

JAGIELLONIAN UNIVERSITY

DOCTORAL THESIS

Magnetic resonance spectroscopy at the nanoscale
utilizing nitrogen-vacancy centers in diamond

Author:

Zuzanna ORZECOWSKA

Supervisors:

prof. dr hab. Wojciech GAWLIK

dr hab. Adam WOJCIECHOWSKI

A thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy

in the

Photonics Department

Marian Smoluchowski Institute of Physics

Kraków, June 2024

*I dedicate this thesis to my Father,
the one responsible for sparking my
interest in tinkering and music.*

Oświadczenie

Ja, niżej podpisana Zuzanna Orzechowska (nr indeksu: 1087536), doktorantka Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. "Magnetic resonance spectroscopy at the nanoscale utilizing nitrogen-vacancy centers in diamond" jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem dra hab. Adama Wojciechowskiego oraz prof. dra hab. Wojciecha Gawlika. Pracę napisałam samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

Jestem świadoma, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

Kraków, dnia

.....

(podpis doktoranta)

ABSTRACT

This thesis delves into the realm of quantum sensing and imaging, centering around the utilization of paramagnetic nitrogen-vacancy (NV) color centers in diamond for magnetic field, current, and temperature measurements. The straightforward optical initialization and readout, coupled with a relatively long coherence time under ambient conditions, position NV centers as promising candidates for applications in many fields.

In the initial stages of nitrogen-vacancy microscopy development, the focus has primarily been on proof-of-concept experiments that highlight its significant potential. However, these early experiments may not have yielded distinctive insights into the studied systems. This cumulative thesis is based on [1-4] articles and aims to advance the progress of sensor technology by applying it to investigate various intricate and complex hybrid glass and diamond samples. Specifically, a wide-field and confocal approach is adopted, employing a dense ensemble of sub-micrometer and nanometer-sized diamonds to capture magnetic fields, current flows, and temperature sensitivity. In each of the presented applications, the intrinsic physics of the test systems and the effects resulting from their interaction with the imaging technique are explored. These observations inspire adjustments to our approach, enhancing the overall utility of the technique.

The results presented in this work originate from a desire to explore the potential of combining nanodiamond powders with easily accessible optical equipment, such as optical fibers and scanning probes, to innovate sensor technology. Consequently, Chapters 1, 2, and 3 serve as an introduction to the subjects discussed in the articles. Chapter 2 delves into the theory of the NV color center found in diamond, providing an explanation of the fundamental phenomena observed within this defect, e.g. initialization process of the center through optical pumping and its readout, the formulation of the ground-state Hamiltonian, and the application of the optically detected magnetic resonance (ODMR) research technique in the examination of the nitrogen-vacancy color center. Chapter 3 presents an overview of the experimental setups built by the author to verify the sensing capabilities of nano- and sub-micron-sized diamond powders containing nitrogen-vacancy color centers, in conjunction with optical fibers and commercially available scanning probes. Chapter 4 provides a concise overview of the results presented in articles [1-4], with a comprehensive account of the author's contribution.

STRESZCZENIE

Niniejsza dysertacja zagłębia się w dziedzinę wykrywania i obrazowania kwantowego, koncentrując się na wykorzystaniu paramagnetycznych centrów barwnych azot-wakancja (*ang. nitrogen-vacancy*, NV) w diamencie do pomiarów pola magnetycznego, przepływu prądu i pomiarów temperatury. Prosta inicjalizacja optyczna i odczyt, w połączeniu z długimi czasami koherencji w warunkach laboratoryjnych, pozycjonują centra NV jako obiecujących kandydatów do zastosowań w wielu dziedzinach.

Rozwój mikroskopii z wykorzystaniem centrów barwnych azot-wakancja w diamencie wykazał, że jest to istotna platforma badawcza, która pozostaje w zainteresowaniu badaczy od lat 70. ubiegłego wieku. Niniejsza praca jest zbiorem artykułów [1-4], a jej początkowe rozdziały stanowią wstęp do tematyki badań złożonych układów z dziedziny nanotechnologii i materii skondensowanej. Wykorzystując znane techniki mikroskopii szerokiego pola oraz konfokalnej oraz unikalną platformę jaką są diamenty o rozmiarach setek nanometrów oraz submikronowych, zaprezentowano ich przydatność do pomiarów pól magnetycznych, elektrycznych oraz temperatury, otwierając tym samym nowe możliwości pomiarowe. W każdym z artykułów przedstawiono możliwości pomiarowe badanych czujników, każdorazowo rozwijając dotychczas stosowane techniki obrazowania.

Wyniki przeprowadzonych eksperymentów przedstawione w tej pracy próbują odpowiedzieć na postawione pytanie badawcze, czy połączenia proszków nano- i submikronowych z dostępnym sprzętem optycznym, takim jak włókna optyczne i komercyjnie dostępne sondy skanujące, mogą doprowadzić do stworzenia innowacyjnego czujnika do pomiarów m.in. pola magnetycznego. Rozdziały 1, 2 i 3 stanowią wprowadzenie do omawianych w artykułach tematów. Rozdział 2 obejmuje niezbędną teorię opisującą centra barwne NV, wraz z wyjaśnieniem podstawowych zjawisk obserwowanych w tym defekcie m.in. proces inicjalizacji centrum poprzez pompowanie optyczne, jego odczyt, hamiltonian stanu podstawowego oraz wykorzystanie techniki badawczej optycznie wykrywanego rezonansu magnetycznego (*ang. optically detected magnetic resonance*, ODMR). Rozdział 3 przedstawia opisy układów eksperymentalnych zbudowanych przez autorkę niniejszej pracy, wykorzystywanych w naszym laboratorium do badań nad kwantowymi czujnikami działającymi w oparciu o centra barwne NV w diamencie. W Rozdziale 4 skrótowo przedstawiono główne konkluzje z artykułów [1-4], z naciskiem na opis wkładu własnego autorki w badania przedstawione w niniejszej pracy.

ACKNOWLEDGMENTS

I am immensely grateful for the invaluable support and guidance I have received throughout my PhD journey, and I wish to extend my heartfelt thanks to those who have played pivotal roles in this transformative experience.

First and foremost, my deepest gratitude goes to my esteemed supervisors, dr hab. Adam Wojciechowski and Professor dr hab. Wojciech Gawlik. Your unwavering commitment, guidance, and encouragement have been instrumental in shaping my research and academic growth. Your expertise and patience have not only enriched my knowledge but have also inspired me to reach for excellence in every aspect of my work. I am truly fortunate to have had the privilege of being under your mentorship.

I also want to express my appreciation to my colleagues and friends in the laboratory. The collaborative spirit, and shared passion for our research have created an environment that fostered creativity and innovation. Special thanks to Mariusz Mrózek, Mona Jani and Paulina Czarnecka for the discussions, shared insights, and the camaraderie that made the challenging moments more manageable and the achievements more meaningful.

To the entire team of Photonics Department, thank you for the knowledge exchange, and the sense of community that made this space a vibrant and intellectually stimulating or at least bearable. Here I want to thank Marek Kopciuch and Michał Padniuk. Your friendship has been a source of motivation and support, turning challenging times into opportunities for growth and learning.

I express my deepest gratitude to Piotr Put—my life partner, a huge source of inspiration, my love, and the scientist I look up to. Piotr's contributions, advice, and endless encouragement throughout this academic rollercoaster have been my rock in navigating the crazy complexities of the PhD process.

I would also like to express my sincere gratitude to my feline companion, Bubu, who has been a constant source of comfort and companionship throughout the duration of my academic pursuits. Bubu's presence, with its quiet and steadfast support, has provided a sense of tranquility during both challenging and serene moments.

Finally, to my parents Barbara and Zdzisław and friends: Agnieszka, Paweł, Magda, Maciek, Misia, Asia, Tomek, Ania, Michał, Gabi, Andrzej, Irena, Tomasz and Justyna for their enduring understanding, unwavering encouragement, and belief in my capabilities. The pillars of strength provided by your support have not only enriched my academic journey but have also contributed significantly to my personal fulfillment.

I also acknowledge support from TEAM NET programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund, project POIR.04.04.00-00-1644/18.

LIST OF ABBREVIATIONS

AFM	atomic force microscopy
CVD	chemical vapor deposition
FWHM	full width at half maximum
GUI	graphical user interface
HPHT	high pressure high temperature
ISC	intersystem crossing
MW	microwave
NV	nitrogen-vacancy color centers
NV ⁻	nitrogen-vacancy color centers negatively charged
NV ⁰	nitrogen-vacancy color centers neutrally charged
ODMR	optically detected magnetic resonance
PL	photoluminescence
ppm	parts per million
RF	radio frequency
S/R	signal-to-noise ratio
ZFS	zero field splitting
ZPL	zero phonon line

CONTENTS

Oświadczenie	v
Abstract	vii
Streszczenie	ix
Acknowledgments	x
List of Abbreviations	xi
1 Introduction	1
2 The diamond's nitrogen-vacancy defect	
2.1 Diamond utilized as a host medium	7
2.2 Impurities in diamond lattice	10
2.3 Color centers: The nitrogen-vacancies	14
2.4 Optical initialization and readout of the nitrogen vacancy center	19
2.5 The Hamiltonian characterizing the ground state of the nitrogen-vacancy center	25
2.6 Magnetic field sensitivity and optically detected magnetic resonance basis	28
3 Experimental Setups	
3.1 Wide-field microscopy setup	33
3.2 MW generation and camera synchronization for wide-field imaging	37
3.3 Confocal spectroscopy setup	41
3.4 Photoluminescence spectroscopy	44
4 Articles	
4.1 Overview of the result	45
4.2 Summary	50

CHAPTER 1

INTRODUCTION

Sensors are devices that detect and respond to physical stimuli. They are used to measure a wide range of physical properties like temperature, pressure, light, sound, and movement. Sensors come in a variety of forms and sizes, and they can be found in many different applications. This thesis is based on four research articles discussing highly adaptable magnetic field sensors [1-4].

In the past decade, there has been a dramatic increase in the number and overall impact of sensors on our lives including integration of technologies into everyday use appliances, e.g. smartphones and watches. This is due to several factors, including improved accuracy, reliability, safety, and efficiency of nowadays sensors [5].

The proliferation of sensors is having a major impact on our lives. They are used to improve the safety and efficiency of transportation, manufacturing, and healthcare. They are also being used to develop new applications in areas such as environmental monitoring and smart homes. For example, the accuracy of sensors has improved thanks to the development of new materials and manufacturing techniques. This has made sensors more reliable and less prone to errors. Sensors have also become safer, thanks to the use of new materials and designs that are less likely to cause injury, e.g. modern smoke detectors, utilizing photoelectric or ionization sensors instead of traditional radioactive materials like americium-241, which led to enhancement of reliability, efficiency, and safety for both consumers and the environment [6].

The efficiency and overall performance of sensors have also improved thanks to the development of new data processing and analysis techniques. This

has made it possible to extract more information from sensor data, which can be used to improve the performance of applications.

In addition to their everyday applications, better sensors are also essential for the discovery and understanding of new physics. For example, the Laser Interferometer Gravitational-Wave Observatory is a sensor to detect gravitational waves, which are ripples in the structure of spacetime caused by massive objects such as black holes and neutron stars. This major breakthrough confirmed the existence of gravitational waves and opened up a new window into the universe [7]. Sensitive particle detectors have allowed scientists to study the fundamental particles that make up matter. The Large Hadron Collider in CERN uses particle detectors to study the collisions of subatomic particles at high energies. This research has helped to understand the basic building blocks of the universe and the forces that govern them [8]. The satellite sensors have enabled scientists to monitor the Earth's climate and environment as well as track the movement of hurricanes and other weather systems [9]. This information is essential to understand and predicting climate change. The last example is the use of medical imaging sensors that have revolutionized the diagnosis and treatment of diseases. Magnetic resonance imaging (MRI) uses powerful magnets and radio waves to create detailed images of the body. This technology is used to diagnose a wide range of medical conditions, including cancer, heart disease, and stroke [10].

As sensors continue to improve, even more applications in science and technology can be expected. For example, better sensors based on quantum physics could be used to develop new medical treatments, create more efficient energy sources, or even detect life on other planets.

Quantum sensors are devices that use the principles of quantum mechanics to measure physical quantities. They have the potential to outperform classical sensors in terms of sensitivity, accuracy, and resolution [11].

The specific domain where sensors have been widely utilized is spectral sensing, e.g. fluorescence spectroscopy or spectrophotometry. Spectral analysis unveils the frequency and magnitude components of signals that change over time, and it holds significance across various domains in natural science and medicine. This is due to its diverse range of practical uses, such as establishing time and frequency standards [12,13]. The accuracy of spectral information is

limited by the laws of physics. Quantum mechanics ultimately determines these limits, and therefore only quantum mechanical detectors can perform quantum spectroscopy at the limits of resolution, sensitivity and still be non-invasive, e.g. due to its nano-size.

This thesis centers around a particularly auspicious quantum sensor, known as the nitrogen-vacancy (NV) center in diamond. Due to its atomic size and electronic spin properties, it exhibits remarkable sensitivity to magnetic fields and offers nanoscale spatial resolution. The fundamental concept behind magnetic field sensing using NV is common to optical magnetometry, in which the energy of spin levels is altered by a magnetic field in direct relation to the field's strength [14, 15].

Nitrogen-vacancy centers in diamond have garnered significant attention in the field of quantum sensing due to their exceptional properties. These centers arise from a substitutional nitrogen atom adjacent to a carbon vacancy within the diamond lattice. In their negative charge state, an electronic ground state of NV center is the spin triplet with a milliseconds-coherence time at room temperature [16]. The electronic spin of the NV center interacts sensitively with both magnetic and electric fields, rendering it an exceptional platform for diverse sensing applications [17]. Notably, the NV center's ability to achieve high sensitivity for magnetic fields and nanoscale spatial resolution has enabled advancements in various fields. Magnetic field sensing based on NV centers operates on the principle of energy level shifts in response to applied magnetic fields, akin to optical magnetometry [18]. This characteristic has found applications in quantum-enhanced metrology [19], as well as biomedical imaging and magnetic resonance spectroscopy [20]. Additionally, NV centers have been harnessed for studies in quantum information processing and quantum communication [21]. Furthermore, their potential integration into solid-state quantum devices has sparked research endeavor to realize practical quantum technologies [22]. NV centers have the potential to serve as nanoscale sensors for temperature [23] or pressure [24]. Given the myriad capabilities of NV centers, ongoing research continues to explore their diverse applications and unlock their full potential in the realm of quantum sensing.

This thesis is based on four articles on the specific research that I have conducted developing NV color centers based sensors. These are:

[1] "Tellurite Glass Rods with Submicron-Size Diamonds as Photonic Magnetic Field and Temperature Sensors." Zuzanna Orzechowska, Mariusz Mrózek, Adam Filipkowski, Dariusz Pysz, Ryszard Stępień, Mateusz Ficek, Adam M. Wojciechowski, Mariusz Klimczak, Robert Bogdanowicz, and Wojciech Gawlik. *Advanced Quantum Technologies* 5.3 (2022): 2100128.

<https://doi.org/10.1002/qute.202100128>

[2] "Preparation and characterization of AFM tips with nitrogen-vacancy and nitrogen-vacancy-nitrogen color centers." Zuzanna Orzechowska, Mariusz Mrózek, Wojciech Gawlik, and Adam M. Wojciechowski. *Photonics Letters of Poland* 13.2 (2021): 28-30.

<https://doi.org/10.4302/plp.v13i2.1095>

[3] "Optically detected magnetic resonance study of thermal effects due to absorbing environment around nitrogen-vacancy-nanodiamond powders." Mona Jani, Zuzanna Orzechowska, Mariusz Mrózek, Marzena Mitura-Nowak, Wojciech Gawlik and Adam M. Wojciechowski. *Journal of Applied Physics* 135 (2024): 203101.

<https://doi.org/10.1063/5.0203870>

[4] "Sensing of Magnetic-Field Gradients with Nanodiamonds on Optical Glass-Fiber Facets." Mona Jani, Paulina Czarnecka, Zuzanna Orzechowska, Mariusz Mrózek, Wojciech Gawlik, and Adam M. Wojciechowski. *ACS Applied Nano Materials* 6.13 (2023): 11077-11084.

<https://doi.org/10.1021/acsanm.3c00887>

These publications, alongside a concise summary constitute a Chapter 4 of this thesis. The results presented in this work provide an answer to the research hypothesis that it is feasible to combine nanodiamond powders with readily available optical equipment, e.g. optical fibers and scanning probes, to create an innovative sensor for measuring temperature, electric currents, magnetic fields, and their gradients. Therefore, Chapters 2 and 3 constitute an introduction into those research topics. Chapter 2 approaches the theory of NV⁻

color center found in diamond, along with an elucidation of the fundamental phenomena observed within this defect. This includes the process of initializing the center through optical pumping and its readout, the formulation of the ground-state Hamiltonian, and the utilization of the optically detected magnetic resonance (ODMR) research technique in the study of the nitrogen-vacancy color center. Chapter 3 provides an overview of experimental setups designed to validate the sensing capabilities of the nano- and sub-micron-sized diamond powders with nitrogen-vacancy color centers combined with optical fibers and commercially available scanning probes.



- [5] Javaid, Mohd, et al. "Sensors for daily life: A review." *Sensors International* 2 (2021): 100121.
<https://doi.org/10.1016/j.sintl.2021.100121>
- [6] Liu, Baojun, et al. "Gamma-free smoke and particle detector using tritiated foils." *IEEE Sensors Journal* 7.6 (2007): 917-918.
<https://doi.org/10.1109/JSEN.2007.895971>
- [7] Abbott, Benjamin P., et al. "Observation of gravitational waves from a binary black hole merger." *Physical Review Letters* 116.6 (2016): 061102.
<https://doi.org/10.1103/PhysRevLett.116.061102>
- [8] Aad, Georges, et al. "Observation of a new particle in the search for the Standard Model Higgs boson with the ATLAS detector at the LHC." *Physics Letters B* 716.1 (2012): 1-29.
<https://doi.org/10.1016/j.physletb.2012.08.020>
- [9] Yang, Jun, et al. "The role of satellite remote sensing in climate change studies." *Nature Climate Change* 3.10 (2013): 875-883.
<https://doi.org/10.1038/nclimate1908>
- [10] Howseman, Alistair M., and Richard W. Bowtel. "Functional magnetic resonance imaging: imaging techniques and contrast mechanisms." *Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences* 354.1387 (1999): 1179-1194.
<https://doi.org/10.1098/rstb.1999.0473>
- [11] Aslam, Nabeel, et al. "Quantum sensors for biomedical applications." *Nature Reviews Physics* 5.3 (2023): 157-169.
<https://doi.org/10.1038/s42254-023-00558-3>
- [12] Diddams, Scott A., et al. "Standards of time and frequency at the outset of the 21st century." *Science* 306.5700 (2004): 1318-1324.
<https://doi.org/10.1126/science.1102330>

[13] Riehle, Fritz. "Frequency Standards: Basics and Applications" *Wiley-VCH*, Weinheim, Germany (2004).

<https://doi.org/10.1002/3527605991>

[14] Redman, D. A., et al. "Spin dynamics and electronic states of N-V centers in diamond by EPR and four-wave-mixing spectroscopy." *Physical Review Letters* 67.24 (1991): 3420.

<https://doi.org/10.1103/PhysRevLett.67.3420>

[15] Gruber, A., et al. "Scanning confocal optical microscopy and magnetic resonance on single defect centers." *Science* 276.5321 (1997): 2012-2014.

<https://doi.org/10.1126/science.276.5321.2012>

[16] Doherty, Marcus W., et al. "The nitrogen-vacancy colour centre in diamond." *Physics Reports* 528.1 (2013): 1-45.

<https://doi.org/10.1016/j.physrep.2013.02.001>

[17] Maze, Jeronimo R., et al. "Nanoscale magnetic sensing with an individual electronic spin in diamond." *Nature* 455.7213 (2008): 644-647.

<https://doi.org/10.1038/nature07279>

[18] Balasubramanian, Gopalakrishnan, et al. "Ultralong spin coherence time in isotopically engineered diamond." *Nature Materials* 8.5 (2009): 383-387.

<https://doi.org/10.1038/nmat2420>

[19] Taylor, Jacob M., et al. "High-sensitivity diamond magnetometer with nanoscale resolution." *Nature Physics* 4.10 (2008): 810-816.

<https://doi.org/10.1038/nphys1075>

[20] Lovchinsky, Igor, et al. "Nuclear magnetic resonance detection and spectroscopy of single proteins using quantum logic." *Science* 351.6275 (2016): 836-841.

<https://doi.org/10.1126/science.aad8022>

[21] Togan, Emre, et al. "Quantum entanglement between an optical photon and a solid-state spin qubit." *Nature* 466.7307 (2010): 730-734.

<https://doi.org/10.1038/nature09256>

[22] Awschalom, David D., et al. "Quantum technologies with optically interfaced solid-state spins." *Nature Photonics* 12.9 (2018): 516-527.

<https://doi.org/10.1038/s41566-018-0232-2>

[23] Toyli, David M., et al. "Fluorescence thermometry enhanced by the quantum coherence of single spins in diamond." *Proceedings of the National Academy of Sciences* 110.21 (2013): 8417-8421.

<https://doi.org/10.1073/pnas.1306825110>

[24] Doherty, Marcus W., et al. "Electronic properties and metrology applications of the diamond NV⁻ center under pressure." *Physical Review Letters* 112.4 (2014): 047601.

<https://doi.org/10.1103/PhysRevLett.112.047601>

CHAPTER 2

THE DIAMOND'S NITROGEN-VACANCY DEFECT

2.1 DIAMOND UTILIZED AS A HOST MEDIUM

Diamonds stand out as a remarkable substance with extensive uses. Renowned for its stunning elegance, it has achieved fame as possibly the most favoured precious stone in the realm of jewellery, often selected for engagement rings to symbolize eternal commitment. However, beyond its aesthetic allure, diamond occupies a crucial position across various domains of industry and scientific exploration due to its superb physical characteristics. In particular, its unparalleled hardness, which is among the best natural materials, underscores its significance in diverse applications beyond the gem sector. This feature arises from the densely packed arrangement of carbon atoms in a crystal lattice, and the robust bonds they form, render diamonds exceptionally suitable for cutting tools and abrasives.

Furthermore, diamond boasts unparalleled thermal conductivity at room temperature, measuring around $2000 \text{ W/(K}\cdot\text{m)}$, with phonons serving as the primary agents for heat propagation. In cases involving highly pure diamond and temperatures close to 100 K, this value can rise to $41,000 \text{ W/(K}\cdot\text{m)}$ [25].

In diamond, each carbon atom undergoes sp^3 hybridization and forms covalent bonds with four adjacent carbon atoms, maintaining a separation of $1.54 \text{ \AA}$. The resultant crystal structure is a face-centered cubic lattice, characterized by a lattice constant of $3.57 \text{ \AA}$ under standard conditions [26], with a two-atom basis located at positions $[(0, 0, 0), (1/4, 1/4, 1/4)]$. Although diamond is not the most thermodynamically stable carbon allotrope under typical conditions, its

transformation into graphite occurs at a low pace due to a notably elevated activation barrier, ranging between 730 to 1160 kJ/mol, with the exact value depending on the specific surface of the diamond involved [27].

Diamond's importance in quantum applications is particularly highlighted by its classification as a semiconductor possessing a substantial indirect band gap measuring 5.47 eV [28]. As a wide-bandgap semiconductor, it also has a remarkable breakdown field of 13 MV/cm and extraordinarily high intrinsic carrier mobilities, which can reach up to 3800 cm²/(V·s) for holes and 4500 cm²/(V·s) for electrons when measured at room temperature [29]. These distinctive properties make diamond exceptionally suitable for advancing the next generation of high-power electronic devices, including applications such as diodes and microwave transistors [30, 31]. The large band gap implies that diamond requires a significant amount of energy to transfer electrons from the valence band to the conduction band, which is essential for facilitating controlled electronic transitions in various quantum devices. This feature allows diamond to act effectively as a platform for quantum information processing, where precise control over the energy states of individual particles is a paramount. Furthermore, the possibility of controllable doping and the exceptional coherence properties achievable in diamond's crystal lattice contribute to its position as a frontrunner in quantum communication systems [32], quantum computing architectures [33] and the field of quantum sensors [1-4], the development of which is the main focus of this thesis.



[25] Wei, Lanhua, et al. "Thermal conductivity of isotopically modified single crystal diamond." *Physical Review Letters* 70.24 (1993): 3764.

<https://doi.org/10.1103/PhysRevLett.70.3764>

[26] Occelli, Florent, Paul Loubeyre, and Rene LeToullec. "Properties of diamond under hydrostatic pressures up to 140 GPa." *Nature Materials* 2.3 (2003): 151-154.

<https://doi.org/10.1038/nmat831>

[27] Davies, G., and Trevor Evans. "Graphitization of diamond at zero pressure and at a high pressure." *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences* 328.1574 (1972): 413-427.

<https://doi.org/10.1098/rspa.1972.0086>

[28] Clark, C. D., P. J. Dean, and P. V. Harris. "Intrinsic edge absorption in diamond." *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 277.1370 (1964): 312-329.

<https://doi.org/10.1098/rspa.1964.0025>

[29] Isberg, Jan, et al. "High carrier mobility in single-crystal plasma-deposited diamond." *Science* 297.5587 (2002): 1670-1672.

<https://doi.org/10.1126/science.1074374>

[30] Umezawa, Hitoshi. "Recent advances in diamond power semiconductor devices." *Materials Science in Semiconductor Processing* 78 (2018): 147-156.

<https://doi.org/10.1016/j.mssp.2018.01.007>

[31] Geis, Michael W., et al. "Progress toward diamond power field-effect transistors." *Physica Status Solidi (a)* 215.22 (2018): 1800681.

<https://doi.org/10.1002/pssa.201800681>

[32] Wang, Jianwei, et al. "Integrated photonic quantum technologies." *Nature Photonics* 14.5 (2020): 273-284.

<https://doi.org/10.1038/s41566-019-0532-1>

[33] Awschalom, David D., et al. "Quantum spintronics: engineering and manipulating atom-like spins in semiconductors." *Science* 339.6124 (2013): 1174-1179.

<https://doi.org/10.1126/science.1231364>

2.2 IMPURITIES IN DIAMOND LATTICE

Electronic defects situated within the band gap of the diamond have significant implications for quantum applications as they have the potential to serve as qubits. The current understanding encompasses over 500 optically active defect variations [34]. The most elementary among these defects is a vacancy resulting from the absence of a carbon atom within the lattice. Additionally, impurity atoms can be identified within diamond's structure. The proximity of boron and nitrogen to carbon in the periodic table confers similar sizes, rendering them prime candidates for replacing carbon atoms in the diamond lattice. This property positions boron and nitrogen as the most prevalent impurities, and their concentration can serve to classify diamonds, as illustrated in [Table 2.1](#).

Defects can significantly affect certain physical characteristics of a host diamond, such as its color. Unlike pure diamonds, which are transparent to visible light because of their wide band gap, defects and impurities can introduce extra energy levels within the energy band gap. These additional energy levels can result in the absorption and emission of light within the visible spectrum, ultimately giving the diamond its distinct coloration. Hence, these imperfections are called *color centers*.

Most natural diamonds belong to the type Ia class due to their elevated nitrogen content ([Table 2.1](#)). However, since both stable nitrogen isotopes (^{14}N and ^{15}N) generate defects with electronic and nuclear spins, causing optical and magnetic interference, samples with excessive nitrogen concentration are generally unsuitable for specific scientific applications. Conversely, diamonds of type II, characterized by a minimal nitrogen content, are more suitable for specific applications where a small amount of nitrogen is advantageous. In this study, all results are derived with type Ib diamond samples.

