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## Faculty of Biomedical Engineering

# Magnetic field imaging in biological systems with nanometric resolution

**Doctoral Thesis** 

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### ANNOTATION

Recent developments of engineered nitrogen-vacancy (NV) centres in diamonds offer promising avenues for the creation of sensitive nanoscale probes, pivotal for quantum measurements and diagnostic applications in nanomedicine. The aim of this work is to enable these sensor applications by studying NV photodynamics, investigating the effects of the environment and developing advanced quantum sensor chips. In this thesis, we include both fluorescent nanodiamond particles (NDs) and NV-containing single crystal diamond. Initially, we study the fundamental physics governing signal generation, exploring the photodynamics of a single NV center and analysing its spin-contrast properties. Subsequently, we probe the impact of the crystal environment on the photoelectrical signals and quantum efficiency, determining the possible origins of non-standard phenomena such as positive photocurrent detected magnetic resonance (PDMR). We demonstrate the usage of ground-state level anti-crossing (GSLAC) in photoelectrical spin-state readout.

In the second part of the thesis, we focused on the development of a quantum chip for both singlecrystal diamond and ND particles. Two types of prototypes were designed and fabricated, with numerical modelling employed to elucidate microwave field distribution and resonance patterns. For single crystal diamond chips, in-depth testing is conducted to mitigate microwave-induced interference, which is critical for detecting low photocurrents from single NV centres. Additionally, we explore the potential for integrating this chip into a microfluidic chamber. The chip for the nanodiamond particles was evaluated for its heating properties, which are crucial for keeping neurons alive, using theoretical calculations and experimental measurements using a nanodiamond probe. Furthermore, we also perform the *in vitro* sensing of the magnetic field at the attached nanodiamonds to the neuron cells.

In summary, our research represents a significant step forward in harnessing the capabilities of engineered NV centers in diamond for quantum sensing applications, offering promising prospects in both fundamental research and practical diagnostics in nanomedicine.

## **KEYWORDS**

Quantum sensing, NV defect, Diamond sensor, Photoelectrical readout, PDMR, Magnetic field detection

### ANOTACE

Nedávné vývoje v oblasti defektu dusík-vakance (NV) v diamantu, nabízejí slibné možnosti pro vývoj citlivých sond s nano-rozlišením, klíčových pro kvantové měření a diagnostické aplikace v nanomedicíně. Cílem této práce je vytvořit koncept kvantových měření studiem fotodynamiky NV defektu, zkoumáním vlivu prostředí a vývojem pokročilých kvantových senzorů. V této práci zahrnujeme jak fluorescenční nanodiamantové částice (NDs), tak NV obsahující monokrystalický diamant. V první části jsme popsali základní fyzikální jevy ovlivňující generaci signálu, zkoumáním fotodynamiky jednotlivých center NV a analýzou spin kontrastu. Dále byly zkoumány vlivy krystalového prostředí na fotoelektrické signály a kvantová účinnost, zároveň jsme určili možný zdroj jevu pozitivní fotoproudem detekovaná magnetická rezonance (PDMR). Demonstrujeme metodu využívající degenerace základního stavu (GSLAC) ve čtení spinového stavu pomocí fotoelektrického signálu.

Ve druhé části práce jsme se zaměřili na vývoj kvantových čipů pro oba typy diamantu monokrystalický a nanodiamantové částice. Byly navrženy a vyrobeny dva druhy prototypů, s využitím numerického modelování k objasnění rozložení mikrovlnného pole a rezonančních profilů. Pro čipsety monokrystalického diamantu jsme vytvořili detailní testování s cílem minimalizovat interferenci způsobenou mikrovlnami, což je klíčové pro detekci nízkých fotoproudů z jednotlivých center NV. Kromě toho zkoumáme možnost integrování mikrofluidní komory do tohoto čipsetu. Čipset pro nanodiamantové částice byl testován pro jeho tepelné vlastnosti, což je klíčové pro udržení neuronů naživu, pomocí teoretických výpočtů a experimentálního měření s využitím nanodiamantové sondy. Kromě toho provádíme *in vitro* měření magnetického pole na nanodiamantech navázaných k neuronálním buňkám.

Shrnutí: Tato výzkumná práce představuje významný krok vpřed ve využívání potenciálu center NV v diamantu pro kvantové senzorové aplikace, nabízející slibné vyhlídky jak v základním výzkumu, tak v praktické diagnostice v nanomedicíně.

## KLÍČOVÁ SLOVA

Kvantová detekce, NV defekt, Diamantové senzory, Fotoelektrický readout, PDMR, Detekce magnetického pole

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## 1. MOTIVATION

Nanomaterials are new, fast-developing kinds of materials with applications in many spheres, including biology and medicine. This kind of material has, thanks to small dimensions, many interesting properties that cannot be observed in "macro materials". Some of many examples of these extraordinary properties are super hardness nanomaterials (nanoalloys), large surface area with the example being nanoparticles (used for, e.g. target drug-delivering) or their quantum properties such as photoluminescence. Similar to nanoparticles photoluminescence can be produced by quantum dots (QDs), which have further applications for example in image technology (used for example in QLED displays). Nanoparticles and QDs are good examples of fast-developing nanotechnology, applied to biologic, pharmaceutical and medical research. Another examples are medically approved nanoparticles that can be used as contrast agents in-vivo [1]. This and many other properties are the reasons why nanomaterials have started to be widely used in different kinds of engineering and medical engineering fields (e.g., electronic, automotive, and biomedical industries) in the past 15 years. [2]

Another example of the field where nanomaterials can be used is the novel type of metrology - quantum sensing and quantum imaging methods. The quantum methodology can be applied in the development of new super-resolution techniques for the detection of nanostructures, individual molecules or atom's behaviour [2]. This thesis is aimed at the development of novel methods for measuring small magnetic fields that can be used in nanoscale nanomagnetic resonance (NMR) detection. In these applications, nitrogen-vacancy (NV) point defect in the diamond crystal lattice, acting as a spin qubit, is used acting as atomistic-scale quantum detector.

## 2. INTRODUCTION

The detection of ultra-low magnetic fields generated within living organisms represents a compelling avenue for extracting valuable insights into biological processes. Such fields are perceptible across diverse anatomical regions and are scrutinized through various clinical methodologies, including neuromagnetography, magnetocardiography, and magnetogastrography. Contrary to electric fields, which strongly depend on the dielectric properties of the tissue between neuronal sources and the recording electrode, magnetic fields travel through tissue without distortion because the respective permeability is essentially the same as free space. However, these ultra-low fields require ultra-sensitive magnetometers that rely on superconducting quantum interference devices (SQUIDs) [3] or, more recently, spin-exchange relaxation-free (SERF) [4] sensors, respectively demanding cryogenic cooling or high-temperature atomic vapour. Alongside other disadvantages, the intrinsically non-biocompatible properties of these sensors mean that they cannot easily be brought into sufficiently close proximity (tens of micrometres) to the target sample necessary for microscopicscale recording, particularly where a solution bath is required to keep tissue alive [5]. Nitrogen vacancy (NV) centre quantum spin states are sensitive to the low fields, and thanks to the fact that sensing doesn't require cooling and can be done at room temperature, it makes it possible to use diamond-based sensors inside in vitro or even in *vivo* sensing (more detail in chapter 3.4.2 Biomedical application).

The NV center, a point defect within the diamond lattice, arises when two neighbouring carbon atoms are substituted by nitrogen and a vacancy in the lattice. One of its important characteristic is its sensitivity to very weak external electric or magnetic fields, often originating from interactions within biological or chemical environments. This sensitivity enables the optical detection of electromagnetic fields—like charge or spin—that interact with a single NV center electron spin. Electron spin resonance (ESR) techniques are employed to monitor transitions between the NV states. Through the discernible differences in photoluminescence intensity during radiative transitions within the electron spin triplet (measured by optical readout), specifically between spins  $m_s=0$  and  $m_s=\pm 1$ , a technique known as optically detected magnetic resonance (ODMR)

directly observes these transitions. Discrepancies between the spins  $m_s=0$  and  $m_s=\pm 1$ , can be further measured by elucidated through the generation of charge carriers, specifically electron-hole pair, emitted from the NV centre. This technique is termed photoelectrically detected magnetic resonance (PDMR), involves the surveillance of photocurrent via electrodes fabricated on the diamond surface (photoelectrical readout). By utilizing microwave (MW) excitation at resonance frequency (approximately 2.87 GHz zero-field splitting) to promote electrons from  $m_s=\pm 1$ , and considering the Zeeman splitting of the degenerate  $m_s=\pm 1$  states, this system proves capable of detecting exceedingly weak magnetic fields on the order of nanoteslas or lower.

This thesis is aimed at developing the concept of a quantum chip for sensing physical fields such as magnetic and temperature field in nanometric resolution based on sensing the NV spin system. The concept is focused on the optical and photoelectrical readout of a signal [6]. Modelling of this photoelectrical readout is challenging, in comparison with optical readout, because the charge dynamics and excitation and recombination processes in conduction and valance bands of diamond need to be introduced. The full quantum mechanical model of the NV defect is essential for further chip development. This requires the implementation of intraband and outerband transition that will allow us to predict the behaviour of the quantum NV chip for different kinds of laser and microwave stimulation and its reaction to the environment. All these features will lead to the characterization of the physical behaviour of the NV defect and point to the essential requirements for further chip design. The model of the NV energy level occupation dynamics (NV photodynamics) can generally be used for all kinds of diamond-based sensors based upon an NV center point defect. (nanodiamond particles (ND), diamond layers or diamond bulks). Various possible chip designs will be created and modelled in terms of the intensity of the photoluminescence/photocurrent signal and will be tested in the selected biological environments.

For the development of the chip prototype, it was necessary to fully understand the physical processes behind the generation of the photoluminescence/photocurrent signal from the NV spin system. Figure 1 shows a generical principle of the NV signal generation. NV defect inside the diamond crystal is excited by the incoming photons and emits photons or charge carriers move under the influence of the bias voltage to the electrodes where they are collected. The local environment reacts with the NV and

changes its energy level positioning. The NV behaviour in the presence of the local environment and stimulation is solved in the MatLab part of the model.



Figure 1 - Schematics of the electrically detected MR setup, visualized in VESTA software.

When the NV photodynamics is resolved, we can implement this obtained knowledge into the COMSOL modelling of the MW field distribution of the chip that best suits the desired applications. Figure 2 shows a visualization of one of the possible chip configurations for the photoelectrical readout. Electrodes on the diamond crystal surface are connected by wire bond to the MW circuit, and the laser is focused on the gap between them. Different types of chip conformation geometries were modelled by the COMSOL environment, and the ability of the microwave stimulation was proved (photocurrent intensity, MW heating).



Figure 2- Schematic representation of chip for photoelectrical readout. Laser is focused on the gap between the electrodes where emitted charge carriers are collected. Electrodes use bias voltage, and the charge carriers are sensed by a lock-in amplifier. Microwaves are applied through the wire at the diamond surface. Taken from [6]

While for the readout techniques discussed above, diamond a slab integrated with a chip is used, another form for quantum sensors containing NV detects are nanodiamonds, e.g. diamond particles with the diameter in nanometric range. Such nanodiamonds presents as a promising candidate for biosensing and bioimaging within biological systems, owing to their inherent biocompatibility, non-toxicity, photostability and possible particle size >5nm. The small particle size holds significant importance in the uptake mechanism, wherein smaller dimensions enhance endosomatic penetration. Leveraging the quantum sensing capabilities of the NDs offers opportunities to monitor weak magnetic or temperature fields in biological processes. Notably, the sensing of the optically detected magnetic resonances was already performed on the HeLa cells [7].

Another interesting application for biological sensing is temperature sensing at nanoscale. Increasing the local temperature around the eukaryotic cells can be linked to the opening/closing of the temperature-sensitive ion channels of the transient receptor potential channels (TRP) [8]. TRP channels are polymodal, non-selective cation

channels involved in a plethora of cellular processes, such as cell excitability, intracellular protein interaction, Ca<sup>2+</sup>, and Mg<sup>2+</sup> homeostasis, as well as cellular proliferation and differentiation [9]. Thermo-sensitive TRP channels exhibit a response profile that collectively covers the entire range of temperatures that mammals can discriminate [10], from noxious cold (TRPA1) and heat (TRPV1, TRPV2) to small changes in physiological temperature (TRPV3, TRPV4). For measuring the local temperature that is affecting TRP channels, it is necessary to have the sensing tool in proximity to the receptor itself, which is a challenge in itself. Until now, there has been no study that links the activation of the TRP receptors and the local temperature. The current approach is limited to the single-pointed heated element. However, this technique leads to multiple artefacts, including the destruction of many cells, which sets free a multitude of toxic intracellular components, leading to a microenvironment with no resemblance to the physiological situation. Nanodiamond can lead to important advances in this field. For this application in this thesis a microreactor integrating ND particles with the chip has been developed to measure in-vitro temperature in biomolecular environment. For this purpose, a chip incorporating microwave and laser heating has been developed to explore the potential of NDs for this type of sensor. This approach affords the unique capability to monitor temperature gradients alongside magnetic field variations within the immediate vicinity of cellular membranes.

## 2.1 Aim of thesis

The objective of this thesis was obtained through the implementation of these methodical procedures:

#### 1. NV defect modelling

A full mathematical model of the NV spin level transitions is developed based on the rate equation description, necessary for designing and operating magnetic field sensors. and theoretical output signal, and its dependency on laser and microwave stimulation will be probed.

#### 2. Crystal environment modelling

The effect of the crystal environment of NV centre is to be modelled and, used for identification of various common diamond impurities (f.e. substitutional nitrogen,  $N_s$ ). This modelling describes fundamental processes occurring in photoelectric spin signal detection such as will be added, and their recombination dynamics. Fulfilling this goal requires the implementation the charge carrier drift implementation into the rate model.

#### 3. Experimental verification

A predicted signal output from the model will be compared with the real measurements on the single NV diamond sample. This goal will be used to validate the proposed physical model.

#### 4. Chip designing and manufacturing.

Multiple sensor designs (a combination of PCB and electrodes) will be proposed for the single crystal and nanodiamond applications. Designs will be developed in terms of the minimalization of crosstalk between the MW line and the electrodes, , the optimisation of scattering parameters (S-parameters), and the direct impact on the NV signal. A prototype of the chips will be manufactured using the crystal and electrode preparation process.

#### 5. Chip testing on fantoms

Sensor prototypes with the diamond crystals will be tested for elementary characteristics like electrode pickup or microwave heating. The results will be compared with the currently used sensors.

#### 6. Chip testing on the biological environment

Sensors developed for the NDs application will be tested for temperature and magnetic field sensing in vitro in the real biological system (NDs will be attached to the neuron

axons). The concept of using the NV as a multisensor for quantum detection will be shown.

## 3. STATE OF THE ART

### 3.1. Diamond

Chemical vapour Deposited (CVD) diamond materials been used in different industries and academic fields for more than past 30 years. From the mechanical properties, it should be mentioned that diamond is the hardest material on the Mohs hardness scale, with a hardness 10<sup>4</sup> kg/mm<sup>2</sup> [11]. Thanks to this property, diamond layers are used f.e. as coating of working tools, drill bits and precise machining. The demand for novel marker targets electrical engineering and bioengineering for the fabrication of different semiconductor devices as well as electrochemical sensor or electrodes for water purifications [12]. From electrical properties should be mentioned high electrical resistivity, breakdown field strength above 10MVcm<sup>-1</sup> and thermal conductivity above 2000W\*m<sup>-1</sup>\*K<sup>-1</sup> should be mentioned [13]. These properties make diamond an interesting material for the fabrication of semiconductor devices that can be used for high frequencies, powers, temperatures, or voltages. With wide-bandgap 5.45eV, it is also well-suitable for defect engineering and optical applications (infrared windows, lenses, X-ray windows etc.) [14]. Another important property is also biocompatibility, so diamond-based sensors can be used for *in vivo* imaging [15].

#### 3.1.1 Crystalline structure

Diamond lattice is a face-centered cubic with sp3 covalent bonding. This sp3 bond makes diamonds an extremely hard and inert material. Figure 3 shows the elementary cell of the diamond crystal. There are two main aspects that are important for modelling, discussed in detail later. The diamond crystal facets have three main types of orientation:  $\{1,0,0\}$ ,  $\{1,1,0\}$ ,  $\{1,1,1\}$  (Figure 3).

The second important quality is the classification of diamonds by impurity content. The most common impurity present in the diamond lattice is nitrogen. Diamonds are classified into two groups, depending on the concentration of nitrogen and the incorporation form (Figure 4). Type I is a diamond that has a large amount of nitrogen impurity. Type I can be divided into Ia and Ib types. Ia stands for aggregate form (IaA), which can be mostly found in natural diamonds due to the long time needed for nitrogen

to aggregate. The Ib group does not contain aggregates, but it contains isolated substitutional nitrogen, which is mostly found in synthetic diamonds. The second main group is group II, where the concentration of nitrogen impurity is below the ~ 1ppm limit. Group IIb is a type II diamond with additional boron impurities. [16]



Figure 3 - Elementary cell of diamond with different crystal planes (100, 110, 111), visualized by author in VESTA software.



Figure 4 – The classification system of diamond, visualized by the author

#### 3.1.2 Nanodiamond synthesis

Nanodiamonds (ND) are crystalline fractions of diamond with dominantly sp3 bonded carbon structure of size  $\sim 1-300$  nm and can be found in different crystalline structural modifications (single, poly, nano and ultra-nanocrystalline structures) [17]. These modifications are related to the method of production, and they suit different kinds of applications (Figure 5). Today, two main types of diamond synthesis are used: detonation synthesis and ball milling.



Figure 5- Production method of different ND types, taken and modified from [18]

#### **Detonation synthesis**

Detonation synthesis is a process that produces a large amount of nanodiamond particles. The way of producing nanodiamonds was introduced by K.V. Volkov, Vyacheslav Danielenko and V.I. Elins from the All-Union Research Institute of Technical Physics (USSR) in 1963. This kind of synthesis enables the production of nanodiamond particles with the size starting from 2 to 10nm. The principle of the synthesis is that in the reactor, one lets explosives be imploded with a certain precursor. In a minute implosion, a high pressure (~20-30 GPa) and temperature (~3000-4000K)

are reached. The typical explosive mixture is TNT (2-methyl-1,3,5-trinitrobenzene) and RDX (1,3,5-trinitroperhydro-1,3,5-triazine), where the volume of TNT is ranging 40%-60%. The standard reactor volume (detonation chamber) is 2-5 m<sup>3,</sup> and it is loaded with 0.5-1kg of the charge. Detonation produces a mixture of ND particles (yielding 30-80% depending on detonation conditions), other carbon allotropes, and metallic impurities. The reactor volume must be filled with an inert medium. By type of medium, we can name the synthesis as "dry" if the medium is a mixture of a gas (usually N2, CO2, or Ar) or "wet" if the medium is water or ice. The medium also acts as a coolant of reaction. [18, 19], [20]

#### Ball milling

Ball milling is a cheap method to produce the NDs in large volumes from larger-scale diamonds, frequently using the HPHT micro diamonds as raw material. The method used is the vibration or rotation ball mill that makes the ball impact, grid and agitate the raw material that is crushed to the nanoscale particles. Created NDs nanoparticles with sizes ranging from 10nm to several um depending on the milling proceed [21, 22]. NDs that are produced this way can contain a large amount of fluorescence active defect (f.e. NV), which makes them suitable for bioimaging.

