

Biological Sensing with NV centres in Diamond

This is the abstract

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I Introduction

II The NV⁻ centre in Diamond

A wide variety of defects occur naturally in diamond. Many of these defects allow the absorption and emission of light [17], often giving their host crystal a natural vivid colour. These colour centres are principally due to site vacancies and impurity defects in the crystal, with elements including boron, silicon, nickel and most commonly nitrogen [16]. The negatively charged nitrogen-vacancy (NV⁻) centre diamond is of particular interest in sensing technologies not only due to their natural abundance, but also due to a number of favourable properties which they possess.

Electronic Structure

The NV centre localises six electrons at the defect site. The nitrogen atom provides two of its valence electrons while a further three are due to dangling bonds of the diamond's carbon atoms [12]. The remaining electron is captured from donor ions in the lattice giving the NV⁻ colour centre a net negative ($-e$) charge [12]. Although the positively charged NV⁺ and neutral NV⁰ defects exist, the NV⁻ is the only variant which is magnetooptically active and is the focus of the vast majority of

research [12]. Indeed, ionisation to NV⁰ poses a challenge to the synthesis of shallow NV⁻ centres [6].

Optical and Spin Properties

The optical properties of NV⁻ centres are crucial to their application in sensing technologies. The essential features of the system can be described by a simple energy-level diagram of Figure.???. The spin triplet ground $|g\rangle$ and excited $|e\rangle$ states lie between the conduction and valence bands and have an energy splitting of ~ 1.945 eV [12]. A metastable spin singlet state $|s\rangle$ lies between $|g\rangle$ and $|e\rangle$ and has a radiative lifetime of ~ 250 ns [12]. The spin triplet states are split into three spin sub-levels labelled by m_S . The m_0 state is lower in energy than the degenerate $m_{\pm 1}$ states due to a zero-field splitting D of 2.87 GHz for $|g\rangle$ and 1.42 GHz for $|e\rangle$ triplets [4]. The triplet $m_{\pm 1}$ degeneracy is lifted by an external magnetic field and thus the system can be used as a magnetic field probe. The metastable long-lived state $|s\rangle$ is primarily populated from the $|e, m_{\pm 1}\rangle$ states while the $|e, m_0\rangle$ state decays more strongly to $|g\rangle$, as a consequence, an optical contrast between m_0 and $m_{\pm 1}$ of 30% arises [12]. This spin dependent luminescence is the basis of many sensing applications.

III Synthesis

AIM: Explain the current possibilities in synthesis/fabrication of diamonds/nanodiamonds for sensing devices.

Focus on how amenable they are to sensing in the biological setting. Elucidate some of the problems in synthesis.

IV Sensing with NV centres

Sensing Protocols

Sensing involves the measurement of perturbations to a system by interrogation. The measurement of EPR frequency shifts is the principal method of interrogation and a number of protocols to this end exist.

Continuous Measurement

Continuous measurement involves the measurement of the EPR spectrum across a suitable range and the subsequent fitting of any resonances observed. The application of an external magnetic field will for instance cause the resonance to shift its centre position. Sensitivity can be increased by observing variations in fluorescence intensity and by collecting photons from

many NV^- centres, this however is detrimental to the nanoscale sensing characteristics of a single NV^- centre [12]. The sensitivity of this measurement technique suffers since the system is continuously being measured, nevertheless sensitivities below $\text{kHz}/\sqrt{\text{Hz}}$ have been achieved [1]. A significant body of work has extended the possibilities of sensing using this technique (see *e.g.* [5, 13]) including the sensing of vector fields using multiple NV^- centres with different orientations [8].

Pulsed Measurement

In pulsed measurements a pump probe scheme is employed in which the system evolves in the perturbing field without any interrogation. The lack of optical pumping during the measurement phase increases sensitivity over long coherent evolution times τ [10]. Furthermore, many pulse schemes have been developed over the years many of which can be employed in these sensing protocols [12].

Relaxometry

Magnetic resonance relaxometry relies upon the fact that the spin relaxation times T_1 and T_2 are dependant on the environmental degrees of freedom of the perturbing system. One particular implementation of relaxometry is the measurement of fluctuating noise in the environment and as in the case of pulsed measurement, many protocols and techniques exist for the sensitive measurement and characterisation of spin relaxation times [14]. MORE CITITATIONS

Measurement Applications

Sensing of magnetic fields is perhaps the most direct measurement application of NV^- centres, however their proper-ties allow for the sensing of other environmental parameters such as temperature, pressure and strain.

Magnetic and Electric Field Sensing

Spin Environment Sensing

Thermometry

It has been shown [2] that the zero field splitting parameter (ZFS), D has a significant dependence on temperature T . Across a variety of samples it was found that $dD/dT = -74.2(7) \text{ kHz/K}$ while the transverse ZFS parameter E had a dependence $dE/dT = -1.4(3) \times 10^{-4} \text{ K}^{-1}$ [2]. This effect is likely due thermal expansion of the crystalline environment and limits the sensitivity of NV^- centres in noisy thermal environments, it can also be exploited as a method to use the NV^- centre as a nanoscale thermometer [15, 11, 7]. Using an ultrapure bulk sample of diamond it was shown [7] that temperature variations of 1.8 mK at a sensitivity of $9 \text{ mK Hz}^{-1/2}$ are possible. Furthermore the local thermal environment could be resolved at 200 nm length scales. These techniques allow the mapping

of subcellular temperature gradients [7] demonstrating the potential of this technique in biological systems (see section

Strain and Pressure Sensing

The effects of hydrostatic pressure on the behaviour of NV^- centres has been investigated [3]. It was found that the variation of the ZFS parameter D with pressure P was highly linear at $dD/dP = 14.58(6) \text{ MHz/GPa}$ [3]. The measurements were performed in a diamond anvil cell capable of reaching extreme pressures and the technique may offer improved sensitivity over current pressure sensing techniques in these environments [3].

Explain how they can be used as quantum sensors for various types of parameters, magnetic field, electric fields, strain temperature etc. nanoscale sensing. mention protocols etc. (protocols which allow sensing)

V Biological Sensing

Aim: Focus on the ways in which the sensing possibilities described in the previous section can be used in biological settings. The advantages/disadvantages/challenges. Give an overview of some of the seminal work done in the area and focus in on the recent developments in the field. many examples. Talk about conventional approaches, compare to quantum dots etc. cytotoxicity etc etc. In Vivo sensing: the possibilities. Biocompatibility

Broad Examples of biological sensing

Recent development 1

Recent Development 2

VI Conclusion

this is to be cited [9]

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