Because type II diamonds are typically not naturally occurring, it becomes necessary to create them artificially. The synthesis of diamonds also offers the added benefit of being able to control properties such as the type and density of impurities and their crystallographic orientation in a diamond lattice. The primary

techniques employed for this purpose are chemical vapor deposition (CVD) and high-pressure high-temperature (HPHT) methods. The predominant source of nanodiamond powders is the detonation nanodiamond (DND) method. While comprehensive accounts of these methods are documented in references [35-37], a concise overview of the fundamental steps in these procedures is provided here

Table 2.1: Types of diamond. Diamonds classification based on their nitrogen [N] content. The majority of naturally occurring diamonds fall into the category of type Ia. However, for scientific applications, diamonds with minimal defects, known as type IIa diamonds, are of greater interest (data extracted from [35]).

	Type	Characteristic
Type I [N] > 1-2 ppm	Ia	common in nature, a pale yellow or brown color due to nitrogen atom aggregations within the carbon lattice
	IaA	Ia subtype, A-centers are created when a duo of nitrogen atoms substitutes carbon atoms in the diamond lattice
	IaB	Ia subtype, B-centers are generated when four nitrogen atoms replace carbon atoms, accompanied by a vacancy (an absence of an atom) within the lattice
	Ib	naturally occurs rarer, substantial nitrogen atoms are more widely spread, found in a broad range of vivid colors that mirrors the nitrogen distribution, known as C-centers that are formed when a nitrogen atom replaces a single carbon atom within the diamond lattice
Type II [N] < 1-2 ppm	IIa	often described as the epitome of purity, featuring minimal impurities and exhibiting transparency across both the visible and ultraviolet (UV) spectra, down to approximately 230 nm wavelengths, resulting in a colorless appearance
	IIb	also have very low nitrogen content despite, typically exhibit a light blue or gray appearance due to the inclusion of small amounts of boron atoms substituting carbon within their crystal lattice

The HPHT technique entails initiating a phase transition from graphite to diamond by subjecting the material to extreme conditions, including pressures ranging from 60 to 150 GPa and temperatures of at least 2000 K. This method is widely employed for the synthesis of synthetic diamonds, as it closely mimics the conditions prevailing in the Earth's mantle, the natural diamond-forming environment. The introduction of metals like iron, cobalt, or nickel can act as catalysts, facilitating the reaction and lowering the necessary pressure and temperature conditions [38, 39]. As impurities are typically present in significant

quantities, the majority of diamonds produced using this method are classified as type Ib crystals. By utilizing exceptionally pure carbon melts and elements that bind to impurities, it becomes feasible to produce diamonds of type IIa [40].

The CVD method involves forming thin layers through the layer-by-layer deposition of atoms from a plasma. It is essential to create suitable conditions for arranging the deposited carbon atoms. Gases, such as methane or hydrogen, are heated to a plasma state, enabling the deposition process. Generating diamond layers involves numerous physical and chemical interactions occurring both in the gaseous phase and at the gas-solid interface. This method allows for a high degree of control over the conditions necessary for producing the nitrogen-vacancy color centers which are the main subject of this thesis.

The detonation method involves triggering an explosion within a potent explosive mixture that includes $C_aH_bN_cO_d$ compounds (with a, b, c, d denote the number of each respective atom in the molecular formula) while ensuring deficiency of oxygen. The resulting shock wave generates extreme pressure and temperature conditions, exceeding 10 GPa and 3000 K. Within this process, approximately 75% of the carbon is transformed into diamond, forming crystallites with dimensions of around 4 nm [41]. This method is commonly employed to produce nano- and microdiamonds. Typical uses for detonation nanodiamonds encompass applications such as electroplating coatings, abrasive polishing compounds and suspensions, polymer composites, lubricating oils, and greases. Additionally, DND has been employed in the seeding of substrates used during the CVD process for growing diamond films [41]. Emerging and innovative uses for nanodiamonds are swiftly evolving across a wide spectrum of fields, including magnetic recording, medical technology, biomedicine, and antifouling applications. Research suggests that DND is not harmful and is compatible with biological systems, rendering it appealing for medical and biotechnological purposes. This appeal is strengthened by its extensive surface chemistry, which can be methodically altered [42].

In following articles included in this thesis HPHT-type diamonds were acquired through commercial procurement from Adamas Nanotechnologies with a range of sizes. These sizes include around 1 micrometer-sized diamonds used for measurements presented in articles [1, 2] and carboxylated fluorescent

nanodiamonds (FND-COOH) with dimensions of 140 nm and a concentration of 1.5 ppm of NV centers in articles [3, 4].



[34] Aharonovich, I., et al. "Diamond-based single-photon emitters." *Reports on Progress in Physics* 74.7 (2011): 076501.

<https://doi.org/10.1088/0034-4885/74/7/076501>

[35] Ashfold, Michael NR, et al. "Nitrogen in diamond." *Chemical Reviews* 120.12 (2020): 5745-5794.

<https://doi.org/10.1021/acs.chemrev.9b00518>

[36] Waldermann, F. C., et al. "Creating diamond color centers for quantum optical applications." *Diamond and Related Materials* 16.11 (2007): 1887-1895.

<https://doi.org/10.1016/j.diamond.2007.09.009>

[37] Neves, A. J., & Nazaré, M. H. (Eds.). (2001). "Properties, growth and applications of diamond." (No. 26). IET.

<https://doi.org/10.1109/MEI.2002.1044323>

[38] Nazare, M. H., & Davies, G. (1994). "Properties and growth of diamond." In EMIS Data Review Series (p. 85). London: INSPEC.

<https://doi.org/10.1180/minmag.1995.59.394.22>

[39] Sung, Chien-Min, and Ming-Fong Tai. "Reactivities of transition metals with carbon: Implications to the mechanism of diamond synthesis under high pressure." *International Journal of Refractory Metals and Hard Materials* 15.4 (1997): 237-256.

[https://doi.org/10.1016/S0263-4368\(97\)00003-6](https://doi.org/10.1016/S0263-4368(97)00003-6)

[40] Balmer, R. S., et al. "Chemical vapour deposition synthetic diamond: materials, technology and applications." *Journal of Physics: Condensed Matter* 21.36 (2009): 364221.

<https://doi.org/10.1088/0953-8984/21/36/364221>

[41] Shenderova, Olga, ed. "Detonation nanodiamonds: science and applications." *CRC Press*, 2014.

<https://doi.org/10.1201/b15541>

[42] Schrand, Amanda M., Suzanne A. Ciftan Hens, and Olga A. Shenderova. "Nanodiamond particles: properties and perspectives for bioapplications." *Critical Reviews in Solid State and Materials Sciences* 34.1-2 (2009): 18-74.

<https://doi.org/10.1080/10408430902831987>

2.3 COLOR CENTERS: THE NITROGEN-VACANCIES

Over the past decade, there has been a significant surge in the engineering of color centers in diamond, particularly for applications in photonic and quantum technologies. Optically active defects with strong luminescence within the visible and near-infrared spectral regions, including impurities associated with vacancies in the diamond lattice, such as nitrogen-vacancy (NV), silicon-vacancy (SiV), germanium-vacancy (GeV), and more recently, lead-vacancy (PbV) and tin-vacancy (SnV) centers, are being explored as potential candidates for generating single photons [43-49]. These developments hold promise for the advancement of solid-state quantum photonics [50, 51].

The NV color centers exhibit stability at room temperature and have the potential to serve as quantum bits (qubits) that operate in everyday ambient conditions. Although it is possible to create these color centers in diamonds through ion implantation [52], the approach of in situ doping during the diamond growth process is the preferred method. This preference arises from the desire to avoid any residual damage caused by the implantation process, which can persist even after high-temperature annealing. A couple of illustrative methods for achieving in situ doping include introducing gaseous precursors such as silane (SiH_4) [53] and germane (GeH_4) [54] into the plasma during the CVD diamond growth process. The concentrations of the respective color centers can be precisely controlled by adjusting the flow rate of the dopant.

Because of the inherent abundance of nitrogen and vacancies, NV centers typically exist within any given diamond. The most straightforward method to augment their quantity involves elevating the diamond's temperature beyond 600°C . At these elevated temperatures, vacancies become mobile and disperse throughout the diamond lattice.

As depicted in Figure 2.1(a), the NV center represents a point defect characterized by a nitrogen atom that replaces a carbon atom and an adjacent vacancy. It exhibits C_{3v} symmetry [56], with its symmetry axis aligned along the

imaginary line connecting the nitrogen atom and the vacancy. Consequently, the NV center can be manifested in four distinct crystallographic orientations, as illustrated in Figure 2.1(b).

NV centers exhibit a range of exceptional characteristics, rendering them highly intriguing candidates for applications in quantum technologies. For example, they demonstrate optical stability when exposed to light. Additionally, NV centers are firmly trapped within the robust diamond lattice, leading to a theoretically boundless lifetime, obviating the necessity for special conditions. Consequently, they remain stable even at temperatures of approximately 1700°C [57]. Compared to other defects found in diamonds, NV centers stand out due to their relatively lengthy relaxation times for electron spin, even under ambient environmental conditions. Another advantage is their optical accessibility, which allows for the initialization and readout of the spin state.

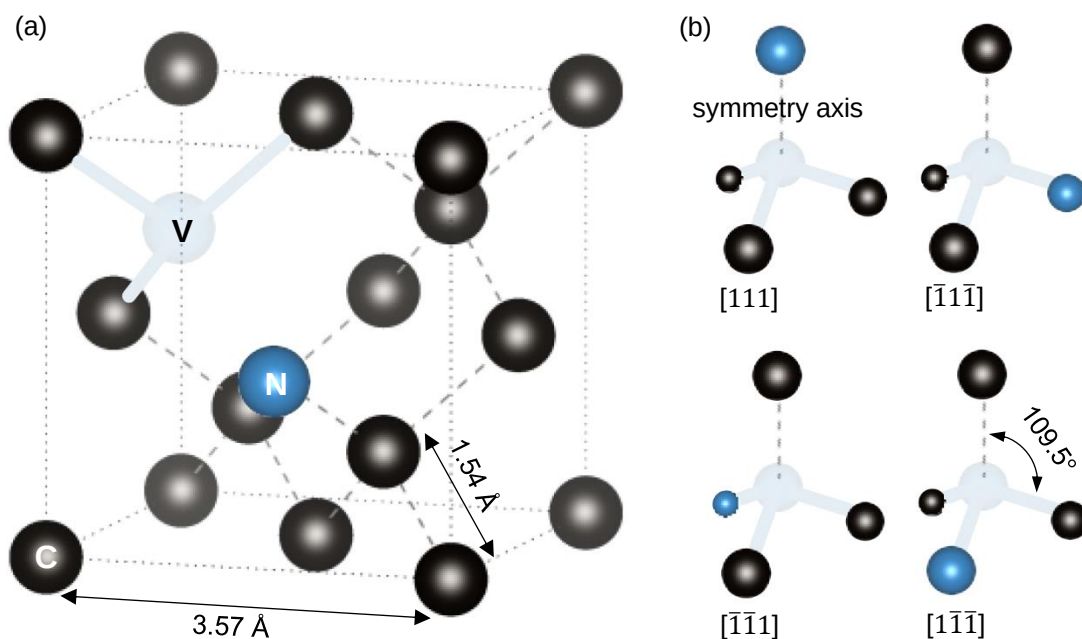


Figure 2.1: The nitrogen-vacancy center in diamond. (a) Illustration of the NV center in diamond, which is composed of a nitrogen atom (depicted in blue) substituting for a carbon atom (shown in black), along with an adjoining vacancy (represented in light blue). (b) Four possible alignments for NV centers within a diamond lattice, with a bond angle of approximately 109.5°.

The electronic structure of NV color center can be described as follows: the nitrogen atom possesses five valence electrons, three of them are bonded to nearby carbon atoms, and the remaining two are close to the vacancy and non-bonded. Three unbounded electrons from neighboring carbon atoms add to a

total number of five electrons that contribute to electronic structure of the color center. This specific arrangement is called a neutral NV color center, and denoted NV^0 . NV^0 , with its neutral charge and paramagnetic properties ($S = 1/2$), appears to hold significant promise for applications in quantum information systems. However, this type of center has received limited research attention, particularly with regard to the absence of optically detected magnetic resonance signals for NV^0 [58]. It is important to highlight that detecting those signals is a crucial milestone in harnessing its potential for qubit applications and magnetic tracking in biomarker studies [59]. When an additional electron from a donor in the lattice, e.g. another nitrogen atom, becomes associated with the vacancy, this defect transforms into the negatively charged color center with $S = 1$, which will be the primary focus of this dissertation and called for brevity of this thesis as NV. A less frequent occurrence involves NV center having only four electrons, resulting in the formation of an NV^+ color center [60].

Diamond is primarily composed of carbon ^{12}C (comprising 98.9% of its composition), characterized by a zero nuclear spin. However, all naturally occurring diamonds contain a trace amount of carbon ^{13}C (1.1%), which has a nuclear spin of $1/2$. This nuclear property renders the presence of carbon ^{13}C particularly significant due to its strong, hyperfine interaction, with the nitrogen-vacancy color center [61].



[43] Rogers, Lachlan J., et al. "Electronic structure of the negatively charged silicon-vacancy center in diamond." *Physical Review B* 89.23 (2014): 235101.

<https://doi.org/10.1103/PhysRevB.89.235101>

[44] Rogers, Lachlan J., et al. "Multiple intrinsically identical single-photon emitters in the solid state." *Nature Communications* 5.1 (2014): 4739.

<https://doi.org/10.1038/ncomms5739>

[45] Sipahigil, Alp, et al. "Indistinguishable photons from separated silicon-vacancy centers in diamond." *Physical Review Letters* 113.11 (2014): 113602.

<https://doi.org/10.1103/PhysRevLett.113.113602>

[46] Sipahigil, Alp, et al. "An integrated diamond nanophotonics platform for quantum-optical networks." *Science* 354.6314 (2016): 847-850.

<https://doi.org/10.1126/science.aah687>

[47] Iwasaki, Takayuki, et al. "Germanium-vacancy single color centers in diamond." *Scientific Reports* 5.1 (2015): 12882.

<https://doi.org/10.1038/srep12882>

[48] Siyushev, Petr, et al. "Optical and microwave control of germanium-vacancy center spins in diamond." *Physical Review B* 96.8 (2017): 081201.

<https://doi.org/10.1103/PhysRevB.96.081201>

[49] Iwasaki, Takayuki, et al. "Tin-vacancy quantum emitters in diamond." *Physical Review Letters* 119.25 (2017): 253601.

<https://doi.org/10.1103/PhysRevLett.119.253601>

[50] Bradac, Carlo, et al. "Quantum nanophotonics with group IV defects in diamond." *Nature Communications* 10.1 (2019): 5625.

<https://doi.org/10.1038/s41467-019-13332-w>

[51] Eichhorn, Tim R., et al. "Optimizing the formation of depth-confined nitrogen vacancy center spin ensembles in diamond for quantum sensing." *Physical Review Materials* 3.11 (2019): 113802.

<https://doi.org/10.1103/PhysRevMaterials.3.113802>

[52] Evans, Ruffin E., et al. "Narrow-linewidth homogeneous optical emitters in diamond nanostructures via silicon ion implantation." *Physical Review Applied* 5.4 (2016): 044010.

<https://doi.org/10.1103/PhysRevApplied.5.044010>

[53] Ralchenko, Victor G., et al. "Monoisotopic ensembles of silicon-vacancy color centers with narrow-line luminescence in homoepitaxial diamond layers grown in $\text{H}_2\text{--CH}_4\text{--}^{[x]}\text{SiH}_4$ gas mixtures ($x = 28, 29, 30$)." *ACS Photonics* 6.1 (2018): 66-72.

<https://doi.org/10.1021/acsp Photonics.8b01464>

[54] Sedov, V., et al. "Growth of polycrystalline and single-crystal CVD diamonds with bright photoluminescence of Ge-V color centers using germane GeH_4 as the dopant source." *Diamond and Related Materials* 90 (2018): 47-53.

<https://doi.org/10.1016/j.diamond.2018.10.001>

[55] Collins, Alan T., and Isaac Kiflawi. "The annealing of radiation damage in type Ia diamond." *Journal of Physics: Condensed Matter* 21.36 (2009): 364209.

<https://doi.org/10.1088/0953-8984/21/36/364209>

[56] Maze, Jeronimo R., et al. "Properties of nitrogen-vacancy centers in diamond: the group theoretic approach." *New Journal of Physics* 13.2 (2011): 025025.

<https://doi.org/10.1088/1367-2630/13/2/025025>

[57] Deák, Peter, et al. "Formation of NV centers in diamond: A theoretical study based on calculated transitions and migration of nitrogen and vacancy related defects." *Physical Review B* 89.7 (2014): 075203.

<https://doi.org/10.1103/PhysRevB.89.075203>

[58] Manson, Neil B., et al. "Assignment of the NV^0 575-nm zero-phonon line in diamond to a ${}^2\text{E--}^2\text{A}_2$ transition." *Physical Review B* 87.15 (2013): 155209.

<https://doi.org/10.1103/PhysRevB.87.155209>

[59] Gali, Adam. "Theory of the neutral nitrogen-vacancy center in diamond and its application to the realization of a qubit." *Physical Review B* 79.23 (2009): 235210.

<https://doi.org/10.1103/PhysRevB.79.235210>

[60] Hauf, M. V., et al. "Chemical control of the charge state of nitrogen-vacancy centers in diamond." *Physical Review B* 83.8 (2011): 081304.

<https://doi.org/10.1103/PhysRevB.83.081304>

[61] Scharfenberger, Burkhard, William J. Munro, and Kae Nemoto. "Coherent control of an NV⁻ center with one adjacent ¹³C." *New Journal of Physics* 16.9 (2014): 093043.

<https://doi.org/10.1088/1367-2630/16/9/093043>

2.4 OPTICAL INITIALIZATION AND REDOUT OF THE NITROGEN VACANCY CENTER

One remarkable characteristic of the NV^- center is its ability to transfer its electron spin $S = 1$ to the $m_s = 0$ state through the process of optical pumping. As illustrated in Figure 2.2, non-resonant laser illumination enables optical excitation from the orbital-singlet, spin-triplet $^3A_2$ ground state [16] to vibronic levels situated above the first excited state.

While the excited ^3E state is characterized as orbital-doublet and spin-triplet, it can be simplified as an effective spin-triplet system, as demonstrated in previous studies [62, 63]. This simplification holds when the temperature exceeds approximately 20 to 25 K, effectively averaging the spin-orbit coupling, resulting in a zero-field splitting of 1.42 GHz [64, 65]. The non-radiative decay into the lowest vibrational band occurs quite rapidly, within a short timescale of approximately 50 fs to 4 ps [66, 67].

In the process of returning to the ground state, two potential pathways are illustrated in Figure 2.2. The immediate decay, with the emission of a photon, preserves the spin (red arrows) and predominantly occurs into the vibronic levels of the ground state. The second decay route entails a non-radiative intersystem crossing (ISC) to intermediate states positioned energetically between the ground and excited states. They comprise an orbital-singlet, spin-singlet state denoted as $^1A_1$ and an orbital-doublet, with a single spin in the ^1E state. These singlet states are coupled by an optical transition with a zero-phonon line (ZPL) occurring at 1042 nm [68]. The ISC from the excited state ^1E to the $^1A_1$ state is primarily driven by spin-orbit coupling and exhibits a significant dependence on the spin state [63]. Specifically, for the $m_s = 0$ spin state, this transition is relatively weak, while it becomes approximately four times more likely for the $m_s = \pm 1$ spin states. Following a rapid transition to the ^1E state, the shift to the ground state displays only a minor spin dependence, as reported articles [69, 70].

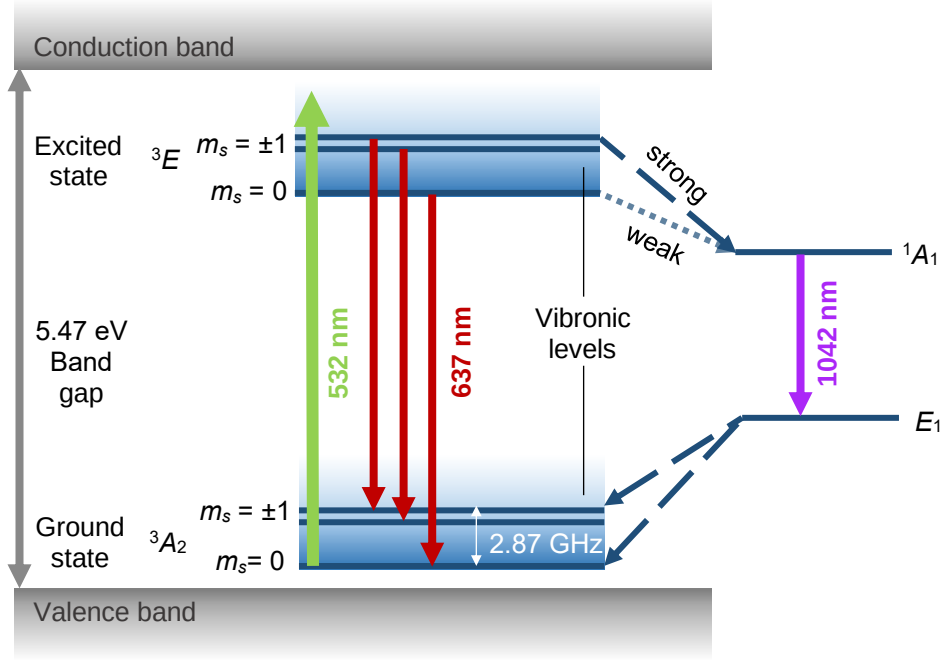


Figure 2.2: Diagram of electron levels of the NV⁻ center. Radiative transitions are represented by solid lines, while non-radiative transitions are indicated by dashed lines. A thicker dashed line denotes a greater likelihood of transitions. Excitation from the $^3A_2$ ground state into vibronic levels above the ^3E excited states is non-resonant and followed by a rapid decay over vibronic states preserving the spin state. In the process of decay to the ground state, there are two pathways. The first pathway involves a direct decay into vibronic levels of the ground state, which also conserves the spin. In this case, the emitted photons exhibit a redshift comparable to that of the zero-phonon line at 637 nm and are marked by red arrows lines pointing down. The second pathway marked by a violet downward arrow encompasses a spin-dependent intersystem crossing towards intermediate states, specifically the $^1A_1$ and ^1E states. This transition is significantly stronger for spin states with $m_s = \pm 1$. Subsequently, the decay from the ^1E state into the $m_s = 0$ ground state exhibits a higher probability. Consequently, this optical cycle enhances the likelihood of populating the $m_s = 0$ spin state.

As a result, the probability of a change in spin state after a single optical cycle is approximately 8% when starting from the $m_s = 0$ state, and approximately 35% if the initial state was $m_s = \pm 1$ [69]. Consequently, on average, the $m_s = \pm 1$ spin states experience depopulation in favor of the $m_s = 0$ state. However, due to the non-zero possibility of both an ISC from the excited $m_s = 0$ state into the intermediate $^1A_1$ state and a transition from the ^1E state to the $m_s = \pm 1$ levels in the ground state, initialization with a perfect spin polarization cannot be achieved in an equilibrium state. The achievable polarizations are reported to be around 80% for ensembles of NV centers [71] and approximately 84% to 92% for single defects [72–74]. When discontinuing optical illumination, the presence of the NV

center in intermediate states cannot be ruled out. Therefore, it is advisable to incorporate an additional relaxation period of not less than 1 μ s before starting subsequent experiments. The time required to achieve the equilibrium state described above depends on the excitation power, as it determines the rate of excitation from the ground state to the excited state.

Numerous techniques for measuring the electron spin of NV centers have been reported. A commonly employed method involves detecting spin-dependent photoluminescence (PL). The change of charge dynamics between NV^0 and NV^- by optical illumination enables application of spin-to-charge conversion techniques. Different charge states can be distinguished optically [73–76] or electrically by detecting released charge carriers [77–79]. At cryogenic temperatures, spin-selective excitation results in fluorescence exclusively from one of the selected states, enabling high-contrast readout [80–82]. In addition, infrared absorption techniques can also be utilized [83]. The following discussion will focus on the readout techniques pertinent to this thesis, while a comprehensive overview of all presently known detection methods can be found in [84].

The process of direct relaxation back to the ground state, which preserves the spin, involves vibronic levels. Consequently, under room temperature, a significant portion of the emitted photons undergoes a redshift relative to the zero-phonon line (ZPL) at 637 nm. Figure 2.3 displays a representative spectrum recorded under ambient conditions. Even at extremely low temperatures, only about 4% of the total fluorescence contributes to the ZPL [85], and the spectrum is predominantly characterized by substantial phonon sidebands, reaching their maximum intensity at approximately 680 – 700 nm. Optical excitation can also lead to switching between the charged and neutral states of the NV center [86, 87]. These transitions alter the electronic configuration, producing photons with a shorter wavelength characterized by the NV^0 zero-phonon line at approximately 575 nm.

There are two primary reasons why fluorescence varies with NV spin state. First, the decay through ISC is considerably more likely for the $m_s = \pm 1$ states, as illustrated in Figure 2.2. Consequently, the likelihood of photon emission during a single optical cycle is lower for these spin states. Second, the slow relaxation rate from the ^1E state to the ground state serves as an effective trap, impeding

further optical excitation. The lifetime of this state depends on the temperature. At the same time, numerous cycles involving direct decay can occur, resulting in the emission of numerous photons. This ultimately leads to a higher PL signal on average for the $m_s = 0$ spin state.

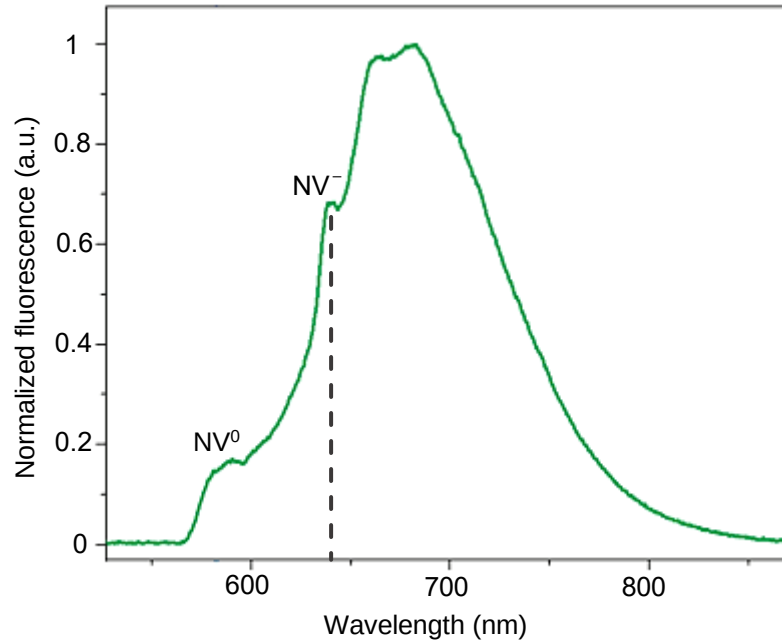


Figure 2.3: Fluorescent spectrum of the NV^- center. Normalized fluorescence spectrum of an NV center registered by the author of this thesis. The vertical dashed line marks the ZPL at 637 nm. The majority of the PL is present in the extensive phonon sideband with longer wavelength than 637 nm. The fluorescence from the NV^0 charge state, resulting from inevitable charge state cycling during illumination, can be partially mitigated by excluding low-wavelength photons. Here we can observe a peak at approximately 575 nm associated with NV^0 centers, its characteristic and broaden shape is due to the high concentration of NV^- centers.



[62] Fu, Kai-Mei C., et al. "Observation of the dynamic Jahn-Teller effect in the excited states of nitrogen-vacancy centers in diamond." *Physical Review Letters* 103.25 (2009): 256404.