#### 3.1.3 Single crystal diamond synthesis

Single crystal diamond is a remarkable variant of diamond, showcases a predominantly sp3 bonded carbon structure. Its crystalline form stands distinguished among various structural modifications, including single crystal, poly crystal, nano crystal, and ultranano crystal structures. Here we present two main types of single crystal synthesis, High-pressure high temperature (HPHT) and Chemical vapour deposition (CVD).

#### **HPHT** synthesis

High-pressure high temperature (HPHT) synthesis is a method for producing single crystal diamonds that are usually bigger than 100µm. Graphite powder is compressed at around 6GPa pressure and temperatures around 1500°C to convert into a diamond in the presence of a catalyst. The phase change can also appear at lower temperatures and

pressures if exotic precursors are used. An example can be a reaction of carbon nanotubes with a NiMnCo catalysator that requires 4GPa and 1300°C. [18, 20]

#### **CVD** synthesis

Chemical vapour deposition (CVD) is the technique that is widely used for the deposition of diamond by homo or heteroepitaxy or for polycrystalline or nanocrystalline diamond growth from the gas phase, layers ranging from several nm thick to crystals of several mm of the thickness can be grown. Various CVD methods have been used for growing diamond layers under low pressure: hot filament CVD, plasma-enhanced CVD and many others [23]. Plasma-enhanced CVD (PECVD) is a widely used method for the deposition of diamond films these days. PECVD uses microwaves (usually with a frequency of 2.45GHz) that are emitted from a generator (typically 500 W to 10 kW power) to a reaction vessel where the ionized the carrier gas (mostly hydrogen) forms a plasma ball. In this carrier gas a few percent of carbon containing gas (usually methane) is mixed in which is then dissociated to carbon atoms and carbon radicals are then formed. The radicals are added on the growing diamond surface forming a thin layer. This process occurs at temperatures ranging from 700 to 1000°C and pressures from typically 3 to 30 kPa. Also, other gases can be added to the growing process, which will lead to a well-controlled concentration of impurities.

## 3.2. Nitrogen vacancy (NV) center

There are more than 500 known colour defect centers in the diamond [24]. Nitrogenrich diamond absorbs blue light and, therefore, have a yellow color. Single substitution form (P1) is a deep electron donor, around 1.7eV below the conduction band (CB). After irradiation with high-energy particles (electrons, protons), followed by hightemperature annealing, N forms a defect called the VN<sub>1</sub> (simply written as NV) defect. The nitrogen-vacancy (NV) colour center (Figure 6) consists of a nearest-neighbour pair of a nitrogen atom in a substitution position and a lattice vacancy [25]. It exists in two charge states, neutral (NV<sup>0</sup>) and negative (NV<sup>-</sup>), with ZPL (zero phonon line) emissions of 575 nm and 637 nm, respectively [26]. Nitrogen can also form more structures with a vacancy (f.e. H3 – vacancy + two nitrogens, H4 – two vacancies and four nitrogens), and this work is related to the most studied structure, NV. [14], [27]



Figure 6 - The elementary cell of a diamond with an NV defect, blue atom N stays for nitrogen, white V for lattice vacancy, and brown C atom for carbon. Visualized by author in VESTA software.

#### 3.2.1 Physical properties

The NV center is a crystallographic point defect. It is formed when one of the four carbon atoms is replaced by nitrogen (N), and the second one is replaced by an empty space (vacancy - V). The NV defect has trigonal symmetry  $C_{3V}$ . Nitrogen is an element from group V in the periodic table, so it has five valence electrons. Three of them are bonded to the neighbouring carbon atoms; two remain free and form a lone-pair orbital, which then interacts with the two free electrons from the carbon lattice induced by the vacancy. If we look closer to the nitrogen-vacancy complex, there are then five electrons localized on the NV defect (two from nitrogen, three from carbon atoms). Each carbon atom in the regular lattice has sp<sup>3</sup> symmetry. During the growth on the (100) facets, the NV can be incorporated in 4 crystallographic directions that are nearly equally populated. Preferable growth was reported, but only in {1,1,1} diamond. Around 97% of all NV growth can be achieved in one direction. [14, 16, 28]

The NV center can exist in two charge states (NV<sup>-</sup>, NV<sup>0</sup>), but we expect that there can also be a third charge state: NV<sup>+</sup> [14]. The charge of the defect mainly depends on the environment. Some impurities that are nearby can act as electron donors and can donate one electron to the vacancy, which leads to the changing of the charge state from NV<sup>0</sup> to NV<sup>-</sup>. The total number of electrons in the NV<sup>-</sup> defect is then six. We can write the equation for donation electron where the donor center is, for example, P1:

$$2N^0 + V^0 \to NV^- + N^+ \tag{3.1}$$

(3.1)

The existence of the NV charge state depends on the local environment, specifically the donor centers. Charge photoconversion is possible via direct illumination of negatively charged NV<sup>-</sup>, where one electron is lost due to the two-photon ionization to the conduction band (NV<sup>-</sup> to NV<sup>0</sup> conversion) or recombination of the NV<sup>0</sup> by ionization of the electron from the valence band (NV<sup>-</sup> to NV<sup>-</sup> conversion). [14, 27].

#### 3.2.2 Formation of defect

The NV defect can be formed by three main techniques: irradiation, ion implantation and incorporation during the CVD growth.

#### Irradiation

Irradiation is one of the most common techniques for manufacturing NV defects in diamonds that already contain some N impurities. In this process vacancies are formed that diffuse towards N atom and form NV centre. Both type I and type II diamonds can be used. The principle of the irradiation method is to focus the beam of ions or electrons on the sample. For example, a large quantity (1.4 g) of diamond powder was prepared in the Nuclear Physics Institute of the ASCR, v. v. i., Prague, Czechia, by irradiation in the cyclic relativistic electron accelerator (Microtron) with the surface charge up to 3C/cm<sup>2</sup> using collimated accelerated electrons extracted with monochromatic energies 6-25 MeV [29]. After (or during) irradiation, the sample is annealed at temperatures higher than 650°C (above this temperature, vacancies start to migrate). Migrating vacancies are

trapped by nitrogen and form stable NV centers. The process usually takes around 1-2 hours, and typical temperatures are in the range of 700 - 800°C. [14]

#### Ion implantation

Ion implantation uses  $N^+$  to implant N toms and at the same time produce vacancies that combine in NV centres. After the exposure, the sample is heated to temperatures around 850°C, which causes the vacancy migration. The vacancy reacts with the  $N^+$  ion (or N atom) and forms a stable NV complex. This technique is mainly used for IIa diamonds, which have very low nitrogen impurities. However, ion implantation has a main problem, that ions cause collateral damage, forming interstitials and other defects, reducing the crystal quality. [14]

#### Incorporation during CVD growth

The NV defects can also be produced during the CVD growth. The formation of the NV is spontaneous when nitrogen is present in the deposition chamber. Usually, it is caused by adding the N2 to the feed gas. Production of the NV is determined by the growth condition, f.e. the amount of nitrogen in the chamber, the temperature of the sample and the pressure [14]. During the growth vacancies are formed as well and combine to the NV centre. The main disadvantage is a low ratio of 1:100 of the NV formed with respect to present N atoms. [16]

#### 3.2.3 Fluorescence of NV

The NV defect has the potential to be widely used as a fluorescence marker. The NV does not show any photo-bleaching because the defect is embedded in the crystal lattice. Diamond biocompatibility makes the NV point defect an interesting tool for *in vitro* cellular imaging. The fluorescence spectrum of the NV center is the sum of NV<sup>0</sup> and NV<sup>-</sup> charge state fluorescence ranging from 575 nm to ~750 nm. The NV- luminescence peaks around 690nm. In the emission spectrum, two significant peaks can be found corresponding to the Zero phonon line (ZPL) of NV- (637nm) and ZPL of NV<sup>0</sup> (575nm). Broad red-shifted phonon sideband for NV<sup>-</sup> is 640-750nm. [27, 30]



Figure 7 - Emission spectra of NV defect for different laser power stimulation (0.01- black trace, 0.3 – green trace, 3W – blue trace). The peak at 573nm is equal to the ZPL of the NV<sup>0</sup> charge state, and the peak at 637nm is equal to the ZPL of the NV<sup>-</sup> charge state [27]

#### 3.2.4 Electronic structure of NV defect

Two main charge states of this defect, neutral NV<sup>o</sup> and negative NV<sup>-</sup>, are known from spectroscopic studies using optical absorption [31, 32] and photoluminescence (PL) [33], NV- can also be detected by electron paramagnetic resonance (EPR) [34–36] and optically detected magnetic resonance (ODMR) [37].

#### NV<sup>0</sup> charge state

The neutral charge state NV<sup>0</sup> contains five electrons. NV<sup>0</sup> can form 3 electronic states, doublets <sup>2</sup>E, <sup>2</sup>A and quadruplet state <sup>4</sup>A<sub>2</sub>. The symbols "A" and "E" refer to specific point group symmetry labels. The label "A" represents a symmetric state, indicating that the wave function remains unchanged under certain symmetry operations (such as rotations or reflections). The label "E" represents the identity operation. The <sup>2</sup>E state is associated with the excited state of the NV center, while the <sup>2</sup>A state is associated with the ground state. Energy spacing between doublets is 2.56eV (ZPL=575nm), and the

position of the quadruplet state is unknown. The  $NV^0$  state does not show optically detected magnetic resonance (ODMR), such as the quality of the  $NV^-$  state (e.g. the electronic spin can not be optically read). [27]



Figure 8 - Electronic structure of NV<sup>0</sup>. Curly arrows stay for the radiative recombination, and labels stay for the doublet states ( ${}^{2}A$ ,  ${}^{2}E$ ) and quarter state ( ${}^{4}A_{2}$ ). Visualised by author.

#### NV<sup>-</sup> charge state - overview

As mentioned before, the  $NV^-$  charge state contains six electrons, two from N, three from neighbouring C atoms, and one from the nearest environment. Two unpaired electrons form one ground state singlet and one ground state singlet and similarly their excited states are one triplet and one singlet; see Figure 9.

The distance between the valence band (VB) and the conduction band (CB) in a diamond is 5.47eV [38]. The energy distance between the ground triplet state <sup>3</sup>A and the excited state triplet <sup>3</sup>E is 1.945eV (zero phonon line (ZPL) is 637nm). Direct excitation from the ground state <sup>3</sup>A to CB is possible with an energy of 2.6eV [6]. Therefore, the position of the excited triplet state <sup>3</sup>E is ~2.6-1.95=0.65eV below CB. The energy difference between the ground singlet state <sup>1</sup>E and the exited state <sup>1</sup>A single was measured as 1.190eV [25] (ZPL=1042nm). The energy difference between the singlet

<sup>1</sup>E and the triplet ground state <sup>3</sup>A is unknown, but it is believed to be approximately  $\sim 0.7 \text{eV}$  [27]. The energy difference between singlet and triplet states arises due to the exchange interaction and spin-orbit coupling [39].

The sublevels of the  ${}^{3}A_{1}$  triplet correspond to the spins states  $m_{s}=0$  and  $m_{s}=\pm 1$  and zero-field energy splitting (ZFS) between the  $m_{s}=0$  and  $m_{s}=\pm 1$  corresponds to microwave frequency  $D_{GS}=2.87$ GHz [30] (at room temperature). A similar fine structure is for the  ${}^{3}E$  state, where the zero-field splitting parameter between the spin states 0 and  $\pm 1$  is  $D_{ES}=1.425\pm 0.003$ GHz. [40].



Figure 9 - Electronic structure of NV-. The excitation transition is indicated by the solid green arrow, the radiative transition is indicated by the curly arrows, the non-radiative transition is marked as dashed arrows. The label stays for the ground  $({}^{3}A_{2})$  and excited  $({}^{3}E)$  state triplet and for excited  $({}^{1}A_{1})$  and ground metastable singlet state. D parameters stay for the zero-field splitting parameter of the ground state (D<sub>GS</sub>) or excited state (D<sub>ES</sub>). Visualised by author

#### Ground state scheme of the NV<sup>-</sup>

Under the interaction with the magnetic field, the level structure of  ${}^{3}A_{1}$  can be described by the Hamiltonian in equation (3.2). The total **Hamiltonian** contains three parts: the electronic spin part  $\widehat{H}_{S}$ , the hyperfine coupling with nitrogen nuclear spin (I=1 for  ${}^{14}N$ )  $\widehat{H}_{SI}$  and the nuclear spin part  $\widehat{H}_{I}$ . [30]

$$\widehat{H_{tot}} = \widehat{H_S} + \widehat{H_{SI}} + \widehat{H_I}$$
(3.2)

Each part of  $\widehat{H_{tot}}$  can be written as:

$$\widehat{H_S} = D_{GS}S_Z^2 + E\left(S_x^2 - S_y^2\right) + g_S\mu_B\vec{B}\cdot\vec{S}$$
(3.3)

$$\widehat{H_{SI}} = A_{\parallel}S_{z}I_{z} + A_{\perp}\left(S_{x}I_{x} + S_{y}I_{y}\right) \tag{3.4}$$

$$\widehat{H_I} = PI_z^2 - g_I \mu_N \vec{B} \cdot \vec{S} \tag{3.5}$$

All constants in the Hamiltonian equation (3.3)-(3.5)are shown in Table 1. In equations (3.3) (3.5), the Pauli spin matrixes are used ( $S_x S_y S_z$ ). For S=1, these have the form [41]

$$S_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \ S_y = \frac{1}{\sqrt{2i}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}; \ S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$
(3.6)

Pauli vector  $\vec{S}$  is defined as [41]

$$\vec{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$
(3.7)

The eigenstates of the Hamiltonian are shown in Figure 10a. Figure 10a shows the fine structure of  ${}^{3}A_{1}$ , the energy difference between m<sub>s</sub>=+1 and m<sub>s</sub>=-1 is determined by the external **magnetic field**. This effect is known as the **Zeeman splitting**. Energy distance when the magnetic field is presented can be estimated by formula  $2g_{s}\mu_{B}B_{z}$  where  $g_{s}$  is electron spin factor,  $\mu_{b}$  is Bohr magnetron, and  $B_{z}$  is the magnetic field part projected to the NV axis. Values of the constant  $g_{s}$  and  $\mu_{b}$  can be found in Table 1. We can estimate that the shift of the m<sub>s</sub>=-1 and m<sub>s</sub>=+1  $\approx$  28MHz/mT. In the hyperfine structure, we can observe the influence of the nitrogen 14 nuclear spin (M<sub>I</sub> = 1) that splits into the fine structure of the eight sublevels. Figure 10b shows all 24 possible magnetic resonances that can appear due to 4 NV orientations, 2 m<sub>s</sub> =0, m<sub>s</sub> = ±1, and the 3 m<sub>I</sub> numbers. This sensitivity to the external field makes the NV defect a tool for vector magnetometry that can measure the magnitude and direction of the external magnetic field. [27, 30]



Figure 10 – A: Structure of GS NV- with fine (Zeeman) and <sup>14</sup>N hyperfine structure. Allowed transitions are marked by double arrows. At fine structure, the influence of the external magnetic field  $B_z$  can be seen. B: snows change in spectra of fluorescence that corresponds to transition for four possible orientations of NV and three different <sup>14</sup>N m<sub>I</sub> levels. A: Visualised by author, B measured at 001 Ib crystal with 2ppm of NV-

Parameter  $D_{GS}$  stays for the axial Zero Field Splitting (ZFS) parameter that was estimated at a value of 2.87GHz at room temperature [42]. The shift of the value of the  $D_{GS}$  can be used for the calculation of the local temperature. **Temperature** dependent  $D_{GS}(T)$  can be described by the following equation [42]:

$$\frac{1}{D_{GS}} \frac{dD_{GS}}{dT} \approx \frac{1}{D_{GS}} \frac{d\langle (r_{12}^2 - 3z_{12}^2)/r_{12}^5 \rangle}{dR} \frac{dR}{dT}$$
(3.8)

Where  $r_{12}$  is the displacement between the two spins,  $z_{12}$  is the component of  $r_{12}$  along the N-V symmetry axis, and R is the distance between two basal carbon nuclei [43]. The effect of thermal expansion on  $\langle (r_{12}^2 - 3z_{12}^2)/r_{12}^5 \rangle$  can be estimated by treating spins, localised near the basal carbon atoms [44], with p-orbitals oriented along axes 110° apart [45].

This effect is expected due to the spin-spin coupling between two unpairing electrons forming the center [44]. The estimated thermal shift of the  $D_{GS}$  parameter from a calculation from *an initio* values [46] and the experimental [43] measurements gives us a value of -74.2 kHz/K. The temperature shift effect in energy level position and ODMR spectra is depicted in Figure 11.



Figure 11 - A: Graphical representation of changing of DGS parameter for the two different temperatures T1 and T2, B: shows the shift in the normalized ODMR spectra for two different temperatures T1=283K, T2=326K. A: visualised by author, B: taken and modified from [43]

As it was mentioned before, the external field magnetic field caused the Zeeman effect, leading to the separation of the  $m_s=\pm 1$  to the two levels  $m_s=+1$  and  $m_s=-1$ . When the field Bz= $\pm 102.4$ mT energy level  $m_s=-1$  degenerates with the energy level  $m_s=0$  and creates a mixed state, causing a sharp drop in the fluorescence spectra, indicates Ground State Level Anti Crossing (**GSLAC**). This microwave free method improves the fidelity

of the classical readout methods by  $\sqrt{3}$  [47]. Schema of the GSLAC and fluorescence spectra are shown in Figure 12. Traces of fluorescence near the GSLAC event show the additional features that can be attributed to the cross-relaxation with the nearby spin bath [48]. GSLAC contrast trace showing narrow magnetic resonance (FWHM  $\approx 38\mu$ T) as a function of  $B_z$  field centred around zero transverse field [49]. More about the usage of the GSLAC method can be found at Chapter '3.3.3 Ground State Level Anti-Crossing assisted spin state readout'.



Figure 12 - A: Graphical representation of the Zeeman splitting with GSLAC when the  $B_z$  field is applied. B- shows the fluorescence spectra as a function of applied  $B_z$  with the sharp drop in fluorescence intensity at 102.4mT caused by GSLAC. Taken and modified from [49]

Constant	description	value	reference
$\mu_B$	Bohr magneton	5.788e-5 eV/T	[25]
$\mu_N$	Nuclear magneton	3.152e-8 eV/T	[25]
$D_{GS}$	Axial ZFS parameter	2.87 GHz	Eqn. (3.8)
<i>gs</i>	Electron-spin g- factor	2.003	[25]
<i>g</i> i	Nuclear-spin g- factor	0.403	[25]
Р	Quadrupole splitting parameter	-4.95 MHz	[25]
Ε	Transverse ZFS parameter	kHz-MHz	[25]
A //	Axial hyperfine constant	-2.16 MHz	[25]
$A_{\perp}$	Transverse hyperfine constant	-2.7 MHz	[25]

Table 1 - Constant used in the ground state (GS) Hamiltonian

## 3.3. Electron spin resonance (ESR)

Electron spin resonance (ESR), also known as Electron Paramagnetic Resonance (EPR), is a method for studying materials that have unpaired electrons [1]. In the presence of an external magnetic field, the electron's magnetic moment aligns itself either antiparallel or parallel to the field, each alignment having a specific energy due to the Zeeman effect. An unpaired electron can change its electron spin by either absorbing or emitting a photon of energy such that the resonance condition is obeyed. ESR is widely used in various fields such as physics, chemistry, archaeology, geology, environmental science, biology, biochemistry, pharmacology, medicine, and industry to study both static properties and dynamic processes in almost any system containing radicals (i.e., molecules with unpaired electrons) [50]. ESR is measured in EPR spectrometers, detecting the spin concentrations down about typically 10<sup>12</sup> cm<sup>-3</sup>. However, the EPR can be directly performed even on a single NV centre by using light excitation combined
with a MW field application. Two main methods for detecting NV ESR under optical excitation are used in the thesis: the Optical Detection of Magnetic Resonance (ODMR) and newly developed methods by UHasselt and CTU: the photocurrent detected magnetic resonance (PDMR). Both methods can be used with pulsed or continuous (CW) microwaves [27, 30].

