

Diamond Quantum Sensors for Biological Application

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Abstract

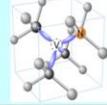
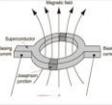
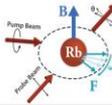
NV (Nitrogen Vacancy) center in diamond has superior physical properties at room temperature for quantum sensors with scalable applications from nanoscale to macroscopic range. We would like to introduce magnetic sensors by applying advanced CVD, nano-device technologies, and quantum protocols. As for AC magnetic field measurements, NMR measurement will enable the direct observation of cells or bio-molecules. As a first step, nanoscale NMR signals from Proton and Fluorine were confirmed by our diamond quantum sensor.

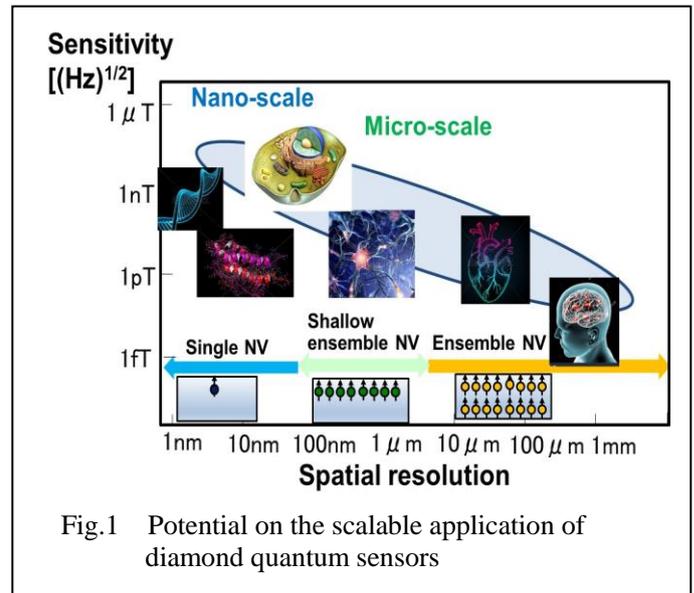
1. Introduction

Negatively charged nitrogen-vacancy (NV) color center in diamond is one of the most promising candidates for quantum sensing of magnetic field, electronic field, temperature, and pressure [1-6]. Spin state ($S=1$) of electrons localized at the NV center can be initialized and read out optically [1]. In conjunction with spin state manipulation using microwave radiation, optically detected magnetic resonance (ODMR) can be performed on a single spin. Photostability and long coherence time even at room temperature make its wide application.

Table 1 shows comparison of the three quantum sensors: diamond NV centers, SQUID, and atomic vapor cells. The diamond sensor has superior performance at room temperature in solid materials and special function of the vector imaging. Figure 1 shows the potential on the scalable application of the diamond quantum sensors. Atomic size NV centers can be brought in proximity to nanoscale targets or it can be packed at enormous density for macroscale applications. Therefore, scalable applications from nanoscale such as protein, cell and neurons activities to macroscale applications such as measurement of heart and brain activity, are all possible with this atomic size NV center.

Table 1 Comparison of three quantum sensors

Quantum sensor	Diamond sensor (NV centers)	SQUID	Atomic vapor
			
Sensitivity (μT^{-1})	< 1 pT	~ fT	< fT
Resolution	10-300 nm	μm -mm	mm
Temp.	RT	LT	>RT
Vector imaging	○	×	×



In this paper, we introduce highly sensitive diamond sensors and discuss on the possibility for the biological applications. Diamond sensors serve as high-sensitivity magnetometers for both the DC and AC magnetic field in application to biological imaging. As for DC magnetic field measurements, our current interest is to observe dynamic reactions of living cells. Super-para-magnetic particles are placed over live cells on a diamond substrate containing high density NV centers in the surface layer. External DC magnetic field is applied to magnetize the super-para-magnetic particles. The spectrum is measured by projecting the fluorescence from the NV centers to an image sensor through an optical microscope. Analysis of the ODMR spectrum at every pixel allows one to determine the positions/angles of the magnetic particles, to extract the live cell reaction. As for AC magnetic field measurements, NMR measurement will enable the direct observation of cells or bio-molecules without marking modifications.

2. Diamond film and sensor devices with high sensitivity

We developed negatively charged NV ensemble centers with longer coherence time. Magnetic detection sensitivity δB (minimally detectable field) is expressed in following equation,

$$\delta B \approx \frac{1}{g_s \mu_B R A \sqrt{\eta}} \frac{1}{\sqrt{N T_2}}$$

where g_s is the NV⁻ electronic Landé factor, R is measurement contrast, A is alignment ratio of the NV axes of magnetic field direction, η is detection efficiency, N is the number

of NV centers, and T_2 is the spin coherence time. We obtained diamond films containing high density ($> 10^{16} \text{ cm}^{-3}$) ensemble NV centers with selectively aligned along the [111] direction ($> 99\%$) by nitrogen-doped microwave plasma CVD [11,12] (Fig.2)[7,8]. For the alignment of the orientation of the ensemble NV centers, it was found that the off direction of the diamond substrate along $\langle \bar{1}\bar{1}2 \rangle$ or $\langle 11\bar{2} \rangle$ is a key factor.