<https://doi.org/10.1103/PhysRevLett.103.256404>

[63] Goldman, Michael Lurie, et al. "State-selective intersystem crossing in nitrogen-vacancy centers." *Physical Review B* 91.16 (2015): 165201.

<https://doi.org/10.1103/PhysRevB.91.165201>

[64] Fuchs, G. D., et al. "Excited-state spectroscopy using single spin manipulation in diamond." *Physical Review Letters* 101.11 (2008): 117601.

<https://doi.org/10.1103/PhysRevLett.101.117601>

[65] Neumann, P., et al. "Excited-state spectroscopy of single NV defects in diamond using optically detected magnetic resonance." *New Journal of Physics* 11.1 (2009): 013017.

<https://doi.org/10.1088/1367-2630/11/1/013017>

[66] Ulbricht, Ronald, et al. "Vibrational relaxation dynamics of the nitrogen-vacancy center in diamond." *Physical Review B* 97.22 (2018): 220302.

<https://doi.org/10.1103/PhysRevB.97.220302>

[67] Huxter, Vanessa M., et al. "Vibrational and electronic dynamics of nitrogen–vacancy centres in diamond revealed by two-dimensional ultrafast spectroscopy." *Nature Physics* 9.11 (2013): 744-749.

<https://doi.org/10.1038/nphys2753>

[68] Rogers, L. J., et al. "Infrared emission of the NV centre in diamond: Zeeman and uniaxial stress studies." *New Journal of Physics* 10.10 (2008): 103024.

<https://doi.org/10.1088/1367-2630/10/10/103024>

[69] Robledo, Lucio, et al. "Spin dynamics in the optical cycle of single nitrogen-vacancy centres in diamond." *New Journal of Physics* 13.2 (2011): 025013.

<https://doi.org/10.1088/1367-2630/13/2/025013>

[70] Tetienne, J. P., et al. "Magnetic-field-dependent photodynamics of single NV defects in diamond: an application to qualitative all-optical magnetic imaging." *New Journal of Physics* 14.10 (2012): 103033.

<https://doi.org/10.1088/1367-2630/14/10/103033>

[71] Harrison, Joanne, M. J. Sellars, and N. B. Manson. "Measurement of the optically induced spin polarisation of NV centres in diamond." *Diamond and Related Materials* 15.4-8 (2006): 586-588.

<https://doi.org/10.1016/j.diamond.2005.12.027>

[72] Fuchs, G. D., et al. "Excited-state spin coherence of a single nitrogen–vacancy centre in diamond." *Nature Physics* 6.9 (2010): 668-672.

<https://doi.org/10.1038/nphys1716>

[73] Waldherr, G., et al. "Dark states of single nitrogen-vacancy centers in diamond unraveled by single shot NMR." *Physical Review Letters* 106.15 (2011): 157601.

<https://doi.org/10.1103/PhysRevLett.106.157601>

[74] Shields, Brendan J., et al. "Efficient readout of a single spin state in diamond via spin-to-charge conversion." *Physical Review Letters* 114.13 (2015): 136402.

<https://doi.org/10.1103/PhysRevLett.114.136402>

[75] Jaskula, J-C., et al. "Improved quantum sensing with a single solid-state spin via spin-to-charge conversion." *Physical Review Applied* 11.6 (2019): 064003.

<https://doi.org/10.1103/PhysRevApplied.11.064003>

[76] Hopper, David A., et al. "Near-infrared-assisted charge control and spin readout of the nitrogen-vacancy center in diamond." *Physical Review B* 94.24 (2016): 241201.

<https://doi.org/10.1103/PhysRevB.94.241201>

[77] Gulka, Michal, et al. "Pulsed photoelectric coherent manipulation and detection of N–V center spins in diamond." *Physical Review Applied* 7.4 (2017): 044032.

<https://doi.org/10.1103/PhysRevApplied.7.044032>

- [78] Siyushev, Petr, et al. "Photoelectrical imaging and coherent spin-state readout of single nitrogen-vacancy centers in diamond." *Science* 363.6428 (2019): 728-731.
<https://doi.org/10.1126/science.aav2789>
- [79] Hrubesch, Florian M., et al. "Efficient electrical spin readout of NV⁻ centers in diamond." *Physical Review Letters* 118.3 (2017): 037601.
<https://doi.org/10.1103/PhysRevLett.118.037601>
- [80] Robledo, Lucio, et al. "High-fidelity projective read-out of a solid-state spin quantum register." *Nature* 477.7366 (2011): 574-578.
<https://doi.org/10.1038/nature10401>
- [81] Blok, M. S., et al. "Manipulating a qubit through the backaction of sequential partial measurements and real-time feedback." *Nature Physics* 10.3 (2014): 189-193.
<https://doi.org/10.1038/nphys2881>
- [82] Cramer, Julia, et al. "Repeated quantum error correction on a continuously encoded qubit by real-time feedback." *Nature Communications* 7.1 (2016): 11526.
<https://doi.org/10.1038/ncomms11526>
- [83] Jensen, Kasper, et al. "Cavity-enhanced room-temperature magnetometry using absorption by nitrogen-vacancy centers in diamond." *Physical Review Letters* 112.16 (2014): 160802.
<https://doi.org/10.1103/PhysRevLett.112.160802>
- [84] Hopper, David A., Henry J. Shulevitz, and Lee C. Bassett. "Spin readout techniques of the nitrogen-vacancy center in diamond." *Micromachines* 9.9 (2018): 437.
<https://doi.org/10.3390/mi9090437>
- [85] Bernien, Hannes, et al. "Two-photon quantum interference from separate nitrogen vacancy centers in diamond." *Physical Review Letters* 108.4 (2012): 043604.
<https://doi.org/10.1103/PhysRevLett.108.043604>
- [86] Manson, N. B., J. P. Harrison, and M. J. Sellars. "Nitrogen-vacancy center in diamond: Model of the electronic structure and associated dynamics." *Physical Review B* 74.10 (2006): 104303.
<https://doi.org/10.1103/PhysRevB.74.104303>
- [87] Gaebel, T., et al. "Photochromism in single nitrogen-vacancy defect in diamond." *Applied Physics B* 82 (2006): 243-246.
<https://doi.org/10.1007/s00340-005-2056-2>

2.5 THE HAMILTONIAN CHARACTERIZING THE GROUND STATE OF THE NITROGEN-VACANCY CENTER

When considering diamond defects with electronic spin, the ground state spin Hamiltonian is typically divided into four components [88]. The initial component, denoted as $\mathcal{H}_{ZF}$, characterizes the interaction among the unpaired electrons. The second term, $\mathcal{H}_Z$, represents the coupling of the electron spin to an external magnetic field, accounting for the Zeeman effect. $\mathcal{H}_{hf}$ deals with hyperfine interactions between the electron spin and associated nuclear spins, while $\mathcal{H}_Q$ describes the quadrupole interaction. Thus, the complete Hamiltonian can be expressed as follows:

$$\mathcal{H}_{NV} = \mathcal{H}_{ZF} + \mathcal{H}_Z + \mathcal{H}_{hf} + \mathcal{H}_Q \quad (1)$$

Figure 2.4 offers a sketched overview of each separate term, and Table 2.2 presents a collection of the pertinent coupling constants. In this context, minor couplings such as the nonsecular Zeeman, nonsecular hyperfine, and nuclear Zeeman interactions have been omitted as they are not relevant to the focus of this thesis [89].

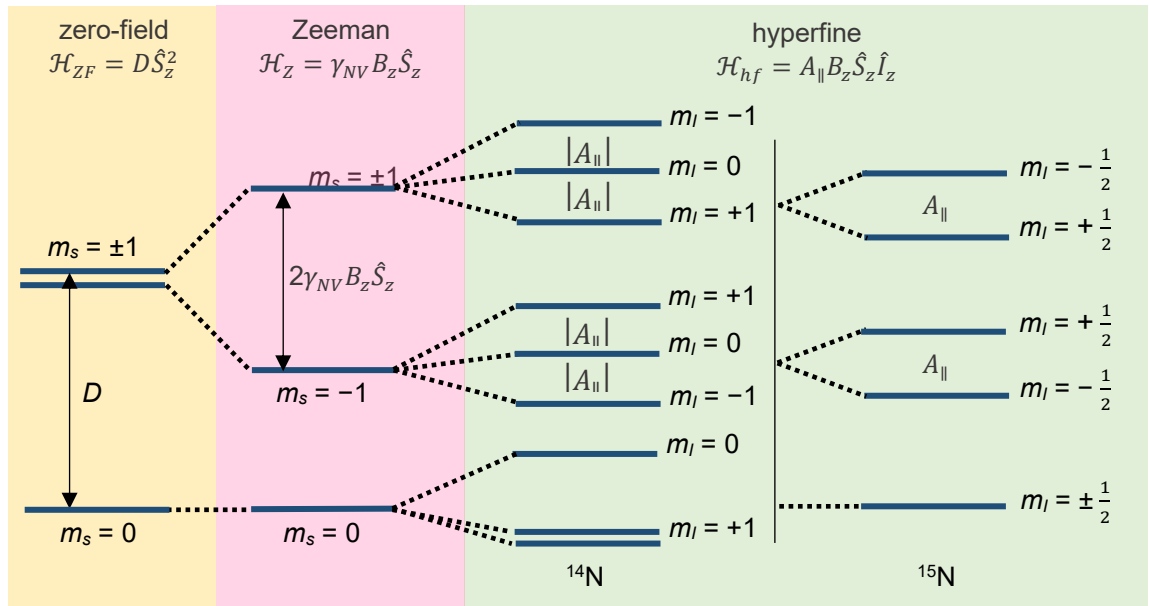


Figure 2.4: Energy manifold of an electronic spin in the $^3A_2$ ground state. The graph illustrates the main interactions of the ground state: zero-field splitting (yellow), the Zeeman interaction (pink) and the hyperfine interaction (green) with the neighboring nitrogen atom, whether either ^{14}N or ^{15}N .

Because the excited state plays a crucial role solely in the optical pumping cycle for both initialization and readout (as described in Sections 2.3), but holds no significance during the sensing phase, it is not elaborated upon in this context. Readers interested in this aspect are directed to [61, 64, 90].

Equation below expresses the Hamiltonian of the $^3A_2$ ground state under the influence of an external magnetic field B :

$$\mathcal{H}_{NV} = DS_z^2 + E(S_x^2 + S_y^2) + g_s\mu_B\vec{B} \cdot \vec{S} + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) + PI_z^2 - g_I\mu_N\vec{B} \cdot \vec{I}. \quad (2)$$

In the given context, μ_B represents the Bohr magneton, μ_N denotes the nuclear magneton, D is the axial zero-field splitting (ZFS) coefficient, E stands for the transverse zero-field splitting coefficient, g_s is Lande g -factor, S_x , S_y and S_z are components of the electron spin vector $\vec{S}$. $A_{\parallel}$ represents the axial hyperfine constant, and $A_{\perp}$ denotes the transverse hyperfine constant. The coefficients $A_{\parallel}$ and $A_{\perp}$ depend on the nitrogen isotopes present in the color center with natural diamond typically consisting of 99.6% nitrogen ^{14}N (with nuclear spin $I = 1$) and 0.4% nitrogen ^{15}N (with nuclear spin equal to $1/2$) [91]. Additionally, P symbolizes the quadrupole moment, I_z represents the longitudinal component of the nuclear spin, and g_I is the nuclear gyromagnetic ratio. The principal axis of the NV^- center aligns with one of the four crystallographic directions $\langle 111 \rangle$ (as depicted in Figure 2.1). The specific values of the coefficients mentioned in equation 2 are detailed in Table 2.2.

Table 2.2: Constants governing the coupling of the NV center. The primary factors influencing the ground-state Hamiltonian typically involve the zero-field splitting parameter D and the Zeeman interaction with the coupling g -factor. Nitrogen isotope-dependent constants encompass the parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) hyperfine couplings, along with the quadrupole parameter P . These values are sourced from [92].

isotope	D (GHz)	g_s	g_I	$A_{\parallel}$ (MHz)	$A_{\perp}$ (MHz)	P (MHz)
^{14}N	2.87	2.003	0.403	-2.14	-2.79	-5.01
^{15}N				3.03	3.65	—



[88] Loubser, J. H. N., and J. A. van Wyk. "Electron spin resonance in the study of diamond." *Reports on Progress in Physics* 41.8 (1978): 1201.

<https://doi.org/10.1088/0034-4885/41/8/002>

[89] Suter, Dieter, and Fedor Jelezko. "Single-spin magnetic resonance in the nitrogen-vacancy center of diamond." *Progress in Nuclear Magnetic Resonance Spectroscopy* 98 (2017): 50-62.

<https://doi.org/10.1016/j.pnmrs.2016.12.001>

[90] Rogers, L. J., et al. "Time-averaging within the excited state of the nitrogen-vacancy centre in diamond." *New Journal of Physics* 11.6 (2009): 063007.

<https://doi.org/10.1088/1367-2630/11/6/063007>

[91] Rabeau, J. R., et al. "Implantation of labelled single nitrogen vacancy centers in diamond using N¹⁵." *Applied Physics Letters* 88.2 (2006).

<https://doi.org/10.1063/1.2158700>

[92] Felton, S., et al. "Hyperfine interaction in the ground state of the negatively charged nitrogen vacancy center in diamond." *Physical Review B* 79.7 (2009): 075203.

<https://doi.org/10.1103/PhysRevB.79.075203>

2.6 MAGNETIC FIELD SENSITIVITY AND OPTICALLY DETECTED MAGNETIC RESONANCE BASIS

The fundamental mechanism behind coupling of the NV electronic spin to magnetic fields is the Zeeman effect. This effect induces shifts in the energies of spin states with a non-zero spin quantum number m_s when exposed to an external magnetic field B . Derived from the Zeeman Hamiltonian outlined in Section 2.5 of this Chapter, the gyromagnetic ratio γ_{NV} of the NV center can be expressed as:

$$\gamma_{NV} = \frac{g_{NV}\mu_B}{h} \approx 28.03 \text{ GHz/T.} \quad (3)$$

To perform vector magnetometry, NV centers aligned with all four possible crystallographic axes orientations can be used [93]. These orientations are responsible for effective gyromagnetic ratios, and hence different Zeeman splitting.

The interaction of the NV center with electric fields occurs through the Stark effect [94, 95]. This interaction is governed by the spin-orbit coupling between the ground and excited triplet states. Nanoscale electric field sensors are of significant importance because numerous particles, such as free electrons, produce electric fields but relatively weak magnetic fields. For instance, the detection of a single charge at a distance of 150 nm is achievable with just one second of averaging, leading to an overall alternating current (AC) electric-field sensitivity of $2.02 \text{ Vm}^{-1}\text{Hz}^{-1/2}$ [96]. Further potential applications of the NV center as an electric field sensor are suggested in [97, 98].

As the NV center constitutes a spin system with $S = 1$, it has a ZFS parameter, which depends on the separation distance of the two unpaired electrons. Consequently, any external factors influencing this distance can alter the ZFS parameter D . Noteworthy examples include pressure p ($dD/dp = 1.46 \text{ kHz/bar}$ [24]) and temperature T ($dD/dT = -74.2 \text{ kHz/K}$ [99]). Hence, NV centers have the potential to serve as nanoscale sensors for temperature [23] or pressure [24].

Most important for this thesis is the capability of NV centers to identify and analyze magnetic signals. To achieve this, various measurement techniques exist, and their suitability and effectiveness hinge on the nature of the magnetic field. The following section outlines the most prevalent techniques. Magnetic resonance is an extensively used and valuable technique, that relies on the absorption (and/or emission) of electromagnetic radiation by paramagnetic particles [100]. As spins possess a magnetic moment, electromagnetic fields resonant to a transition between two spin levels can be absorbed. Consequently, an unknown frequency can be identified by adjusting the energy difference between the spin levels and detecting the absorption.

Given that the fluorescence of the NV center is spin-dependent, optically detected magnetic resonance (ODMR) emerges as a straightforward yet robust spectroscopic technique [15]. The underlying principle is illustrated in Figure 2.5 (a). The NV center is subjected to a continuous light irradiation and is simultaneously exposed to the magnetic field oscillating at microwave frequency. Light consistently populates (pumps) the $m_s = 0$ state, while the microwaves (MW) induce spin transitions if their frequency is resonant with transitions to other magnetic substates. When the MW frequency does not match with the energy splitting between the $m_s = 0$ and $m_s = -1$ or $+1$ spin states, the recorded fluorescence remains high. Conversely, if the microwaves are absorbed, the spin state can change, leading to a reduction in fluorescence. As the NV center is continuously illuminated, an equilibrium is established between these two competing mechanisms, dependent on the excitation power of the laser and the driving amplitude of the microwave field. In the absence of an external magnetic field, the spin states $m_s = -1$ and $m_s = +1$ are degenerate and shifted by $D = 2.87$ GHz compared to the $m_s = 0$ level. Owing to Zeeman interactions, both states with a non-zero spin quantum number are split, allowing for selective addressing of transitions with $m_s = 0$ state, as illustrated in Figure 2.5 (a). The splitting ν_Δ , measured in frequency units, is defined by:

$$\nu_\Delta = \Delta m_s \gamma_{NV} B_z \approx B_z \cdot 2 \cdot 28 \text{ GHz/T}, \quad (4)$$

where $\Delta m_s = 2$ represents the difference in spin quantum numbers, γ_{NV} is the gyromagnetic ratio of the NV center's electron spin, and B_z is the projection of

the magnetic field onto the symmetry axis of the NV center. Based on the selection rules, the spin quantum number can only change by one, allowing direct driving of the $m_s = 0 \leftrightarrow m_s = -1$ and $m_s = 0 \leftrightarrow m_s = +1$ transitions.

When considering the zero-field splitting D , the resonance frequencies are as follows:

$$\nu_{res} = D \pm \gamma_{NV} B_z = 2.87 \text{ GHz} \pm 28 \frac{\text{GHz}}{\text{T}} \cdot B_z. \quad (5)$$

In Figure 2.5 (c) and (d), the ODMR spectra for various magnetic bias fields (B_z) are depicted for the [111] orientation of magnetic field. In this context, the fluorescence was recorded while varying the microwave frequency (ν) of a generated microwave field.

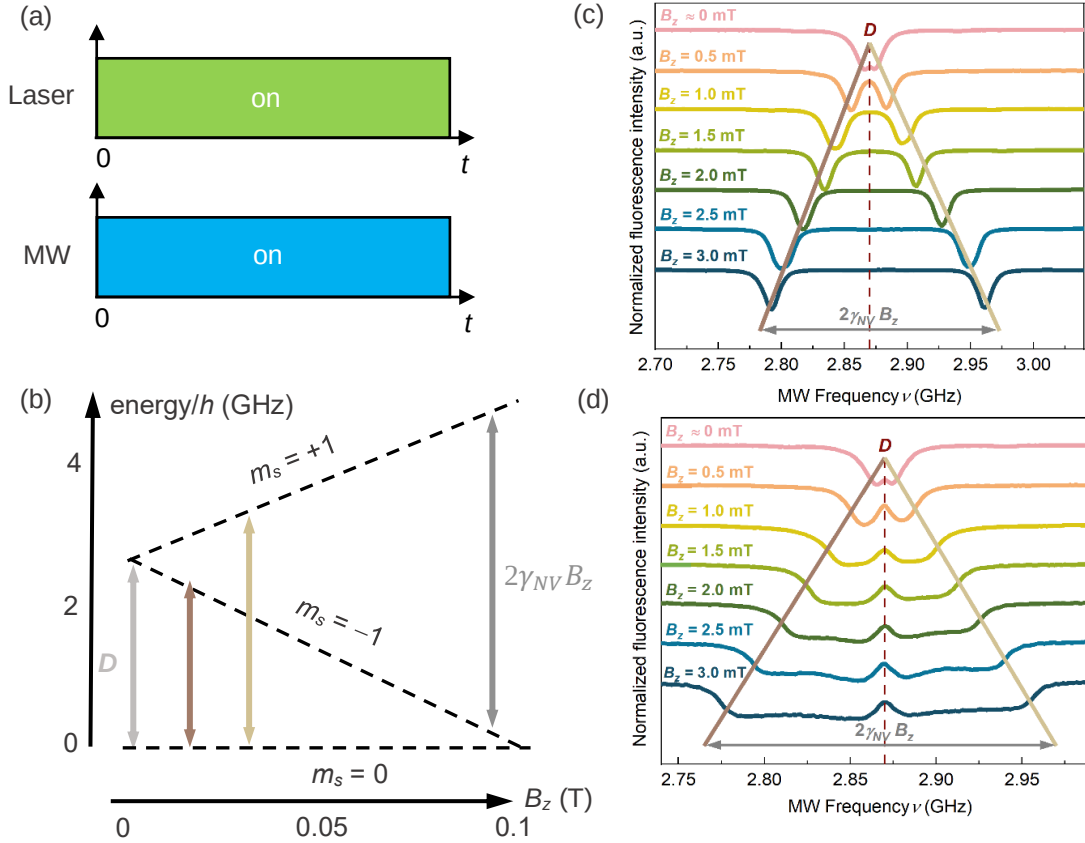


Figure 2.5: Basis of the ODMR technique. (a) The NV centre is constantly illuminated and simultaneously subject to a microwave field in time domain. (b) The transition frequency between the spin states m_s as a function of the magnetic field B_z . If the microwave frequency is in resonance with either the $m_s = 0 \leftrightarrow m_s = -1$ transition (brown arrow) or the $m_s = 0 \leftrightarrow m_s = +1$ transition (beige arrow), absorption occurs. The $m_s = -1 \leftrightarrow m_s = +1$ transition is forbidden due to selection rules. Figures (c) and (d) presents the ODMR spectra for different magnetic fields. The resonances split symmetrically with increasing bias field. (c) represents the spectra collected for bulk crystal sample with an external magnetic field along <111> direction and (d) are ODMR signals from 140 nm ND powder visible broadening of the spectra is caused by the coexistence of all possible magnetic field orientations.

When $B_z = 0$, a single peak is observed around $\nu = D$, marked by red dashed line. As the magnetic field increases, two lines, beige and brown, correspondingly follow minima that extend apart from each other in Figure 2.5 (c) and (d). Consequently, the strength of an unknown magnetic field can be directly determined by determining position of these peaks at MW scale. Using the same principle, an oscillating field (e.g. various frequencies are used for different measurements techniques 0.1 Hz to 10kHz in ODMR, 100 kHz to 1 MHz for dynamical decoupling and 1 to 10 GHz for T_1 relaxometry) with an unknown frequency can be recorded by sweeping a well-known bias field [103]. As illustrated in Figure 2.5 (c), ODMR spectra can be gathered for a bulk crystal sample. In Figure 2.5 (d), a typical spectrum for a nanodiamond sample is depicted. In contrast to bulk samples, changes in the magnetic field cannot be determined by straightforwardly recalculating the minima of peak positions. The coexistence of all possible magnetic field orientations leads to a broadened net spectrum. Therefore, the magnitude of the external magnetic field is determined by calculating the second derivative of the ODMR signal [101].



[93] Steinert, Steffen, et al. "High sensitivity magnetic imaging using an array of spins in diamond." *Review of Scientific Instruments* 81.4 (2010).

<https://doi.org/10.1063/1.3385689>

[94] Van Oort, Eric, and Max Glasbeek. "Electric-field-induced modulation of spin echoes of NV centers in diamond." *Chemical Physics Letters* 168.6 (1990): 529-532.

[https://doi.org/10.1016/0009-2614\(90\)85665-Y](https://doi.org/10.1016/0009-2614(90)85665-Y)

[95] Tamarat, Ph, et al. "Stark shift control of single optical centers in diamond." *Physical Review Letters* 97.8 (2006): 083002.

<https://doi.org/10.1103/PhysRevLett.97.083002>

[96] Dolde, Florian, et al. "Electric-field sensing using single diamond spins." *Nature Physics* 7.6 (2011): 459-463.

<https://doi.org/10.1038/nphys1969>

[97] Iwasaki, Takayuki, et al. "Direct nanoscale sensing of the internal electric field in operating semiconductor devices using single electron spins." *ACS Nano* 11.2 (2017): 1238-1245.

<https://doi.org/10.1021/acsnano.6b04460>

[98] Bassett, L. C., et al. "Electrical tuning of single nitrogen-vacancy center optical transitions enhanced by photoinduced fields." *Physical Review Letters* 107.26 (2011): 266403.

<https://doi.org/10.1103/PhysRevLett.107.266403>

[99] Acosta, Victor M., et al. "Optical properties of the nitrogen-vacancy singlet levels in diamond." *Physical Review B* 82.20 (2010): 201202.

<https://doi.org/10.1103/PhysRevB.82.201202>

[100] Slichter, Charles P. "Principles of magnetic resonance". *Vol. 1. Springer Science & Business Media*, 2013.

<https://doi.org/10.1007/978-3-662-09441-9>

[101] Fedotov, I. V., et al. "Fiber-optic magnetometry with randomly oriented spins." *Optics Letters* 39.23 (2014): 6755-6758.

<https://doi.org/10.1364/OL.39.006755>

CHAPTER 3

EXPERIMENTAL SETUPS

3.1 WIDE-FIELD MICROSCOPY SETUP

All the measurements outlined in this thesis and articles gathered in Chapter 4 were conducted using the wide-field microscopy setup, built by the author of this thesis. While this system has a relatively straightforward design, it provides the synchronized management of NV diamond substrate illumination and photoluminescence collection, manipulation of the NV spin state through a microwave field, application of an external magnetic field to offset the NV spin state energy levels, and control/modulation of the device or system while investigating various diamond sample. This section introduces the elements common to the wide-field microscope that can perform ODMR measurements, encompassing optics configuration, sample mounting, microwave antennas, and alignment of the external magnetic field in different configurations to interact with diamond samples, e.g. powders and powder-covered optical fiber facets, bulk diamond samples or thin membranes.

The optical components in any experiment with NV spins need to facilitate the initialization and readout of the NV spin state, involving excitation from a light source, e.g. a laser, and efficient collection of the photoluminescence. In most applications, the laser excitation needs to be gated, allowing it to be used for time-dependent spin-state pumping and optimized for sensitive readout. In wide-field imaging experiments, the excitation laser must deliver sufficient power across a field of view of typically tens or hundreds of micrometers in diameter. The NV photoluminescence collected from the same area must be projected onto a camera for imaging. This can be done in various ways, and this section reviews

the methods used throughout this thesis. Additional details can be found in the references [93, 102, 103].

Figure 3.1 illustrates the configuration of optical components employed in constructing a wide-field microscope for NV-diamond imaging. This schematic serves as a representation for custom-built wide-field microscopes built by the author of this thesis and utilized in articles [1-4].