Figure 13 shows the typical ODMR spectra of the NV center. Spectra are obtained by scanning the frequency of the MWs. When the MW frequency matches resonantly the energy difference between ground state spin sublevels (ZFS), the PL intensity is reduced, and a decrease of output PL signal can be seen (discussed more in detail below). The central  $m_s$ = +- 1 resonance can be split by an external magnetic field into two transitions. The first one (left one) is caused by the transition  $|0\rangle\rightarrow|-1\rangle$ , and the second one (right one) is due to transition  $|0\rangle\rightarrow|+1\rangle$ . The energy difference between resonance lines is equal to the Zeeman splitting of energy levels of the GS.



Figure 13 - ODMR spectra of the NV center for different values of external magnetic field 8.3, 5.8, 2.8 and 0mT. Drop in fluorescence at frequency  $\omega 1$  stays for transition  $|0\rangle \rightarrow |-1\rangle$ ,  $\omega 2$  between the  $|0\rangle \rightarrow |+1\rangle$  [30]

### 3.3.1 Optical readout

Continuous-wave optically detected resonance (CW-ODMR) is a simple and widely used ESR method. In the CW method, the optical excitation, the MW spin driving, and the photon readout occur continuously and simultaneously (see Figure 13).

The laser excitation of the NV center transfers electrons to the higher excited state, from which they recombine either radiatively or non-radiatively and end up in the  $m_s = 0$  state. It is called spin polarization. The laser light then continuously polarizes the NV-ground state  $m_s = 0$  (GS0, bright state), MW near-resonant frequency drives the population to ground state  $\pm 1$  (GS $\pm 1$ ). From this sublevel, the electron is excited to the  $m_s = +1$  excited state, and it returns to the ground state with 70% radiatively and 30% non-radiatively (dark transition). The ratio between the bright and the dark transition is called the spin contrast.

This transition has a 30% reduced fluorescence (radiation relaxation transition from ES to GS state) due to non-radiative decay through the metastable state. Figure 14 shows a typical CW-ODMR confocal photoluminescence setup. A confocal microscope is an optical system that uses a single optical objective for focusing and collecting fluorescence light. By placing the sample on the movable stage and directing light through filters and a detector, the setup is able to visualize and capture a fluorescence image of the sample. This setup is also widely used in life and material sciences [51]. The laser beam is guided and focused by optical elements to the sample, and photons emitted from the NV center in the sample are focused on the detector, typically the avalanche silicon photodiode (APD). The advantage of the ODMR is that this method has been known since the 1920s (Hg vapor, Fermi, Rasetti) [52]. Many studies have already used the ODMR for different kinds of applications; therefore, this method is well-developed. The disadvantage of this method is the low efficiency of photon collection due to the high refraction index of the diamond. In the case of the flat diamond efficiency, it is ~4%. If a SIL (solid immersion lens) is fabricated from diamond around the NV centre, the maximum collection efficiency about ~50% can be reached. [6]



Figure 14 - Schema of the CW-ODMR method. Excitation laser 532nm goes through the mirrors and is the objective of the sample. Photons from the fluorescence of the sample go through mirrors and a green filter (green rectangle) to the avalanche photodiode (APD). NV is stimulated by the laser 532nm (green light path) and microwave in the sample and emits fluorescence photons (red light path). Visualised by author.

#### 3.3.2 Photoelectric readout

Photoelectric-detected magnetic resonance (PDMR) has been developed jointly in the last decade for the detection of ESR by UHasselt and CTU (Prof. Nesladek's group). The principle of this method is that an electron can be promoted from ground state of  $NV^{-}$  (GS) charge state to conduction band (CB) by two-photon ionization (one photon is required for the excitation electron to the excited state, and the second photon is required for the excitation from excited state (ES) to CB). In this process,  $NV^{-}$  loses one electron and becomes  $NV^{0}$ . This system can be reinitialized by pumping the electron from VB to  $NV^{0}$ , and then NV0 is transformed back into  $NV^{-}$ . This process is called back conversion. These charge carriers are transported under a bias voltage to the collecting electrodes. Unlike ODMR, the PDMR requires a diamond sample to be electrically connected. Figure 15 shows one possible chip for the PDMR readout. Electrodes are fabricated on the diamond surface by a standard lithography technique and are connected to the source of the bias voltage via the SMA ports  $p_{3}$  and  $p_{4}$ . The current is measured by a lock-in amplifier. Microwave is connected via port  $p_{1}$ , and they

are terminated at  $p_2$  with a 50 $\Omega$  load. PDMR leads to increased detection efficiency, higher spatial resolution, and easier on-chip integration compared to the ODMR technique. The absence of optics for photon collection unlocks the possibility of miniaturizing the quantum chip size (chip size ~50nm can be achieved). [6]



Figure 15 - Schematic representation of chip conformation, PCB with diamond crystal in center excited by 532nm laser,  $p_{1-4}$  stays for SMA port,  $p_1$  is used for MW source,  $p_2$  is connected to 50 $\Omega$  terminator,  $p_{4-3}$  is connected to bias voltage and to the detector. Visualized by author.

#### 3.3.3 Ground State Level Anti-Crossing assisted spin state readout

One of the prominent advantages of the Ground State Level Anti-Crossing (GSLAC) assisted readout lies in its utilization of the fluorescence variation to obtain the value of external magnetic field close to the value of external magnetic field close to the GSLAC value (~100 mT). The circumvention of the usage of microwaves avoids negative effects such as spurious harmonics within the measurement or the undesired propagation of microwave-induced heat, which could introduce temperature fluctuation in the signal that limits the usage of the sensor [53]. Sensors based on the GSLAC method have already been used in various applications, ranging from magnetometry [30], nuclear magnetic resonance (NMR) spectroscopy [31], optical or

hyperpolarization [54]. These applications are interesting in the biomedical fields, where high-power microwave driving is undesirable. Photoelectric Detection of Magnetic Resonance suing GSLAC was developed in this thesis.

## 3.4. Applications

## 3.4.1 Magnetometry

One of the widest application fields of diamond-based sensors is the detection of low external magnetic fields. Current magnetometer sensors can achieve few femto Tesla resolutions (f.e. SQUID, SERF), but they need to operate at low temperatures, high vacuum levels, etc.. the NV-diamond sensor can work at pressures to 60GPa [55] and temperatures from cryogenic to 700K [56]. Diamond-based sensors allow sensing signals in DC or AC mode up to 50MHz. Both AC and DC sensitivity are limited by the NV<sup>-</sup> relaxation time [47]. DC sensitivity is limited by the inhomogeneous dephasing time  $T_2^*$  (~1µs), AC sensitivity is limited by longitudinal relaxation time  $T_1$  and homogeneous spin decoherence time  $T_2$ . Over the past years, various magnetic sensing methods using the NV centers in bulk, at the diamond surface and as well in diamond nanoparticles have been developed. [57]. Various recent studies show the usage of the single NV quantum sensor for the detection of nuclear spins [58], external single electron spin [59] or the concept of the single molecule 3D nano MRI that uses the quantum imaging technique with the super-resolution [60]. The nano MRI technique shows promising new technology that can be used for the study of chemical reactions in small volumes (drug synthesis) or for non-invasive imaging of the interior of living cells.

### **DC magnetometry - ESR**

One of the simplest methods for measuring the static magnetic field is CW magnetometry, which extracts the shift of the ESR resonance under the application of a measured external magnetic field. Eqns. (3.3)-(3.5) show that the Zeeman splitting is proportional to the projection of the magnetic vector to the NV symmetry axis. When external known field  $B_0$  is applied, the ESR spectrum splits into four pairs of resonant peaks, one for each corresponding to one NV orientation. When an unknown magnetic field  $\delta B$  is present, the ESR resonances will shift depending on the field strength and the

field orientation. The external unknown  $\delta B$  vector field can be calculated by using three different NV orientations. [30]



Figure 16 - Example of ESR-based magnetometry a- show a sketch of 4 possible NV orientations, the known external magnetic field  $B_0$ , the unknown magnetic field  $\delta B$  and total magnetic field  $B_{net}$  b- ESR spectra, blue for the known magnetic field  $B_0$ , red for total magnetic field  $B_{net}$  [30]

#### AC magnetometry

In place of CW, laser pulses and MW pulses are used for AC magnetometry. The widely used method is Hahn echo (also noted as spin echo) [57]. The pulse protocol starts by preparing the superposed state between Ms = 0 and Ms = +-1 by MW  $\pi/2$  pulse, followed by a second pulse ( $\pi$ ) to invert the accumulated phase, and then the second  $\pi/2$  pulse is applied. Hahn echo enables measuring the AC field that is determined by the full pulse sequence of the duration  $\tau$  (with ideal frequency  $f_{AC}=1/\tau$ ), the alternative is the Ramsay protocol. [30]

### 3.4.2 Biomedical application

Nanodiamonds containing fluorescent Nitrogen-Vacancy (NV) centres are nanodiamond particles, of which, by recording NV spectral shifts or changes in spin

relaxation rates, various physical and chemical quantities can be measured, such as the magnetic field, orientation, temperature, radical concentration, pH or even NMR. This turns NV-nanodiamonds into nanoscale quantum sensors, which can be read out by a sensitive fluorescence microscope equipped with an additional magnetic resonance upgrade [61].

These two main properties make diamonds a promising material for *in vitro and in vivo* sensing. ND particles have been used as fluorescence markers since the late 2000s. ND markers do not show negative phenomena such as photobleaching or photo blinking. Sub diffraction of ND size allows tracking of intercellular processes with high spatial-temporal resolution and high contrast from the surrounding environment [14]. Another interesting applications is nano-Magnetic Resonance Imaging (nano-MRI) wen placing FND in chemical or biological environment. This method has the potential to revolutionize many chemical analyses and bio-medicine. This chapter is dedicated to up-to-date research studies and their impact on the usage of diamond materials in the biomedical field.

#### Bioimaging

Biocompatibility, fluorescence without bleaching and operating at room temperature make NDs a promising candidate for fluorescence markers. In addition, the majority of fluorescence emission is in the near infra-red region that overlaps the biological window, and it has a longer wavelength than cell autofluorescence. These facts make NDs a suitable tool for bioimaging in tissues and living cells *in vivo* applications. In the past, several studies[62–64] used NDs as fluorescence markers in cells and tissues of different creatures (*Caenorhabdis elegans, Escherichia Coli, Mus musclus, Sus domesticus*). Research on *C. elegans* [62] shows that NDs, when they are injected, can stay in the organism for its whole lifespan and that there is no difference in lifespan compared to the control group. When the worms were fed by dextran-coated NDs and with bacteria *E. Coli* that contains ND (particles with a diameter of about 40nm ), NDs were concentrated at the intestinal wall and lumen (Figure 17). *C. elegans* that contain NDs from digesting the *E. Coli* was under continuous measurement for 48 hours. Measurement showed no photobleaching of NDs. In general, no harmful effect of the NDs on the worms was observed. A study [64] performed *in vivo* on laboratory mice

showed a preferable accumulation of the injected functionalized NDs (ND-PG-Cy7, Nanodiamond-PolyGlycol-Cyanine7) onto the tumour surface, increasing the total fluorescence over time. The study shows the usage of functionalized NDs for the high-resolution imaging of the tumour morphology over the eight days. Another study [63] examined the usage of functionalized NDs for selective cell therapy *in vivo* in miniature pigs. NDs were coated with HAS (human serum albumin) with attached MSC (Mesenchymal stem cells) and injected into the specimen. The study shows background-free imaging of the NDs and quantitative tracking of human MSC beyond the rotten model with single-cell accuracy. As mentioned FND can be combined with spin detection this combing tracker with local NMR or EPR:



Figure 17 – Epifluorescence/DIC-merged images of *C. elegans* fed with dextran-coated NDs (A), BSA-coated NDs (B-C), fed with *E. Coli* that contain NDs. Blue markers show NDs in intestinal cells, and yellow markers show NDs in the lumen. The scale bars are 50µm. Taken from [62]

#### Drug delivery

One of the important characteristics of NDs that was not mentioned before is their good dispersibility in the water, and the large surface area makes this nanomaterial suitable for targeted drug therapy. Drugs can be chemically or physically attached to the ND surface by bounding to the functional group at the surface. The principle of the targeted/non-targeted drug delivery (in this case, anti-tumour drug Dox (doxorubicin) is depicted in Figure 18. Most of the studies aim to deliver anti-tumour drugs to the tumour cell lines (HeLa, HepG2, MCF-7). In [65], the authors compare the Dox that was cell targeted with nanocomposite material ND-UCNP (Nanodiamond-NaYF4:Yb,Er) with a non-targeted application. Results show high concentration dependent anti-tumour activity in the case of a targeted application that opens the possibility of reducing the dose of the drug in therapy, which may decrease the side effects of the treatment. In another complex study [41], authors test uptake and cytotoxicity of the ND-PEG-GLY-DOX complex (Nanodiamond-polyethylenglycoleglycine-doxorubicin) at tumour cell lines in vivo. The authors achieved a pH-induced target drug delivery system in an intercellular lysosome environment that provides a new way of exploring a theragnostic drug delivery system.



Figure 18 – Schematic representation of transporting of Dox drug to the cell with method 1) NDs-Dox complex via endocytosis. 2. Passive diffusion of Dox via the cell membrane, 3. Transport Dox via the ABC transporter proteins. Taken from [67]

### 3.4.3 Temperature sensing

NV-based sensors can also be used to measure precise physical properties like temperature strain or electric fields with nanoscale precision. For temperature, a wide-range temperature sensor (~90K) with a resolution of a few mK was reported [68, 69]. The advantage of the usage of NDs as a temperature probe is the possibility of monitoring the probe's close environment and sub-cellular temperature gradient, which is essential for the understanding of temperature-involved fundamental functions like the genesis of an action potential or cell metabolism. The first pioneering study that uses NDs as a quantum temperature probe has been published recently [70]. A study [70] finds evidence of temperature increase and the firing activity of cultivated hippocampal neurons at single-cell level monitoring. The combination of MEA can create a complex

tool for the synchronized monitoring of cellular metabolic activity with the propagation of electromagnetic signals.



Figure 19 – Confocal fluorescence micrograph of hippocampal neurons. The cytoplasm is stained green, the red emission is from NDs, and the yellow is for internalised NDs. Taken from [70]

## 3.5. Summary

The negatively charged nitrogen-vacancy defect in diamond is widely used due to its unique opto-magnetic properties. The position of the energy levels in the ground state of the NV<sup>-</sup> is sensitive to crystal lattice stress and temperature. The presence of an external magnetic field causes splitting of the energy level in GS  $|\pm1\rangle$  to  $|+1\rangle$  and  $|-1\rangle$ . This energy level separation is known as the Zeeman split and is proportional to the strength of the magnetic field [30]. Broadening of the energy gap between the GS  $|0\rangle$  and GS  $|\pm1\rangle$  can be used for precise temperature detection [43]. This property makes NV-based sensors a promising tool for ultra-sensitive metrology that is fully functional in a wide range of temperatures (up to 800K) with sub-kelvin resolution [56]. In combination with the biocompatibility of the diamond, it becomes possible to develop sensors *in vivo* (f.e. for tracking the cellular processes, nanoscale biological imaging or drug delivery) [62, 65, 66, 71].

## 4. METHODS AND MATERIALS

The thesis deals with the concept of NV quantum sensing theoretically as well as experimentally. The theoretical part consists of the in-depth exploration of the photon and charge carrier photodynamics inherent in the NV defect and its interaction with the crystal environment, such as lattice defects. The investigation was performed using the MatLab software, which provides a robust framework for analysing complex NV photodynamics. In the experimental section, the focus is directed to the validation of the experimental model on the single NV defect measurements. In the experimental section, the focus is directed to the validation of the experimental model on the single NV defect measurements verify theoretical models and elucidate the potential applications in diverse fields. Furthermore, we tested the quantum probes for sensing physical fields (in particular temperature) in complex biological systems, notably neurons.

## 4.1. NV defect model

A full understanding of the generations of the photoluminescence or photocurrent signals from the NV defect is crucial in the sensing concept. Here, we model NV defect as a six-energy level system within a one-electron approximation. NV<sup>-</sup> charge state considers five energy levels: The  $m_s=0$  and  $m_s=\pm 1$  for the unsplit Ground State (GS) and the Excited State (ES) triplet states, the metastable-state singlet is approximated by the one energy level since the singlet  ${}^{1}A_{1}$  has a short relaxation time which does not play a significant role in the modelling. We consider the presence of zero external magnetic field, which means there is no Zeeman splitting presented. The NV<sup>0</sup> charge state is presented as a one level system (the inner dynamics of the NV<sup>0</sup> are not conceded is taken into the account by using effective photoionization time). Photoionization is realized from the valence band to the NV<sup>0</sup> charge state by the two-photon process determined by the eqn. (4.5). In this process, the extra electron is photoionized to the NV<sup>0</sup> and the defect changes its charge to the NV<sup>-</sup> and a hole charge carrier is produced in the valence band (VB). The electron that is responsible for the charge state transition can end at the GS (with a probability~80%) or at the metastable-state singlet (with a

probability~ 20%) [72]. The second part of the defect ionisation consists of the excitation of the electron from the GS of the NV<sup>-</sup> to the ES by a single photon, in ES the electron has the possibility to excite the second photon to the conduction band (CB) and NV<sup>-</sup> change the charge state back to the NV<sup>0</sup>. One-photon excitation is the principle of the ODMR signal (low laser power regime), while two-photon ionisation is the principle of the PDMR signal generation (high laser power regime). The process generates the free electron in the CB. If the electron in ES is not excited, the electron will relax by the radiative (emitting fluorescence photon) or non-radiative (via the metastable-singlet) way back to the NV<sup>-</sup> GS. All the possible transitions are shown in Figure 20.



Figure 20 - Energy level system of NV defect. Levels 1-2 represent the GS of NV<sup>-</sup>, 3-4 the ES of NV<sup>-</sup>, 5 the metastable state (MS), 6 denotes the NV<sup>0</sup> charge state, VB denotes the valence band and CB the conduction band. The colour of the arrows defines excitation (green) and relaxation (red). The solid lines relate to ionisation or radiative relaxation, and the dashed lines relate to non-radiative relaxation.  $k_i$  denotes the following transitions between energy levels of NV<sup>-</sup> charge state: k<sub>1</sub> (GS to ES), k<sub>2</sub> (ES to GS), k<sub>3</sub> (ES m<sub>S</sub>= 0 to MS), k<sub>4</sub> (ES m<sub>S</sub>=±1 to MS), k<sub>5</sub> (MS to GS m<sub>S</sub>=0), k<sub>6</sub> (MS to GS m<sub>S</sub>=±1). *ion*<sub>1</sub> denotes the ionisation transition from ES of NV<sup>-</sup> to CB, *ion*<sub>2</sub> the ionisation transition from VB to NV<sup>0</sup> charge state, *rec*<sub>1</sub> stands for the recombination transition between GS of NV<sup>-</sup> and VB, *rec*<sub>2</sub> for the recombination transition

between the CB and NV<sup>0</sup>,  $k_{mw}$  stays for the microwave transition between the energy levels (m<sub>s</sub>=0, m<sub>s</sub>=±1) of the GS.

