurations shown in Fig. 3. Figure 3 (a) shows a configuration in which the target molecule is placed on the flat diamond surface at the position right above the embedded NV^- center. Figure 3 (b) shows a diamond cantilever with a single NV^- at the tip, which can be used to conduct atomic force microscopy and access the target molecule directly. While the method in Fig. 3 (b) is more versatile than the method in Fig. 3 (a), many groups are adopting the method shown in Fig. 3 (a)

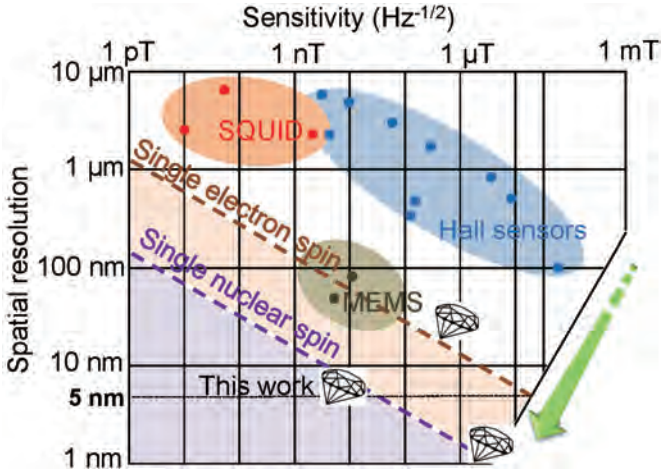

Fig. 4: Comparison of the performance of the magnetic sensors. The vertical axis is the spatial resolution and the horizontal axis is the sensitivity. The diamond marks represent the performance of the NV sensors.

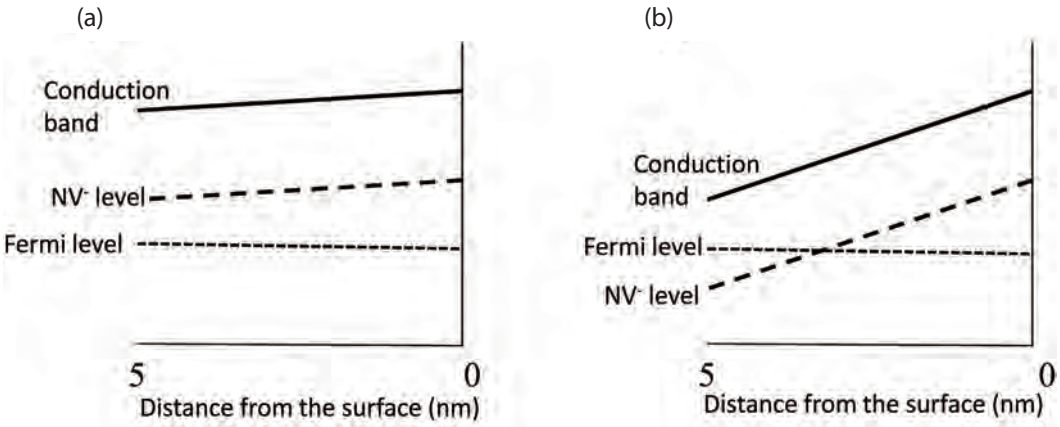

Fig. 5: Band bending of the diamond near the surface. (a) Intrinsic diamond. (b) n-type diamond.

as it is significantly simpler than that shown in Fig. 3 (b). In both cases, achievement of atomic spatial resolution is expected.

Figure 4 shows a comparison of various magnetic sensing technologies. This is an updated version of the presentation that was developed originally by Degen.[7] Here the vertical axis is the distance between the sensor and the target (which determines the spatial resolution) and the horizontal axis is the minimum magnetic field detectable (which corresponds to the sensitivity). The region below the dashed line labeled single nuclear spin (single electron spin) is where the condition to detect a single nuclear spin (single electron spin) is fulfilled. The sensitivity of classical sensors such as Hall sensors and MEMS (force detection using a cantilever) is lower than that of quantum-assisted sensors like SQUIDs (superconducting quantum interference devices). SQUIDs also have a wide detecting area, typically $\sim(\mu m)^2$, which is a big advantage when the source of the target magnetic field is situated far away. On the other hand, it is not possible to achieve nano meter spatial resolution with SQUIDs. The NV^- center having a very small detecting area, about the size of an atom, can achieve nano meter spatial resolution and high quantum–assisted sensitivity simultaneously if the NV^- sensor can be placed a few nm from the source of the magnetic field. This allows for single nuclear spin detection, as we will discuss later.[8]