We confirmed the magnetic sensitivity by AC magnetic field measurements is higher than $30 \text{ nT Hz}^{-1/2}$ of 300 nm scale. In a large sensor volume ($8.5 \times 10^{-4} \text{ mm}^3$), the sensitivity would reach $0.14 \text{ pT Hz}^{-1/2}$. This high estimated sensitivity originates from the high contrast because of the perfectly aligned NV ensembles.

The charge state control of NV centers in diamond is an important issue because only negatively charged NV centers have the attractive spin properties. To control of the charge state band-gap engineering techniques using pn junctions are applied to the sensing devices. We fabricated p-i-n junction to modulate the charge state of NV centers in i-layer to NV⁻ state [9]. The electrical property of p-i-n junction with good rectification ratio of 10^5 was obtained. We observed that the charge state of ensemble NV centers is depend on the voltage range. The NV⁻ ratio could successfully be increased by tuning electron quasi Fermi energy if almost no current flow through the p-i-n junction, while it is decreased by hole current.

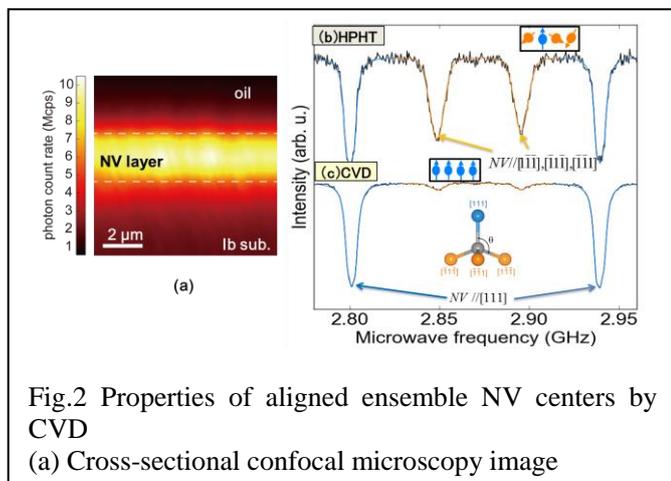


Fig.2 Properties of aligned ensemble NV centers by CVD
(a) Cross-sectional confocal microscopy image

3. Perfectly aligned shallow ensemble NV centers for nanoscale NMR

As for AC magnetic field measurements, NMR measurement will enable the direct observation of cells or bio-molecules without marking modifications. As a first step, NMR signals from proton and fluorine were confirmed with 10 nm shallow (delta-doped) ensemble NV centers [10]. We developed that a highly aligned high-density shallow NV centers ensemble is formed by step-flow growth using MPCVD growth on (111) substrates. More than 10^{16} cm^{-3} NV centers are detected from confocal scan. The results demonstrate highest NV density in the vicinity of the surface with a perfect alignment of more than 99%. Surface sensitive magnetic field measurements were performed by observing the thin layer of

proton and fluorine contained in Fomblin oil by nanoscale NMR using the XY8-80 pulse sequence (Fig. 3). The single NV center approximation indicates that the depth of the NV centers is approximately 9–10.7 nm from the surface with the error of less than 0.8 nm.

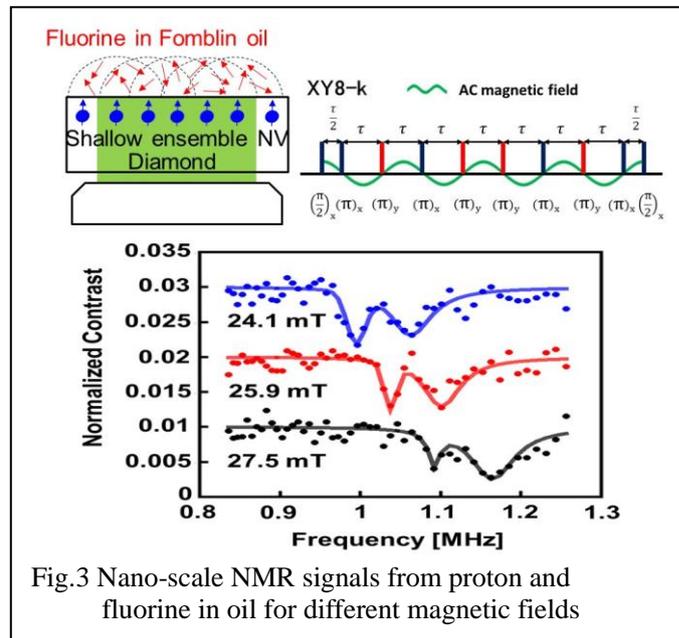


Fig.3 Nano-scale NMR signals from proton and fluorine in oil for different magnetic fields

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