#### 4.1.1. NV<sup>-</sup> ground state manipulation

Spin dynamics of the ground state triplet state can be divided into transitions due to the resonant microwave application. The spin relaxation rate 1/T1 is where T1 is longitudinal relaxation, and the k rate represents excitation and relaxation to or from other energy levels. Microwave (MW) manipulation can be done with a pulse sequence or by continuous stimulation (CW). The transition from  $|0\rangle \rightarrow |\pm 1\rangle$  can be achieved by applying resonant MWs with a frequency equal to ZFS (energy gap between  $|0\rangle$  and  $|\pm 1\rangle$ ). This two-level system can be described by a semi-classical model. The model shows the dependency of the population of spin sublevels and the coupling strength of the MW field. This strength is given by the Rabi frequency equation: [73]

$$\Omega_R = \frac{g_e \mu_B}{\hbar} \cdot B_{MW} \tag{4.1}$$

Where  $\hbar$  is the reduced Planks constant,  $B_{MW}$  is the amplitude of the applied MW field (the constants are indicated in Table 1). The MW stimulation is only effective if the MW vector is perpendicular to the NV axis. The probability of  $|0\rangle$  is written as [74]

$$p_{(\omega)} = \frac{1}{2} + \frac{\Omega_R^2}{2\Omega^2} \cos(2\pi\tau\Omega)$$
(4.2)

Where  $\Omega$  is the generalized Rabi frequency [73]

$$\Omega = \sqrt{\Omega_R^2 + \Delta^2} \tag{4.3}$$

Where  $\Delta$  is the detuning parameter, the transition rate from  $|0\rangle \rightarrow |\pm 1\rangle$  and  $|\pm 1\rangle \rightarrow |0\rangle$  can be described by the effective rate  $k_{MW}$ . [75]

$$k_{MW} = k_{MW0} + \frac{2\Omega/T_m}{(2\Omega)^2 + (1/T_m)^2}\Omega$$
(4.4)

Where  $k_{MW0}$  is a population relaxation rate that can be computed from the spin-lattice relaxation time  $T_1$ ,  $k_{MW0} = (1/T_1)/2$ . The total dephasing rate  $T_m$  can be calculated from the spin dephasing  $T_2$  and the ionisation rate k(1). The total dephasing rate is then  $1/T_m = 1/T_2 + k(1)$ . [75]

### 4.1.2. Photodynamic model of the NV defect

The photodynamics of the NV level occupation can be described by a set of rate equations. These equations describe the population of energy state level in time, and they are characterized by the rate constant. We can distinguish two rates of constant type: Ionisation rates, where the incoming photon is absorbed, or recombination rates, where the energy is released by photon (radiative) or phonon (non-radiative).

#### **Ionisation** rates

The ionisation rate  $ion_2$ , from the VB to the NV<sup>0</sup> charge state, can be described by the following equation [76]:

$$ion_2 = \frac{W_A \cdot W_B \cdot P_{laser}^2}{(1 + W_A \cdot P_{laser})}$$
(4.5)

Where ion<sub>2</sub> is the ionisation rate from the valence band to the  $NV^0$ ,  $W_a$  and  $W_b$  are the ionisation coefficients, and  $P_{laser}$  is the laser power.

Ionisation rates  $ion_1$  and  $k_1$  can be denoted as the multiplication of the pumping parameters with the laser power:

$$k_1 = W_{k1} \cdot P_{laser} ; ion_1 = W_{ion1} \cdot P_{laser}$$

$$(4.6)$$

Where ion<sub>2</sub> is the ionisation rate from the valence band to the NV<sup>0</sup>,  $W_{k1}$  is the ionisation coefficient from NV<sup>-</sup> GS to ES,  $W_{ion1}$  is the ionisation coefficient from NV<sup>-</sup> ES to CB, and  $P_{laser}$  is the laser power.

All of the ionisation rates consider the stimulation photons with a wavelength of 532nm.

### **Recombination rates**

Recombination constants of the inner cycle of the NV<sup>-</sup> charge state ( $k_{2-4}$ ) are well known from the literature, other ones are still under debate ( $k_{6-5}$ ,  $rec_2$ ,  $rec_1$ ). The recombination rates can be either radiative ( $k_2$  - here, for simplicity, we consider that, due to their short lifetimes, the  $m_s = 0$  and  $m_s = \pm 1$  spin sublevels have identical radiative recombination rates) or non-radiative ( $k_{3-6}$ ). The last group of recombination paths relates to transitions involving the conduction or the valence bands, in particular, the recombination rate of electrons from the NV<sup>-</sup> ground state to the valence band ( $rec_1$ ) or the recombination of the electron from the conduction band to NV<sup>0</sup> ( $rec_2$ ), or recombination via defect levels, discussed later.

### Rate equations of NV defect

The total photodynamic of the NV defect level occupation probability can be described by a set of partial differential equations. A table of all used parameters inside the equation can be found in Appendix A. Six equations correspond to the different energy levels of the NV defect and two extra equations to the conduction (|CB)) and the valence band (|VB)):

$$\frac{p_{|1\rangle}}{dt} = -k_1 \cdot p_{|1\rangle} + k_2 \cdot p_{|3\rangle} + k_5 \cdot p_{|5\rangle} + A_k \cdot ion_2 \cdot p_{|6\rangle} \cdot p_{|VB\rangle} - k_{MW} \cdot p_{|1\rangle} + k_{MW} \cdot p_{|2\rangle} + A_k \cdot rec_2 \cdot p_{|6\rangle} \cdot p_{|CB\rangle} - D_k \cdot rec_1 \cdot p_{|1\rangle} \cdot (1 - p_{|VB\rangle})$$
(4.7)

$$\frac{p_{|2\rangle}}{dt} = -k_1 \cdot p_{|2\rangle} + k_2 \cdot p_{|4\rangle} + k_6 \cdot p_{|5\rangle} + k_{MW} \cdot p_{|1\rangle} - k_{MW} \cdot p_{|2\rangle} 
+ B_k \cdot rec_2 \cdot p_{|6\rangle} \cdot p_{|CB\rangle} - E_k \cdot rec_1 \cdot p_{|2\rangle} \cdot (1 - p_{|VB\rangle}) 
+ B_k \cdot ion_2 \cdot p_{|6\rangle} \cdot p_{|VB\rangle}$$
(4.8)

$$\frac{p_{|3\rangle}}{dt} = k_1 \cdot p_{|1\rangle} - (k_2 + ion_1 + k_3) \cdot p_{|3\rangle}$$
(4.9)

$$\frac{p_{|4\rangle}}{dt} = k_1 \cdot p_{|2\rangle} - (k_2 + ion_1 + k_4) \cdot p_{|4\rangle}$$
(4.10)

$$\frac{p_{|5\rangle}}{dt} = k_3 \cdot p_{|3\rangle} + k_4 \cdot p_{|4\rangle} - (k_5 + k_6) \cdot p_{|5\rangle} + C_k \cdot ion_2 \cdot p_{|6\rangle} \cdot p_{|VB\rangle} + C_k \cdot rec_2 \cdot p_{|6\rangle} \cdot p_{|CB\rangle}$$

$$(4.11)$$

$$\frac{p_{|6\rangle}}{dt} = -ion_2 \cdot p_{|6\rangle} \cdot p_{|VB\rangle} + ion_1 \cdot (p_{|4\rangle} + p_{|3\rangle}) - rec_2 \cdot p_{|6\rangle} \cdot p_{|CB\rangle} + rec_1 \cdot p_{|1\rangle} \cdot (1 - p_{|VB\rangle})$$

$$(4.12)$$

Where

the

Eqn.

(4.7) represents the rate equations for the  $m_s=0$  spin sublevel of NV<sup>-</sup> GS, Eqn. (4.8) stands for the  $m_s=\pm 1$  spin sublevel of NV<sup>-</sup> GS, Eqn. (4.9) for the  $m_s=0$  spin sublevel of NV<sup>-</sup>ES, Eqn. (4.10) for the  $m_s=\pm 1$  spin sublevel of NV<sup>0</sup> ES, Eqn. (4.11) for the metastable singlet state of NV<sup>-</sup>, Eqn. (4.12) for NV<sup>0</sup> charge state. Here, *p* stands for the population of each specific energy sublevel (see Figure 20), *CB* and *VB* stand for Conduction and Valence bands, *rec* stands for recombination rates, *ion* for ionisation rates, and A<sub>k</sub>-E<sub>k</sub> stands for the recombination.

Inside the equation are denoted recombination coefficients:  $A_k$ - $G_k$  denote the adjustment of the recombination fluxes to or from the different energy levels,  $A_k$ - $C_k$  stand for the recombination coefficient for the flux from the NV<sup>0</sup> to the NV<sup>-</sup> GS0, GS±1 and metastable singlet [72].  $D_k$  and  $E_k$  stand for the recombination coefficients from NV<sup>-</sup> GS to the VB.

Two additional equations for the valence and conduction band need to be included in the full scheme and can be determined by the following equation:

$$\frac{p_{|CB\rangle}}{dt} = -rec_2 \cdot p_{|6\rangle} \cdot p_{|CB\rangle} + ion_1 \cdot \left(p_{|4\rangle} + p_{|3\rangle}\right) + (1/e) \cdot \nabla j_{CB}$$

$$\tag{4.13}$$

$$\frac{p_{|VB\rangle}}{dt} = -ion_2 \cdot p_{|6\rangle} \cdot p_{|VB\rangle} + rec_1 \cdot p_{|1\rangle} \cdot \left(1 - p_{|VB\rangle}\right) + (1/e) \cdot \nabla j_{VB}$$
(4.14)

Where  $p_{CB}$  stands for the population of the conduction band, pVB stands for the population of the valence band, and *e* stands for the electric charge of the electron.  $V_{jCB}$  and  $V_{jVB}$  are the divergences of the drift currents.

## 4.2. Model of the crystal defects' environment

Diamond crystals contain several types of point defects that have a significant effect on the photoelectrically detected signal. To address the full picture of the PDMR method, it is necessary to include this type of defect in the numerical model.

## 4.2.1. Substitutional nitrogen

One of the most common defects is the substitutional nitrogen -  $N_s$ .  $N_s$  plays a significant role in photocurrent detection through the recombination and trapping processes. Characterisation of the  $N_s$  occupation dynamics is crucial for the full understanding of photocurrent generation. In the PDMR Ns, photoionisation can cause a decrease in NV photocurrent, by increasing the recombination lifetime of charge carriers on non-occupied Ns and decreasing photoelectrically detected spin-contrast [77–79]. We considered Ns as one energy level system (Figure 21) with the two possible charge states, Ns0, that after photoionisation became  $N_s^{+}$ , making the  $N_s$  defect level relax in energy about 4.6 eV [80]. Consequently, the photo-induced back conversion from  $N_s^+$  to  $N_s^0$  is not possible under the 532nm illumination. The  $N_s^+$  can be back-converted to the  $N_s^0$  by the recombination of the  $N_s^+$  with the free electron from

the conduction band. When an  $N_s$  defect is included, an extra equation must be implemented into the system.

$$\frac{p_{|8\rangle}}{dt} = -ion_3 \cdot p_{|8\rangle} + rec_3 \cdot (1 - p_{|8\rangle}) \cdot p_{|CB\rangle} - rec_4 \cdot p_{|8\rangle} \cdot (1 - p_{|VB\rangle});$$

$$ion_3 = W_{ion3} \cdot P_{laser}$$
(4.15)

Where *p* stands for the population of energy levels and indexes of *p* stand for 8 ( $N_s^0$ ), CB (conduction band), VB (valence band), rec stands for recombination rates: *rec<sub>3</sub>* (CB to  $N_s^0$ ) and *rec<sub>4</sub>* ( $N_s^0$  to VB). Ionisation rate *ion<sub>3</sub>* stands for the ionisation rate from  $N_s^0$  to CB, and it is calculated by the multiplication of the laser power *P*<sub>laser</sub> with the pumping parameter *W*<sub>*ion*3</sub>.



Figure 21 - Model of the  $N_s$  defect. The system is considered here as a one energy level system  $|8\rangle$  with recombination rates rec<sub>3</sub> and rec<sub>4</sub> and ionisation rate ion<sub>3</sub>.

### 4.2.2. Acceptor defects

Even in the highest-purity CVD-diamond samples, in addition to N<sub>s</sub>, several other types of defects can be present, for example, neutral and charged vacancies, di-vacancies, interstitials, and their complexes with N or hydrogen [57, 81]. The influence of these defects on the optical and photoelectric spin contrast has not been studied in detail so far. Recently, our experimental results suggested the existence of such an acceptor level [82]. This defect level (noted level X) has the ability to trap an electron or to serve as a recombination centrum (as depicted in Figure 22) [82, 83]. We found earlier that the presence of acceptor defects could lead to intriguing behaviour, such as the inversion in the sign of the PDMR contrast [82]. In [82] we tentatively attribute this level to the single vacancy V. Acceptor defect X, represented as a one-level system with charge states  $X^0$  and  $X^+$  (Figure 22). We consider that the charge state transition from  $X^0$  to  $X^+$ by the excitation of the electron from the defect to the CB is not possible. The defect X population dynamics can be characterised as follows:

$$\frac{p_{|7\rangle}}{dt} = (1 - p_{|7\rangle}) \cdot ion_4 \cdot p_{|VB\rangle} + rec_5 \cdot (1 - p_{|7\rangle}) \cdot p_{|CB\rangle} - rec_6 \cdot (1 - p_{|VB\rangle}) \cdot p_{|7\rangle}$$

$$ion_4 = W_{ion4} \cdot P_{laser}$$

$$(4.16)$$

Where *p* stands for the following levels' population: 7 (X<sup>0</sup>), CB (conduction band), VB (valence band), *rec* stands for recombination rates:  $rec_5$  (CB to X<sup>0</sup>) and  $rec_6$  (X<sup>0</sup> to VB). Ionisation rate ion<sub>4</sub> stands for the ionisation rate from VB to X<sup>0</sup> and is a product of multiplication between pumping parameter W<sub>ion4</sub> and the laser power *P*<sub>laser</sub>.



Figure 22 – The proposed structure of the acceptor level X, represented by a one-level system for simplicity. The level is designed as a strong hole producer; rate  $rec_5$  is the recombination rate from the Conduction band (CB) to X<sup>+</sup>,  $rec_6$  is the rate of recombination of X<sup>0</sup> electron to the valence band (VB), rate ion4 is the ionisation rate from VB to X<sup>+</sup>. This ionisation process leads to the production of holes in the VB.

## 4.3. Model of drift of the free charge carriers

Important part of this thesis was to develop a model describing photocurrent and photoluminescence under the spin manipulation, which is the essence of the proposed sensor. In the following text we derive this model that was fully developed during the PhD work.

The charge carrier drift is a crucial component of the PDMR scheme and also plays an important role in the recombination and trapping processes, as well as charge carrier collection by electrodes. The drift leads to the redistribution of charge onto defects outside the illumination spot. By including it in the model, we account for interaction of the drifting charge carrier with defects such as recombination and trapping present on the way to the collecting electrode, which, as we show, have an effect on the photocurrent spin contrast. In order to model the charge carrier drift, we represent the

gap between the electrodes as a one-dimensional space that we sample to the finite number of elements. Each element can contain one or multiple defects (NV, N<sub>s</sub> or X). The bins in the illumination spot contribute to the photocurrent by the photogeneration of charge carriers, balanced by recombination. The total photocurrent is the sum of all current sub-sources (eqn. (4.26), (4.27)). The bins outside the illumination spot can shift the charge carrier from the previous bin. The charge carrier can also be annihilated by the recombination with defects located in these bins. Free charge carrier drift elements are denoted at (4.13) (4.14),  $j_{CB}$  for the electrons in the conduction band, and  $j_{VB}$  for the holes in the valence band. Figure 23 shows the schema of the electrode gap divided into the spatial bins, with single NV and Ns defects inside of the illumination spot. The figure shows the drift of the charge carriers dependent on the electrode polarity.



Figure 23 – Representation of the electrode gap with single NV and Ns defect. Electrodes are connected to the bias voltage, and charge is detected by the detector. Arrows stand for the migration of the electron-hole pair generated by NV, the blue arrow for the electron, red arrow for the hole.

## 4.4. Steady-state calculations

When the system reaches the steady state, the luminescence or photocurrent do not change with time and in this situation we can study integral characteristics such as the laser power dependency of fluorescence intensity and photocurrent for the microwave off-and-on. This allows us to calculate the MW-induced optical and photocurrent contrasts. The intensity of the fluorescence response of NV<sup>-</sup> can be calculated as:

$$I_f = k_2 \cdot \left( p_{|3\rangle} + p_{|4\rangle} \right) \tag{4.17}$$

Where  $I_f$  stands for the intensity of fluorescence intensity,  $p_{|3\rangle}$  stands for the population of NV excited state ES0,  $p_{|4\rangle}$  population of NV<sup>-</sup> excited state ES±1 and  $k_2$  represent the relaxation rate from NV- ES to GS.

The total photocurrent  $I_p$  of the system can be calculated as the sum of electron  $I_e$  and hole  $I_h$  currents:  $I_p = I_e + I_h$ . Each sub-current can be calculated by the formula:

$$I_e = e \cdot G_e \cdot \tau_e \cdot \mu_e \cdot E \tag{4.18}$$

$$I_h = e \cdot G_h \cdot \tau_h \cdot \mu_h \cdot E \tag{4.19}$$

Where *e* represents the charge of the electron, *E* stands for the applied external electrical field,  $\mu_e \ \mu_h$  stands for the mobility of the electron and the hole charge carriers,  $\tau_e, \tau_h$  stands for the recombination lifetime and the  $G_e$ ,  $G_h$  stands for the photogeneration rate.

The photocurrent is proportional to the charge carriers' generation and recombination lifetime. Generation of the charge carrier can be defined by the creation of the charge carrier in the band by defect-induced photoionisation. The generation of charge carriers by the single NV defect is determined by the formula:

$$G_e = ion_1 \cdot \left( p_{|3\rangle} + p_{|4\rangle} \right) \tag{4.20}$$

$$G_h = ion_2 \cdot p_{|6\rangle} \cdot p_{|VB\rangle} \tag{4.21}$$

Where the *ion*<sub>1</sub> stands for the ionisation rate from NV<sup>-</sup> ES to CB, *rec*<sub>1</sub> stands for the ionisation rate from VB to NV<sup>0</sup>,  $p_{|3\rangle}$  stands for the population of the NV<sup>-</sup> ES0,  $p_{|4\rangle}$  is the population of the NV<sup>-</sup> ES±1,  $p_{|6\rangle}$  is the population of the NV<sup>0</sup>,  $p_{|VB\rangle}$  is the population of

the VB,  $G_e$ ,  $G_h$  stands for the photogeneration rate,  $W_{ion1}$  is the pumping parameter of ionisation transition from NV ES to CB and  $P_{laser}$  stands for the laser power.

The lifetime of the charge carrier is the essential component of the photocurrent and represents the average time till the charge carrier is recombined. In the case of a single NV defect, it can be described as:

$$\tau_e = \frac{1}{rec_2 \cdot (p_{|6})} \tag{4.22}$$

$$\tau_h = \frac{1}{rec_1 \cdot (p_{|1\rangle} + p_{|2\rangle})}$$
(4.23)

Where  $rec_2$  is the recombination rate from CB to NV<sup>0</sup>,  $rec_6$  is the recombination rate from NV<sup>-</sup> GS to VB,  $\tau_e, \tau_h$  is the recombination lifetime, and  $p_i$  stands for the population denoted in Figure 20.