PLACING NV^- CENTERS CLOSE TO THE SURFACE OF THE DIAMOND

The remaining tasks appear rather simple: placing the NV^- centers close to the surface of the diamond (within 2-3 nm), putting the target object on top of the surface, and measuring. However, placing the NV^- centers within a couple of nms of the diamond surface turns out to be a very difficult materials-science challenge. Unlike standard doping by donors or acceptors, it is necessary to dope with nitrogen and to find the correct conditions for

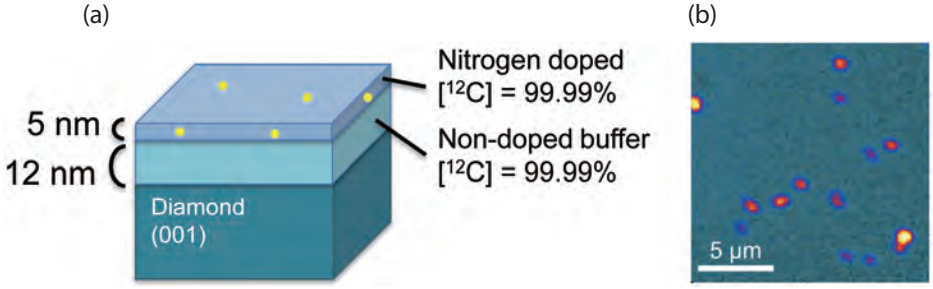

Fig. 6: (a) The structure of the sample employed in this work. (b) Photoluminescence mapping of the sample showing emissions from single NV centers.

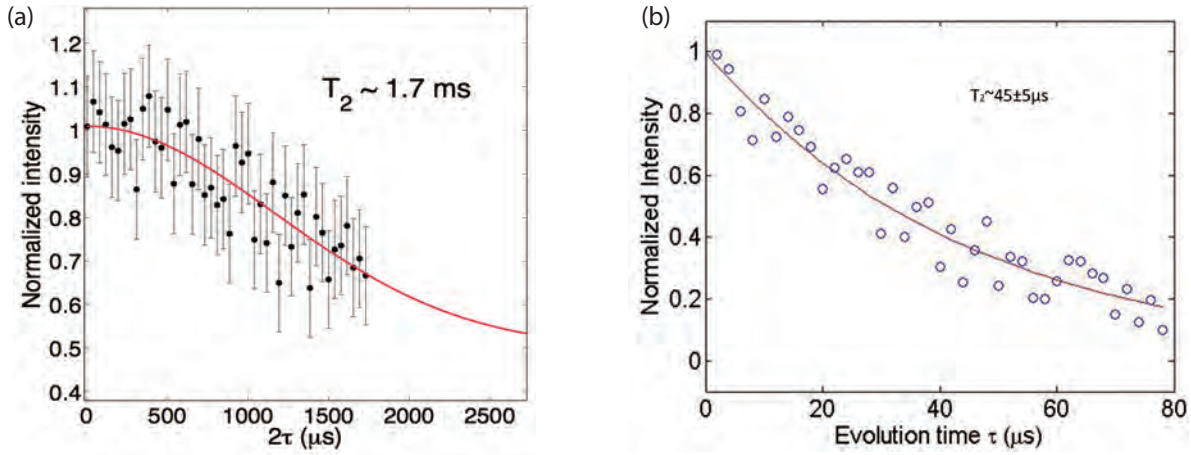

Fig. 7: (a) Spin-echo of a single NV center in a 100nm thick ^{12}C diamond film.[11] (b) The same in a 5nm thick sample.[8]

the vacancies to come next to the nitrogen atoms. A variety of methods, such as the ion-implantation of nitrogen[9] and the doping of nitrogen during the chemical vapor deposition of diamond,[10] have been developed, but the most challenging part turns out to be keeping the NV center close to the surface in the negatively charged state. Due to the presence of the surface states, the band bends like the Schottky barrier towards the surface as shown in Fig. 5 and the NV^- state tends to come above the Fermi level near the surface as shown in Fig. 5 (a). As such, NV centers near the surface prefer to be in their neutral states (NV^0), thus losing the single electron spin that works as a sensor. In order to overcome this problem, the present group[8], 11 and the UC Santa Barbara group[12] independently developed a method to dope the surface layer very heavily with nitrogen in order to push the Fermi level upwards even near the surface so that the NV^- level remains below the Fermi level.