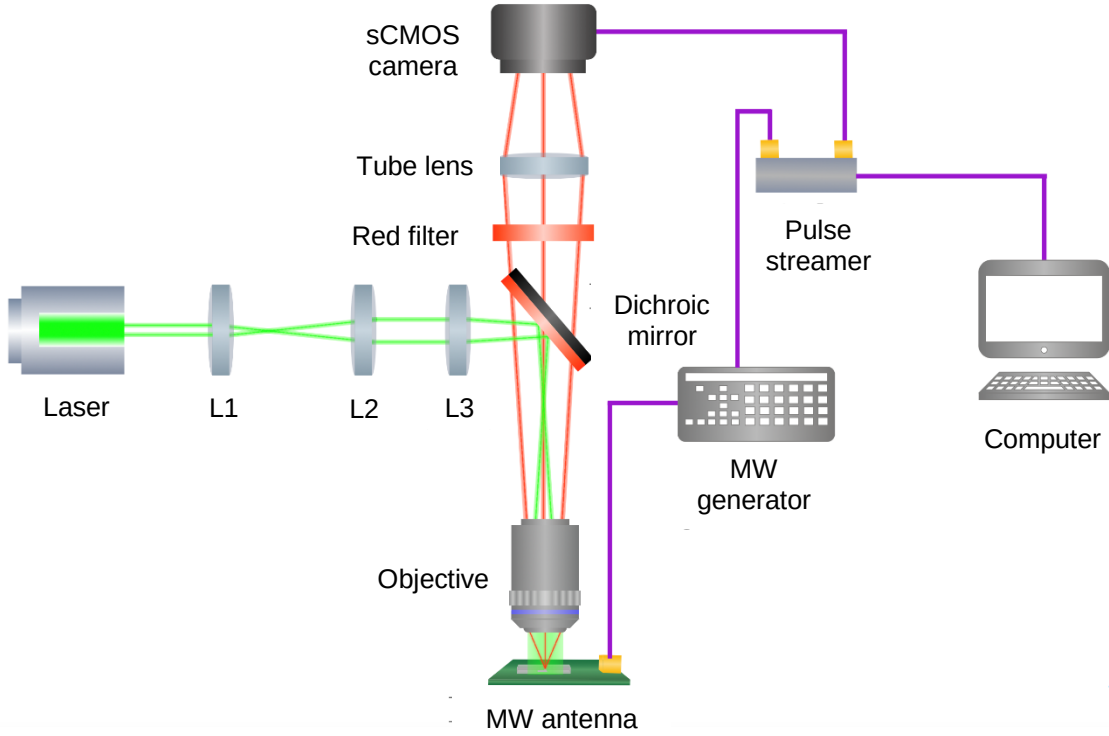


Figure 3.1: Illustration outlining the optical and electronic components of the wide-field NV diamond microscope built by the author. A CW laser beam with a wavelength of 532 nm (green) passing through a beam expander (lenses L1 and L2) to adjust the beam waist and subsequent field-of-illumination. The beam is then focused (lens L3) on the back focal plane of a microscope objective which provides wide-field illumination of the sample. The resulting NV red photoluminescence is gathered through the objective, separated from the excitation laser using a dichroic mirror, and filtered before being concentrated onto an sCMOS camera for imaging. Signals from the sCMOS camera sensor and MW generator are synchronized with a pulse streamer and controlled by the computer.

A continuous wave (CW) diode-pumped solid-state laser (Sprout G, Lighthouse Photonics) operating at a wavelength of 532 nm is employed to both initialize and read out the NV spin state. The laser's output power can reach up to 10.0 W, providing power stability at higher operating levels. The laser power is kept at maximum for stability reasons but most of its energy is dumped and only 1 W is distributed among different experiments on the optical table using beam splitters. The typical power used in experiments, measured before the dichroic

mirror in the C1 cage, was approximately 60 mW. In the setup involving a wide-field microscope, half-wave plates are utilized to attenuate the laser power (usually in the tens of milliwatts range) while preserving the laser's polarization. The beam passes through a beam expander to adjust its waist. By employing a half-wave plate, the linear polarization of the beam is rotated. This rotation allows for optimization of the pumping process of a specific NV group in a particularly oriented diamond plate (see Figure 2.5), leading to enhanced optical spin state contrast [104]. Alternatively, the polarization can be balanced across multiple groups to reduce background in vector ODMR measurements [105].

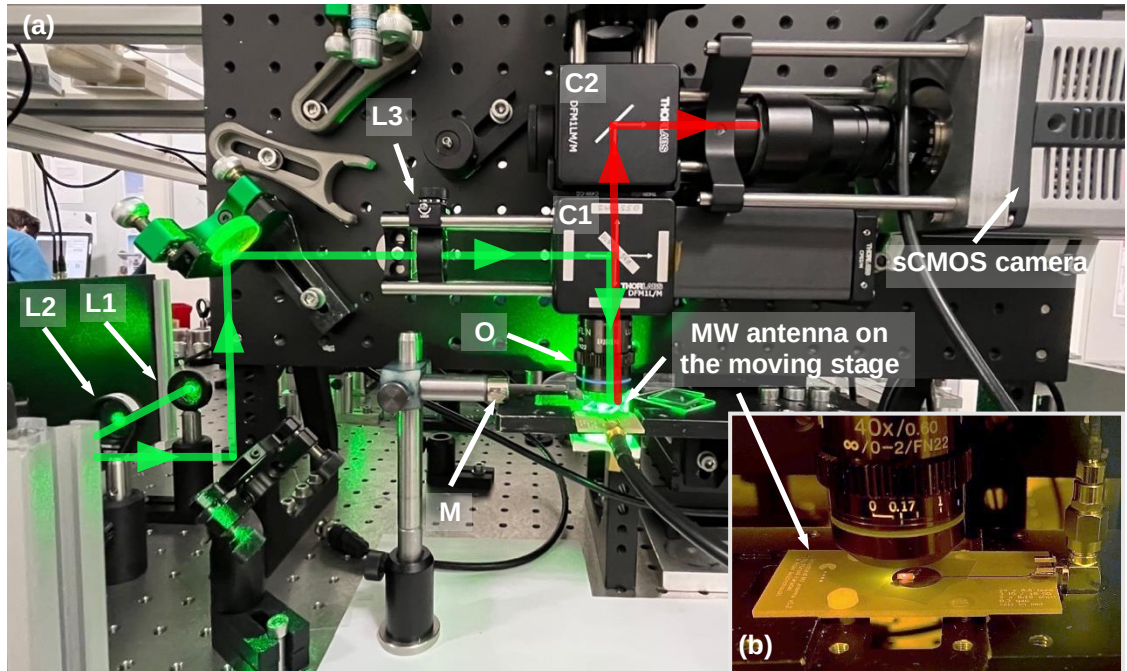


Figure 3.2: A photograph of the wide-field microscope. The picture (a) shows the custom setup built by the author utilized in the research presented in articles [1-4]. The laser beam is safely separated within the experiments using black laser-safe boards visible next to L1 and L2 lenses. Elements corresponding to the schematic representation in Figure 3.1 are labelled accordingly, such as the lenses of the beam expander marked as L1, L2 and the lens L3 which is responsible for focusing the beam onto the back focal plane of the objective. Additionally, the setup includes a camera, MW antenna with a diamond on a moving stage, objective (O) and a permanent magnet (M) is positioned to the left of the sample stage. The dichroic mirror and filter are integrated into a cage cube (Thorlabs), and marked as C1. The C2 cage cube holds a mirror directing the fluorescence towards the camera (sCMOS). The inset picture (b) was taken with the use of green light filter (Laser safety glasses LG3, Thorlabs, with transmission less than 0.00001% for a light wavelength 180 to 532 nm) and shows an objective (40x/0.6 LUCPLFN, Olympus) which directs laser light on a nanodiamond sample lying on the MW antenna. The red fluorescence from the NV^- color centers is visible due to filtering of strong 532 nm green laser and passing red spectrum of light.

The expanded beam is directed into the back focal plane of an objective (40x/0.6 LUCPLFN, Olympus), which illuminates a substantial area of the diamond bulk or powdered sample. The emitted red photoluminescence from the illuminated NV centers is collected by the same microscope objective and separated from the excitation laser using a dichroic mirror. Any extraneous light collected along with the NV photoluminescence is filtered out (by the filter FEL0550, Thorlabs, with the cut-off wavelength 550 nm and transmission region 559 - 2150 nm) before the photoluminescence is focused onto the sCMOS camera photosensor for imaging (Zyla 5.5 megapixels, Andor, Oxford Instruments) using a tube lens ($f = 100$ mm). A neodymium permanent magnet is positioned near the sample stage on either a magnetic post holder or a goniometer, enabling precise manipulation of the external magnetic field at the sample's location as can be seen in [Figure 3.2](#). This magnetic field can be oriented to align with the orientation of a specific NV centers within the imaging ensemble or to form the same angle with all four possible NV orientations, aligning them to degeneracy.



[102] Pham, Linh My, et al. "Magnetic field imaging with nitrogen-vacancy ensembles." *New Journal of Physics* 13.4 (2011): 045021.

<https://doi.org/10.1088/1367-2630/13/4/045021>

[103] Levine, Edlyn V., et al. "Principles and techniques of the quantum diamond microscope." *Nanophotonics* 8.11 (2019): 1945-1973.

<https://doi.org/10.1515/nanoph-2019-0209>

[104] Alegre, Thiago P. Mayer, et al. "Polarization-selective excitation of nitrogen vacancy centers in diamond." *Physical Review B* 76.16 (2007): 165205.

<https://doi.org/10.1103/PhysRevB.76.165205>

[105] Lillie, Scott E., et al. "Magnetic noise from ultrathin abrasively deposited materials on diamond." *Physical Review Materials* 2.11 (2018): 116002.

<https://doi.org/10.1103/PhysRevMaterials.2.116002>

3.2 MW GENERATION AND CAMERA SYNCHRONIZATION FOR WIDE-FIELD IMAGING

The majority of NV sensing methods necessitates the utilization of a pulsed resonant microwave field to manipulate NV spin states. In the context of our wide-field vector imaging, the typical microwave frequencies applied fall within the range of 2.7 to 3 GHz. However, certain applications may demand the driving of NV spin resonances to frequencies as low as a few MHz or exceeding 3 GHz [106, 107].

By employing microwave and radio frequency (RF) fields, it becomes feasible to manipulate the electron spin states of the NV center. In our wide-field microscope used for ODMR experiments, the microwave signal is produced by the generator (SG386, Stanford Research Systems) is transmitted through coaxial cables to the microwave antenna. While the term "antenna" is commonly used in the context of NV color centers in diamonds, it's important to emphasize that in this context, a magnetic field generated by a current-carrying wire (near-field) is utilized rather than a radiated electromagnetic far-field. Thus, from a classical perspective, the structures delivering microwaves do not fit the traditional definition of antennas. Nonetheless, for the sake of brevity, we refer to these elements of the apparatus using the term antenna, as many of them share the similar or identical design to the proper-use, oftentimes resonant, radiating antennas. The antenna is positioned either behind or beneath the diamond sample. Various orientations of experimental samples in relation to the antenna are illustrated in Figure 3.3. The antenna is mounted to the custom-made board, which is then attached to the XYZ translation stage (PT3/M - 25.0 mm, Thorlabs). This setup enables external control of the sample's movement in three orthogonal directions: two within the plane of the optical table and one perpendicular to it, through motors (KDC101 Thorlabs) featuring a DC servo motor actuator with a 25 mm travel range and a minimal repeatable step of 0.2 μm (Z925B, Thorlabs). The microwave signal travels through a switch and power amplifier with a maximum power of 42 dBm, i.e. 16 W (ZHL-16W-43-S+, Mini-Circuits), subsequently being directed to the antenna.

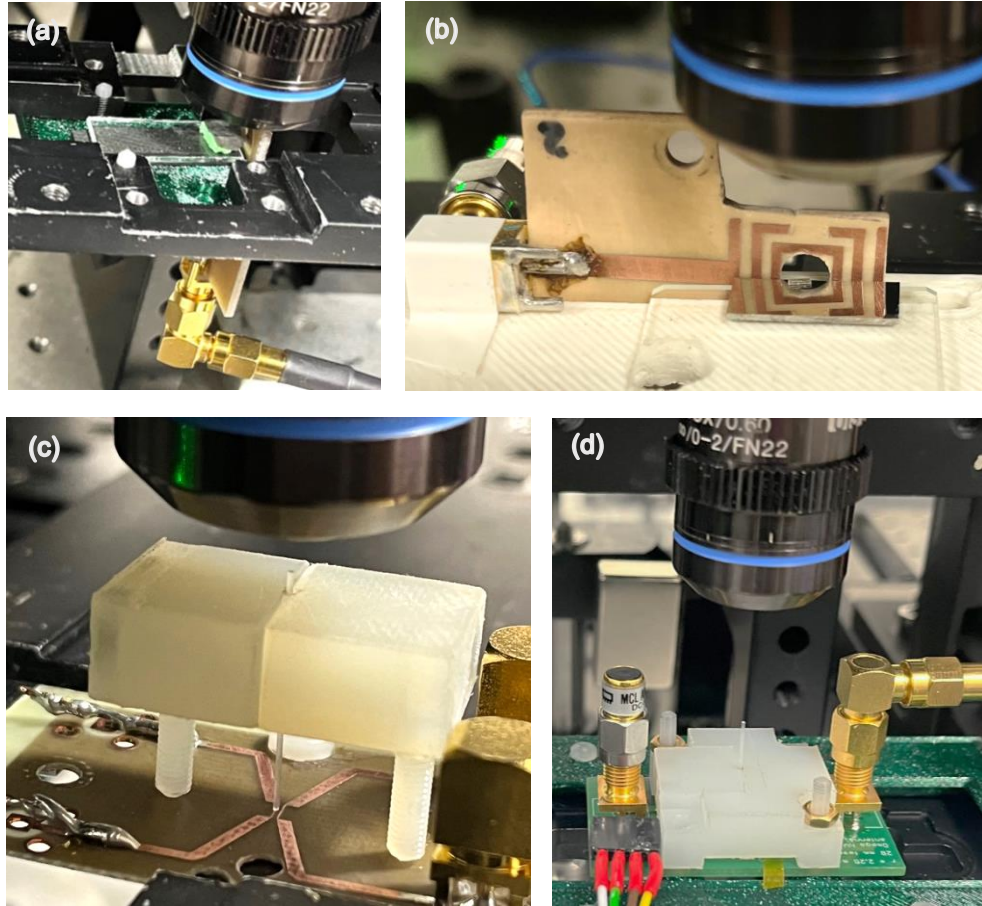


Figure 3.3: Photographs depicting different orientations of samples and antennas employed in the described experiments. The figure illustrates the range of orientations and challenges associated with varying sample sizes and shapes that needed to be taken into consideration during experiments. All sample holders visible on these pictures were custom made and designed by the author to meet the need of effective delivery of MWs as close as possible to the NV color centers in diamond samples. Picture (a) presents the vertical orientation of an antenna employed when the sample absorbs microwaves, and there is no other way of efficient delivery of this field to diamonds. An antenna used in this experiment is described in [107]. Picture (b) depicts a horizontally positioned antenna. A CVD diamond sample with NVs near the surface is positioned on a Si wafer with surface magnetic domains. This antenna is called double splitting resonator (DSRR) and effectively and uniformly couples microwave magnetic fields into nitrogen-vacancies over a large area [109]. On the image (c) a visible plastic tripod serves as a holder for an imaging fibers bundle, with its facet coated with nanodiamonds, positioned in close proximity to an antenna. This specific sample orientation is described in article [4]. This antenna is a printed circuit board (PCB) designed to generate circular polarization [110], two parallel lines, spaced 320 μm apart are visible. Image (d) presents another approach to sensing with imaging fiber bundle and uses of Ω -shaped, microstrip line antenna similar to one described in [111]. This antenna features multiple pins, allowing for the connection of various structures, such as gold-printed crosses that facilitate currents flowing in various directions.

The effective utilization of this entire infrastructure relies on the synchronized control of each component. Continuous laser and microwave pulses are applied to initialize, manipulate, and read out the NV spin state in synchrony with the photoluminescence collection by the sCMOS camera. This synchronization is achieved through a digital pattern generator (Pulse Streamer 8/2, Swabian Instruments) configured and controlled in LabVIEW by a custom script written by the author of this thesis. As illustrated in Figure 3.4, the microwave signal from the amplifier is directed to the digital pattern generator which synchronizes the microwave signal and the image capture process in the wide-field microscope.

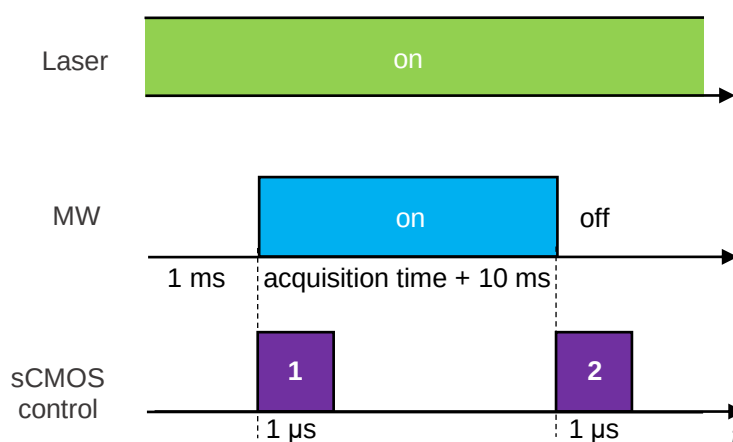


Figure 3.4: Timing of MW generation and camera synchronization for wide-field imaging.

Under continuous light illumination, two images (1, 2) are captured, with microwaves sequentially activated for about 10 ms (on) and deactivated (off) for each microwave frequency. The acquisition time corresponds to the exposure duration of a signal collected by the sCMOS camera, 10 μ s – 100 ms configured for each measurement in the LabView program made by author of this thesis. The camera is triggered to capture a picture within a time frame of 1 μ s.

In the presence of continuous light illumination, two images are taken with microwaves alternately turned on and off for each MW frequency. This is done to subtract the background and compute the normalized fluorescence contrast, effectively mitigating variations in fluorescence intensity caused by laser power drifts and fluctuations. This process enhances the overall signal-to-noise ratio (S/N). The signal timing pattern is presented in Figure 3.4.



[106] Stepanov, Viktor, et al. "High-frequency and high-field optically detected magnetic resonance of nitrogen-vacancy centers in diamond." *Applied Physics Letters* 106.6 (2015).

<https://doi.org/10.1063/1.4908528>

[107] Broadway, David A., et al. "Quantum probe hyperpolarisation of molecular nuclear spins." *Nature Communications* 9.1 (2018): 1246.

<https://doi.org/10.1038/s41467-018-03578-1>

[108] Sasaki, Kento, et al. "Broadband, large-area microwave antenna for optically detected magnetic resonance of nitrogen-vacancy centers in diamond." *Review of Scientific Instruments* 87.5 (2016).

<https://doi.org/10.1063/1.4952418>

[109] Bayat, Khadijeh, et al. "Efficient, uniform, and large area microwave magnetic coupling to NV centers in diamond using double split-ring resonators." *Nano Letters* 14.3 (2014): 1208-1213.

<https://doi.org/10.1021/nl404072s>

[110] Mrózek, Mariusz, et al. "Circularly polarized microwaves for magnetic resonance study in the GHz range: Application to nitrogen-vacancy in diamonds." *Applied Physics Letters* 107.1 (2015).

<https://doi.org/10.1063/1.4923252>

[111] Opaluch, Oliver Roman, et al. "Optimized planar microwave antenna for nitrogen vacancy center based sensing applications." *Nanomaterials* 11.8 (2021): 2108.

<https://doi.org/10.3390/nano11082108>

3.3 CONFOCAL SPECTROSCOPY

NV⁻ color centers are commonly examined using a confocal microscope system [14, 112-114]. The fundamentals of confocal imaging, originally introduced and patented by Marvin Minsky in 1961 [115], differ from wide-field microscopy or fluorescence microscopy. In the wide-field microscopy, the entire object is illuminated by a light source, and the sample reflects, absorbs, or fluoresces light, which is then collected by the objective. However, the lens not only gathers light from the focal plane but also from the entire volume of the illuminated sample along the beam axis. This leads to unwanted, out-of-focus signals that contribute to a blur and noise and reduce signal-to-noise ratio (S/R). To address this issue, confocal microscopes use a small diaphragm, such as a pinhole, iris, or an optical fiber with a small core, placed at the focus of a lens in front of the detector. This diaphragm eliminates signals originating from outside the focal plane, significantly enhancing image contrast and quality and essentially limits the image to a thin slice in the focal plane. The main drawback of this configuration stems from signal collection from one point (in reality a tiny, diffraction limited volume) at a time and the necessity of scanning to obtain an image.

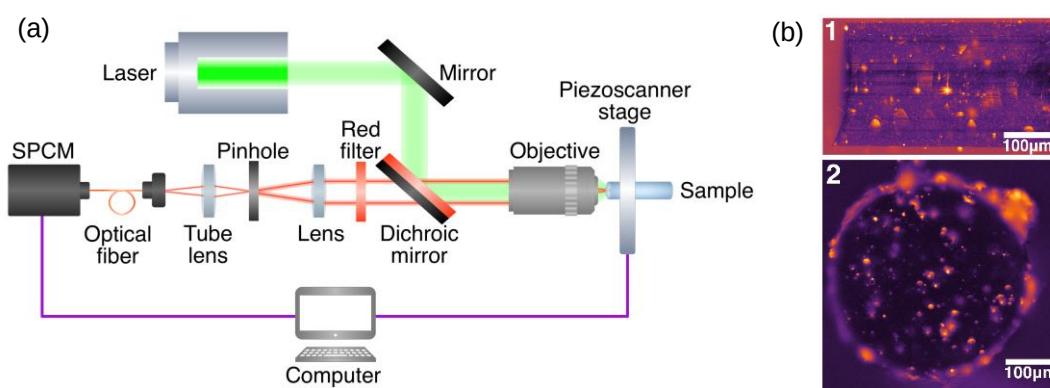


Figure 3.4: Schematic representation of a confocal microscope employed with NV diamond. (a) a green laser is directed into an oil-immersion objective, allowing scanning over the diamond surface in increments ranging from approximately 10 nm to 1 μ m. To exclusively capture the red-shifted fluorescence from the confocal volume, a pinhole is employed before reaching the single-photon counting module (SPCM). In the confocal image (b), individual grains with NV centers manifest as distinct bright spots, 1 is a side view and 2 from the fiber facet.

Figure 3.4 illustrates the configuration of the confocal microscope employed in the measurements presented in articles [2-4]. A CW diode-pumped solid-state laser (Sprout G, Lighthouse Photonics) generates a collimated and linearly polarized beam of monochromatic light at a wavelength of 532 nm. The light is then directed towards a dichroic mirror (Thorlabs DMLP567L), which predominantly reflects the light with λ below 550 nm and efficiently transmits spectral components with λ above 584 nm. The reflected light is guided to an oil-immersion objective (100 $\times$ /1.3, UPLFLN Olympus) positioned on a piezo stage (Nano-LP200, Mad City Labs) with a scan range of 200 $\times$ 200 $\times$ 200 μ m and an accuracy of 0.4 nm. This arrangement allows for the precise positioning and scanning of the sample placed above the objective, which is responsible for focusing the laser light. The light emitted from NV centers is collected by the objective and directed to the dichroic filter, which allows the transmission of red-shifted fluorescence. Subsequently, the light is focused onto a pinhole (Thorlabs PS30, 30 μ m diameter) to enable the passage of light emitted from the confocal volume to the detector. The remaining fluorescence is focused onto a single-photon counting module (SPCM-AQRH-14-FC, Excelitas Technologies). For protection against stray light, this section of the setup is enclosed within an additional box.

The dimensions of the confocal volume are determined by the characteristics of the objective, the laser wavelength λ and the refractive index n of the immersion medium. The axial resolution (distance along a line that is parallel to the laser beam) of an ideal confocal microscope, assuming an infinitely small pinhole, is expressed in terms of the full width at half maximum (*FWHM*) of the Airy spot and is defined by [116]:

$$FWHM = \frac{0.64\lambda}{n - \sqrt{n^2 - NA^2}}, \quad (6)$$

and the lateral resolution (distance in a plane of sampling object perpendicular to the laser beam) is given by:

$$FWHM = \frac{0.37\lambda}{NA}, \quad (7)$$

where NA is the numerical aperture of the objective.

To manage the experiment, including command and parameter input, as well as data visualization, a PC was employed. Ensuring the synchronized operation of all hardware devices necessitates a dependable control software. Consequently, for all presented experiments in articles [1-4] that mention confocal microscopy, the Qudi software was utilized. Qudi serves as a comprehensive, modular, and multi-operating system suite written in Python [117]. The scientific modules within Qudi can be classified into three domains. The logic modules oversee and coordinate specific experiments, convey input parameters, and analyze measurement data. The graphical user interface (GUI) modules facilitate parameter input, visualize data, and provide a user-friendly interaction with the logic modules. Third domains is “translation”, often an experimental hardware varies significantly in their command structures, sometimes even within products from the same manufacturer. In response, hardware modules are tasked with translating commands from the logic modules into the language compatible with the used hardware.



[112] Acosta, Victor M., et al. “Diamonds with a high density of nitrogen-vacancy centers for magnetometry applications.” *Physical Review B* 80.11 (2009): 115202.

<https://doi.org/10.1103/PhysRevLett.112.047601>

[113] Davidovits, Paul, and M. David Egger. “Scanning laser microscope.” *Nature* 223.5208 (1969): 831-831 (7).

<https://doi.org/10.1038/223831a0>

[114] Davidovits, Paul, and M. David Egger. “Scanning laser microscope for biological investigations.” *Applied Optics* 10.7 (1971): 1615-1619.

<https://doi.org/10.1364/AO.10.001615>

[115] Minsky, Marvin. “Memoir on inventing the confocal scanning microscope.” *Scanning* 10.4 (1988): 128-138.

<https://doi.org/10.1002/sca.4950100403>

[116] Amos, Brad, McConnell, Gail, and Wilson, Tony “2.2 Confocal Microscopy, in Comprehensive Biophysics”, edited by E. H. Egelmann, volume 2, *Elsevier* (2012), Amsterdam, pp. 3–23.

<https://doi.org/10.1016/B978-0-12-374920-8.00203-4>

[117] Binder, Jan M., et al. “Qudi: A modular python suite for experiment control and data processing.” *SoftwareX* 6 (2017): 85-90.

<https://doi.org/10.1016/j.softx.2017.02.001>

3.4 PHOTOLUMINESCENCE SPECTROSCOPY

One of the distinctive features of the wide-field microscope built by the author is its easy adaptability into a confocal setup. In addition to being utilized for confocal imaging, this configuration was successfully applied for PL measurements in articles [1, 3]. Spectral measurements of the NV photoluminescence can serve as a valuable sensing technique independently, providing swift and efficient insights into the surrounding environment.

Similarly, as detailed in the description of the wide-field microscope setup in section 3.1, light is passing through all optical elements with slight modifications. After the beam is expanded by the combination of L1 and L2 lenses, an iris enables the adjustment of the expanded beam's size, extending it up to 0.3 mm, making the lens L3 redundant. Additionally, one of the cubes, C2, which directs fluorescence to the camera can also be eliminated. As illustrated in [Figure 3.5](#), light is focused by a lens onto a facet of the fiber, which then collects and guides the light to the spectrometer (AvaSpec-3648, Avantes).

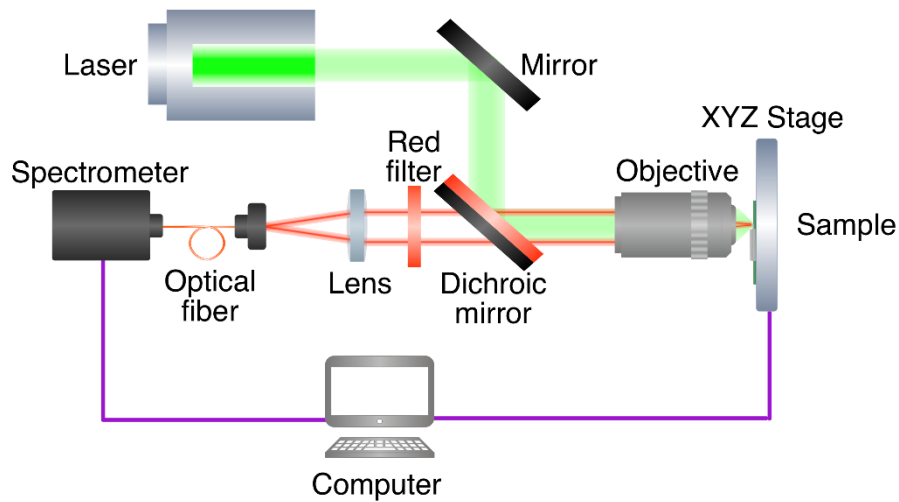


Figure 3.5: Confocal photoluminescence spectroscopy setup. The signal collected in this setup is depicted in [Figure 2.3](#) and in article [1].