When multiple defects are present, the total charge carrier generation rate can be calculated as the sum of all sub-generation rates [84]:

$$G_{tot} = \sum_{i=1}^{N} G_i \tag{4.24}$$

Where  $G_{tot}$  is the total generation of charge carriers in the system,  $G_i$  is the generation from an i<sup>th</sup> bin, and *N* is the total number of bins.

In a similar way, the lifetime of the charge carrier can be calculated as [84]:

$$\frac{1}{\tau_{tot}} = \sum_{i=1}^{N} \frac{1}{\tau_i}$$
(4.25)

Where  $\tau_{tot}$  is the total recombination lifetime,  $\tau_i$  is the recombination lifetime from the sub-bin, and *N* is the total number of space resolution bins.

The total hole and electron photocurrent can then be expressed as:

$$I_{e,tot} = e \cdot G_{e,tot} \cdot \tau_{e,tot} \cdot \mu_e \cdot E \tag{4.26}$$

$$I_{h,tot} = e \cdot G_{h,tot} \cdot \tau_{h,tot} \cdot \mu_h \cdot E \tag{4.27}$$

The meaning of the symbols was introduced in equations (4.18)-(4.19), (4.24)-(4.25). The total photocurrent can be calculated as the sum of the total electron current  $I_{e,tot}$  and total hole current  $I_{h,tot}$  as  $I_{tot} = I_{e,tot} + I_{h,tot}$ 

When the total fluorescence intensity and photocurrent output for MW off and on are known, we can calculate the theoretical spin contrast of the system by the formula:

$$C = \frac{I_{off} - I_{on}}{I_{off}} \tag{4.28}$$

Where *C* is the calculated spin contrast,  $I_{off}$  is the fluorescence intensity/total photocurrent in off-resonance, and  $I_{on}$  is the fluorescence intensity/total photocurrent in resonance.

When the model is fully resolved, we can calculate the quantum efficiency of the single NV defect. For this, we need to calculate the ratio of the PL or photocurrent and the number of incoming photons. In the case of fluorescence quantum efficiency, we use the formula:

$$QE_f = \frac{l_f}{k_1(p_{|1\rangle} + p_{|2\rangle}) + G_{tot}}$$
(4.29)

Where  $QE_f$  is the quantum efficiency of fluorescence,  $I_f$  is the intensity of fluorescence,  $k_1$  ionisation rate from the GS to ES of NV- charge state, p is the population of energy level 1 (GS0) or 2 (GS±1),  $G_{tot}$  is the total generation of charge carriers.

In the denominator of equations (4.29) and (4.31), we can use  $G_{tot}$  as a substitution of ionisation flux from VB to the NV<sup>0</sup> charge state and from ES NV<sup>-</sup> to the CB.

Internal quantum efficiency from the experimental data is obtained by the formula:

$$QE_{f,exp} = \frac{I_{f,exp}}{I_{laser}}$$
(4.30)

Where  $QE_{f,exp}$  stands for the quantum efficiency of fluorescence from experimental data,  $I_{f,exp}$  is the intensity of fluorescence from experimental data [count/s], and the  $I_{laser}$  stands for the intensity of the laser.

In the formula for the internal quantum efficiency of the photocurrent response of the single NV, we need to compare the total generation of charge carriers with the number of incoming photons, which gives us the equation:

$$QE_p = \frac{G_{tot}}{k_1(p_{|1\rangle} + p_{|2\rangle}) + G_{tot}}$$
(4.31)

Where  $QE_p$  stands for the quantum efficiency of photocurrent,  $G_{tot}$  is the total generation of charge carriers. The rest of the symbols are defined at eqn. (4.29).

In the case of quantum efficiency of photocurrent when the multiple  $N_s$  defects are presented in the system, we need to modify the quantum efficiency formula (4.31) with respect to the total collected photocurrent:

$$QE_{p,tot} = \frac{I_{tot}}{k_1(p_{|1\rangle} + p_{|2\rangle}) + G_{tot}}$$
(4.32)

Where  $QE_{p,tot}$  – quantum efficiency of the total collected,  $I_{tot}$  is the total photocurrent and the rest of the symbols are defined at (4.31) and (4.29).

Formula (4.32) allows us to compare the quantum efficiency of the photocurrent calculated from the model and compare one that is calculated from data by:

$$QE_{p,exp} = \frac{I_{tot,exp}}{I_{laser}}$$
(4.33)

Where  $QE_{p,exp}$  is the quantum efficiency of the total collected,  $I_{laser}$  is the intensity of the laser, and  $I_{tot,exp}$  is the total collected photocurrent from the experiment.

When we like to compare the difference between the population of the energy level in off and on resonance, we are using the modified formula (4.28) for the population as:

$$dP = \frac{P_{off} - P_{on}}{P_{off}} \tag{4.34}$$

Where dP is the difference in energy level population,  $P_{off}$  is the energy level population in off-resonance, and  $P_{on}$  is the energy level population in resonance.

## 4.5. Numerical simulation of NV defect

Solving the set of differential equations (Eqn. (4.7)-(4.14)) is a complex numerical calculation that can be split into three main parts: construction of the problem array, solving of the problem array in a numeric way, and calculation of the fluorescence or charge carrier generation from the result matrix.

The problem description contains the six time-dependent equations (Eqn. (4.7)-(4.12)) that determine NV occupation dynamics and the two equations for the conduction and the valence bands occupation dynamics (Eqn. (4.13)-(4.14)), i.e. 8 equations representing energy level occupation (10 equations in case Ns and X defects are present). The one dimensional charge carrier transport path is divided to mesh of cells. The set of equations is executed for every mesh cell that represents spatial resolution, in our case, 11 over 5  $\mu$ m electrode distance, which gives us a total maximum number of 110 equations. The interval of integration was set as a 1D matrix with t<sub>0</sub>=0 and t<sub>end</sub>=1ms (where we assume the steady state) with 10<sup>5</sup> time steps. This time resolution provides acceptable accuracy for the time-dependent photodynamic.

### Solver part

Solving the problem is done in the MatLab environment using the embedded function ode23tb. This function is used for numerical integration of the stiff differential equation using a trapezoidal rule with a backward differentiation formula[85]. The system is integrated over the interval of integration. When convergence is reached, we obtain a 3D matrix of results (Figure 24). The calculated result matrix is a three-dimensional matrix with the size (M, N, Z) corresponding to the occupation of the n<sup>th</sup> level (M), spatial resolution (N), and integration time (Z) (see Figure 24). The calculation (and, therefore, the resulting 3D matrix) can be performed for different situations, such as for various laser powers. The last submatrix in the time coordinate (the green slice) is considered to be the result of the steady state. The time dependence of the level occupations can be extracted as well.



Figure 24 - Resolving the obtained 3D matrix of results, the green 2D matrix contains the result of energy levels occupation in the steady-state;  $m_i$  stands for the energy levels where M is the number of energy levels, n stands for the space resolution where N is the number of sub bins, tstands for the time samples where Z is the selected time resolution of the system. Each element of the matrix contains the probability of energy level occupation ( $p_{mi,nj}$ ) in every time step.

# 4.6. Chip design

The diamond chip was designed using the simulator COMSOL Multiphysics 6.0 (Sweden) employing the RF and AC/DC modules for technical drawing and for the investigation of the microwave (MW) induced magnetic field in the area of interest. Two chip variants were developed depending on the area of application. First model is for the single crystal diamond, and the second model is for the nanodiamond (NDs) application.

Table 2 shows the requirements for each type of chip.

Characteristic	Chip A	Chip B
Sample type	Single crystal	NDs
Dimension [cm]	5x5	5x5
Simulation	RF	RF + MW heating
Measured field	Magnetic	Temperature + Magnetic
Application	QNMR, MRI	Temperature probe
Sample	Molecules in liquid media	Neurons in liquid media
Readout	Electrical and Optical	Optical

Table 2 – Characteristics of the two designed chip

#### **Geometry and Mesh**

The chip was fully modelled in a 3D in COMSOL Multiphysics. The chip has dimensions standardized to 5x5cm, a common configuration within our setups. Microwave signal connectivity was established by the SMA ports while microstrip impedance is calculated to  $50\Omega$ . The bottom of the chip contains the metal layer that serves as the ground plane and is connected to the SMA outer conductor. Surrounding the domain of the chip is a sphere representing the local air environment. The air domain has a diameter of 10cm and has its centre at the center of the chip. A diamond sample is positioned at the centre of the chip. Geometry was divided to the tetrahedral elements, with a maximum size of 0.1 mm in the case of the diamond crystal domain, and with 'Fine' size free tetrahedral elements for the remaining geometry, ensuring optimal resolution for probing the microwave field inside the crystal with requested precision.

#### Design Study

For the purpose of microwave stimulation, we set one SMA port as the microwave feed with 1W input power. The second SMA was configured as the MW output, terminated by an absorbing condition. Microstrips and the ground plane were represented as 2D structures with the material set as Perfect Electrical Conductor (PEC). As a boundary condition, a Perfectly Matched Layer (PML) was implemented at the surface of the air sphere. A simulation was conducted in the 'Frequency domain (emw)' spanning the microwave frequencies from 2-4GHz with step 0.5GHz (chip A, chip B), or in specific cases (chip B), on a single frequency of 2.87GHz, the corresponding resonance frequency of the NV<sup>-</sup> ground state.

#### Material simulations

For optimised performance of the sensor, materials used for chip construction needed to be verified by the simulation. The chip uses the Rogers substrate for the PCB material, copper for the outer SMA, Teflon for the inner SMA and Air for the air sphere. In the simulation where we are using diamond crystal, defined by dielectric properties. The table shows the dielectric properties of the used materials, and values were taken from the COMSOL Material Library [86].

	ε <sub>r</sub> [-]	σ [S/m]
PCB – RO4350B	3.48	0.035
SMA - dielectricum	2	5.1.10-17
SMA - conductive	1	$5.9 \cdot 10^{7}$
Tracks	PEC	PEC
Air environment	1	0
Diamond	5.7	1.10-12

Table 3 – Dielectric properties of the material used in the simulation.

## 4.6.1 Chip for single crystal diamond

The chip that utilises a single crystal diamond configuration is designed primarily for photoelectrical readout applications but also allows the photoluminescence readout. The design is conceived to ensure uniform excitation of the microwave field across both the crystal volume and frequency spectrum. The magnetic component of the microwave field is oriented perpendicular to the z-axis of the model. Electric tracks that conduct the charge carriers towards electrodes, are shielded by two ground planes, providing minimalization of the electrostatic environmental interference.

The main configuration of the model is outlined in the previous chapter 4.6. The difference that is specific to this chip is that we investigate the impact of MW stimulation on the single crystal sample measuring 4x4x1mm. Specifically, our focus is on the magnetic part of MW, which induces the spin-flip transitions between the ground state of NV<sup>-</sup> (as detailed in eqn. (4.4)). We examine the potential cross-talk between the microwave excitation structure and electrodes that we try to minimise. The electrodes are designed to cover the center region of the sample, perpendicular to the MW microstrip, with an electrode gap of 5 to 20µm. Visualisation of the chip can be seen in Figure 25.



Figure 25 – Modelled chip for single crystal diamond. A: shows the magnification of the laser aperture at the 'top' plate at XY plane. The red rectangle represents the diamond crystal, which is 4x4mm in size, between the chip plates. At the surface of the crystal, a black line representing the electrodes can be seen. Electrodes are connected to the electric tracks via. B: shows the complete plate with the SMA ports dedicated for MW stimulation. C: Shows the magnified XZ plane of the chip with 'top' and 'bottom' plates. The blue area stays for the simple port of the electrode line, and the red box stays for the diamond crystal.

The chip comprises two main components: the 'bottom' and the 'top'. Each part consists of two layers, with one microwave substrate housed in each layer. The 'bottom' part features a cavity with the size of 4x4x1mm to accommodate the diamond crystal, while the 'top' part includes a rectangular aperture positioned at the center of the crystal for the laser beam. The aperture in the V3 and V4 layers differ in size, ensuring that the laser beam is not shadowed by the V4 layer. The full stack-up of the chip can be seen in Table 4. Fabrication was carried out by Pragoboard company.

the bottom surface of the chip			
Ground plane 35um			
Ro 4350B 1.524 mm	V1		
MS line 35 um		bottom part	
Prepreg 0.101 mm			
Ro 4350B 0.813 mm	V2		
Ro 4350B 0.1 mm	\/2		
Ground plane	V3		
Prepreg 50 um		top part	
MS line18 um		top part	
Ro 4350B 0.1 mm	V4		
Ground plane 18um			
the top surface of the chip			

Table 4 – Stack-up of the chip for the single crystal applications. In the first column, the Orange background of cells stands for the conductive (copper) layers, blue for the prepreg dielectric glue, and the grey background of cells stays for the MW substrate Rogers 4350B. Chip consists of two parts, 'bottom' and 'top' parts. Each part consists of two layers of substrate denoted as V1-4.

In the simulation, we modelled the electrodes as 2D planar structures (Figure 26A) oriented perpendicular to the microwave excitation line, utilising the 'Transition boundary condition' with a thickness of 120nm. This approximation closely mimics the behaviour of real sputtered electrodes. Electrodes are fabricated to the crystal surface using the standard lithography procedures. Sputtering is performed within a two-target system, employing targets composed of titanium (Ti) and gold (Au) targets. The resulting electrode structure consists of 20nm of titanium followed by 100nm of gold (Figure 26B).



Figure 26 - A: Design of electrode mask for the lithography, electrodes contain multiple tracks to cover the bigger surface of the diamond crystal, and aligning crosses helps position the crystal. B: Image of fabricated electrode structure at the diamond surface

In the second iteration of the prototype (Figure 27), we rectified the errors identified in the initial production phase. Specifically, we addressed the absence of the cuts for the SMA ports in the 'top' plate and implemented grounding of the middle ground plane through the microwave stitching between the middle metal layer (Table 4 - V3 plane) and upper ground (Table 4 - V4 plane) of the top plate. Additionally, we augmented functionality by incorporating two pairs of electrodes to extend coverage over the diamond surface. This enhancement not only expands measurement capabilities but also can serve us with a multipixel sensor, unlocking the possibility of sensing, e.g., the gradient of the magnetic field.



Figure 27 – Second iteration of the chip for single crystal diamond. Microwave features are marked by a yellow color, electrode features a blue color and laser-related features with red colour.

## Chip for single crystal diamond, QNMR variation

A potential application of single crystal diamond is the detection of NMR signals from very small amount of analytes (attolitre – picolitre) i.e. mass-limited samples. In conventional high-field NMR setups, the signal-to-noise ratio (SNR) changes linearly by the volume of the sample [87]. Although they work quite well for micro-litre samples, they fail at nano and pico-litre scales. However, single crystal diamonds are a promising platform for detecting MR signals from such small-volume samples [88]. We explore the utilisation of a proposed chip as a promising tool for constructing microfluidic chambers. In our experimental setup, we fabricate a microfluidic channel sealed with a transparent glass plate covered with copper tape, serving as the ground
plane. The initial prototype undergoes modifications and testing to evaluate its microfluidic properties, such as pressure and flow dynamics, as well as their compatibility with pulsed protocols, including Rabi, Ramsay and Hans-Echo sequences. Figure 28 shows the adaptation of the Quantum Nuclear Magnetic Resonance (QNMR) chip for incorporating a single crystal diamond membrane with a thickness of 50 $\mu$ m. An alumina piece is securely affixed to the ground plane of the sensor chip atop the chip. The microfluidic channel is crafted by drilling through both the alumina block and sensor chip, subsequently sealed with a 0.5mm thick glass slide. The diamond membrane is then positioned within the microfluidic channel. Connection to the external microfluidic part is facilitated by <sup>1</sup>/<sub>4</sub>-28 superflangless male nuts. Additionally, the entire bottom surface, except the laser aperture, is covered with black tape to mitigate the multi-reflection of the sensing laser, thereby ensuring operator safety and minimising reflection to the photodiode detector placed near the microfluidic chip. In this microfluid configuration, we could achieve a flow rate of up to 400  $\mu$ L/s.



Figure 28 – Chip modification for microfluidic QNMR. A microfluidic channel is placed through the aluminium sensor chip, sealed with the glass plate. Copper tape serves as the ground plane, and masking tape reduces the laser reflection.

#### 4.6.2 Chip for NDs

The chip that is used for photoluminescence signal detection from the nanodiamond particles (ND) is conceived to achieve ND particle excitation via a uniform MW field across a 1mm circle area, facilitated by a resonance structure operating at a resonant frequency of 2.87GHz. Furthermore, the MW at off resonance frequency serves in maintaining the temperature of the liquid media to 38 °C (i.e. by MW absorption), which is crucial for the viability of neural cells.

The setup was further described in the previous chapter 4.6. The microwave stimulation structure has been designed in the shape of an omega, featuring the drilled hole inside the omega structure that serves as a place for placement of the liquid neuron imaging media containing NDs. The omega-shaped structure has an inner diameter of 4.5mm. Notably, the chip incorporates a single electrical pathway equipped with two SMA ports dedicated to microwave stimulation, but the circuit for the photocurrent readout is not presented. The frequency-dependent dielectric properties of the imaging media were determined through the application of a fitted 2-pole Cole-Cole model [89], that is frequently used for the characterisation of disperse mediums. Furthermore, a chip has been designed for optical readout detection.



Figure 29 – Modelled chip for the NDs application. A: shows the complete plate with two SMA ports dedicated to the microwave stimulation line. B: shows the magnification of the omega feature in the XY plane. The blue area represents the liquid medium with the NDs that are used for sensing.

Fabrication of the prototype was made at PXL Makerspace of Hasselt University from the sheet of the Rogers 4350B PCB using frilling techniques. The sheet has a thickness of 8mm and was covered at both planes with 35µm of copper cladding. A liquid sample with NDs is put inside the hole, and the structure is sealed by a coverslip for the bottom. NDs can be stimulated by the laser beam that is focused from the bottom of the chip. Stac-kup of the is presented at

the bottom surface of the chip
Ground plane 35um
Ro 4350B 0.76 mm
Copper plane 35 um
the top surface of the chip

Table 5 – Stack-up of the omega shape chip for NDs application. The orange background of cells stands for the conductive (copper) layers, and the grey background of cells stands for the MW substrate Rogers 4350B.

Figure 30 shows the fabricated omega-shaped chip that is ready for ND imaging. Before doing so, the cover slip needs to be attached to the chip surface, and the created cavity needs to be filled with the liquid sample that contains the ND particles.



Figure 30 – Fabricated chip for nanodiamond application. Two MW SMA ports are soldered to the conductive tracks. One port serves as the feed of the microwave, while the second port accommodates a  $50\Omega$  match.

# 4.7 Optical setup

The photo of the experimental optical setup for the spectroscopic measurements can be seen in Figure 31. This setup is specifically designed for detection of magnetic resonances of NV centre and can be used for optical as well as photoelectrical readout. A solid-state continuous wave laser emitting at 532nm is used as the optical pumping source. The laser beam traverses an optical-acoustic modulator (AOM – AOMO 3200-146) and is focused onto the sample by an air objective (Olympus MPLANAPO NA95). The diamond sample, affixed to the chip, rests atop an XYZ piezo stage (Physical Instruments P-545), offering precision movement capabilities on the order of approximately 10nm, giving us a possible 200x200  $\mu$ m scanning area. Photoluminescence signals emitted from the sample are collected by the same objective and directed through a dichroic mirror. These signals pass a long-pass filter (FELH05550) that has a cutoff wavelength of 550nm, effectively filtering the excitation wavelength. The filtrated beam traverses the set of lenses and pinholes before reaching a single photon counter (Excelitas technologies). In the case of photoelectrical signal

detection, charge carriers are collected by ohmic electrodes that are manufactured by standard lithography at a diamond crystal surface. Electrodes are typically composed of Ti/Al or Ti/Au materials with a thickness of 20/100nm. These electrodes are subjected to a bias voltage (0-5 V/ $\mu$ m) applied via a voltage source and picoampere meter (Keithley 487 with down 10fA sensitivity). Microwave is generated by microwave source (Windfreak SynthHD), and subsequently amplified by microwave amplifier (MiniCircuits ZHL-1W), and then routed through an excitation structure within the chip before being terminated by a 50 $\Omega$  load. The system is controlled from a PC using a program constructed in LabVIEW. Figure 32 shows the fluorescence map acquired through the optical setup.