Figure 6 (a) shows a sample structure grown by the present group. The top 5 nm thick, isotopically enriched ^{12}C layer is doped heavily with nitrogen ($\sim 10^{18}$ cm^{-3}). Photoluminescence mapping of this sample using the set up shown in Fig. 2 led to the observation of dispersed bright spots corresponding to individual NV^- centers [Fig. 6 (b)].[8] Here, all the bright spots arise from the NV centers placed less than 5 nm from the surface. Next, we evaluated the coherence properties of each NV^- center using the spin-echo method. We measured the phase coherence time T_2, a characteristic time during which the phase of the precessing electron spin is preserved. Such phase coherence typically decays exponentially so that T_2 is the time constant in the exponent. As mentioned already, since our goal is to measure the small change in phase resulting from a small change in the external magnetic field, the sensitivity (minimum magnetic field measureable) depends on the coherence time T_2 as $1/\sqrt{T_2}$. Thus, the longer T_2 the more sensitive the sensor becomes. Figure 7 (a) shows that $T_2 \sim 1.7$ ms for an NV^- electron spin observed in a 100 nm thick, isotopically enriched ^{12}C diamond[11] sample and Fig. 7 (b) shows that $T_2 \sim 0.045$ ms in the 5 nm thick sample shown in Fig. 6.[8] The value $T_2 \sim 1.7$ ms found in the 100 nm thick sample is the same as the value 1.8 ms observed in the bulk, isotopically enriched ^{12}C diamond.[13] The time $T_2 \sim 0.045$ ms measured in the 5 nm sample appears short, but even with such a value of T_2, the detection of a magnetic field as weak as ~ 3 nT is theoretically possible. This is

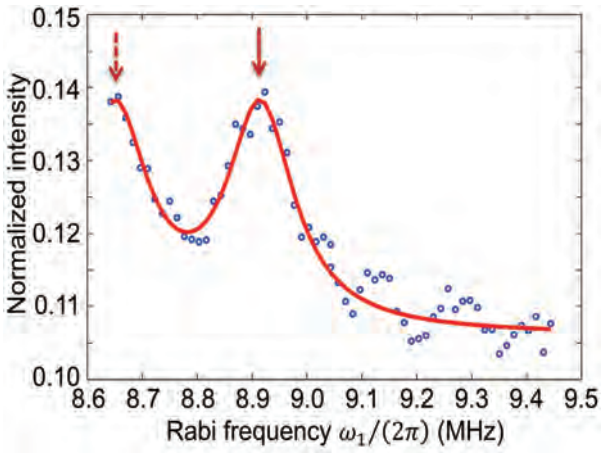

Fig. 8: An example of proton NMR detection using a single NV center as a sensor.

significantly smaller than the ~10 nT field we expect to require for the detection of a single proton nuclear spin when using conventional techniques. The diamond mark labeled "This work" in Fig. 4 is plotted at the intersection of 3 nT and 5 nm, and is situated in the region where the condition for single nuclear spin detection is fulfilled.

PROTON NMR DETECTION USING A SINGLE NV CENTER

Figure 8 shows an example of using a single NV center as a detector to sense the magnetic field arising from the precession of ensemble of proton nuclear spins. The proton nuclear spins were contained in a drop of emulsion oil placed on top of the diamond surface.[8] The peak at 8.9 MHz corresponds to proton NMR and the peak at 8.65 MHz corresponds to proton NMR shifted by the hyperfine interaction with ^{14}N nuclear spins. Here about 6,000 protons have been detected successfully. Prior to our work, there were two examples of the successful detection of a small number of protons using a single NV.[14, 15] More recently, there are two groups who have reported successful single nuclear spin detection using single NV sensors.[16, 17] The next step is to establish methods to perform nuclear magnetic resonance imaging within a single molecule. Such a goal is extremely meanin gful for technological applications. Moreover, it is of great interest to fundamental research to explore what and how much can be sensed using single electron spins.

SUMMARY

The forefront of quantum assisted sensing using single NV centers in diamond has been reviewed. Detection of single proton NMR using a single NV center as a sensor at room temperature has been realized already. A wide variety of applications utilizing NV sensors can be expected in the future.

Acknowledgments

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