CHAPTER 4

ARTICLES

4.1 OVERVIEW OF THE RESULTS

Following chapter builds upon preceding introduction to NV physics and experimental systems to provide a brief introduction and summary of the findings presented in articles [1-4].

The previous chapters served as an introduction to fundamentals of the NV color center in diamond. This theoretical framework provides an explanation of the essential phenomena associated with this defect, in particular, an explanation of the processes involved in initializing the center through optical pumping and subsequently reading its state. Additionally, the formulation of the ground state Hamiltonian, which outlines the quantum mechanical properties of the NV center, is discussed. Furthermore, the application of the optically detected magnetic resonance (ODMR) research technique is highlighted as a crucial tool for examining characteristics of the nitrogen-vacancy color center in diamond. In this thesis, a central point of every experiment is a wide-field microscope. This microscope enables imaging applications of NV centers in nanodiamonds and confocal PL measurements. The unique configuration described in Chapter 3 was not only conceptualized but also physically constructed and programmed by the author of this thesis.

The extreme flexibility of this setup facilitated its involvement in numerous experiments conducted on various types of samples. These included fiber bundles with facets coated with nanodiamonds, tellurite rods with sub-micron-sized diamonds incorporated into glass during the melting process, AFM scanning probe with cantilever coated with nanodiamonds. Additionally, the

research considered bulk CVD diamonds not discussed in detail here. These diamond plates used for the magnetic mapping, including a 50-micrometer-thick diamond membrane with NV centers close to the surface. The utilization of this imaging system allowed for corroborating measurements and an exploration of the utility of the researched temperature, magnetic and electric field sensors, as presented in the subsequent articles. Each project not only provided novel insights into the systems but also prompt refinements to the NV imaging technique to alleviate interactions that may hinder imaging or affect the observed phenomena. As a result, a robust and intuitive approach to wide-field imaging with NV ensembles in diamond has been developed, poised for future applications in many systems.

The limitations of the imaging technique constitute a crucial factor when dealing with absorbing materials or those sensitive to temperature variations. Studying phenomena such as magnetic fields in samples with ferromagnetic domains or current flows in wires necessitates minimal substrate requirements and fabrication. In other cases, the direct transfer of nanodiamond onto substrates is deemed a viable and appropriate approach. To address this challenge, an unconventional yet effective solution is explored, allowing to characterize samples by endoscopic methods. Subsequently, one such extraordinary samples, is an imaging fiber bundle coated with nanodiamond enabling imaging and measuring current flows remotely, through the fiber. This method combines the flexibility of NV experiments with the numerous benefits of fiber imaging, e.g. endoscopy, thereby expanding the potential range of future applications.

In this section a summary of following articles [1-4] is presented, emphasizing the author's input to each one. The article [1] "Tellurite Glass Rods with Submicron-Size Diamonds as Photonic Magnetic Field and Temperature Sensors." Zuzanna Orzechowska et al. proposes a novel type of photonic sensor based on tellurite glass rods doped with submicron diamonds. This type of sensor can be used to measure magnetic fields and temperatures with high sensitivity. The sensors are fabricated by doping tellurite glass rods with submicron diamonds containing nitrogen vacancy and nitrogen-vacancy-nitrogen (NVN) centers. As a result, it was demonstrated that this type of sensor measures magnetic fields up to 50 G with a sensitivity of $10^{-5} \text{ T} \cdot \text{Hz}^{-1/2}$, and temperature

shifts of up to 8 degree at room temperature with a sensitivity of $2.2 \text{ K} \cdot \text{Hz}^{-1/2}$. The obtained sensor is small, lightweight, and the signal can be collected from its side in contrary to the optical fiber. This makes them promising candidates for a variety of applications, such as medical imaging or environmental monitoring. Samples were prepared through collaborative efforts with the research groups from Gdansk and Warsaw. Despite the fragility of tellurite glass, the author of this thesis successfully conducted challenging measurements, leading to a pivotal discovery that the samples not only contained NV color centers but mainly NVNs. This newfound information constituted a novel contribution to the field of sensing properties with different types of color centers. The author assumed responsibility for coordinating the description of primary findings, composing the major sections of the published article, conducting measurements, and analyzing data to succinctly summarize the research within the article.

The article [2] “Preparation and characterization of AFM tips with nitrogen-vacancy and nitrogen-vacancy-nitrogen color centers” by Zuzanna Orzechowska, et al. discusses a simple method for coating AFM tips with submicron-sized diamonds containing color centers. This coating enables convenient visualization of AFM tips above transparent samples as well as potentially using the tip for performing spatially resolved magnetometry. In this article we also showed its sensitivity for magnetic field. The principal content of this article, including obtaining the AFM probes, planning and execution of the methodology and measurements, was undertaken by the author of this thesis. The standard silicon AFM probes were dip-coated in a suspension of submicron-sized diamonds in isopropyl alcohol. The used diamonds contained two types of color centers: NV and NVN. The AFM tips were characterized by measuring their fluorescence intensity and magnetic field sensitivity. It was found that the tips can be visualized using microscopy, e.g. on a fluorescent microscope with AFM attachment module and that they have a magnetic field sensitivity of $2.2 \text{ nT} \cdot \text{Hz}^{-1/2}$. The proposed method is a simple and a cost effective way to create AFM probes with both optical and magnetic sensing capabilities. These probes have the potential to be used in a variety of applications, such as nanoscale magnetic mapping and imaging.

The article [3] “Optically detected magnetic resonance study of thermal effects due to absorbing environment around nitrogen-vacancy-nanodiamond

powders” by Mona Jani et al. shows the impact of Fe^+ ion implantation on optical properties of nanodiamonds containing nitrogen-vacancy color centers. Observed decrease in the NV^- peak intensity and a blue shift in Raman spectra, indicated a transition from sp^3 to sp^2 carbon hybridization. The ODMR spectra showed a red shift in the resonance position, suggesting local heating due to absorption of laser energy. This shift disappeared after annealing, suggesting that it is caused by absorptive impurities in the environment. To confirm this the iron oxide and graphite powder were added to the nanodiamond suspension, leading to a substantial increase in the ODMR red shift. This suggests that the shift is caused by local heating of the NV centers by absorptive impurities. The study highlights the importance of considering the local environment in NV-based nanodiamonds experiments. It becomes a crucial consideration, particularly when attempting to measure magnetic fields within living organisms containing iron-laden erythrocytes, its potential impact on experimental outcomes cannot be omitted. As the second author of this article, I undertook planning and performing ODMR and PL measurements within an experimental setup built by me and described in this thesis. Additionally, I provided guidance to the primary author in the analysis of the acquired data and proposed the idea of sample analysis after annealing, thus contributing to proving the reversibility of the observed local heating phenomenon primarily caused by ion implantation.

The article [4] "Sensing of Magnetic-Field Gradients with Nanodiamonds on Optical Glass-Fiber Facets." by Mona Jani et al. describes a method for detecting magnetic field gradients using nanodiamonds covalently attached as a thin film on one facet of an optical fiber bundle. Through ODMR signal measurements from individual fibers within an ~ 0.5 -mm-wide imaging bundle, variations in local magnetic field strengths and gradients across the bundle facet were determined. These gradients result from direct electric currents in a wire near the nanodiamond film. The measurement facilitates determining the net magnetic field for different current directions and their associated magnetic field gradients. Using my prior expertise in optical fiber measurements, I made relevant contributions to this manuscript through the experiment planning, execution, and analysis of ODMR measurements utilizing developed and programmed wide-field microscope. Experiments presented in the article,

indicate prospects for compact fiber-based endoscopy, offering possibilities for remote and highly sensitive magnetic field detection with sub micrometer spatial resolution in ambient conditions.

4.2 SUMMARY

This cumulative thesis is based on 4 research articles investigating paramagnetic nitrogen-vacancy color centers in nano- and submicron-sized diamonds.

The initial phase involved designing and constructing a wide-field microscope system, easily convertible into a confocal microscope, and programming a new sCMOS camera that provided high sensitivity imaging functionality not available before in the laboratory. This system enabled various measurements, including the examination and observation of ODMR and fluorescence spectra in micro- and nanodiamond samples. By combining diamond powders with known photonic equipment such as imaging optical fiber bundles, tellurite glass rods, or AFM scanning probes, unique sensors based on NV^- and NVN color centers were developed.

Beyond creating innovative research equipment and conducting detailed characterization on nitrogen-vacancy color centers in diamonds, this work opens new opportunities for further research. The analyses and measurements conducted herein can serve as the foundation for future projects. For example, exploring magnetic fields in flowing liquids using nanodiamonds embedded in optical fibers, magnetic mapping using nanodiamond-coated AFM probes, or mapping magnetic domain fields beneath thin-film diamond samples. The author has already initiated work on mapping magnetic fields using 50 μm thin diamond crystal with NV color centers and wide-field microscopy, which holds promise due to its potential for significantly accelerating magnetic field mapping with nanoscale resolution on microscale surfaces compared to currently used diamond-based AFM magnetic microscopes.

This thesis presented several hybrid platforms that combine common measurement tools, such as optical fibers and scanning probes, with nanodiamond powders containing nanoscale defects. In the course of this work, I have successfully proven the research hypothesis that these systems can function under ambient conditions and serve as practical sensors for measuring magnetic fields and their gradients, electric currents, and temperature.

Tellurite Glass Rods with Submicron-Size Diamonds as Photonic Magnetic Field and Temperature Sensors

Zuzanna Orzechowska, Mariusz Mrózek, Adam Filipkowski, Dariusz Pysz, Ryszard Stępień, Mateusz Ficek, Adam M. Wojciechowski,* Mariusz Klimczak, Robert Bogdanowicz, and Wojciech Gawlik

The results of work on a hybrid material composed of a tellurite glass rod doped with submicron diamonds containing nitrogen-vacancy-nitrogen and paramagnetic nitrogen-vacancy color centers are presented. The reported results include details on tellurite glass and cane fabrication, confocal and wide-field imaging of the submicron diamond distribution in their volume, as well as on the spectroscopic characterization of their fluorescence and optically detected magnetic resonance measurements of magnetic fields and temperatures. Magnetic fields up to 50 G were examined with a sensitivity of $10^{-5} \text{ T Hz}^{-1/2}$, whereas temperature measurements are simultaneously performed with a sensitivity of $2.2 \text{ K Hz}^{-1/2}$ within the 8 K range at room temperature. In that way, the suitability of such systems for fiber magneto- and thermometry with a reasonable performance are already demonstrated in the form of glass rods. At the same time, the rods constitute an interesting starting point for further processing into photonic components such as microstructured fibers or fiber tapers for the realization of specialized sensing modalities.

1. Introduction

Nitrogen-vacancy-nitrogen (NVN) and negatively charged nitrogen-vacancy (NV^-) color centers are point defects in the diamond lattice which find increasingly more important applications in photonics, sensors, and biomedical diagnostics.

The NVN (also known as H3), structure is formed by a nitrogen pair trapped near a vacancy and is one of the most commonly present lattice defects in natural diamonds after the thermal annealing process. In particular, the H3 color centers are used as *in vivo* fluorescent markers due to their low toxicity, strong green fluorescence,^[1–3] and long fluorescent lifetime.^[4] Very good thermal stability, even at temperatures as high as 500 °C, makes NVN centers interesting candidates for room temperature color center lasers.^[5] H3 centers can be taken into consideration in thermometry applications

based on the frequency shift of their zero-phonon line (ZPL).^[6]

The NV^- are diamond defects where a substitutional nitrogen atom replaces the carbon and an adjacent lattice site is left empty creating a vacancy. In addition to applicability as fluorescent markers for biological systems caused by their strong red fluorescence,^[7,8] the NV^- centers are paramagnetic, hence exhibit very interesting magnetic properties. For example, they can be used as qubits in quantum information science,^[9,10] and sensors of electric^[11] or magnetic^[12,13] fields.

Large sizes of typical commercial high-quality magnetometers motivate new developments of small-scale devices combining optical fibers with color centers in diamonds. That approach was realized in several ways: by attaching a diamond to the optical fiber,^[14–16] incorporating it into photonic crystal fibers,^[17] growing the diamond material at the outer fiber core,^[18] coupling them with tapered optical fibers,^[19] or designing miniaturized hybrid magnetometers.^[20,21]

One promising direction of these developments is based on the melt mixing of diamonds and glass material during the drawing process. Such an approach has been notably advanced by the Monro group.^[22–24] We followed their recipe for glass preparation and similarly chose the tellurite glass which is well-suited as a host material for submicron diamonds (SDs). The reason for that is the relatively low melting point temperature of 600 to 700 °C

Z. Orzechowska, M. Mrózek, W. Gawlik
Institute of Physics
Jagiellonian University in Kraków
Kraków 30-348, Poland

A. M. Wojciechowski
Institute of Physics
Jagiellonian University in Kraków
Kraków 30-348, Poland
E-mail: a.wojciechowski@uj.edu.pl

A. Filipkowski, M. Klimczak
Department of Photonics
University of Warsaw
Warsaw 02-093, Poland

A. Filipkowski, D. Pysz, R. Stępień
Łukasiewicz Research Network
Institute of Microelectronics and Photonics
Warsaw 02-668, Poland

M. Ficek, R. Bogdanowicz
Department of Metrology and Optoelectronics
Gdańsk University of Technology
Gdańsk 80-233, Poland



The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/qute.202100128>

DOI: 10.1002/qute.202100128

minimizing the oxidation of SDs when mixing them into the glass melt. Moreover, tellurite dioxide (TeO_2) based glasses are transparent in the range of 500–4000 nm and possess highly non-linear optical properties.^[25] Embedding SDs in a tellurite glass host enables efficient coupling of single-photon emission to the bound modes of rods drawn from this material. These features, together with high transparency and low transmission losses (around 1 dBm^{-1} for wavelengths 550–900 nm^[26]) determined mainly by the NV^- centers absorption are essential in exploiting the unique properties of NV^- doped SDs and application of such material in various photonic devices.

In addition to their interesting optical properties, a more important feature of the negatively charged NV defect is its magnetic properties due to the nonzero electronic spin ($S = 1$) that enables magnetic resonance studies and, together with a long coherence time, makes these centers suitable for sensing applications. The sensing principles are extensively described (e.g., in refs. [27–29]), so we just briefly summarize the main features which make it possible. The ground state of the color center defect NV^- is a spin triplet. In the absence of a magnetic field, the ground state sublevels $m_s = 0$ and $m_s = \pm 1$ are split by 2.88 GHz, while the application of a magnetic field splits the $m_s = \pm 1$ levels with a slope of 2.8 MHz per G of the field component along the NV axis. Using optical pumping (excitation by a green light), the ground state of the NV^- defect becomes spin-polarized. Application of the resonant microwave (MW) field allows the manipulation of the m_s sublevel populations with energy splitting depending on the magnetic field projection on the NV axis and temperature, while the fluorescence signal can be used to probe the spin-state population difference in an optically detected magnetic resonance (ODMR) measurement. The ODMR experiments performed here are based on collecting the red fluorescence from the tellurite glass rods enriched with NVs as a function of the MW frequency and magnetic field.

In this paper, we describe the development of incorporating two kinds of fluorescent SDs into tellurite glass for photonic sensing applications. We use high-pressure high-temperature (HPHT) submicron-size diamonds of size around 750 nm, with both nitrogen-vacancy-nitrogen and nitrogen-vacancy color centers. The former offers green fluorescence (with the maximum at $\approx 520 \text{ nm}$), while the latter fluoresces in the red ($\approx 670 \text{ nm}$), which allows for their independent detection and addressing. In the studied samples, we observe the contributions of the NVN and NV centers and extend the previous studies by demonstrating measurements of magnetic fields in a wide range, up to 50 G, and by employing the thermometry based on the ODMR. Glass rods doped with color centers appear to be a convenient material platform for further modification for the development of various photonic devices, for example, ending of rods with needle shapes, tapers, fiber extruding, making microlenses, plates, etc.

2. Experimental Results

For initial characterization of the fabricated tellurite glass rods, the distribution of diamond particles was investigated with the help of confocal fluorescence microscopy, which is described in Section 2.1. This allowed us to evaluate the doping process, particularly the amount of SDs detectable in the drawn rod. In Section 2.2, we analyze the fluorescence spectra of the doped rod in

order to compare them with the raw SDs material. Finally, Section 2.3. is devoted to the observation of optically detected magnetic resonance signals and its use for sensing applications in the wide-field microscopy setup.

2.1. Confocal Imaging

Figure 1a schematically presents the beam paths and relevant optical components of the home-built confocal setup used for imaging SDs containing NV centers in the rod volume. 2D sample scans were performed along the planes indicated schematically in Figure 1b. The resulting fluorescence images recorded are shown in Figure 1c. Images α and β , obtained for planes marked 1 and 2, respectively, visualize the SDs containing NV centers as bright spots. To visualize both kinds of SDs, that is, also those containing NVN centers, the image γ in Figure 1c was obtained with a commercial microscope equipped with several excitation sources and suitable filter sets. By merging the images recorded at the green and red wavelength bands under blue and green excitation, respectively, we confirmed that the developed tellurite glass contains comparable densities of SDs with the NVN and NV^- color centers.

The amount of diamonds present in the glass matrix after rod fabrication may be affected by many factors, such as melting temperature, glass cane drawing speed at the fiber drawing tower, the concentration of SDs added to the melt, and the size of particles.^[22,23] As mentioned in Section 4.1 of this paper, the concentration of SDs at the input was 0.001% (w/w) and from the obtained images we were able to calculate the average number of submicron diamonds with color centers that were visible after (survived) the drawing process. We use the same methodology as presented in ref. [23]. 25 SDs with both NV^- and NVN color centers were identified on six merged confocal images of known focal depth $1.44 \mu\text{m}$ and the volume of $\approx 4.2 \times 10^9 \mu\text{m}^3$. The initial number of diamond particles incorporated into the glass was $\approx 2.6 \times 10^9$. Based on the confocal images acquired and assuming the identical distribution of SDs along the full length of the drawn rod, $\approx 93\%$ of the initial number of diamond particles survived the drawing process which is significantly more than in ref. [23]. This confirms our prediction that larger-sized diamonds are more resilient for mixing with glass and the tellurite glass with a low melting point is a well-suited host material for diamonds with NV^- and NVN color centers.

2.2. Fluorescence Spectra

Figure 2a shows the fluorescence spectra of NV^- color centers of the submicron-size diamond incorporated (SD-doped) tellurite glass rod obtained with 532 nm excitation light. The spectra were collected in three geometrical configurations: first, associated with the excitation and fluorescence detection from the rod side (Figure 2c) corresponding to the spectrum depicted by the blue curve; second, associated with the excitation and detection from the top end of the rod (Figure 2d) and corresponding to the spectrum marked with the red curve in Figure 2a; third, with the excitation from the side and fluorescence detection from the top presented in Figure 2e which corresponds to the green line in

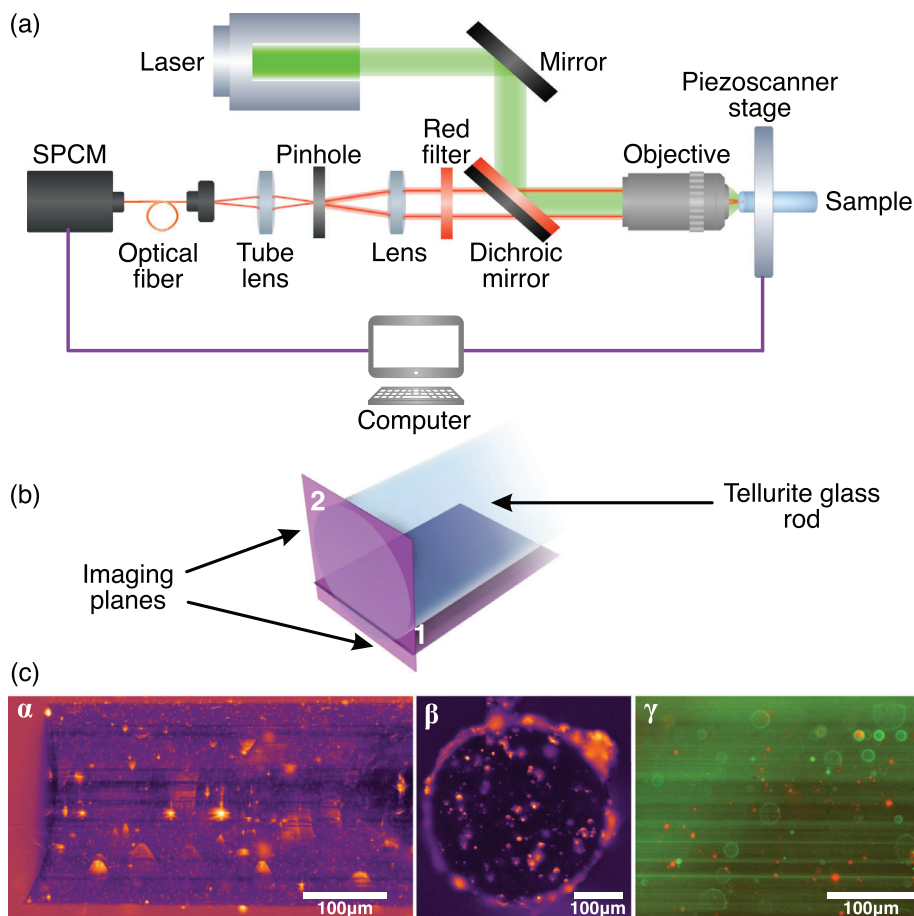


Figure 1. a) Beam path and optical elements used in the confocal setup. b) Schematic view of the tellurite rod with indicated planes 1 and 2 which correspond to the images depicted below. c) Images of the front face (α) and side of the rod (β) were recorded with the scanned confocal microscope. Image α was collected with the rod of 245 μm diameter at the depth of 42 μm . Image β shows the front face of the 400 μm diameter rod (bright spots on the outer edge of its face are recognized as dust particles and are also visible with a standard optical microscope). Both images α and β are a result of merging 6 and 9, 200 $\times$ 200 μm single scans, respectively. Images α and β were taken with red spectral filters transmitting the NV^- emission, whereas image γ was taken with different spectral filters selectively transmitting the green (NVNs) and red (NV^- s) fluorescence.

Figure 2a. Each of these spectra exhibits a 637 nm ZPL peak of NV^- as shown in detail in inset Figure 2a, which confirms that the developed glass indeed contains submicron-size diamonds with NV^- color centers. The peak observed around 555 nm was also present in the undoped glass and only marginally contributes to the overall fluorescence level.

Interestingly, all three spectra of the tellurite rod have their amplitudes in the short-wavelength wing (below 637 nm), significantly higher than the reference spectrum of the used SD powder under the same (532 nm) excitation (Figure 2b). Since the undoped tellurite glass does not possess any spectral feature in the range 560–800 nm, we have to associate the observed spectral changes with the SD admixture. In addition to the well-evidenced spectrum of NV^- there are other principally possible sources of the fluorescence below 637 nm: one is the possible green H3 emission, the second is the NV^0 fluorescence with ZPL at 575 nm. The first possibility, however, cannot be realized with the excitation by 532 nm light used in our experiment, thus we assign the enhancement of the short-wavelength fluorescence

wing in Figure 2a to NV^0 . The exact nature of this enhancement is an open question at the moment and deserves future detailed studies. Definitely, a thermal conversion between NV^- and NV^0 and increase of vacancy mobility with temperature play an important role here, as noticed in ref. [30]. For wavelengths above 637 nm, in Figure 2a different amplitudes of the phonon sidebands can be noticed. They may be caused by the different ratios of NV^0 to NV^- for various SDs observed in three configurations. The influence of NV^0 on the NV^- shape and intensity of the spectral line is described in ref. [31]. The observed spectra may be compared with the fluorescence spectrum of the starting material, MDNVN1 diamond powder, presented in Figure 2b for various excitation wavelengths. For excitation at 405 nm, we have a characteristic emission peak for green (NVN) color centers at 520 nm; for excitation at 488 nm, the mixed spectra of the green/red color centers exhibit a significant peak at 575 nm associated with NV^0 color centers; and the spectrum recorded for 532 nm excitation, has a peak emission at 680 nm characteristic for red fluorescing color centers.

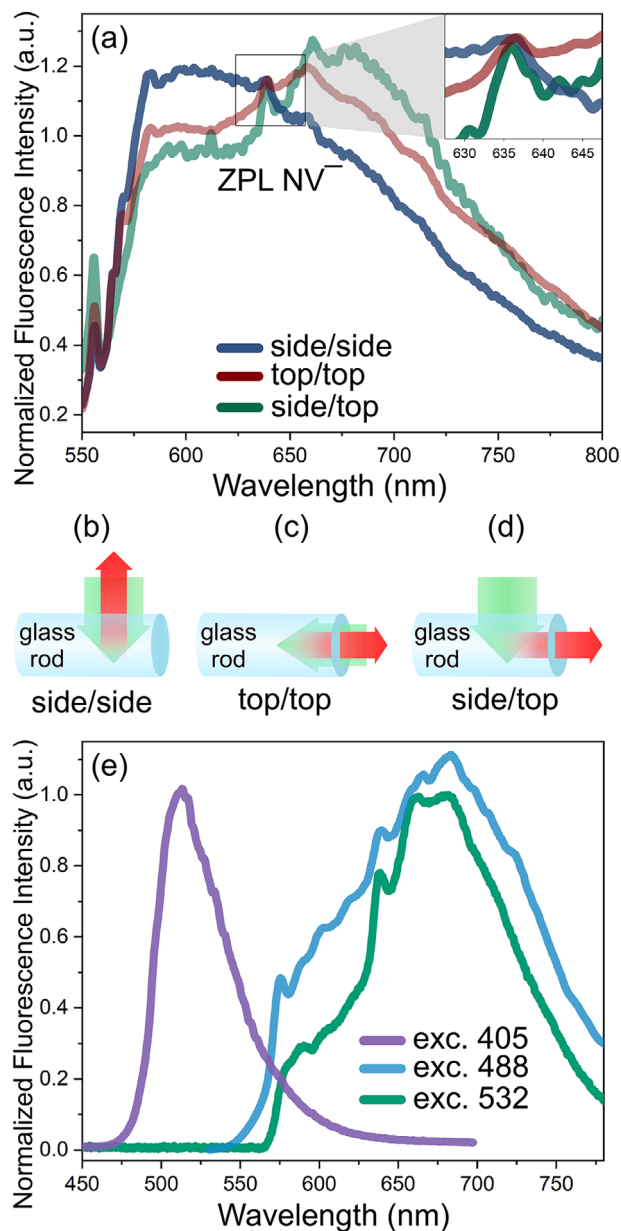


Figure 2. a) Fluorescence spectra of the SD-doped tellurite glass rod excited at 532 nm. Various spectra correspond to different excitation and detection directions, color coded as: b) green excitation from the rod side and detection of the red side fluorescence—labeled as side/side; c) green excitation from the top of the rod and detection of the backward red fluorescence—labeled as top/top; d) excitation from the rod's side and detection of the red fluorescence emitted along the rod—labeled as top/side. The inset to (a) shows details of the NV[−] ZPL at 637 nm. e) Fluorescence spectra of the starting material, MDNVN1 powder, obtained for excitation wavelengths 405, 488, and 532 nm with a proper set of filters.

2.3. ODMR in Magnetic Field and Temperature Measurement

The dependence of the NV energy-level structure on external perturbations enables various sensing applications, with the most important being the magnetic field and temperature probing. The signal detection relies upon shifts of energy levels caused

by the magnetic field and temperature, which can be monitored by the corresponding shifts of fluorescence and/or ODMR spectra.