Figure 31 – Photo of the optical setup. The green path stands for the laser excitation line of 532nm, and the red path stands for the fluorescence emission from the mounted sample (blue box). Fluorescence emission is detected with the use of a single photon counter placed in the blue box detection unit.



Figure 32 – Fluorescence map of the electrode gap containing NV defects. The electrode gap is 3um, and no bias voltage is applied. Laser power (532nm) is 2mW. The yellow cross marks the individual NV center.

# 4.8. Diamond material

### Single crystal diamond

In chapter 5.1 (5.1 NV defect population) and 5.2.1 (5.2.1. Effect of Ns centre) we used a single type IIa crystal diamond from the NDT (New Diamond Technology) company. by HPHT method with 3x3x0.5mm (±0.05mm) size and {1,1,1} face orientation. Surface roughness was approximately 5nm. Notably, the concentration of the impurities was approximately 50 ppb for Boron and 10 ppb for Nitrogen.

In chapter 5.2.2 (5.2.2. Effect of acceptor level (level X)) we used a single type IIa optical grade CVD diamond with  $Ns^0$  concentration less than 1ppm. Sample was

electron-irradiated (14 MeV,  $10^{16}$  cm<sup>-2</sup>) and annealed (700 °C, 4h). Sample contain ~10ppb of bulk NV ensembles.

In chapter 5.3 (5.3. GSLAC-assisted electrical readout) we used a single-crystal  $\{1,1,1\}$  with size 2.1x2.3x0:65 mm diamond, synthesized using a high-temperature high-pressure (HPHT) method. The initial nitrogen concentration of the sample was specified as <200 ppm. To produce NV centers, the sample was electron-irradiated at 14MeV (dose:  $10^{18}$  cm<sup>-2</sup>) and then annealed at 700 °C for three hours. The resulting NV centers are randomly oriented along all four  $\{1,1,1\}$  crystallographic axes of the diamond.

In chapter 5.4.1 (5.4.1 Chip for single crystal diamond) we used a Ib single-crystal diamond  $\{1,0,0\}$  with size 2x1mm with thickness of 35 µm. Sample contain 14ppm of Ns with the 2ppm of NV.

### Nanodiamond particles

Nanodiamond particles sourced from Microdiamant Switzerland were utilized in this work. These particles possess a size median of 0.125µm with a moderate distribution of 0.105-0.145µm and contain 100-200 ppm of nitrogen impurities. The oxidation of the NDs particles was performed in air at 510 °C for 5 hours, followed by wet oxidation in a mixture of hydrofluoric and nitric acid (in a 2:1 ratio) at 160 °C for two days within a PTFE container. Acid residues were removed by successive centrifugation and washing followed by lyophilization, resulting in the isolation of monodisperse NDs. Monodisperse particles were irradiated at 870 °C within an external target for a duration of 80 hours using a 15.7 eV electron beam, with particle flux od 2.5\*10<sup>19</sup> cm<sup>-2</sup>, extracted from the MT-25 microtron. Following irradiation, the NDs underwent annealing at 900 °C for 1 hour under an argon atmosphere, followed by oxidation in the air for 5 hours at 510 °C. The resultant fluorescence-enhanced NDs were further subjected to wet oxidation in a hydrofluoric and nitric acid mixture in a 2:1 ratio, washed and lyophilized, yielding final NDs with NV centres.

# 4.9. Biological samples

Cells and cell media were prepared in collaboration with BIOMED (Department of Neurobiology) at BroneRigo lab. The comprehensive methodology regarding the incubation and cell preparation protocols will be elucidated in a forthcoming published [90]. Here, we provide a succinct overview of the cell cultivation process and incubation with nanodiamonds.

## Cells:

All experimental procedures were conducted according to the protocol approved by the Institutional Animal Care and Use Committee. Primary cortical neurons were isolated from postnatal day 0 to day 2 (P0-P2) mouse pups. The cortical tissues were dissected, cleaned of the meningeal layer, and then dissociated. First, enzymatically (1% trypsin and 0.1% DNAse I in HBSS 0.2% glucose solution) for 5 minutes at 37 °C. Then mechanically in (0.05% DNAse in growth medium: Neurobasal supplemented with B27, 1mM L-glutamine and penstrep) using a glass pasteur pipette until the solution is homogeneous. The solution is then strained with a 70µm cell strainer and added to FBS to centrifuge for 10 min at 1000RPM. The pellet was then mixed with growth medium, and cells were plated (40 000 cells per well) on Poly-D-lysine (100mg/ml- Gibco) precoated glass coverslips. Neurons were plated in the growth medium, and the medium was changed 2 hours after plating.

# Immunofluorescence:

Four days after culture, primary neurons were fixed in 4% paraformaldehyde 5% sucrose solution for 15min at 4°C. The cells were then incubated with blocking buffer (PBS 5% BSA) after three PBS washes. The cells were incubated with primary antibody at 4°C overnight and then with fluorescent-conjugated secondary antibody for 1 hour at room temperature. Last, the coverslips were mounted on microscope slides (ThermoScientific) in fluorescent mounting medium (Immu-Mount, ThermoScientific).

### ND incubation and live staining:

Four days after culture, neurons were incubated with 1µg/ml NDs overnight at 37°C, 5% CO2. On the next day, cells were washed 3 times with the culture medium then they were dyed using Cell Mask Deep Red Actin (Invitrogen) at 1:10 000 for 30min at 37°C, 5% CO2. Then, after 3 washes, the cells were taken to IMO for imaging.



Figure 33 – Fluorescence image of a cortical neuron in culture (4div) (Green, immunofluorescence) incubated overnight with 2µg/ml NDs (Red, NV- fluorescence).

# 5. RESULTS

The first part of the work (Chapter 4) focused on the design of the theoretical the NV centre photon and photocurrent response related to microwave and laser excitation. We probed the photodynamic of the single NV defect at the time domain and its laser power dependency. We performed the simulation for the different rate sets of the relaxation from the metastable singlet to the ground state, where the true value is at the ongoing discussion. The next chapter is dedicated to the interaction of the crystal environment with the photoelectrical signal generated by NV. We investigate the effect of the most common point defect in diamond, Ns, and its influence on the PDMR contrast. We also investigate the rare phenomenon of positive PDMR and discuss the origin of the positive PDMR signal. We also model the photoelectrical detection of the microwave-less GSLAC-assisted readout, which is essential for further chip development. The last part shows the usage of the quantum sensing concept in the biological system, NDs attached to the neuron axon.

# 5.1 NV defect population

The behaviour of the single NV defect was probed at 1D simulation without additional defects. Charge state dependency was probed as the function of laser power. In the simulation, charge state neutrality was respected. NV charge state at the simulation time t=0 is in its neutral state, p(NV0)=1.

### 5.1.1. Time simulation

Figure 34 shows the simulated time dependency of the charge state probability with the three different laser powers: 0.1mW, 1mW and 5mW. The first part of the trace shows an increasing population of the NV<sup>-</sup>charge state with elapsed time. A steady state is reached faster for the higher laser powers, and the population of the NV<sup>-</sup>charge state at equilibrium increases with the laser power as expected. Steady-state is reached after 5.6  $\mu$ s at the laser power of 0.1mW, after 190ns at 1mW, and after 78ns at 5mW with a charge state distribution (NV<sup>0</sup>/NV<sup>-</sup>) of ~31/69 % at 0.1mW, ~8/92 % at 1mW and ~2/98 % at a 5mW laser power. When the laser power excitation is increased to 5mW (Figure 34, blue trace), an inflection point in the NV<sup>-</sup> population can be seen at t = 6ns. This is

due to the saturation of the excited state of NV<sup>-</sup> whose population is rising faster than the population of the metastable singlet state. After the occupancy of the metastable singlet state reaches its maximum, which is determined by its lifetime, a second saturation occurs. This is a consequence of the long-lived metastable singlet ground state with a lifetime of ~ 200 ns at room temperature [91]. The visibility of the second inflexion point increases with the laser power, in accordance with [92]. Based on the knowledge of the population of each of the individual sublevels, we can calculate the spin contrast using equation (4.28).



Figure 34 - The simulated time-dependent population of the NV<sup>-</sup> defect charge state without the presence of any other defects in the diamond crystal and without the resonant microwave field application. The system of partial differential equations was solved for three different laser powers (red -0.1 mW, black -1 mW, blue -5 mW).

### 5.1.2. Laser power-dependent simulation

Figure 35 shows the simulated charge state populations of the NV<sup>-</sup> triplet and of the metastable singlet state at steady state as a function of the laser power, with a resonant microwave field on or off. These traces are used for the calculation of the spin contrast

in Figure 36. The population of the NV charge state starts to saturate at 1mW and is followed by saturation of the metastable singlet state at 1.5 mW. The population of NV<sup>-</sup> reaches a value of approximately 0.92. Results of the model show that saturation of the population of the NV<sup>-</sup> charge state is linked with the saturation of the metastable singlet state, where most of the charge is stored. This is also in accordance with ref [72], where it is shown that at high laser powers, the charge is stored at the metastable singlet state. Figure 36 shows the optically/photoelectrically read spin-contrast of the single NV defect. Spin contrast has a maximum of 0.35mW of laser power with a value of 30%. Optical pumping parameters  $W_{kI}$  and  $W_{ionI}$  were obtained by fitting experimental data. The Result shows that in the case of no recombination, the PDMR contrast curve copies the ODMR one.



Figure 35 - The simulated laser power dependence of the population of the NV<sup>-</sup> charge state and the metastable state singlet at the steady state. The population of the NV<sup>-</sup> charge state is calculated with and without the resonant microwave field in black (MW off) and red colour (MW on), while the metastable singlet state population is represented in green (MW on) and blue colour (MW off).



Figure 36 – Laser power dependency of the spin-contrast at the single NV defect, ODMR (red trace, dashed line) and PDMR contrast (blue trace, solid)

# 5.1.3. Relaxation rates discussion

Two different values (Wirtitsch - [72], Tetienne - [93]) for rates of relaxation from the metastable state singlet to the ground state ( $m_s=0$ ) are still under discussion. The simulation was performed with the ionisation rates (taken from the fitting of experimental data). Only results for the ODMR spin-contrast are shown here. The PDMR is strongly affected by the presence of other optoelectrically active defects and is discussed in chapter 5.2. The two modelled cases (Wirtitsch and Tetienne) differ slightly in the position of the maximal contrast in the PL intensity, and contrast decreases faster in the case of Tetienne's rate set due to the faster dropping of the initialisation efficiency. In particular, when using the data from Wirtitsch, the ODMR maximum contrast shifts slightly towards the higher laser power.



Figure 37 – Simulated laser power dependence of the CW-ODMR spin contrast in case of single NV and defect in the steady state. The figure shows ODMR contrast with the usage of Wirtitsch rates (black trace) and Tetienne rates (red trace).

# **Conclusion and author contribution**

Photodynamics of the single NV defect occupation for each energy level in time, and spin-contrast with laser power dependency were modelled. Computer simulation shows that for high large laser powers, the probability of NV- exceeds the probability of NV0, and most of the charge is stored at the metastable state singlet. This is confirming the results in reference [72]. We have shown that without the influence of recombination by other defects, PDMR contrast copies the ODMR contrast.

The author designed a comprehensive model of the photodynamics of the NV centre level occupation. The model integrates the interaction between laser and microwaves with defects alongside the transport of charge carriers crucial for modelling of photocurrent signals. Various simulations were conducted by the author to investigate relaxation rates from the metastable singlet and discusses disparities observed in the optical spin-contrast dependence on laser power.

# 5.2. Influence of environment on spin contrast

We probed the influence of several other optoelectrical active defects in the diamond crystal lattice, the substitutional nitrogen (Ns) and acceptor level X (vacancies, divacancies, etc.), on the spin contrast. We consider the charge states  $N_S^0$  and  $N_S^+$  in our calculations [76, 94]. We assume that in the initial state, there is an equal probability for  $N_s$  to be in the  $N_S^0$  and  $N_S^+$  charge states [76, 94], i.e.  $p(N_S^0) = 0.5$ . In the same way, we are considering the charge and initial states of level X. The charge state neutrality was compensated by adding a hole with a probability of 0.5 inside the valence band.

# 5.2.1. Effect of Ns centre

We placed an N<sub>S</sub> centre into the central bin of the 1D mesh, i.e. in the same place as the NV defect (Figure 23). The total spin contrast is defined by (4.28) and is influenced by photoionisation from the N<sub>S</sub> level [92]. With our model, we can monitor the changes due to photoionisation and recombination of the charge carriers on individual defect levels. Figure 38A shows the laser power dependence of the occupation change in the total NV<sup>0</sup>, NV<sup>-</sup> excited state and N<sub>S</sub> populations when the MW excitation is changed from "on" to "off" (Formula (4.34)).



Figure 38 - A shows modelling of the occupation changes (dP) of NV<sup>-</sup> excited state, NV<sup>0</sup> and N<sub>s</sub> when the resonant microwave field is turned on and off when 1  $N_s^0$  centre and 1 NV centre under a 10 G microwave excitation is considered. B shows the laser power dependence of the total PDMR spin contrast for different numbers of N<sub>s</sub> present. The total photocurrent (resulting from NV and N<sub>s</sub> centres ionisation) is considered here. Traces of different colours represent the output of the model for 1 NV centre and various numbers of N<sub>s</sub> centres, ranging from 0 (reference) to 10 (fraction N<sub>s</sub>/NV of 10/1).

The calculation is done for a situation of 1 Ns centre and 1 NV centre. Occupation change of the NV<sup>-</sup> excited state coincides with the ODMR contrast as well as with the PDMR contrast for the case of 0 N<sub>s</sub>. That is because the photoluminescence is proportional to the excited state population, as is the photocurrent in the absence of N<sub>s</sub>. Notably, N<sub>s</sub><sup>0</sup> occupation is influenced by the microwave field. This is to be expected as NV<sup>0</sup> occupation drops, which leads to the creation of a hole in the valence band. Also, the NV<sup>0</sup> occupation change is practically identical to the NV<sup>-</sup> occupation change, meaning that the changes in the m<sub>S</sub> = 0/±1 can also be potentially monitored by the NV<sup>0</sup> population change, or with less contrast even by N<sub>S</sub><sup>0</sup> population change, which brings interesting alternatives for the PDMR detection and spin readout applications.

Figure 38B depicts the predicted spin contrast on the total photocurrent as a function of the number of Ns centres placed in the central bin together with an NV centre. A significant decrease and a shift of the maximum in the electron spin contrast to higher powers is observed when the number of Ns defects introduced to the system increases, as already documented experimentally [92]. As a direct use of the modelling, from the

detected shift in the maximum of the PDMR contrast as a function of the laser power, we are able to evaluate how many  $N_S$  centres are present in the close vicinity of the NV centre. As the  $N_S$  presence also has consequences on the reduction of the  $T_2$  and  $T_2$ \* times, our model can be useful for evaluating the number of  $N_S$  centres in the close vicinity of NV, helping thus devising the origin of the spin decoherence in single NV centres.

#### Comparison with the experimental results

We apply the model to the experimentally measured dependence of the optically and photoelectrically detected spin contrasts of a single NV centre. Considering the 20ppb nitrogen concentration and the focus point volume of roughly  $1\text{um}^3$ , we estimate the number of N<sub>s</sub> that have an impact on PDMR contrast to be around 10. All of the rates, except for ionisation and recombination, were taken from the literature (see Appendix A for details). Concerning the rates k<sub>5</sub> and k<sub>6</sub>, there is no consensus at this point on these rates, therefore we apply the model twice – first, we consider the rates from Wirtitsch et al.[72], then the rates from Tetienne et al.[93], and get the ionisation and recombination rates for both cases (Figure 39C).



Figure 39 - Laser power dependence of the ODMR/PDMR spin contrast for a diamond quantum chip. A: shows experimental (red crosses), modelled with Wirtitsch rates [72] (blue trace) and with Tetienne [93] rates (black trace) photoluminescence contrast. B: shows experimental (red crosses), modelled with Wirtitsch rates [72] (blue trace) and with Tetienne rates [93] (black trace) photocurrent contrast leading to an estimated N<sub>s</sub> concentration of 10 N<sub>s</sub> for 1 measured NV. For this reason, we used the same N<sub>s</sub> concentration for ODMR modelling. C: contains values of the FIT for the rate set of Tetienne [93] and Wirtitsch [72] and shows the result of the model in the form of ionisation and recombination rates for the two different sets of input rates (mainly differing in  $k_5$  and  $k_6$ ).

Figure 39 shows a comparison of experimental contrast (red crosses) with the output of the modelled system (blue trace) for both OMDR (Figure 39A) and PDMR (Figure 39B). Figure 39A shows that the ODMR contrast peaks at approximately 30 % at about 0.4 mW laser power. Figure 39B shows the experimental and modelled PDMR contrast reduced by Ns defects, where the maximum is approximately 18 % under 1.2 mW laser power (blue trace). Figure 39B also shows a clear significant shift of PDMR contrast maximum that is believed to be caused by the effect of the Ns defect, as shown by modelling.

The ODMR modelling trace for Figure 39A is then recalculated for an identical number of  $N_s$  centres. From the modelling, we can conclude that, as expected, the ODMR spin contrast is not significantly influenced by the  $N_s$  presence, while the PDMR contrast is. From the output of the model (Figure 39), we can see that the recombination rate "rec<sub>3</sub>" is significantly closer to the previously reported value of 3ns [95] for the case of the input rates from Wirtitsch et al.

#### Quantum efficiency

Notably, by using our theoretical model for the measured ODMR and PDMR spin contrast, we can also calculate the quantum efficiency (QE) for both optical and photoelectric detections. ODMR quantum efficiency has been modelled so far from experimental data [76]. With the fully resolved model, we can theoretically calculate quantum efficiency and compare it with measured data as a function of laser power.

Figure 40 shows the laser power dependence of the fluorescence and photocurrent QE calculated by Eqn. (4.29)-(4.33). In the low laser power regime, we can see a maximum optical QE of 84% in the presence of MW and 69% without MW. The optical QE decreases with the laser power. As concerns PDMR, above 2.2mW, the photocurrent QE increases with the laser power and starts to dominate the optical QE, reaching ~ 44% at 4mW; however, at this laser power, the photoelectrical spin contrast drops to 10% (see Figure 38B). The results of our model are in good agreement with the experimental data of QE (that was obtained by fitting eqn. (4.30)). In particular, the PL quantum efficiency calculated using our model is very close to the results presented in reference [96], where the PL QE of the NV centre was measured. In addition to this work, our modelling enables us to obtain the QE for the case of photoionisation. Modelling shows that for higher laser powers, the charge carrier generation becomes more effective than the photon generation by photoluminescence. Despite the decrease in spin contrast, the total photocurrent signal increases with the laser power without saturation, which can be effectively used to reach a higher sensitivity for spin magnetometry. Interestingly, as the photocurrent and PL are complementary, one could extend this measurement concept to measure electron and photon count correlations, which we plan in the future. Further on, we can see from Figure 40 that the experimental photocurrent QE that is calculated from total collected photocurrent (Eqn.