The relevant energies are described by the Hamiltonian of the NV color center which takes into account the interaction of electronic spins with the magnetic field, the thermal expansion of the crystal lattice, and the electron-phonon interactions. The simplified form of the NV Hamiltonian, which ignores the diamond anisotropy and the effects of electric fields has the following form:

$$H_{NV} = DS_z^2 + g_{NV}\mu_B \mathbf{B} \mathbf{S} + \mathbf{S} \mathbf{A} \mathbf{I} \quad (1)$$

with D as a zero-field splitting parameter along the z -axis equal to 2.87 GHz, S_z being the spin component along the axis of a defect, $\mathbf{S}$ being the electronic spin operator, g the electron Landé factor, μ_B the Bohr magneton, $\mathbf{B}$ the applied magnetic field, $\mathbf{A}$ the hyperfine tensor, and $\mathbf{I}$ the nitrogen nuclear spin operator. The first and second terms in Equation (1) represent the main contributions enabling thermometry and magnetometric applications, respectively.

ODMR measurements of the developed tellurite glass rods containing NV[−] color centers were conducted in a wide-field setup at room temperature. The tellurite rod with submicron diamonds was mounted on a microstrip patch antenna where the MW field around 2.87 GHz was delivered (the measurement configuration is presented in Figure 3d). The MW antenna was designed similarly to the one described in ref. [32]. A movable neodymium magnet was used to create the magnetic field varying in the 0–5.0 mT range and an additional laser (532 nm) was employed to heat the sample for temperature measurements.

Figure 3a presents the ODMR spectra collected from the area around 24 μm^2 corresponding to different magnetic field strengths with the individual signals vertically offset for clarity. In this configuration, the maximum ODMR contrast without the magnetic field was 6% and reduced to around 2% with the applied magnetic field, consistently with the observation of NV ensembles in bulk diamond mono-crystals.^[33] The geometry of the ODMR signal collection in the present work was different from the one reported in ref. [24] as a large area was illuminated at once in a wide-field type configuration. This resulted in the detection of the signal from an ensemble of SDs at the same time. Additionally, we have also observed a slightly higher ODMR contrast, which we attribute to an improvement of MW field strength at the probed fiber volume.

The ODMR signals collected for the camera full-frame area of around $3.5 \times 10^4 \mu\text{m}^2$, covering dozens of diamond particles, are presented in Figure 3b. The observed spectra in a nonzero magnetic field reflect the fact that the sensing volume contains many NV color centers oriented in arbitrary directions relative to the direction of the magnetic field. With a small detection volume, this averaging is not complete and, hence, the ODMR spectra are a mixture of discrete and structure-less components. Despite this orientation-related averaging, the broadened spectra still enable measuring the magnetic field intensity by detecting the outermost edges of the spectrum.^[34]

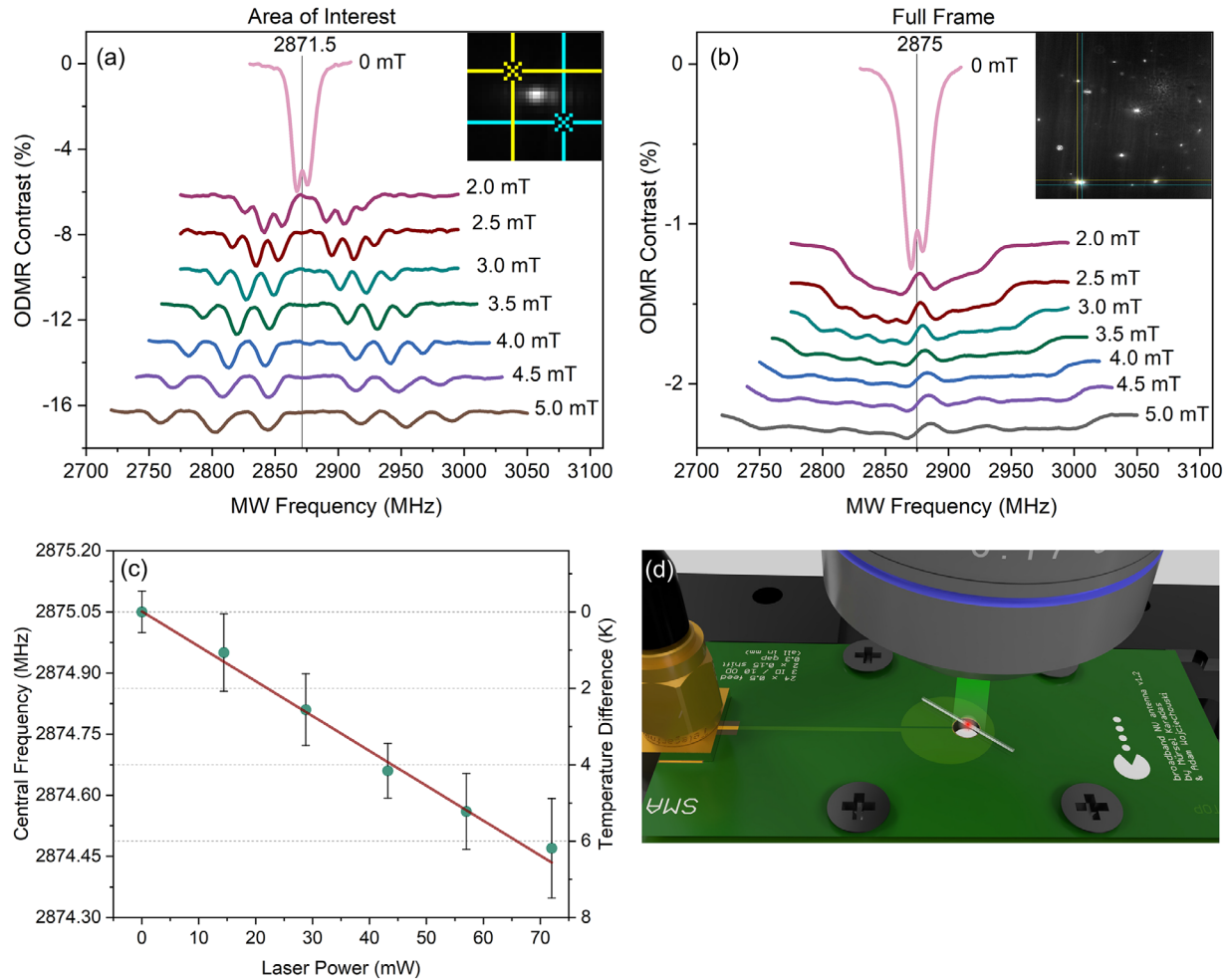


Figure 3. a) ODMR spectra as a function of the external magnetic field collected from the area of interest where a single particle was visible. The inset presents a sensing area of about $24 \mu\text{m}^2$ selected with the cursors. b) ODMR spectra as a function of the external magnetic field collected from the Full Frame area of $205 \times 173 \mu\text{m}$. c) Dependence of the resonance frequency (left vertical axis) on the heating-laser power (horizontal axis). The temperature difference corresponding to the resonance frequency shift is displayed on the right vertical axis. The straight line shows a linear fit to the collected data. d) Illustration of the wide-field setup used for the described ODMR measurements: the tellurite rod was placed on MW antenna and the excitation and fluorescence light was passing through the same objective. The illuminated area of about $3.6 \times 10^6 \mu\text{m}$ contained many SDs.

The magnetic sensitivity can be estimated following ref. [35] as

$$\eta_{\text{DC}} = \sqrt{e/(8\ln 2)} \frac{h}{g_{\text{NV}} \mu_{\text{B}}} \frac{\delta}{C\sqrt{N}} \quad (2)$$

where C is the ODMR contrast in a nonzero magnetic field, $C = 0.04$, the ODMR linewidth is $\delta = 27 \pm 0.5 \text{ MHz}$, and h is the Planck's constant. The number of photons per second detected at the output end of the glass rod was $N = 3 \times 10^6 \text{ s}^{-1}$, and resulted in a projected magnetic sensitivity of around $10^{-5} \text{ T Hz}^{-1/2}$, consistent with the sensitivity obtained for tellurite fibers in ref. [24].

Similarly, based on ref. [36] one can estimate the sensitivity of measuring the temperature of the SD and its environment as

$$\eta_T = \frac{1}{|dD/dT|} \frac{\delta}{C\sqrt{N}} \quad (3)$$

where dD/dT is a linear slope, resulting in a projected temperature sensitivity of around $2.2 \text{ K Hz}^{-1/2}$, that is, consistent with the sensitivity obtained in ref. [36].

3. Conclusion

Results presented in this work demonstrate that the hybrid material, tellurite glass rods doped with submicron-size diamonds containing NVN and NV^- color centers, is a promising platform for temperature and magnetic field sensing. While the tellurite rods used in this work are larger than previously employed optical fibers, the projected magnetic sensitivity around $10^{-5} \text{ T Hz}^{-1/2}$ obtained in this work is comparable to the one achieved in fibers covered with submicron diamonds^[19,37] and to that of tellurite fiber incorporated with 40–50 nm nanodiamonds studied by Ruan et al.^[24] The bigger size of diamond particles used in this work lead to a significantly larger number of observed fluorescing diamonds that survived the melting and drawing process. We

observed the effect of broadening and reducing of the ODMR contrast from 6% to $\approx 2\%$ with an increase of the magnetic field, similarly to the results reported in refs. [24, 37]. This is caused by the random orientation of individual SDs as well as the increased strain in the diamond lattice due to the SD placement inside the glass matrix.

The ability to use NVN and NV⁻ color centers implemented in the tellurite glass increases the versatility of the developed material and enables its wide applications. For example, temperature measurements based on the shift of ZPL of NVN became also possible with the described material as demonstrated in ref. [6], albeit with a lower sensitivity than the NV⁻ ODMR measurement enables. For further increasing the sensitivity, the MDNVN1 powder used in this work can be replaced with the one containing SDs with higher concentrations of NV⁻ color centers. On the other hand, in light-sensitive applications where exposure to red and/or green light needs to be limited, it may be useful to trade the sensitivity offered by NV⁻ centers for a blue-shift of optical excitation and detection bands offered by NVN centers.

Temperature measurements based on ODMR studies presented in this paper demonstrate that this type of sensors can be used to simultaneously detect magnetic fields and temperature changes. Spatial dispersion of diamonds inside the tellurite rod can be thus seen as an advantage enabling temperature and magnetic field gradient measurements. Submicron-size diamonds dispersed in the tellurite glass can thus be a versatile platform for measuring local microscopic magnetic fields and temperature sensing in the microscale. Furthermore, the drawn structure can be easily connected to an undoped optical fiber, offering much better light transmission over larger distances, to act as a remote sensor probe with the SD-doped sensing volume localized only at the fiber end.

4. Experimental Section

Sample Preparation: Submicron diamond incorporated tellurite glass was fabricated using a four-component system with the following chemical composition [mol%]: TeO₂ (73), ZnO (20), Na₂O (5), La₂O₃ (2) (abbreviated as TZNL) identical to that reported in ref. [22]. High purity chemical reagents were used to make batches for glass melting. The glass was synthesized at a maximum temperature of 825 °C and stirred twice during melting to homogenize the glass. Next, the glass was cooled down to 650 °C and 2 mg of SD powder was added to 200 g of TZNL, stirred again, and inserted into a furnace at 650 °C for 10 min. The resulted concentration of the diamond powder in the glass was 0.001 %w/w. Recently, Kumar et al.^[38] reported that annealing of SDs at 750–1000 °C increases the concentration of NV⁻ centers thanks to the vacancy migration in the lattice. The glass was then cast into a preheated graphite form and annealed from 335 °C to room temperature at a cooling rate of 0.5 °C min⁻¹. The drawing process was carried out in a fiber drawing tower at a temperature of 440 °C. Rods about 400 μ m in diameter were obtained and used for ODMR magnetic field and temperature measurements in this study. The SD powder (MDNVN1 from Adamas Nanotechnologies with 750 nm particle size, as determined via DLS measurements) was used as a carrier for H3 and NV⁻ color centers. The use of a powder resulted in random positioning of diamond particles inside the glass matrix and yielded measurable green and red fluorescence from the manufactured tellurite rods. For undoped glasses, the measured refractive index was $n_d = 2.0655$ and the coefficient of linear thermal expansion measured in a range of 20–200 °C was equal to $17.5 \times 10^{-6} \text{ K}^{-1}$. When the undoped tellurite glass was excited with a green light (532 nm) laser, it did not exhibit noticeable fluorescence in the red

(600–800 nm) wavelength range as verified with an optical spectrometer (AvaSpec-3648, Avantes). Hence, any fluorescence in the doped glasses was attributed to the introduced SDs.

Fluorescence Spectra Collection: Optical fluorescence spectra presented in Figure 2a were recorded using a 0.3 m monochromator (SR303i, Andor—Oxford Instruments) equipped with a 1200 grooves mm⁻¹ grating and an intensified charge-coupled device (ICCD) detector (DH740, Andor—Oxford Instruments). The spectra in Figure 2b were collected with commercial confocal microscope (LSM710, Zeiss) equipped with spectrometer (SP2150, Acton) and ICCD camera (PI-MAX2, Princeton Instruments).

Confocal Microscopy and ODMR Technique: Optical excitation was achieved using a 532 nm laser (Sprout G, Lighthouse Photonics) with an output power of ≈ 1 mW for confocal imaging, and ≈ 60 mW (for wide-field ODMR measurements). In the home-made confocal setup the oil immersion objective with a magnification of 100 $\times$ (100 $\times$ /1.3 UPLFLN, Olympus) was used to illuminate and collect fluorescence from the sample. The movement of a sample in three directions with 200 $\times$ 200 $\times$ 200 μ m steps size and resolution of 0.4 nm was enabled by the piezo-scanner stage (Nano-LP200, Mad City Labs). Detection of the emitted fluorescence was performed by a single photon counting module (SPCM-AQRH-14-FC, Excelitas Technologies). The pinhole (30 μ m) placed just before the fiber connected to the SPCM eliminated the fluorescence emitted out of the focal plane by spatial filtering. Instruments of the in-house build confocal setup were controlled by a computer with the Qudi software.^[39] Confocal image γ presented in Figure 1c was taken with a commercial wide-field microscope (Axio Observer Z1, Zeiss) equipped with an sCMOS camera (Orca 4.0 V2, Hamamatsu). The ODMR spectra were collected in a wide-field setup. For wide-field illumination, the green laser was focused onto the back-focal plane of the objective (40 $\times$ /0.6 LUCPLFLN, Olympus), the optical excitation of SDs was achieved in the same way as with the confocal setup. The collected fluorescence was projected onto a 704 $\times$ 594 pixel photosensitive sensor of a camera (Zyla 5.5 sCMOS, Andor—Oxford Instruments) and the used optics yielded an effective pixel size of about $\approx (0.29 \mu\text{m})^2$ with the field of view of 205 $\times$ 173 μ m. The camera was connected to a computer which controlled the experiment and collected data. The MWs were delivered from a signal generator (SG386, Stanford Research Systems).

Acknowledgements

The authors would like to acknowledge the financial support of the Foundation for Polish Science under the project Team-NET No. POIR.04.04.00-00-1644/18.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

tellurite glass, submicron diamonds, Nitrogen-vacancy-nitrogen (H3) color centers, nitrogen-vacancy color centers, magnetometry, thermometry, sensors

Received: October 14, 2021

Revised: November 12, 2021

Published online:

- [1] S.-J. Yu, M.-W. Kang, H.-C. Chang, K.-M. Chen, Y.-C. Yu, *J. Am. Chem. Soc.* **2005**, *127*, 17604.
- [2] Y.-R. Chang, H.-Y. Lee, K. Chen, C.-C. Chang, D.-S. Tsai, C.-C. Fu, T.-S. Lim, Y.-K. Tzeng, C.-Y. Fang, C.-C. Han, H.-C. Chang, W. Fann, *Nat. Nanotechnol.* **2008**, *3*, 284.
- [3] B. R. Smith, M. Niebert, T. Plakhotnik, A. V. Zvyagin, *J. Lumin.* **2007**, *127*, 260.
- [4] N. Nunn, N. Prabhakar, P. Reineck, V. Magidson, E. Kamiya, W. F. Heinz, M. D. Torelli, J. Rosenholm, A. Zaitsev, O. Shenderova, *Nanoscale* **2019**, *11*, 11584.
- [5] S. Rand, L. DeShazer, *Opt. Lett.* **1985**, *10*, 481.
- [6] G. Davies, *J. Phys., C: Solid State Phys.* **1974**, *7*, 3797.
- [7] A. M. Wojciechowski, M. Karadas, A. Huck, C. Osterkamp, S. Jankuhn, J. Meijer, F. Jelezko, U. L. Andersen, *Sci. Instrum.* **2018**, *89*, 031501.
- [8] G. Balasubramanian, I. Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, C. Shin, C. Kim, A. Wojcik, P. R. Hemmer, A. Krueger, T. Hanke, A. Leitenstorfer, R. Bratschitsch, F. Jelezko, J. Wrachtrup, *Nature* **2008**, *455*, 648.
- [9] D. A. Golter, T. Oo, M. Amezcua, K. A. Stewart, H. Wang, *Phys. Rev. Lett.* **2016**, *116*, 143602.
- [10] P. Jamonneau, G. Hétet, A. Dréau, J.-F. Roch, V. Jacques, *Phys. Rev. Lett.* **2016**, *116*, 043603.
- [11] R. Schirhagl, K. Chang, M. Loretz, C. L. Degen, *Annu. Rev. Phys. Chem.* **2013**, *65*, 83.
- [12] V. M. Acosta, E. Bauch, M. P. Ledbetter, C. Santori, K.-M. Fu, P. E. Barclay, R. G. Beausoleil, H. Linget, J. F. Roch, F. Treussart, S. Chemerisov, W. Gawlik, D. Budker, *Phys. Rev. B* **2009**, *80*, 115202.
- [13] T. Wolf, P. Neumann, K. Nakamura, H. Sumiya, T. Ohshima, J. Isoya, J. Wrachtrup, *Phys. Rev. X* **2015**, *5*, 041001.
- [14] T. Van der Sar, E. Heeres, G. Dmochowski, G. De Lange, L. Robledo, T. Oosterkamp, R. Hanson, *Appl. Phys. Lett.* **2009**, *94*, 173104.
- [15] I. Fedotov, L. Doronina-Amitonova, A. Voronin, A. Levchenko, S. Zibrov, D. Sidorov-Biryukov, A. Fedotov, V. Velichansky, A. Zheltikov, *Sci. Rep.* **2014**, *4*, 5362.
- [16] A. K. Dmitriev, A. K. Vershovskii, *J. Opt. Soc. Am. B* **2016**, *33*, B1.
- [17] T. Schroder, A. W. Schell, G. Kewes, T. Aichele, O. Benson, *Nano Lett.* **2011**, *11*, 198.
- [18] D. Bai, M. H. Huynh, D. A. Simpson, P. Reineck, S. A. Vahid, A. D. Greentree, S. Foster, H. Ebendorff-Heidepriem, B. Gibson, *APL Mater.* **2020**, *8*, 081102.
- [19] X. Liu, J. Cui, F. Sun, X. Song, F. Feng, J. Wang, W. Zhu, L. Lou, G. Wang, *Appl. Phys. Lett.* **2013**, *103*, 143105.
- [20] Y. Hatano, J. Shin, D. Nishitani, H. Iwatsuka, Y. Masuyama, H. Sugiyama, M. Ishii, S. Onoda, T. Ohshima, K. Arai, T. Iwasaki, M. Hatano, *Appl. Phys. Lett.* **2021**, *118*, 034001.
- [21] F. M. Stürner, A. Brenneis, T. Buck, J. Kassel, R. Rölver, T. Fuchs, A. Savitsky, D. Suter, J. Grimm, S. Hengesbach, M. Förtsch, K. Nakamura, H. Sumiya, S. Onoda, J. Isoya, F. Jelezko, *Adv. Quantum Technol.* **2021**, *4*, 2000111.
- [22] H. Ebendorff-Heidepriem, Y. Ruan, H. Ji, A. D. Greentree, B. C. Gibson, T. M. Monroe, *Opt. Mater. Express* **2014**, *4*, 2608.
- [23] Y. Ruan, H. Ji, B. C. Johnson, T. Ohshima, A. D. Greentree, B. C. Gibson, T. M. Monroe, H. Ebendorff-Heidepriem, *Opt. Mater. Express* **2015**, *5*, 73.
- [24] Y. Ruan, D. A. Simpson, J. Jeske, H. Ebendorff-Heidepriem, D. W. Lau, H. Ji, B. C. Johnson, T. Ohshima, S. Afshar, L. Hollenberg, A. D. Greentree, T. M. Monroe, B. C. Gibson, *Sci. Rep.* **2018**, *8*, 1268.
- [25] M. Yamada, M. Shimizu, *J. IEICE* **2003**, *86*, 234.
- [26] M. R. Oermann, H. Ebendorff-Heidepriem, Y. Li, T.-C. Foo, T. M. Monroe, *Opt. Express* **2009**, *17*, 15578.
- [27] L. Rondin, J.-P. Tetienne, T. Hingant, J.-F. Roch, P. Maletinsky, V. Jacques, *Rep. Prog. Phys.* **2014**, *77*, 056503.
- [28] V. M. Acosta, Ph.D. Thesis, University of California, Berkeley **2011**.
- [29] D. J. Kimball, E. Alexandrov, D. Budker, *Optical Magnetometry* (Eds: D. Budker, D. F. J. Kimball), Cambridge University Press, Cambridge **2013**, pp. 3–24.
- [30] R. Guo, K. Wang, Y. Zhang, Z. Xiao, G. Jia, H. Wang, Y. Wu, Y. Tian, *Appl. Phys. Lett.* **2020**, *117*, 172104.
- [31] J. Jeske, D. W. Lau, X. Vidal, L. P. McGuinness, P. Reineck, B. C. Johnson, M. W. Doherty, J. C. McCallum, S. Onoda, F. Jelezko, T. Ohshima, T. Volz, J. H. Cole, B. C. Gibson, A. D. Greentree, *Nat. Commun.* **2017**, *8*, 14000.
- [32] K. Sasaki, Y. Monnai, S. Saijo, R. Fujita, H. Watanabe, J. Ishi-Hayase, K. M. Itoh, E. Abe, *Sci. Instrum.* **2016**, *87*, 053904.
- [33] S. Steinert, F. Dolde, P. Neumann, A. Aird, B. Naydenov, G. Balasubramanian, F. Jelezko, J. Wrachtrup, *Sci. Instrum.* **2010**, *81*, 043705.
- [34] A. M. Wojciechowski, P. Nakonieczna, M. Mrózek, K. Sycz, A. Kruk, M. Ficek, M. Głowacki, R. Bogdanowicz, W. Gawlik, *Materials* **2019**, *12*, 2951.
- [35] A. Dréau, M. Lesik, L. Rondin, P. Spinicelli, O. Arcizet, J.-F. Roch, V. Jacques, *Phys. Rev. B* **2011**, *84*, 195204.
- [36] J. F. Barry, J. M. Schloss, E. Bauch, M. J. Turner, C. A. Hart, L. M. Pham, R. L. Walsworth, *Rev. Mod. Phys.* **2020**, *92*, 015004.
- [37] I. V. Fedotov, L. V. Doronina-Amitonova, D. A. Sidorov-Biryukov, N. A. Safronov, A. O. Levchenko, S. A. Zibrov, S. Blakley, H. Perez, A. V. Akimov, A. B. Fedotov, P. Hemmer, K. Sakoda, V. L. Velichansky, M. O. Scully, A. M. Zheltikov, *Opt. Lett.* **2014**, *39*, 6755.
- [38] R. Kumar, D. K. Singh, P. Kumar, C. T. Trinh, K.-G. Lee, R. Kumar, S. Dhakate, *Diam. Relat. Mater.* **2021**, *114*, 108337.
- [39] J. M. Binder, A. Stark, N. Tomek, J. Scheuer, F. Frank, K. D. Jahnke, C. Müller, S. Schmitt, M. H. Metsch, T. Unden, T. Gehring, A. Huck, U. L. Andersen, L. J. Rogers, F. Jelezko, *SoftwareX* **2017**, *6*, 85.

Preparation and characterization of AFM tips with nitrogen-vacancy and nitrogen-vacancy-nitrogen color centers

Zuzanna Orzechowska,¹ Mariusz Mrózek,¹ Wojciech Gawlik,¹ and Adam M. Wojciechowski^{*,1}

¹*Faculty of Physics, Astronomy and Applied Computer Science,
Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland*

Received March 23, 2021; accepted April 28, 2021; published June 30, 2021

Abstract—We demonstrate a simple dip-coating method of covering standard AFM tips with nanodiamonds containing color centers. Such coating enables convenient visualization of AFM tips above transparent samples as well as tip using for performing spatially resolved magnetometry.

Atomic force microscopy (AFM) is a well-established field of research that offers multiple measurements including surface topology mapping, magnetic force measurements and electric conductance imaging with high-spatial resolution in various environments, like air, vacuum and/or liquids modalities [1–2]. Studies of nanomechanical properties of biological molecules, organella and living cells may be performed through local indentation by the AFM probe [3–4]. Measurements performed on optically transparent objects often require fluorescence imaging and the acquired AFM signal needs to be spatially correlated with the optical image [5].

In this work, we demonstrate a simple way of coating AFM tips and cantilevers with fluorescent nanodiamonds (NDs), which enables their localization using fluorescence microscopy techniques. Standard silicon AFM probes were dip-coated in a suspension of NDs in isopropyl alcohol and the NDs used contained two types of color centers: nitrogen-vacancy (NV) and nitrogen-vacancy-nitrogen (NVN, also designated as H3). They can be easily imaged under blue (for NVN centers) or green (for NV centers) light excitation with their fluorescence detected in the green and red wavelength bands, respectively. In the case of NV diamonds, additional measurement modalities are possible, e.g., magnetic field sensing [6]. While there have been many examples of scanning probe microscopy with diamond probes, including the use of single NV centers for nanoscale magnetometry [7–15], we focus here on the customization of more standard, silicon-based probes.

NV color centers are atom-like systems finding many practical applications in science and nanotechnology owing to their bright and stable fluorescence and spin properties, particularly when they are in their negative electronic charge state, NV⁻ [16–18]. The NV⁻ defect possesses a spin-triplet ground state which enables magnetic and electric field sensing using so-called, optically detected magnetic resonance (ODMR) [19], [20]. Green laser light is used for the spin polarization and

readout while a microwave (MW) field around 2.87 GHz is used for the spin manipulation. Small (~1 – 10 %) fluorescence dips are observed when the MW field is in resonance with the NV spin transition. External fields shift the resonance frequency which is monitored by the fluorescence change. The ODMR spectrum can be used to determine the magnitude and, in some arrangements, even the vector orientation of the perturbing field.

The spatial resolution of a magnetometer based on ND with an ensemble of NV centers, is a function of the size of the crystal used and its distance from a field source. Thus, to achieve good spatial resolution, placing NDs close to the tip apex is desired.

Our experiments were performed with commercially available silicon AFM probes (type PPP-CONTR, Nanosensors). The overall chip size is $3.4 \times 1.4 \times 0.3$ mm with the cantilever thickness, length, and width being 2.0 ± 0.1 μ m, 450 ± 10 μ m, and 50 ± 7.5 μ m, respectively. The tip height is within 10 – 15 μ m range. For dip-coating, the chip tip was carefully immersed for a few seconds into a suspension of nano-diamonds (MDNVN1 μ m powder with a 750 nm mean particle size, Adamas Nanotechnologies Inc.) in isopropyl alcohol and then allowed to dry in air. This type of ND powder contains on average ~2 ppm of NVN centers and estimated ~0.1 ppm of NV centers. Importantly, observations under the microscope indicated fluorescence of individual crystals being dominated by either the NV or NVN centers. Therefore, to achieve a satisfactory coating with less abundant NV diamonds, the dipping process was repeated, and two repetitions were found to be typically sufficient.

Fluorescence imaging of coated cantilevers and ODMR measurements have been performed with a wide-field microscope setup schematically presented in Fig. 1. Excitation of the NV color centers is ensured by a green (532 nm), PM-fiber-coupled laser (532-L-OE-115-1W, Integrated Optics) with an output power of 60 mW. The laser beam after the fiber was expanded to ~9 mm diameter and collimated, and then focused at the back focal plane of the microscope objective (LUCPLFLN 40x, NA = 0.6, Olympus) with a help of a dichroic mirror (DMLP567, Thorlabs). Fluorescence light collected by the objective was filtered by a 600-nm long-pass filter (FEL0600, Thorlabs) and projected onto a CMOS camera

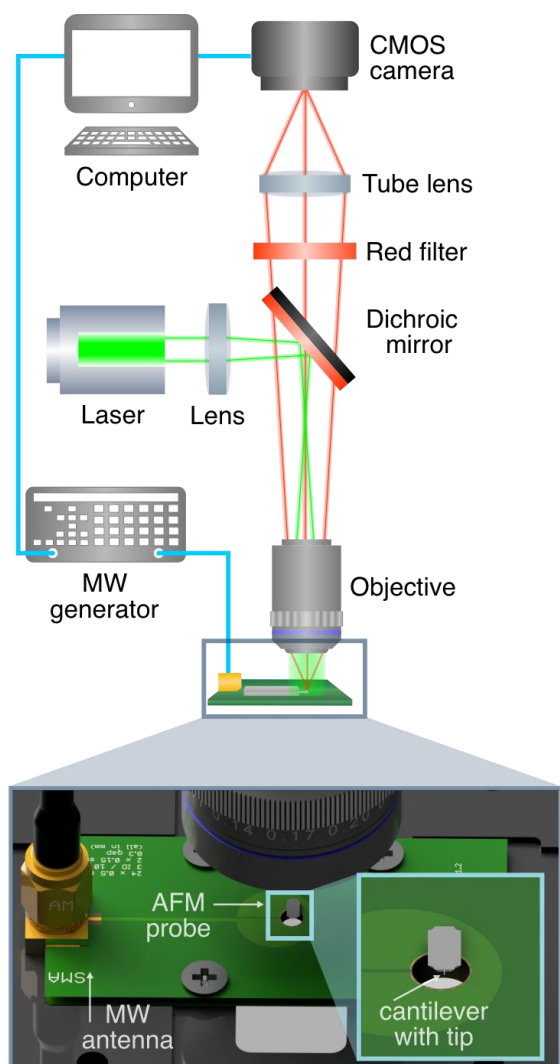


Fig. 1. Experimental apparatus for wide-field fluorescence microscopy and ODMR measurements. Inset shows the position of the AFM chip on the MW antenna.

sensor (IDS, UI-3240CP Rev. 2) using a 100-mm focal distance lens, which resulted in a field of view of $305 \times 244 \mu\text{m}$. For the ODMR measurements, the MW field was generated using a signal generator (SG396, Stanford Research Systems), amplified by a high-power amplifier (ZHL-16W-43+, Mini-Circuits) and delivered to a loop-gap type microstrip patch antenna [21] which has a 2-mm-diameter central hole size and ensures spatially uniform magnetic field over the whole cantilever area (see the inset in Fig. 1). An additional coil (not shown in Fig. 1) was used for applying a static magnetic field of up to 1 mT induction.

The fluorescence image of the ND-coated AFM cantilever is shown in Fig. 2. Under green light illumination, NDs containing NV centers are well visible as bright spots located randomly on the surface of the cantilever, which enables a convenient way of localizing the structure with a fluorescence microscope. Additionally,

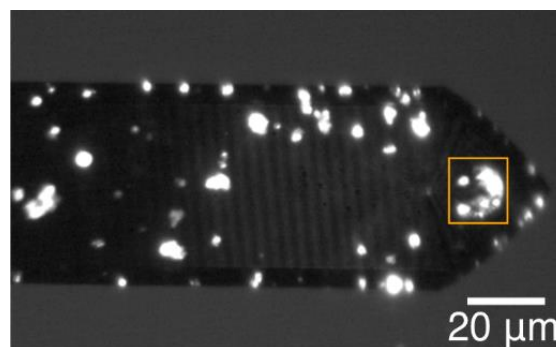


Fig. 2. Fluorescence image of the AFM cantilever coated with 750-nm-size nanodiamonds. The orange square marks the area from where the ODMR signal was collected.

there is a number of NDs visible around the tip area marked with the orange square in Fig. 2. The tip extends there from the cantilever plane towards the microscope objective and, due to the limited field depth of the optical setup, some NDs do not form a sharp image. However, this doesn't preclude ODMR measurements as long as fluorescence is integrated over the area containing a blurred image of all NDs. If the integration area is set too small, any drifts occurring during the MW frequency scans may cause fluorescence signal variations which can easily hinder the visibility of the ODMR signal.

Figure 3 shows the ODMR signals acquired for several magnetic field values with the fluorescence signal integrated over the region marked in Fig. 2. While in a zero magnetic field the measured nanodiamond ODMR spectrum resembles closely the single-crystalline one [16], the spectra recorded in non-zero fields are significantly different. Rather than exhibiting discrete pairs of resonances corresponding to four possible NV orientations along the $[111]$ crystallographic direction in a bulk diamond, they are inhomogeneously broadened because of the random orientation of fluorescing NDs with respect to the direction of the magnetic field. Because of adding fluorescence from multiple randomly oriented NDs, the orientation of the magnetic field vector cannot be retrieved. However, the information on the field magnitude still can be extracted from the overall width of the spectrum [22], [23]. For the accurate readout of the field strength, this requires multiple, truly randomly oriented NDs contributing to the signal, but a less rigorous or qualitative magnetic field mapping is feasible with any number of NDs.

In this work, we have demonstrated a simple and efficient method of making the AFM chips visible under a fluorescence microscope by dip-coating them with fluorescent NDs. The method can be useful for the localization of the AFM tip position with respect to optically transparent but fluorescing samples. Moreover, we have successfully recorded ODMR spectra from a group of NDs located around the pyramidal tip of the

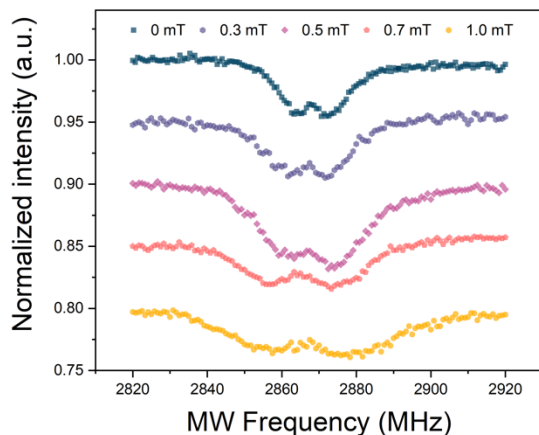


Fig. 3. ODMR signal for different value of magnetic fields. The visible broadening of a signal is caused by an increase in the applied magnetic field.

cantilever. This enables performing local magnetic field and temperature measurements with the same chip used for AFM measurements. The spatial resolution in the case of ND magnetometry is strongly dependent on the size of NDs and their positioning around the tip and may be improved by applying smaller diamond particles and limiting the fluorescence collection area to the tip apex. Since the NDs are addressed optically, the ultimate limit on spatial resolution is coming from the optical diffraction limit and is on the order of hundreds of nanometers. Despite offering significantly worse spatial resolution than the AFM, this modality may find practical applications for discerning nanostructures characterized by similar topography but different magnetic properties.

Authors acknowledge stimulating discussions with Robert Bogdanowicz and Marta Targosz-Korecka. This work was supported by the Polish National Science Centre under Grants No. 2016/21/B/ST7/01430 and the Foundation for Polish Science under the project Team-NET No. POIR.04.04.00-00-1644/18.

References

- [1] G. Binnig, C. F. Quate, C. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).
- [2] F.J. Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003).
- [3] S. Kasas, G. Dietler, *Eur. J. Appl. Physiol.* **456**, 13 (2008).
- [4] C. Roduit *et al.*, *Biophys. J.* **97**, 674 (2009).
- [5] L.A. Kolodny *et al.*, *Anal. Chem.* **73**, 1959 (2001).
- [6] L. Rondin *et al.*, *Rep. Prog. Phys.* **77**, 056503 (2014).
- [7] C.L. Degen, *Appl. Phys. Lett.* **92**, 243111 (2008).
- [8] J.M. Taylor *et al.*, *Nat. Phys.* **4**, 810 (2008).
- [9] J.R. Maze *et al.*, *Nature* **455**, 644 (2008).
- [10] L. Rondin *et al.*, *Appl. Phys. Lett.* **100**, 153118 (2012).
- [11] J.P. Tetienne *et al.*, *Science* **344**, 1366 (2014).
- [12] R. Nelz *et al.*, *Appl. Phys. Lett.* **109**, 193105 (2016).
- [13] G. Balasubramanian *et al.*, *Nature* **455**, 648 (2008).
- [14] P. Maletinsky *et al.*, *Nat. nanotechnol.* **7**, 320 (2012).
- [15] L. Thiel *et al.*, *Nat. nanotechnol.* **11**, 677 (2016).
- [16] F. Jelezko *et al.*, *Appl. Phys. Lett.* **81**, 2160 (2002).
- [17] M. W. Doherty *et al.*, *Phys. Rep.* **528**, 1 (2013).
- [18] C. Kurtsiefer, S. Mayer, P. Zarda, H. Weinfurter, *Phys. Rev. Lett.* **85**, 290 (2000).
- [19] A. Gruber, A. Dräbenstedt, C. Tietz, L. Fleury, J. Wrachtrup, C. Von Borczyskowski, *Science* **276**, 2012 (1997).
- [20] F. Dolde *et al.*, *Nat. Phys.* **7**, 459 (2011).
- [21] K. Sasaki *et al.*, *Rev. Sci. Instrum.* **87**, 053904 (2016).
- [22] A.M. Wojciechowski *et al.*, *Materials* **12**, 2951 (2019).
- [23] I.V. Fedotov *et al.*, *Opt. Lett.* **39**, 6755 (2014).

RESEARCH ARTICLE | MAY 22 2024

Optically detected magnetic resonance study of thermal effects due to absorbing environment around nitrogen-vacancy-nanodiamond powders

Mona Jani ; Zuzanna Orzechowska ; Mariusz Mrózek ; Marzena Mitura-Nowak ; Wojciech Gawlik ; Adam M. Wojciechowski 



J. Appl. Phys. 135, 203101 (2024)

<https://doi.org/10.1063/5.0203870>



Applied Physics Letters

Special Topic:

Quantum Networks

Guest Editors: David Awschalom, Ronald Hanson, Stephanie Simmons

Submit Today!

Optically detected magnetic resonance study of thermal effects due to absorbing environment around nitrogen-vacancy-nanodiamond powders

Cite as: J. Appl. Phys. 135, 203101 (2024); doi: 10.1063/5.0203870

Submitted: 17 February 2024 · Accepted: 7 May 2024 ·

Published Online: 22 May 2024



Mona Jani,^{1,2,3,a)} Zuzanna Orzechowska,¹ Mariusz Mrózek,¹ Marzena Mitura-Nowak,^{3,4}
Wojciech Gawlik,¹ and Adam M. Wojciechowski^{1,a)}

AFFILIATIONS

¹Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland

²School of Engineering and Applied Science, Ahmedabad University, 380009 Gujarat, India

³Laser Centre, University of Latvia, Jelgavas street 3, Riga LV-1004, Latvia

⁴Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, Kraków 31-342, Poland

^{a)}Authors to whom correspondence should be addressed: mona.jani@lu.lv and a.wojciechowski@uj.edu.pl

ABSTRACT

We implanted Fe⁺ ions in nanodiamond (ND) powder containing negatively charged nitrogen-vacancy (NV⁻) centers and studied their Raman spectra and optically detected magnetic resonance (ODMR) in various applied magnetic fields with green light (532 nm) excitation. In Raman spectra, we observed a *blue shift* of the NV⁻ peak associated with the conversion of the electronic sp³ configuration to the disordered sp² one typical for the carbon/graphite structure. In the ODMR spectra, we observed a *red shift* of the resonance position caused by local heating by an absorptive environment that recovers after annealing. To reveal the *red shift* mechanism in ODMR, we created a controlled absorptive environment around ND by adding iron-based Fe₂O₃ and graphitic sp² powders to the ND suspension. This admixture caused a substantial increase in the observed shift proportional to the applied laser power, corresponding to an increase in the local temperature by 150–180 K. This surprisingly large shift is absent in non-irradiated NV-ND powders, is associated only with the modification of the local temperature by the absorptive environment of NV-NDs, and can be studied using ODMR signals of NV⁻.

© 2024 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0203870>

I. INTRODUCTION

Taking advantage of their unique quantum properties, nitrogen-vacancy (NV) color centers in nanodiamonds (NDs) have been research strategy for highly sensitive and spatially resolved room temperature nanothermometry and nanomagnetometry applications^{1–4} with numerous applications, including those studied for electronic devices and biological sample objects that can operate under ambient and extreme conditions.^{2,5–7} NV color centers in the ND occur in two optically distinguishable electronic states: negatively charged (NV⁻) and neutral (NV⁰). When excited with green light (532 nm), the photoluminescence (PL) contains signatures of both centers, NV⁻ and NV⁰. Specifically, the sharp lines at 637 and 575 nm represent the zero-phonon lines (ZPLs) of NV⁻ and NV⁰, respectively. In the PL spectrum, the relative ratio of NV⁻ to NV⁰

for each charge state depends on the excitation wavelengths, as discussed in numerous articles, e.g., in Ref. 8. For green light (532 nm) excitation, the ZPL of NV⁻ is significantly stronger than that of NV⁰. NV⁻ has a nonzero electronic spin ($S=1$) and a triplet ground level.⁹ The superior photostability of NV⁻ enables precise optical detection of the electron spin resonance and, thus, conducting fundamental studies, such as on interactions with the nearby electronic and nuclear spins. Most of the existing applications of NDs with NV centers explore the exceptional optical and spin properties of NV⁻, in particular their dependence on electric¹⁰ and magnetic fields,⁶ strain,¹¹ and temperature.¹² After illumination with green light, the NV⁻ centers emit a spin-state-dependent fluorescence. The optically detected magnetic resonance (ODMR) technique relies on recording the fluorescence intensity while driving the spin transitions with appropriate microwave (MW) fields. This

07 June 2024 15:30:55

allows us to read out the populations of the ground-state magnetic sublevels, $m_s = 0$ and ± 1 split by the zero-field splitting (ZFS) parameter D (equal to about 2870 MHz at zero magnetic field) at room temperature. The dependence of the energies of the states $m_s = \pm 1$ on the external magnetic field enables many sensing applications,¹³ also on the nanoscale. For nanoscale temperature sensing/monitoring, one uses the fact that the ZFS parameter D decreases in response to a temperature increase due to lattice thermal expansion,¹² whereas for nanoscale magnetic field sensing with arbitrary oriented NDs, such as in powders or suspensions, one can benefit from the broadening of the overall ODMR spectrum that enables the determination of the external magnetic field strength.¹⁴

NV⁻ centers have been widely used to investigate magnetic nanostructures,¹⁵ paramagnetic ions in solution,¹⁶ spin-labeled molecules, detection of temperature changes,¹⁷ functionalized surfaces, measurements within living cells,¹⁸ increase in the sensitivity of biosensors, etc.¹⁹ Most applications that use NV-ND rely on interactions between the NV⁻ centers and the environment close to the ND surface.²⁰ NV⁻ centers provide significant information on various environmental influences.^{7,17,21,22} For example, the highly sensitive surface of ND enables complex surface immobilizations, grafting chemical moieties or biomolecules that strongly affect the surface reactivity of NDs, and can even induce chemical contaminations or surface graphitization.^{2,23–25} The presence of non-diamond carbon impurities reduces the fluorescence efficiency of ND.²⁶ In addition, the fluorescence intensity of NV-NDs depends on their ambient magnetic and fluctuating environment. Defects on the surface of the ND, such as hydrogen, vacancies, and trapping states, reduce the stability of NV⁻ centers.^{25,27,28} Because for many NV-ND-based applications, a very specific, uniform, and homogeneous surface is vitally important, we apply ODMR signals of NV⁻ to study the environment around the NV-ND powder surface.

In this work, we implanted NDs with Fe ions. Metal ions that transform to the sp^2 -graphitic phase are used in field emission sources²⁹ and as magnetic biomaterials,³⁰ and this was the motivation to start initially with the implantation of metal-Fe ions. When performing spectral diagnostic of the Fe irradiated samples, we observed a characteristic *blue shift* of the 1570 cm^{-1} Raman line typical for a graphitic/non-carbon phase and a large additional *red shift* of the ODMR. To obtain a closer view of the observed shifts, we admixed controlled amounts of iron-based Fe_2O_3 and graphitic (sp^2) powders into the ND suspension used for sample preparation. This admixture caused a substantial increase in the observed *red shift* in the magnetic resonance proportional to the applied laser power, corresponding to an increase in the local temperature by 150–180 K. This resonance shift is absent in non-irradiated NV-ND powders and is associated only with the modification of the local temperature by the absorptive environment of NV-NDs. Although it is generally well known that admixtures and contaminations cause enhanced absorption of external radiation (optical and MW) in the pure crystal structure, the huge size of the observed local heating studied using ODMR was quite unexpected and motivated this specific detailed study.

Our results confirm that the shift is caused by thermal effects arising from our modification of the ND environment and can be detrimental to sensitive measurements. Dried NDs are poorly thermally anchored and can heat up significantly before dissipating the heat elsewhere. While our focus was on implantation of Fe ions, we

recognize that similar outcomes could be anticipated for various types of ions. We hope that this work contributes to a specific understanding of the interaction between NV⁻ spins in NDs and the surrounding environment and should be useful for the implementations of thermometry and magnetometry methods and the development of NV relaxometry for material and bioscience research.

II. EXPERIMENTAL METHOD AND SETUP

We used a 140 nm carboxylated ND slurry with a mean diamond particle size of 140 nm, having a concentration of 1.5 ppm of NV centers, dispersed in de-ionized water (DI) (1 mg/ml) obtained from Adamas Nanotechnologies, USA. The spectroscopic properties of these NDs have been previously characterized in Ref. 31. From the suspension, $40\text{ }\mu\text{l}$ was dropped onto precleaned glass substrates and left to form a dry deposit.

Subsequently, the samples were implanted with Fe^+ ions using the ion implanter at the Institute of Nuclear Physics (Kraków Poland) described in Ref. 32. The implantation was carried out with ions having 30 keV energy and current density in the range of $0.8\text{--}1.0\text{ }\mu\text{A}/\text{cm}^2$, with substantial ion doses: 10^{14} and 10^{15} ions/ cm^2 . We labeled these samples ND14 and ND15, respectively. For the comparison of samples before and after the implantation process, samples were annealed in vacuum at $600\text{ }^\circ\text{C}$ for 3 h.

To create an iron-based and graphitic environment around NV-ND, we separately mixed and thoroughly sonicated $\sim 3\text{ mg}$ of iron-containing Fe_2O_3 (Warchem, Poland) and graphite powders in 2 ml of DI. From this, $75\text{ }\mu\text{l}$ was mixed with $50\text{ }\mu\text{l}$ of ND slurry and $40\text{ }\mu\text{l}$ was drop-dried on precleaned glass substrates. We labeled them NDF and NDG, respectively.

Here, we use five samples that are non-irradiated NV-NDs; non-irradiated NV-NDs implanted with Fe^+ ions at dose 10^{14} (ND14) and 10^{15} ions/ cm^2 (ND15); and NDs embedded with Fe_2O_3 (NDF) and NDs embedded with graphitic (NDG). ND14 and ND15 were annealed for comparison.

Depth profile simulations for ^{56}Fe ion implantation in NDs were obtained by a popular simulation routine Stopping and Range of Ions in Matter (SRIM).³³ Raman scattering spectra were recorded with a laser excitation of 532 nm in the range of $110\text{--}4000\text{ cm}^{-1}$ with a spectral resolution of 2 cm^{-1} using a confocal micro-Raman spectrometer (Almega XR, Thermo Electron Corp.) and WITec Alpha 300 confocal Raman microscope (Ulm, Germany).

ODMR signals were obtained in a home-built wide-field epifluorescence microscopy setup.³⁴ Samples on glass substrates were mounted close to the printed-circuit board of MW and excited by a 532 nm green laser (Sprout G, Lighthouse Photonics) with $\sim 65\text{ mW}$ laser power focused onto the back-focal plane of the $40\times/0.6$ objective (LUCPLFLN, Olympus). The continuous wave MW field was generated by a signal generator (SG386, Stanford Research Systems) plus the (ZHL-16W-43+ Mini-Circuits) amplifier, and its frequency was swept around the resonance frequency of the $m_s = 0 \leftrightarrow m_s = \pm 1$ transition of the ground state of NV⁻ of about 2870 MHz with 1 MHz steps. An external uniform magnetic field (B) of 1 and 3 mT was applied to the sample using a permanent magnet. To elucidate the heating effects due to MW and laser on the samples, the ODMR signals were collected by changing the MW power between -30 and $+10\text{ dBm}$ at a constant laser power of

07 June 2024 15:30:55

~ 65 mW and by varying the laser power between 5 and 80 mW at a constant MW power of $-10/-20$ dBm (before amplifier). The red fluorescence ($\sim 600-800$ nm) emitted from the sample was collected with the same microscope objective, filtered, and projected onto a 704×594 pixel photosensitive sensor of the sCMOS camera (Andor Zyla 5.5). The objective used produced an effective pixel size of about $(0.29 \mu\text{m})^2$ with a field of view of $205 \times 173 \mu\text{m}$. The ODMR data collection was carried out in LabView software, which controlled the camera, the signal generator, and the digital pattern generator (Pulse Streamer 8/2, Swabian Instruments). The laser spot on the sample has an area of $1.02 \times 10^5 \mu\text{m}^2$, and the laser energy flux on the NV-NDs is $\sim 6.3 \times 10^{-7} \text{ W}/\mu\text{m}^2$. During continuous light illumination, two images were captured with MWs turned on and off for every frequency to subtract the background and calculate the normalized fluorescence contrast, which helped to reduce fluorescence intensity variations due to laser power drifts and improved the overall signal-to-noise ratio.

III. RESULTS AND DISCUSSION

A. Implantation: Raman spectroscopy and ODMR

The depth profile (target depth) of the Fe ion implantation in diamond was modeled with the SRIM package³³ and is shown in Fig. 1(a). Simulations performed for an ion energy of 30 keV, an atomic density of $3.52 \text{ g}/\text{cm}^3$, and a displacement threshold energy of 45 eV for direction (111)³⁵ predict that the mean distribution of the depth of implantation is between 5 and 30 nm with the maximum peak at 15.8 nm. The inset in Fig. 1(a) depicts the predicted number of vacancies produced by the Fe ion beam inside the diamond for the ion depth range up to 140 nm, corresponding to the size of the NDs used. For the ND layer (in the form of an air-dried ND suspension) on a flat substrate, the implantation depth corresponds to a local distance from the ND surface. As seen, the entire implantation profile fits within ~ 50 nm depth, much less than the size of the ND. However, at high-ion fluences used, some damage of the diamond lattice is expected.

To monitor the characteristic structural changes caused by Fe ion irradiation, we recorded fluorescence spectra of the investigated ND samples [Fig. 1(b)]. Generally, two competing mechanisms contribute to net light emission, Raman scattering, and photoluminescence. However, for high NV densities and green-light excitation, the specific Raman characteristics are overwhelmed by strong NV fluorescence.³¹ To reveal weak Raman contributions on a strong fluorescence background, we performed a baseline correction of the spectra of Fig. 1(b) (fifteen-point spline in Origin software). Figure 1(c) depicts the resulting corrected spectra with pronounced peaks at wavenumbers of 1426 (576 nm) and 3129 cm^{-1} (638 nm) that are signatures of zero-phonon lines (ZPL) of NV^0 , NV^- for nonimplanted and implanted NDs, respectively.³⁶ Here, the characteristic diamond Raman band corresponding to the active phonon mode F_{2g} at $\sim 1332 \text{ cm}^{-1}$ is barely visible in nonimplanted ND and in ND14 due to the overwhelming contribution of highly fluorescent NV centers.³¹ The unidentified peak at 2975 cm^{-1} could be due to structural defects, surface chemistry, and/or undefined sample impurities. For the ND15 sample, a broad asymmetric peak is observed between 1200 and 1700 cm^{-1} . This broad structure comes from partially merging peaks due to a

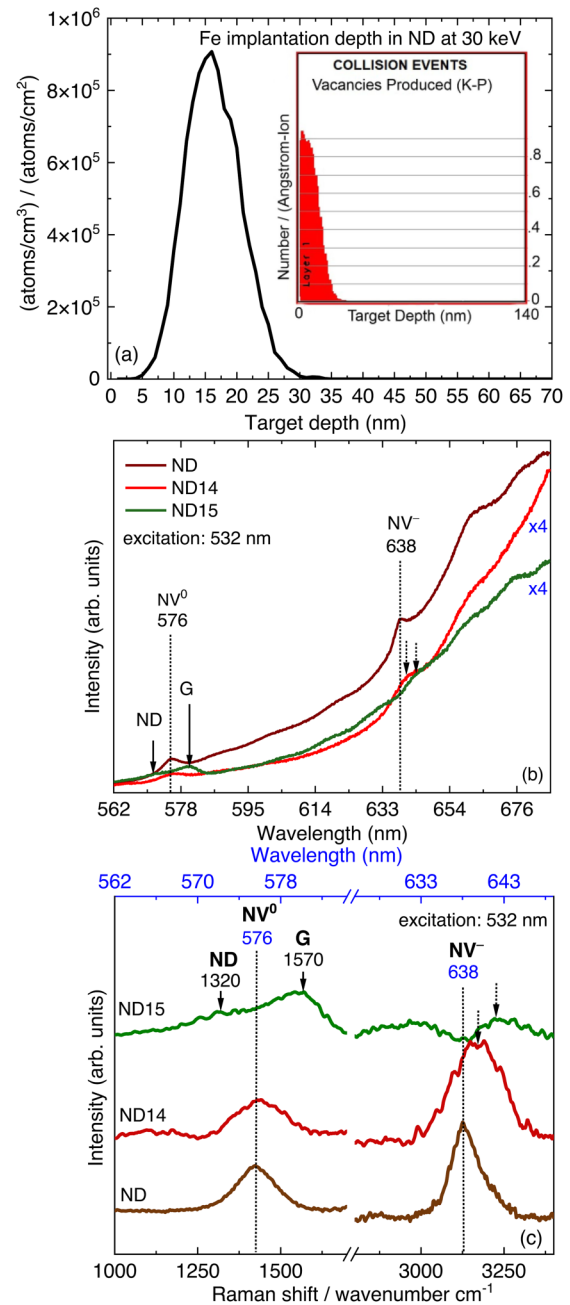


FIG. 1. (a) Simulated Fe ion concentration depth profile and damage (inset) at 30 keV. (b) Fluorescence spectra of the Fe-implanted 140 nm-sized NDs with no implantation (brown line), implantation doses of $10^{14} \text{ ions}/\text{cm}^2$ (ND14) (red line) and $10^{15} \text{ ions}/\text{cm}^2$ (ND15) (green line) at 532 nm laser excitation. The marked arrow at $\sim 1320 \text{ cm}^{-1}$ is attributed to the diamond Raman band in combination with disordered/amorphous carbon and that at 1570 cm^{-1} to the graphitic material. The dotted lines at 1426 (576 nm) and 3129 cm^{-1} (638 nm) are signatures of zero-phonon lines (ZPLs) of NV^0 , NV^- . The dotted arrows indicate blue shifted NV^- resonance, and (c) shows the Raman spectra of NV centers (zoomed-in) after the subtraction of a strong fluorescence background.