(4.33)) is lower than the theoretical QE trace for 1 NV without  $N_S$  defect that is calculated from the generation of charge carriers (Eqn. (4.31)). The decrease in the QE is caused by the fact that the lifetime of the charge carriers is shorter due to the presence of the other defects (Ns). On the contrary, if we do the modelling for 10 N<sub>s</sub>, the modelling matches the experiment well.



Figure 40 - Laser power dependence of quantum efficiency. The figure shows the quantum efficiency model of the photoluminescence without (black trace) and with (red trace) microwave excitation for single NV and experimental PL data (black crosses) and the model photocurrent quantum efficiency without (blue trace) and with (pink trace) microwave excitation for 1 NV. The traces are calculated from the PL and photocurrent dependence as a function of the laser power. For the PL data, we scaled the experimental data onto the theoretical curve to compare the experimental trace shape with the model. The orange trace is the modelled photocurrent quantum efficiency for the case of 1 NV and 10 Ns, and blue crosses correspond to the experimental photocurrent data. The experimental photocurrent data are fitted directly without any scaling-

### 5.2.2. Effect of acceptor level (level X)

For the study of the acceptor defect, we consider the density of N<sub>s</sub>/NV as 11/1, and we vary the density of the acceptor level [X]=0 to [X]=7. Calculations performed using this model before show that when only NV and  $N_s^0$  are present, the magnetic resonances formed in the photocurrent are always negative, regardless of the green laser power applied or of the value considered for the different recombination rates. Indeed, as expected, the photocurrent calculated considering only the free charge carriers resulting from NV<sup>-</sup> and NV<sup>0</sup> ionisation systematically decreases under the application of a resonant microwave field (i.e., presents a negative resonance). In the absence of defect X, the photocurrent calculated considering only the free electrons resulting from  $N_s^0$ ionization also shows a difference in the off and on resonance (Figure 38A). This difference in  $N_s^0$  population is due to the fact that in the presence of the microwave field, the reduction in the amount of free charge carriers resulting from NV<sup>-</sup> ionization induces a decrease in the rate of electron capture by  $N_{S}^{+}$  and thus a decrease in the rate of  $N_s^0$  ionisation (given that the capture of an electron by  $N_s^+$  leads to the formation of  $N_{s}^{0}$ ). The modelling results confirm thus that the presence of  $N_{s}$  defects in large excess leads to a limitation of the total PDMR contrast, which is in good agreement with experimental observations. [77]



Figure 41 - Experimental PDMR (A) and ODMR (B) contrast as a function of the light focusing depth (z parameter)

The reversed sign of the PDMR contrast was experimentally measured at various IIa bulk samples (Figure 41A, sample characteristic can be found in Appendix B) under green illumination (532nm), where in microwave resonance conditions, increasing the photocurrent can be seen. Spin contrast in Figure 41 was measured under the external magnetic field to induce Zeeman splitting between NV<sup>-</sup> ground state spin levels m<sub>s</sub>=-1 and  $m_s=+1$ , where resonances were detected in both ODMR and PDMR spectra with the identical shape but a different sign, that confirms NV<sup>-</sup> electron spin resonance. The formation of positive resonances phenomena requires the introduction of an acceptor level and to consider that the positively charged state of this defect  $(X^+)$  presents a large electron capture cross-section (considered 20 times higher than the electron capture cross-section of  $N_{s}^{+}$  to obtain the data presented in Figure 42). It can be observed in Figure 42A that the introduction of a small amount (1 to 4) of acceptor defect X in the model leads to an increase in the absolute value of the negative PDMR contrast. Indeed, the recombination of free electrons with X<sup>+</sup> (considered to have a large capture crosssection) competes with their recombination with  $N_{s}^{+}$ , further reducing the reformation of  $N_s^0$  and thus decreasing the photocurrent associated with  $N_s^0$  ionisation. This leads to an increase in the absolute value of the negative contrast in Ns<sup>0</sup>-photocurrent (up to-11.3% for [X]=4). Due to the higher number of defects, in the range [X]=1 to [X]=4, N<sub>S</sub>associated photocurrent dominates over X-associated photocurrent, and the overall PDMR contrast remains negative in the whole range of excitation power. If a sufficient number of defect X is introduced into the mathematical model ( $[X] \ge 6$  in Figure 42A), the calculated green-light power dependence of the PDMR contrast appears qualitatively similar to the experimentally observed dependence (transition from negative to positive contrast upon reduction of the illumination power, followed by a light decrease of the positive contrast when the illumination power approaches zerosee Figure 41A). In the case [X]=6, calculations of the microwave-induced spin contrast (Figure 42B) indicate that the photocurrent resulting from NV<sup>-</sup> and NV<sup>0</sup> ionization decreases at resonance (negative contrast up to-20%). N<sub>s</sub><sup>0</sup>-associated photocurrent also presents a large negative contrast (up to -22%), resulting, as explained above, from charge exchanges between  $NV^-$  and  $N_S^+$ . The microwave-induced contrast in the electron photocurrent (resulting from NV<sup>-</sup> and N<sub>S</sub><sup>0</sup> ionisation) is, therefore, always negative. On the contrary, under low illumination, the photocurrent associated with X<sup>+</sup> ionisation increases at resonance, as expected, considering the capture of free electrons resulting from NV-ionization by this defect. In case the concentration of defect X with

respect to NV and  $N_S$  is sufficient, this causes an augmentation of the hole photocurrent at resonance and ultimately leads to the positive contrast observed in the total photocurrent under low-power green illumination. These simulations clearly suggest that in the presence of acceptor defects, the hole photocurrent limits the PDMR contrast and, in some particular conditions, can lead to an inversion in the sign of PDMR resonances.



Figure 42 – A: Calculated green-light power dependence of the PDMR contrast for the different numbers of acceptor defects X. [X]: number of defect X, considering 1 NV center and 11 N<sub>s</sub> defects. B: In the case [X]= 6, the MW-induced contrast in the total hole photocurrent and the total electron photocurrent was calculated, as well as in the photocurrent associated with NS, X, and NV ionisation.

#### **Conclusion and author contribution**

The author investigated the impact of the crystal defect environment on photocurrent generated from the NV defect by modelling. This involved influence of substitutional N<sub>s</sub> and an additional acceptor level X and varying the density of the N<sub>s</sub> defect and analysing the response of the PDMR contrast. Observations reveal a decrease in PDMR contrast and a shift of its maximum to higher laser power with increasing N<sub>s</sub> density. The model was validated by fitting experimental data from a single NV with the modelled contrast for both spin contrast (ODMR and PDMR). Alternations in model outputs were further discussed using different rates (proposed by Wirtitsch and Tetienne

[72, 93]). Quantum efficiency (QE) modelling was conducted for the single NV defect, which was consistent with prior research, as well as for NV and N<sub>S</sub> defect systems. Comparison of experimentally and theoretically obtained QE values demonstrated good agreement. The author developed the modelling of a new acceptor level X that accounts for the recently discovered positive resonances in the spectra of PDMR, particularly IIa crystals (Author worked on relevant publication  $\{1\}$ ).

The author conducted simulations to assess the combined impact of various densities of other defects (Ns, X) on the photocurrent signal. Absolute values for NV ionisation, as well as other defects, were derived by fitting of experimental data. Furthermore, the author quantified the optical and photoelectrical quantum efficiencies of an individual NV centre, as well as the photoelectrical quantum efficiency of the NV complex within the crystal environment. Measurements of single NV were made by a PhD student, Michael Petrov (UHasselt, Quantum Science and Technology), and measurements of positive PDMR were performed by an experienced senior researcher, Emillie Bourgeois (UHasselt, Quantum Science and Technology).

# 5.3. GSLAC-assisted electrical readout

Microwave free detection of magnetic fields is a novel way for magnetometer sensor, utilising the GSLAC, developed in the thesis. Investigation of the magnetic resonance that originated from the ground state level anti-crossing (GSLAC) was performed for both types of read-out (optical as well as photoelectrical) and using irradiated the HPHT diamonds. On the surface of the diamond ohmic Ti/Al coplanar electrodes with a 5µm gap were fabricated by standard lithography process. The magnetic field was applied by a custom-made electromagnet [49]. A schematic representation of the experiment can be seen in Figure 43. Optical and photocurrent detection was performed simultaneously. The laser beam waist was estimated to be around  $6\mu$ m, and the Rayleigh range  $\approx 200$  µm. We focused the laser beam on different z positions (z=0 is the surface of the crystal) and collected the photoluminescence (PL) and photocurrent (PC) signals. We observe the fast drop in the intensity of the PC signal due to the decreasing of the laser intensity that is necessary for the two-photon mechanism of PC generation and the

rapidly decaying electric field. PL signal showing different behaviour where a 30% drop can be observed due to the shadowing of the laser beam by electrodes. Figure 43 shows that PC readout provides a small effective volume compared to fluorescence.



Figure 43 -A: Schematic representation of the setup that is used for the PC detection. A static magnetic field ( $B_S$ ) is applied along the NV axis (z-direction). Laser 532nm is focused between the electrodes. The PC signal  $I_{phc}$  is detected by a lock-in amplifier with reference to the modulation frequency of the laser light by an acusto-optic modulator (AOM). The projected side view shows the effective region of detection of PC (blue region) and PL (red region).

Figure 44 shows the GSLAC-assisted photoelectrical and photoluminescence signal as a function of the applied  $B_z$  field (parallel to the NV axe). Visible features can be seen at 51 mT (cross relaxation [97] and possible excited level anti-crossing [98]) and around 102.5mT (GSLAC), where PC contrast can be seen but detected spin-contrast of the PC signal is lower than the contrast obtained from PL signal.



Figure 44 – Photocurrent (A) and photoluminescence (B) signal in arbitrary units as a function of the magnetic field. The magnetic field was scanned from 0-110mT in 5s. The green laser beam of various powers is modulated, and the PC is synchronously detected by a lock-in amplifier. The data are normalised to the signal at zero field. The laser power is indicated in the corresponding colours of the legend. For visual clarity, the traces in Figure B are manually shifted. The electrical potential applied to the electrodes was 17V.

To compare the experiment with the model, we calculated PC and PL signals from experimental and geometrical conditions and reproduced them using the proposed model. Figure 45A and Figure 45B show the predicted and measured laser power dependency at the total PL and PC signal. It can be seen that the photocurrent signal did not reach saturation, which is consistent with the previously published models. The photoluminescence signal should saturate due to the limit established by the NV<sup>-</sup> exited state lifetime and be stacked into the metastable state singlet. The deviation in the PL model output and experiment can be accounted for by the shadowing of the diamond by electrodes, resulting in the reduction of the effective laser power. Figure 45C shows the total PC and PL signal as the function of depth (z axe) below the crystal surface. The local contribution is indicated by a blue (PC) or red (PL) shaded area (in arbitrary units). Results show that 90% of the PC signal comes from the region 0-30µm below the surface where the NV defects experience sufficient both optical excitation and electric field to drive the charge carriers towards the electrodes. PL signal is produced throughout the diamond slap and detected once photons get out of the high E-field region beneath the electrodes. Based on the simulation, we estimate the ratio of effective interrogation volumes of PC to PL detection to be the order of 1:20.



Figure 45 A: calculated (orange) and experimental (green) total photocurrent vs laser power. B: calculated (orange) and experimental (green) photoluminescence signal vs laser power. C: calculated accumulated photocurrent (black) and photoluminescence (red) signal as a function of penetrating depth into the diamond chip. Blue (red) shaded area indicates local contribution to the photocurrent (photoluminescence) signal in arbitrary units.

## **Conclusion and author contribution**

A microwave-free diamond quantum sensor based on GSLAC-assisted photoelectrical readout for measuring weak magnetic fields was developed in this work in collaboration with the scientific group at Mainz University. Generation of both types of signals (photoluminescence as well as photocurrent) was quantitatively modelled in this thesis and relevant publication. (Author work in relevant publication {2}). GSLAC features were observed for the first time by photoelectrical readout. Information obtained from this work can be used to build hybrid gradiometers, taking advantage of observed detection volumes of PC and PL signals and improving spatial resolution.

The author determined the dependence of photoelectrical and fluorescence signals with crystal depth using his model developed in the thesis. The author also calculated the cumulative signal as a function of laser power. Measurements were performed by Huijie Zheng et al. at Mainz University.

# 5.4. Chip testing

Numerical modelling on both proposed chips in frequency ranges from 2GHz to 4GHz for 1W microwave power input was performed.

## 5.4.1 Chip for single crystal diamond

PCB components of the chip were fabricated by Pragoboard corporation (Czechia), while the final assembly of the chip itself took place at IMO UHasselt (Belgium). The crystal was affixed to the lower surface of the upper segment of the chip by the soldering of sputtered electrodes onto the vias using a low-temperature silver paste, followed by bounding of two segments of the chip ('top' and 'bottom'). Chip was equipped with four SMA ports, two allocated for microwave excitation and two for electrode connectivity.

# Numerical simulation

The initial phase of testing was focused on modelling of the chip's capability to deliver adequate microwave excitation. Figure 46 shows the result of the magnetic part of the microwave, which is responsible for spin-flip from the ground state ms=0 to  $ms=\pm 1$ (magnitude field is calculated by  $Hnorm = (H_X^2 + H_Y^2 + H_Z^2)^{\frac{1}{2}}$ ). Red arrows denote the orientation of the magnetic field flux (determined by  $H_x$  and  $H_y$ ), while their lengths is proportional to the field intensity. Figure 46A shows a comprehensive view of the chip from the YZ plane. Results show that the highest field intensity occurs around the edges of the microstrip as expected, diminishing towards the upper surface of the diamond (highlighted by the red square). The region of interest for sensing lies beneath the laser aperture, roughly spanning from the diamond's upper surface to 100µm below it (indicated by a yellow ellipse). In this region, the generation of fluorescence and photocurrent signals is predominantly from NV centers (as also discussed in chapter 5.3. GSLAC-assisted electrical readout). Figure 46B shows the magnified the area pertinent for sensing. The diamond crystal is highlighted by the red square, while the laser aperture is marked by a green square. V3 and V4 stay for the layers of the 'top' part of the chip (detailed in Table 4). Results show that beneath the laser aperture, the microstrip established a homogeneous field with a strength of ~40A/m. The disparity in field intensity between the crystal surface and 100µm below it is approximately 10%. The direction of the field indicates that NV defects aligned with their axes parallel to the Z-axis of the model experience maximum microwave stimulation.





Figure 46 – Microwave field distribution (H part) in YZ plane. The green box represents for the laser aperture, red box for the single crystal diamond sample. A: Total microwave H field distribution in chip in A/m for at frequency of 2.75GHz, yellow circle stays for the magnified area depicted at B. B: the magnified area around the laser aperture. V3 stays for layer 3 and V4 for layer 4. The description of the layer is denoted in Table 4

Another pivotal characteristic of the chip is reflected and transmitted power represented by scattering parameters (S-parameter) values. We used S-parameters to probe the influence of direct microwave pickup and to examine potential resonance profiles. Figure 47 shows the computed S-parameters delivered from the numerical model, where |S11| denotes microwave power reflected to the source port (reflection coefficient), and |S21| transmitted power to the terminator. Results exhibit an anticipated profile in both |S11| and |S21| parameters, consistent with microstrip behaviour. Notably, minimal microwave power is transmitted to the electrode lines, which is a crucial aspect for detecting small photocurrents, such as those generated by a single NV.



Figure 47 - S parameters of the chip for a single crystal diamond. |S11| represents power reflected back to the microwave source, |S21| represents microwave power transmitted to the terminator, and |S31| and |S41| represent microwave transmitted to the electrode lines.

### **Experimental measurements**

A chip with a mounted diamond crystal was tested for microwave-induced frequencydependent photocurrent. Microwave-associated crosstalk effects were observed causing the fluctuation in the photocurrent intensity. Reasons behind these fluctuations are still not fully understood, but potentially come due to direct interactions between microwaves and electrode pathways (induction). Figure 48 shows experimental data demonstrating the microwave-induced variation in the photocurrent for the three different chip types. Results indicate that the proposed chip design exhibits minimal fluctuation in photocurrent intensity compared to conventional 'parallel' (Figure 49B) and 'perpendicular' (Figure 49A) chips commonly used by the UHasselt group. All of the experiments were performed on the same diamond crystal and electrodes (described in chapter 4.6.1 Chip for single crystal diamond). Microwave excitation in the case of 'parallel' and 'perpendicular' chips was made by a wire which laid on the microwave surface (depicted in Figure 2 and Figure 15). A flat frequency response to photocurrent is crucial for accurately measuring low-intensity photocurrent, particularly photocurrent from the single NV defect.



Figure 48 – Microwave involved pickup response to the DC photocurrent. Parallel represents the chip with parallel lines (measured with lock-in), perpendicular represents for the chip with perpendicular lines (measured with lock-in), A is for the proposed chip, point1 and point2 are two different focus points on the diamond crystal.



Figure 49 – Conventional chip for photocurrent signal detection from the diamond sample. Green lines highlight the microwave path, red lines highlight the electrode pathways. A: chip with the 'perpendicular' traces, B: chip with the 'parallel' traces. Diamond crystal is not mounted.

# Chip for single crystal diamond, pulse measurements

We performed multiple series of ODMR pulse sequences, including Rabi, Ramsay, and Hans echo, on the designed chip to assess its functionality for microfluidic applications for measuring NMR. While comprehensive usage of this chip for NMR is currently underway, here we present the Rabi sequence, which is the basis of the NMR protocol in which nuclear spins are detected using the NV centre as a sensor (showed in Figure 50). To demonstrate coherent control of quantum states ( $m_s = 0$  and  $m_s = \pm 1$ ), we perform the Rabi protocol, which starts with a laser polarization pulse to put the electron spin population into the  $m_s = 0$  state. The polarization pulse typically takes 3-5µs. A MW pulse with a width of  $\tau_{MW}$ , follows a polarization pulse to drive transition between the ground and excited states. Immediately after, a 2µs laser readout pulse is applied to measure the state of the electron spin. This represents a typical Rabi protocol without lock-in detection. To suppress the effect of the low-frequency noise sources in our measurement, we have implemented a lock-in detection technique. To implement lock-in detection, we periodically modulate the amplitude of the MW with a frequency typically of 20 kHz. To reveal Rabi oscillations, we varied  $\tau_{MW}$  and monitor the inphase signal of Lock-in (Figure 51).



Figure 50 -: Sequence of events in modulated Rabi protocol. t is the delay between the end of laser pulse and start of the MW pulse.  $\tau_{MW}$  is the duration of MW pulse.



Figure 51 – Rabi oscillation performed on QNMR chip for five different microwave powers. Amplitudes represent the output of the MW source before being amplified by a MW amplifier with a nominal gain of 45 dB.

# 5.4.2 Chip for NDs

Another important application was the design of a chip for measuring functionalised nanodiamonds (FNDs) in living nerve cells, decorated with FNDs. In this measurement, nerve cells are measured on a droplet of medium that is placed in the chip. Essential problem is the temperature control of the medium with neurons, as well as the ability to perform ODMR measurement at the same time. PCB components of the chip were manufactured by Makerspace PXL (Hasselt University, Belgium) using a drilling technique on a microwave substrate sheet coated on both sides with copper cladding. Assembly of the chip was finished at IMO UHasselt (Belgium), where an SMA connector was mounted to the MW tracks, and a coverslip was glued to the omega structure. This configuration established a space where the liquid medium with NDs can be placed. The dispersion of the diamond particles was achieved through sonification within the imaging media, resembling a biological phantom. To prevent liquid evaporation and serve as a grounding plane, the hollow space was sealed using copper tape, effectively closing the aperture.

## Numerical simulation

The geometric of the omega-shape structure was varied to investigate their influence on the resonance profile, particularly in terms of the |S11| (denotes microwave power reflected to the source port (reflection coefficient)) parameter, in proximity to the 2.87GHz frequency.

Alternations were made on both the inner diameter of the omega and the diameter of the aperture to discern their impact on the resonance characteristics. Figure 52 shows the frequency dependence of the |S11| parameter for the different inner diameter of the omega structure. Results show that optimal diameter for the omega is 4.5mm. This fulfils the criteria for potential resonance patterns, and also provides ample space for neuron cultivation.



Figure 52 – Frequency dependence of the |S11| parameter on the inner diameter of omega. Values in mm represent the corresponding omega diameter value.

#### **Experimental measurements - Biosensing**

The performance of omega-shaped antenna in terms of its ability to regulate the temperature regulation through off-resonance MW absorption in the liquid was evaluated by modelling. To characterise the performance, a single microwave fluorescence sweep was conducted at two different temperatures with 1mW of laser excitation. Normalised fluorescence is presented in Figure 53. Spectra show temperature-induced shifts alongside Zero Field Split with an observed spin contrast (ODMR) of approximately 3%. Using the local minimum algorithm (employing the key MatLab function 'islocalmin'), we accurately determined the peak positions (+1 and -1 energy levels of ground state NV<sup>-</sup>) in each spectrum. The peak detection enables realtime monitoring of the temperature within the imaging medium, determining the assessment of microwave-induced heating and its correlation with the temperature stabilisation capabilities of the omega-shaped structure. Results of microwave-induced temperature maintenance of the imaging media can be seen in Figure 54. The blue curve shows the temperature prediction by the model, and the orange curve represents experimental data measured via the nanodiamonds. Both spectra show similar trends, with a sharp rise in temperature within 5 minutes followed by a slow rise towards a steady state of 40°C. For the simulation, we used a microwave power of 5W. For the experiment, we used a microwave power of 10W and a laser power of 1mW of laser power, whilst microwave frequency was 2.87GHz. The difference between microwave power used in simulation and in measurements is caused by power loss in MW cables and connections as well as the discrepancy between the material and environmental temperature.


Figure 53 – Normalised intensity of fluorescence emission from NDs using the omega shape chip. Data represent two different media temperatures, 23.5 and 56 °C. Two peaks correspond to the split of energy level (+1 and -1) of NV- ground state due to Zero Field Split (ZFS). Spectra were taken with 1mW of laser excitation by a green 532nm laser and 1W microwave power.



Figure 54 – Microwave (2.87GHz) induced temperature of the liquid sample modelled (blue) and sensed by NDs (orange) with the usage of an omega-shaped antenna. For the excitation, 1mW laser power (532nm) and 10W microwave power were used, and for the modelling, 5W of microwave power was used.

Figure 55 shows the photoluminescence map of neurons with attached nanodiamonds (red ellipse). Figure 56 shows ODMR spectra for the attached nanodiamond from the ND particle marked by green ellipse in Figure 55. Spectra was taken at a laser power of 1mW and 2W microwave power. ODMR spectra show Zero Field Splitting. Figure 55 also shows the successful anchoring of functionalised nanodiamond particles on the extracellular part of the cell membrane. Nanodiamonds were equipped with a poly(glycerol) coating and modified with a ligand which selectively and tightly binds to the CXCR4 receptor. CXCR4 is a non-internalizing receptor enabling a long-term anchoring of the nanodiamonds on the membrane. The biocompatibility of the modified NDs is evidenced by the sustained fluorescence signal emitted by the particles throughout the neuron's one-hour lifespan within the chip. These observations are consistently reproducible across multiple measurements. The stable attachment of NDs on the neural membrane is an important research question and neuron receptor targeting was demonstrated in the work caried out here. It should be mentioned that the CXCR4 has been linked at the Institute for Organics Chemistry and Biochemistry.

Our results demonstrate the efficacy of nanodiamonds as a biocompatible tool for in vitro quantum sensing of both magnetic and temperature fields. The chip functionality corresponding well the design predicted by the COMSOL simulations.



Figure 55 – Photoluminescence map of a neurons with attached nanodiamonds (in red ellipses), green ellipse marks the ND from which spectra were taken. For excitation, a 532nm laser with 1mW power was used. Photoluminescence of neurons comes from immunofluorescence, which is described in chapter 4.9. Biological samples.



Figure 56 – ODMR spectra taken from a nanodiamond attached to the neuron. Spectra was taken at lab temperature with a laser power 1mW and 1W microwave power.

#### **Conclusion and author contribution**

Both types of quantum chips, designed for use with single-crystal diamond and nanodiamond particles, were subjected to both theoretical and experimental scrutiny. Theoretical testing was conducted through numerical modelling, focusing on microwave-related characteristics such as S parameters and field distribution. Additionally, the single crystal diamond chip was tested for microwave pickup theoretically by examining |S31| and |S41| parameters (microwave transmitted to the electrode lines). Experimentally, we designed and conducted measurements of the microwave-induced pickup, where the proposed chip exhibits improved performance compared to currently employed chips. We verified the device functionality by performing series of pulse sequences, including Rabi, Ramsay, and Hans echo, on at chip modification used for microfluidic QNMR. Results show that the chip gives good spin manipulation possibilities and suits for microfluidic manufacturing. The Omega-

shaped chip underwent examination of its heating properties alongside measurements conducted on ND particles heating. Numerical modelling was employed to analyse heating characteristics, while microwave heating of liquid media, sensed by NDs, was experimentally determined. Optical detection of Zeeman splitting was conducted using liquid imaging, which is considered representative of biological samples, as well as nanodiamonds attached to neurons. Our finding substantiates the viability of utilising ND quantum probes to measure physical fields, including temperature and magnetic fields, for *in vitro* applications.

The author tested both models theoretically and iterated the chip design using numerical model output. Measurements were carried at the UHasselt, Quantum Science & Technology Group in collaboration with UHasselt BIOMED. Neurons were cultivated by PhD student Sarra Zaghbouni. Measurements on the Omega antenna were performed by a PhD student, Alevtina Shmakova, measurements on the single crystal chip were performed by a PhD student, Michal Petrov, and the QNMR variation chip was experimentally tested by senior expert researcher Reza Tavakoli. Nanodiamonds particles were functionalised by Synthetic Nanochemistry Group in Prague.

# 6. CONCLUSION

This thesis's main aim was to study quantum chips for sensing the environmental interactions with a future use in biological systems utilizing the nitrogen-vacancy (NV) point defect within the diamond's crystal lattice. The NV defect exhibits energy level shifts in response to external electromagnetic fields, which can be readout in optically or photoelectrically. For understanding of the relationship between the output signal, microwave/laser excitation and crystal environment, a sophisticated model was developed, containing the intrinsic behaviour of the NV defect, its interaction with laser and microwave fields, and its interplay with other defects, notably substitutional nitrogen (Ns). Understanding the physical processes behind signal generation is essential for the advancement of quantum sensors. Based on the described NV behaviours, two types of quantum chips were designed and fabricated: one for single crystal diamond application and the other for sensing within nanodiamonds (NDs). Both chips underwent rigorous numerical modelling and experimental verification. Furthermore, the chip designed for single crystal diamond exhibited promise for future application in microfluidic devices, while the ND-based quantum sensor was tested with particles affixed to the neuron bodies, showcasing its potential in biological sensing applications. All goals were fulfilled and are listed below:

## • Rate equation model of the NV defect in presence of the drift

The author developed a full mathematical model describing the temporal dynamics of the occupation of the NV defect in the diamond lattice based on the differential rate equation for each energy level, taking into account laser and microwave interaction, charge carrier drift and recombination kinetics. This original model is essential for the enabling highly performing NV quantum chips based on photoelectric spin state readout.

#### • Crystal defect environment modelling of the NV defect

The author investigated the effect of the crystal defect environment on NV defects by incorporating additional defects (substitutional nitrogen and acceptor defects) into the nearby diamond lattice. Their influence on the photocurrent signal was examined. The author systematically characterised the dependency of the photocurrent signal on the density of these defects. To account for defect interactions, conduction and valence bands were introduced alongside the migration of charge carriers. The author modelled total quantum efficiency for both the single NV defect and the crystal environment containing NV and Ns. The developed model allows to estimate Ns concentration in the close vicinity of the NV centre, which has important effect on the spin dynamics and consequently on the spin contrast which is inherent part of the magnetic field and temperature sensor.

#### • Experimental verification of the proposed models

The author experimentally verified the proposed model through the measurements of fluorescence and photocurrent signals of individual NV centre. The author conducted data fitting to determine ionisation rate values, which are dependent on the optical system. It was shown that the simulated spin-contrast closely matched experimental data. The author also investigated the influence of the acceptor defect on the positive PDMR phenomena. Additionally, the author explored signal generation as a function of the depth beneath the crystal surface. The varication of the model confirmed its applicability on the control of the NV spin sensor, and it is important for setting up operational parameters of device for optimal detection performance.

## • Chip designing and manufacturing.

Based on the physical understanding of NV behaviour, the author developed two quantum chips, the first for the single crystal diamond application and the second for nanodiamond applications. Each design was simulated for microwave field distribution and resonance patterns. The author developed electrodes specific to single crystal diamond, aimed at minimalizing potential microwave crosstalk interference. Subsequently, prototypes were assembled by the author and primed for experimental interrogation. These prototypes are currently used for designing practical sensors. As future step we will use the developed methodology for measuring the temperature in TRPV channels using nanodiamond, which application brings an important hope for studying of neuropathologic diseases.

#### • Chip testing on phantoms

The author's quantum sensor for single-crystal diamond applications has been tested for microwave-coupled sensing. Additionally, a QNMR microfluidic variant was employed to evaluate basic qubit manipulation using pulse schemes. Furthermore, the heating capabilities of the omega-shaped sensor for ND particles were assessed in liquid media.

#### • Chip testing on the biological environment

The sensor developed for the ND application has been tested for magnetic field sensing in the real biological system, where NDs are attached *in vitro* to neuron axons. The concept of using NV as a sensor for quantum detection was shown.

## 6.1 NV defect model

The author modelled the NV defect at two possible charge states, NV- (five energy levels) and NV0 (single energy level). Photodynamics were elucidated by a set of rate equations formulated to describe the transition between energy levels. Spin contrast was modelled for both types of readout methods, optical and photoelectrical. Notably, the steady-state probability distribution of the charge states as a function of laser power was characterised alongside the time dependency of the metastable state singlet. Results show that the majority of the charge state probability in the charge probability in the metastable singlet state causes an increase in the charge probability in the metastable singlet state, causing an increase in the charge probability in the NV<sup>-</sup> charge state at higher laser powers. Furthermore, analysis of laser-dependence spin-contrast shows that with the absence of the recombination centres, PDMR contrast copies that of ODMR one.

#### **Future perspectives**

Future perspectives of the NV photodynamic model, together with the influence of other defects, are discussed in Chapter 6.2.

# 6.2 Influence of the environment and GSLAC-assisted readout on spin contrast

Two additional defect structures, namely substitutional nitrogen (Ns) and a proposed acceptor level X, were incorporated into the model, each considered as a single energy level structure with possible positive  $(Ns^+ X^+)$  or neutral  $(Ns^0, X^0)$  states. Variation in the density of Ns centres was systematically explored, elucidating its impact on the photocurrent readout of spin-contrast. Our analysis shows that an increase in Ns led to a reduction in the PDMR contrast, accompanied by a shift of its maximum to higher laser power, which is consistent with experimental observations. The validity of the model was further substantiated through spin-contrast measurements of individual NV centres employing both optical and photoelectrical readout, demonstrating excellent agreement with experimental data. Upon comprehensive model determination, we calculated quantum efficiency for both optical and photoelectrical readout, as well as for NV and Ns complexes. Introducing acceptor level X into the simulated crystal environment enabled modelling of non-standard phenomena such as positive PDMR. Computer simulations of level X density showed that the origin of the positive PDMR may come from the proposed acceptor level. Furthermore, we investigate the depth-dependent origin of the signal, revealing theoretically and experimentally that 90% of the photoelectrical signal comes from the region 0-30µm below the crystal surface, in contrast to fluorescence signals, which originate from the entire volume. Based on the simulation, we estimate the ratio of effective interrogation volumes of photocurrent to photoluminescence detection to be the order of 1:20.

## **Future perspectives**

Understanding physical processes and dependency of external electromagnetic fields and defect concentrations within the crystal constitutes a fundamental aspect in the development of advanced quantum sensors, pulse sequence design, and determination of the effects of the crystal environment. Describing the recombination mechanism occurring at the electrode/crystal boundary or in proximity to the surface can explain phenomena such as high PDMR contrast, where observed PDMR contrast may exceed 50% or the dependency of the NV charge state flipping with the applied bias voltage. The calculated quantum efficiency is important in optimizing the pulse protocol to increase the efficiency of electrical readout and its dependency on the Ns defect concentration. Leveraging the COMSOL-MatLab interface facilitates direct examination of output signals in newly designed chip/electrode configurations. Furthermore, the utilization of microwave-free GSLAC-assisted readout chip sensors enables the deployment of diamond-based quantum sensors in biological systems, circumventing the need for microwave exposure. Coupled with precise modelling, this approach aids in determining crystal thickness and doping profiles to maximise the efficacy of photoelectrical readout via GSLAC.

# 6.3 Chip designing and testing

Two chips were developed and fabricated: one tailored for single crystal diamond and another for sensing via nanodiamond particles. Designs for both chips were optimized for microwave field distribution and potential resonance patterns. Single crystal diamond chips employed a tri-plate configuration engineered to achieve a homogenous magnetic part of the microwave field intensity surrounding the laser aperture, aligned parallel to the z-axis of the model. S-parameters within the frequency range exhibited flat characteristics, and no resonance pattern was present. Unique electrodes were designed to mitigate microwave interference with the detected photocurrent signal. Chip microwave pickup was modelled, demonstrating minimal interference on the electrode lines (-40 and -50dB). Chip evaluation for the microwave-involved pickup revealed a consistently flat response across different focal points within the frequency range, outperforming currently used chips at the UHasselt group. Moreover, the chip demonstrated promise as a candidate for microfluidic QNMR. An initial prototype was developed and subjected to pulse protocol spin manipulation tests (including Rabi, Ramsay, and Hans Echo). Further optimisation efforts will be focused on refining microwave field distribution. A quantum chip designed for nanodiamonds was developed to exhibit a resonance pattern around 2.87 GHz. Heating properties were modelled and experimentally validated through temperature sensing by nanodiamonds within an imaging media, which we consider to be a biological phantom. ODMR spectra were acquired, and algorithms successfully detected temperature shifts and

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Zeeman splitting. Additionally, ODMR spectra were collected from nanodiamond particles attached to the neurons, confirming the retention of Zeeman splitting and thus demonstrating *in vitro* quantum sensing of magnetic fields.

#### **Future perspectives**

The chip developed in this thesis for the single crystal diamond will be tested to measure individual NV defects. The QNMR setup will be upgraded so that one can apply sophisticated pulse sequences to detect NMR signals from aL-pL samples and tune the direction of the main magnetic field. An example of these sequences is XY8 [99]. To detect NMR signals, one can thermally polarize a sample inside a 1.5 T polarization magnet developed at UHasselt group and then transfer the sample as quickly as possible to the microfluidic chip through a high-pressure flow path. Then, the flow will be stopped, and the detection pulse sequence will start. This process will be repeated over and over again until a reasonably good signal-to-noise ratio is achieved. Further setup upgrades can be done by 1) implementing a double resonance pulse sequence [100], 2) Improving the main field uniformity to achieve a 10Hz linewidth resolution. This can be done through an improved design of the magnetic field, e.g., the Halbach array incorporated by gradient fields. 3) Monitoring the temperature of the NMR sample through temperature sensing protocol. 4) Using a CPC lens and light guide to collect as much PL as possible 5) Stabilizing the main magnetic field drift through active monitoring of its magnitude and compensating it by the feedback mechanism. This can be done by installing an auxiliary NV sensor alongside the membrane.

For perspective neuron measurements, we will investigate the dynamics of spontaneous axon growth during development as well as the regenerative plasticity of axonal networks after trauma on diamond-based probes. We will combine the measurement of local temperature gradients using diamond NV centers as a powerful and highly innovative tool for neuroscientific research. Temperature gradients will be defined to represent the skin-to-body core temperature differences (min: 33.5 to max: 37.7 °C) or the differences between healthy and inflamed tissue (~36.6 °C to 42 °C).

# 7. REFERENCE

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# APPENDIX A

## Table of used constants:

Constant	Value (532nm)	Unit	Source
$W_{k1}$	74.2	[MHz/mW]	FIT
W <sub>ion1</sub>	17.7	[MHz/mW]	FIT,[72]
ion <sub>2</sub>	-	[MHz]	eqn S5,[76]
Wion3	9.976	[MHz/mW]	FIT
Wion4	0.8	[MHz/mW]	FIT
rec <sub>1</sub>	6.2	[MHz]	FIT,[101]
rec <sub>2</sub>	3.1	[MHz]	FIT,[101]
rec <sub>3</sub>	10.18	[MHz]	FIT,[101]
rec <sub>4</sub>	0.059	[MHz]	FIT,[101]
rec <sub>5</sub>	40	[MHz]	FIT
rec <sub>6</sub>	5.6	[MHz]	FIT
$T_1$	250	[Hz]	measured
T <sub>2</sub>	5	[kHz]	measured
WA	22.10-3	[MHz/mW]	FIT
W <sub>B</sub>	26.10-3	[1/mW]	FIT
A <sub>k</sub>	0.3844	[-]	[72]
B <sub>k</sub>	0.4104	[-]	[72]
$C_k$	0.2052	[-]	[72]
D <sub>k</sub>	0.5	[-]	FIT
E <sub>k</sub>	0.5	[-]	FIT

Table A1 – Parameters and constants used in rates equations.

For the internal relaxation rates of  $NV^{-}$  charge state, we used two sets of rates (published in the work of Wirtitsch[72] and Tetienne[93]) and discussed their differences in the thesis).

k <sub>2,W</sub>	76.9231	[MHz]	[72]
k <sub>3,W</sub>	10.6952	[MHz]	[72]
k4,w	66.7557	[MHz]	[72]
k <sub>5,W</sub>	5.3729	[MHz]	[72]
k <sub>6,W</sub>	0.3674	[MHz]	[72]
k <sub>2,T</sub>	67.7	[MHz]	[93]
k <sub>3,T</sub>	6.4	[MHz]	[93]
k <sub>4,T</sub>	50.7	[MHz]	[93]
k <sub>5,T</sub>	0.7	[MHz]	[93]
k <sub>6,T</sub>	0.6	[MHz]	[93]

 Table A2 – Relaxation rates proposed in the work of Wirtitsch[72] (subscript W) and

 Tetienne[93] (subscript T)

# APPENDIX B

Sample	Initial sample	Treatment	NV- density	Sign of PDMR resonances
n6	Type-Ila optical grade CVD diamond with [Ns0] < 1 ppm	Electron-irradiation (14 MeV, 1016 cm–2), annealing (700 °C, 4h)	10ppb (bulk NV sample)	Variable

Table A3 – Characteristics of the sample used for the measuring of positive PDMR, taken from  $\{1\}$