07 June 2024 15:30:55

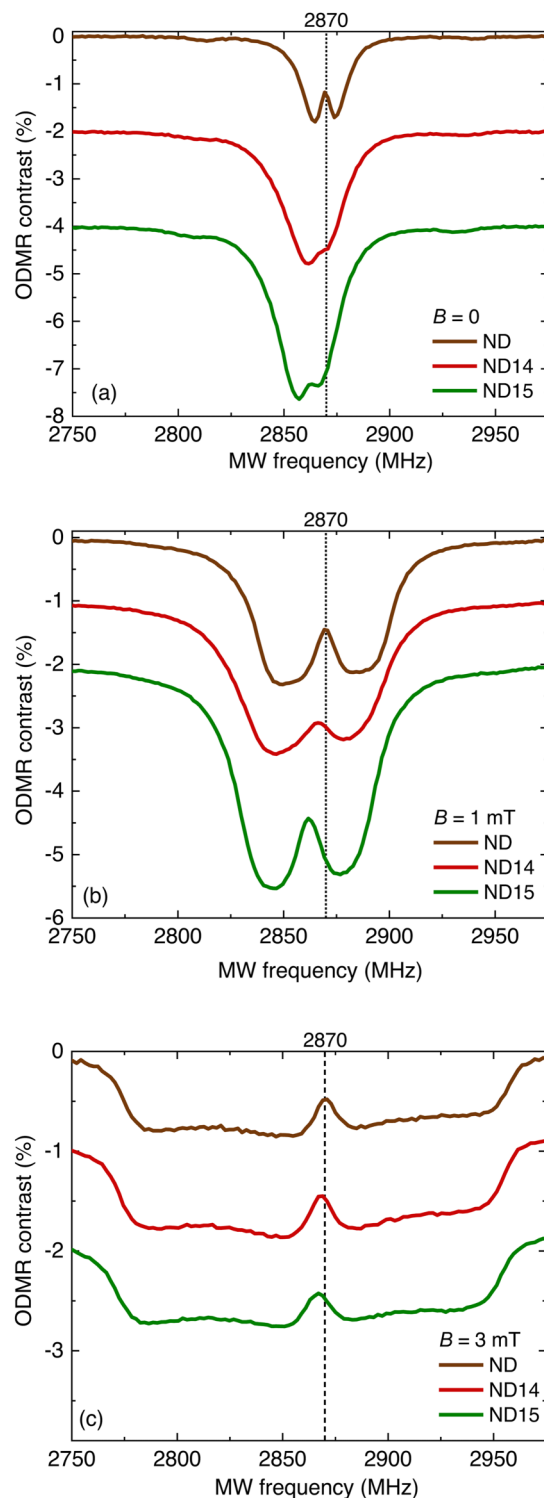


FIG. 2. ODMR spectra of ND for various implanted doses and magnetic field intensities: (a) $B = 0$, (b) $B = 1$ mT, and (c) $B = 3$ mT.

combination of disordered and amorphous carbon sp^2 (1320 cm^{-1}), the “G-band” of graphitic materials arising from mixing of carbon structures sp^2 and sp^3 (1570 cm^{-1}), and from the contribution of NV^0 ($\sim 1426\text{ cm}^{-1}$).³⁷ At higher irradiation doses, other processes may also affect the surface structure, such as the formation of multiple vacancy defects. Furthermore, with Fe ions implanted in ND, distinct *blue shifts* of Raman peak positions of

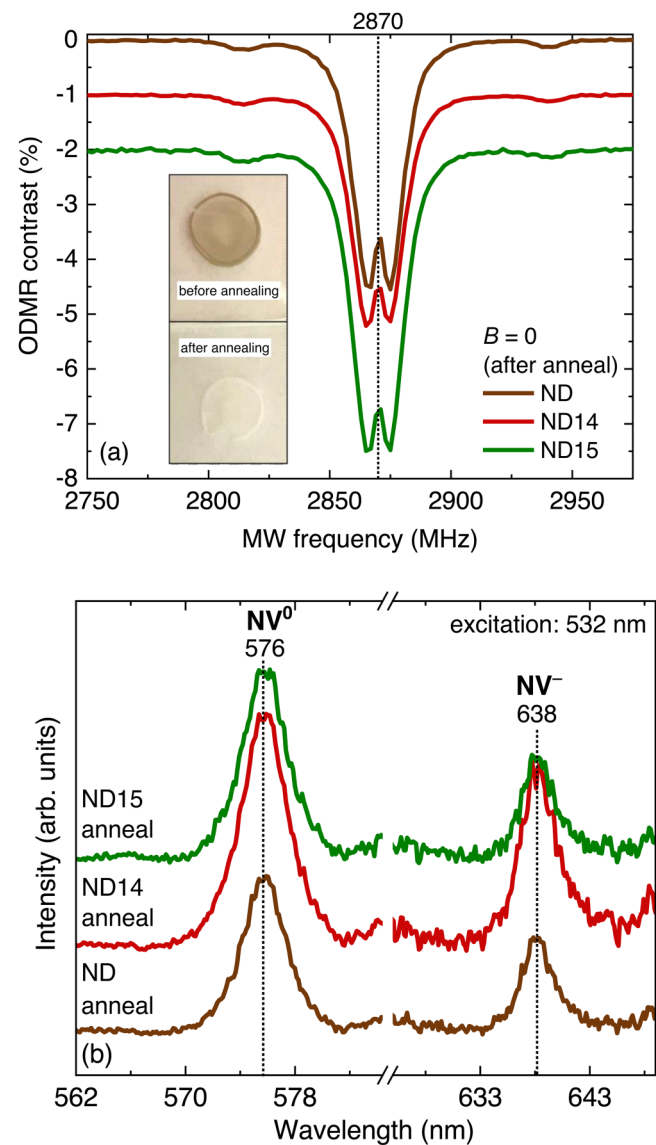


FIG. 3. (a) ODMR spectra of ND samples for various implanted doses collected at $B = 0$ after annealing. The inset shows the images of the implanted samples before and after annealing (the samples were drop-dried droplets of 140 nm ND water suspension on a glass surface); (b) fluorescence spectra of NV centers after implantation and annealing of NDs, with the subtracted strong fluorescence background.

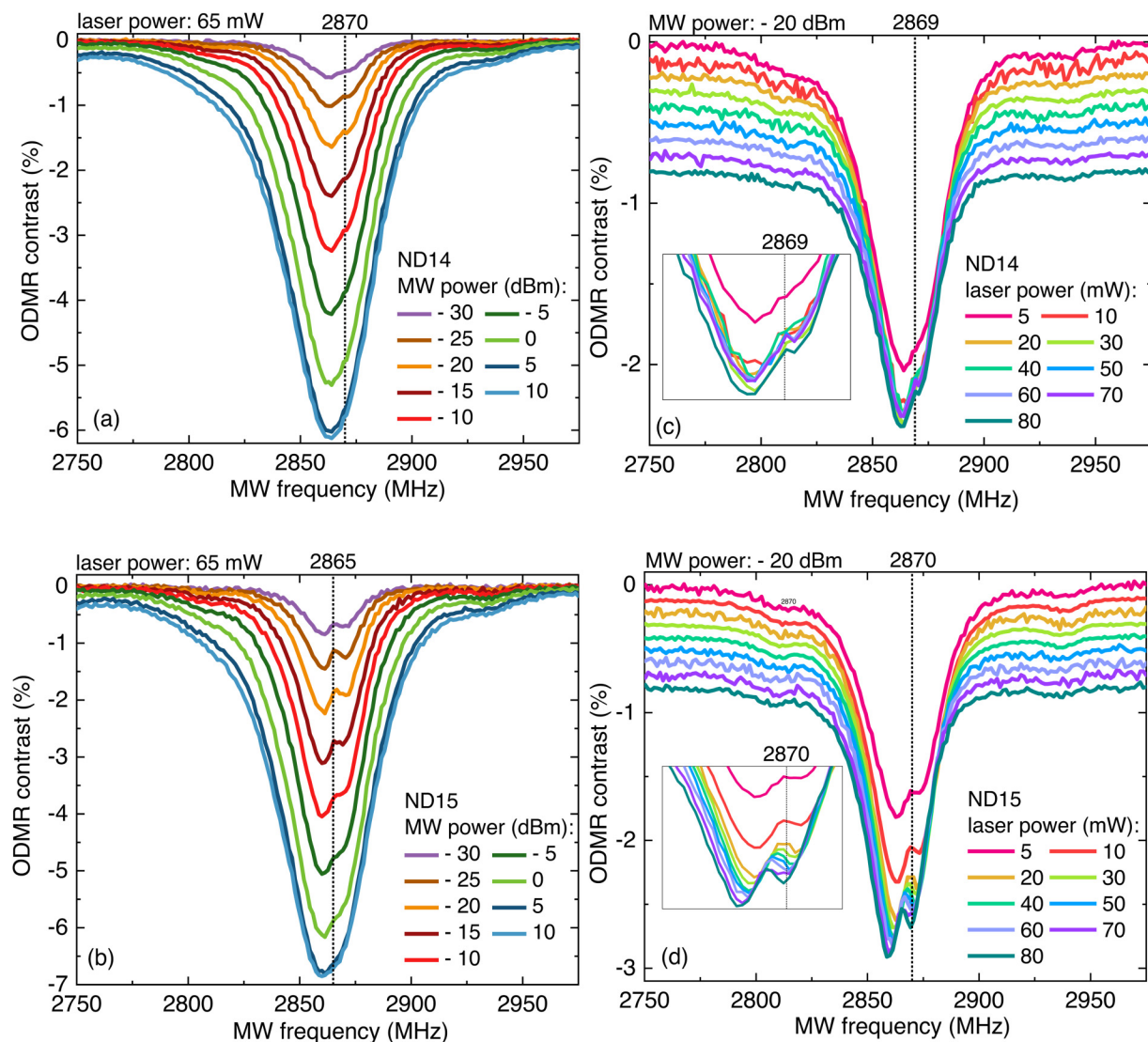
07 June 2024 15:30:55

NV^- are visible: $\sim 33 \text{ cm}^{-1}$ for ND14 and about 110 cm^{-1} shift for ND15 [indicated by arrows in Figs. 1(b) and 1(c)].

To the best of our knowledge, the specific process behind such a large upshift in the wavenumbers is not known. Based on the spectra presented in Figs. 1(b) and 1(c), we attribute the observed large *blue shift* of the Raman spectra caused by the implantation to surface changes in the local lattice environment (e.g., disordered carbon/graphite sp^2) that affect the NV^- centers.

In addition to the described changes in the Raman spectra, such as the formation of disordered carbon/graphite sp^2 , we also observed modifications of the ODMR by ion implantation. The detection of ODMR is based on recording spontaneous fluorescence

of excited states of NV centers in a diamond, with a physical mechanism different from that of a Raman scattering where a scattering occurs often without a sizeable population of excited states. Although Raman and fluorescence spectra generally differ,^{38–40} there are cases, like in NV diamonds, where they overlap and become indiscernible (particularly for high-NV-density samples, see, e.g., Ref. 31). Figure 2 shows the normalized ODMR spectra recorded in the absence of the magnetic field ($B = 0$) and with applied magnetic fields ($B = 1$ and 3 mT). The spectra exhibit a characteristic decrease in the fluorescence intensity around the central resonance frequency $D = 2870 \text{ MHz}$. The decrease is due to the repopulation of the $m_s = \pm 1$ sublevels induced by the presence of the MW field. For



07 June 2024 15:30:55

FIG. 4. ODMR spectra of ND14 and ND15 before annealing collected (a) and (b) at a laser power of 65 mW at various MW powers and (c) and (d) with a MW power of -20 dBm at various laser powers. Insets in (c) and (d) show the zoomed-in image of the *red shift* observed in the ODMR central resonance frequency.

NDs [Fig. 2(a), at $B = 0$], two resonances caused by strain splitting of about 6 MHz, predicted by the NV spin Hamiltonian,⁴¹ are clearly resolved. A small resonance asymmetry is attributed to MW polarization and the frequency dependence of the antenna efficiency.^{42,43} The vertical dotted line indicates the ZFS resonance frequency ($D = 2870$ MHz at $B = 0$). As can be seen in Fig. 2(a), the ODMR signals with Fe-implanted samples are visibly *red shifted*. The shift increases with increasing implantation dose reaching about 2 MHz for a dose of 10^{15} ions/cm².

The ODMR spectra recorded with $B \neq 0$ are significantly broadened compared to the zero-field spectra, due to random crystallographic orientations of small NDs [Figs. 2(b) and 2(c)]. However, the overall width of the broadened spectrum scales with the applied strength of B , allowing magnetometric applications.¹⁴ Additionally, there is a small upshift in the central frequency (vertical dotted line) at 2875 MHz [Fig. 2(c), ND14] and an asymmetry in the left and right sides of the spectra that is due to the nonlinear Zeeman effect.⁴⁴

To understand the effects of Fe ion implantation on NV centers in NDs, samples were not only analyzed using confocal Raman³¹ and ODMR spectroscopy. The implanted samples were also analyzed using luminescence spectroscopy and spin relaxometry. The corresponding spectra are shown as supporting information. Figure S1 in the [supplementary material](#) shows acquired luminescence spectra, and Figs. S2(a) and S2(b) in the [supplementary material](#) present the results of measurements of the spin-lattice and spin-spin relaxation times, T_1 and T_2 . These additional studies demonstrate that Fe⁺ implantation does not impact NV⁻ luminescence or spin relaxation in a meaningful way.

Implantation introduces damage to the irradiated crystal lattice that can be repaired by thermal annealing.⁴⁵ As shown in the inset in Fig. 3(a), the *red shift* of the central frequency of the ODMR signal, caused by irradiation, disappears after annealing. In addition, as shown by the photograph in white light in the inset, there is a color change back to the transparent original ND sample. In the Raman spectra [Fig. 3(b)], it is seen that the peaks are restored to their original positions and that the peaks related to the disordered surface bonds of sp^2 disappeared. This clearly indicates that, by annealing, the diamond structure is preserved to the original without inclusions of unwanted graphitic structures.

To elucidate the *red shift* observed in the ODMR central resonance frequency, we collected ODMR spectra for ND14 and ND15 as a function of MW and laser powers. From Figs. 4(a) and 4(b), we observe that the ODMR central resonance frequency remains 2870 MHz (ND14) and *red shifted* to 2865 MHz (ND15) for various applied MW powers between -30 and $+10$ dBm, at a constant laser power of 65 mW. On the other hand, at a constant MW power of -20 dBm, a gradual *red shift* in the ODMR central resonance frequency is observed with changing laser power from 5 to 80 mW as seen in Figs. 4(c) and 4(d). The ODMR spectra and the central resonance frequencies after annealing (Fig. S3 in the [supplementary material](#)) are similar to those for NDs [see Figs. 5(a) and 6(a)]. We attribute the *red shift* observed in the NDs implanted with ions (before annealing) to the local thermal effects arising from the heating of the NDs. To provide more insight into the mechanism of that effect, we admixed absorbing powders to the investigated ND samples. Specifically, we prepared the samples NDF and NDG where

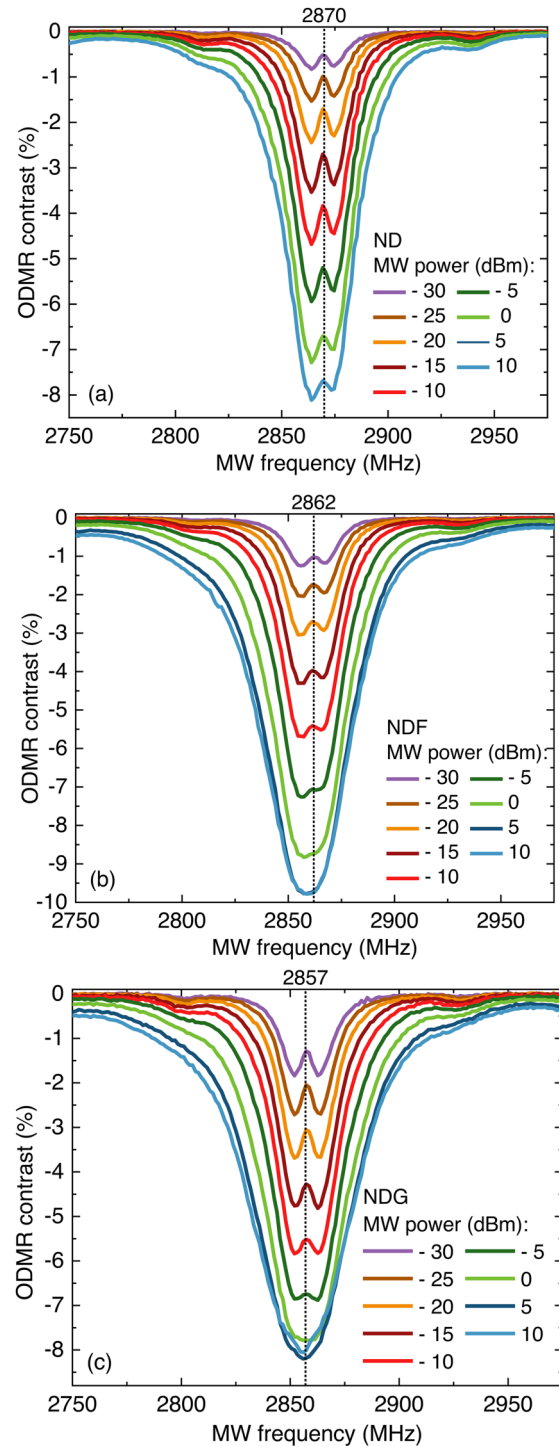


FIG. 5. ODMR spectra of (a) ND with admixtures and ND with admixtures of (b) iron (Fe_2O_3) and (c) graphite collected at a laser power of 65 mW at various MW powers. Note: In (a), the curves corresponding to 5 dBm and 10 dBm overlap.

07 June 2024 15:30:55

magnetic iron-containing Fe_2O_3 and graphite powders created a light-absorbing environment of the investigated NV-NDs and studied their ODMR spectra as functions of varying MW and laser power.

B. Iron-based and graphitic environment: ODMR

1. Microwave-dependent ODMR signals

Figure 5 shows the ODMR signals from NDs by varying the MW power from -30 to $+10$ dBm, while keeping the laser power constant at 65 mW. Figure 5(a) displays the resulting ODMR spectrum for NDs as a function of increasing MW power. ODMR signals lead to the observation of a power broadening of the central resonance frequency (2870 MHz) and increase their contrast to saturation by

approximately 8% and become power broadened.^{46,47} For absorber-enriched NDF and NDG samples, both broadening and contrast increase with increasing MW power [Figs. 5(b) and 5(c)], similar to that observed in Fig. 5(a). Furthermore, for both samples, the strain-split ODMR peaks merge into a single broad fluorescence dip.

Most importantly, the central resonance frequency, 2870 MHz for the sample without admixtures, is red shifted to 2862 MHz for NDF and 2857 MHz for NDG samples due to the presence of iron and graphite admixtures.⁴⁸

2. Laser power-dependent ODMR signals

Figure 6 shows the dependence of the ODMR signal with varying laser power from 5 to 80 mW at -10 dBm MW power. The

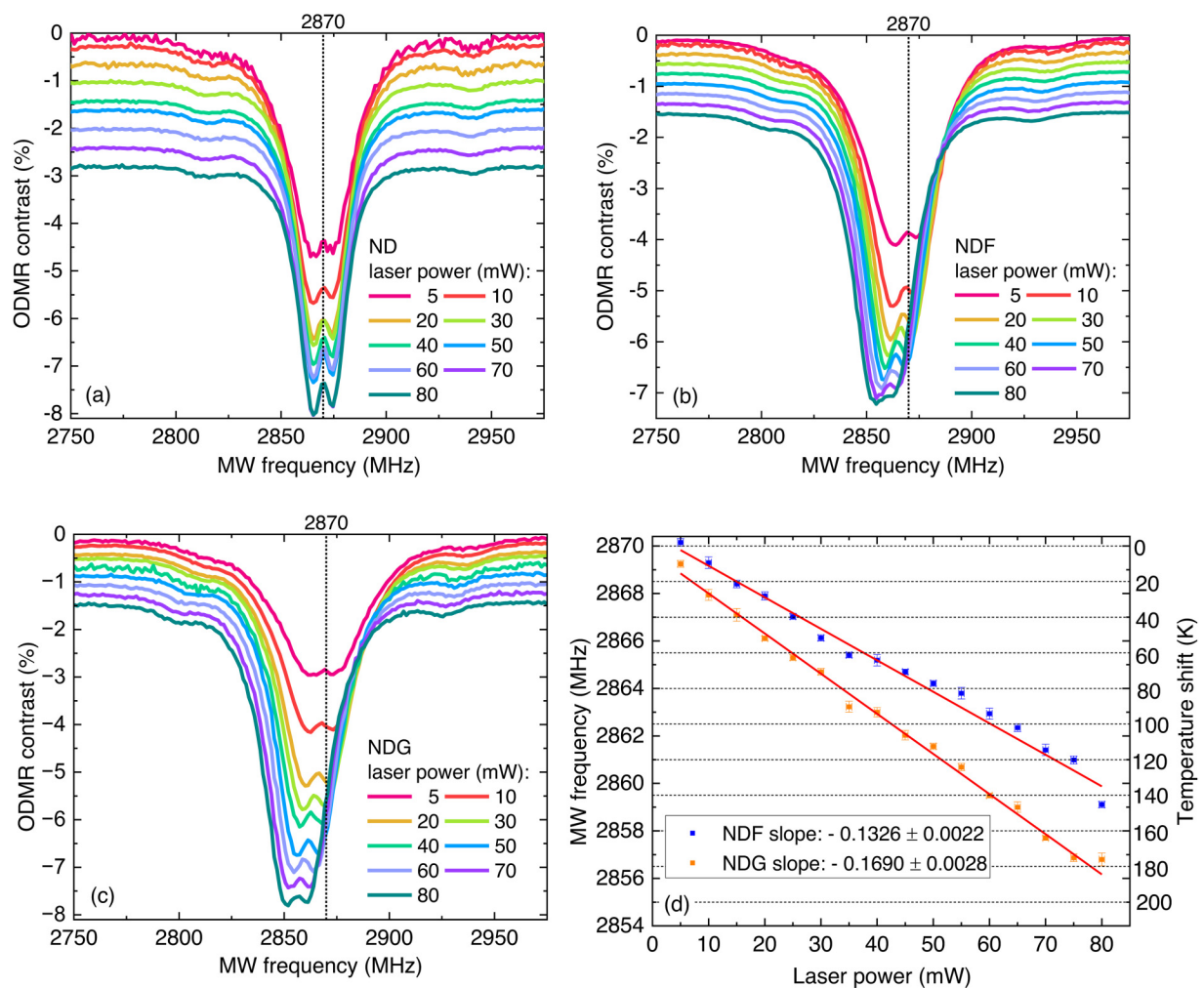


FIG. 6. ODMR spectra collected with a MW power of -10 dBm at various laser powers of ND samples (a) without admixtures, and ND with admixtures of (b) iron (Fe_2O_3), and (c) graphite. (d) Temperature change due to the local environment around NV-ND calculated from the shift observed in the ODMR spectra (b) and (c). Lorentz fitting was performed on each resonant position in (a), (b), and (c), and the values were averaged to calculate the central resonance frequency and errors. The temperature shift was determined using the formula $dD/dT = -75$ kHz/K.^{21,49}

ODMR signals procured for NDs show no significant changes in the ODMR contrast and/or broadening, and all resonances remain centered at 2870 MHz with no shift within the applied laser power range [see Fig. 6(a)]. As can be seen from the figure, the applied laser power is sufficiently low to avoid heating of the ND samples with no admixtures. However, for the same laser power that was used to collect ODMR signals for NDs, we observe a significant shift of the central frequency of the ODMR spectra taken with samples with an iron-based and graphitic environment [Figs. 6(b) and 6(c)]. In contrast, the spectral shape of the ODMR signals remained unaffected. Here, we used the Lorentzian function to determine the central position of the structured resonance. We fitted the two central dips and calculated the average frequency to determine the central resonance frequency “ D .” For the NDF sample, the ZFS parameter D is linearly *red shifted* with increasing laser power from 2870 MHz at 5 mW to 2859 MHz to 80 mW, and for the NDG sample, the shift reached even 2856 MHz. The change from the center position $D = 2870$ MHz is equivalent to a shift of 11 MHz (NDF) and 14 MHz (NDG) [Fig. 6(d)]. The temperature response in NV-ND reveals a thermal shift of ZFS (D) at 2870 MHz ($m_s = 0$ to $m_s = \pm 1$) or the zero-phonon line (ZPL) at 637 nm²¹. From Fig. 6(d), this is a direct indication that the frequency shift corresponds to an increase in the temperature due to the presence of iron and graphite surroundings, as optically detected using NV⁻ spin resonance. The surrounding environment absorbs laser light, becomes warmer, and further heats the NDs, thus increasing the local temperature. For bulk diamonds, the zero-field resonance frequency D changes approximately linearly with temperature around room temperature, with a slope of $dD/dT = -75$ kHz/K,^{21,49} while the resonance width remains temperature independent.⁵⁰ The measured ODMR frequency is temperature dependent; hence, by measuring the ODMR frequency shift, the temperature change can be inferred directly. Taking into account the dD/dT reported values, the temperatures are calculated for the frequency shift and plotted as the temperature axis on the right-hand side scale of Fig. 6(d). The calculated temperature shifts appear to be quite strong, exceeding 140 K (NDF) and 180 K (NDG), respectively. The temperature shifts linearly as a function of laser power, as shown in Fig. 6(d), the slope for Fe₂O₃ surrounding NDs is ≈ -0.13 MHz/mW, corresponds to the temperature shift ≈ -1.73 K/mW, different from the slope for graphite surrounding ND, which is ≈ -0.17 MHz/mW, and corresponds to ≈ -2.26 K/mW.

IV. CONCLUSION

In this work, we describe the effects of implantation of Fe ions in ND matrices containing NV⁻ color centers. The implantation becomes responsible for the formation of sp²-structures in NDs, resulting in a *blue shift* of Raman spectra. Furthermore, the ODMR signals of NV⁻ are shifted to low frequencies due to local thermal effects caused by a magnetic and non-carbon matter.

We have demonstrated that the ODMR shifts are significantly enhanced by creating optically absorptive iron oxide (Fe₂O₃) and graphitic (sp²) environments of the investigated NDs. In this way, we have evidenced extreme temperature changes in NDs that exceed 150 K. We have verified that these changes are not caused by direct heating of non-irradiate NDs by a laser or by microwaves.

We attributed these shifts to the modification of the local temperature by the absorptive environment of NV-NDs.

The reported ODMR observations shed light on the dynamics of interaction between surfaces of color-center containing nanoparticles with various non-carbon moieties and their temperature dependence. In particular, they reveal the importance of thermal effects associated with various admixtures and/or graphitization in various NV-based experiments, which may enable precision *in situ* thermometry on a nanoscale.

SUPPLEMENTARY MATERIAL

See the supplementary material for acquired luminescence spectra and the inset showing amplitudes of the NV⁰, NV⁻ peaks and their ratios NV⁻/NV⁰ obtained from the average of ten PL spectra for Fe ions implanted in ND (ND14 and ND15) (Fig. S1); the results of measurements of the spin-lattice and spin-spin relaxation times, T_1 and T_2 for various Fe-ion-implanted doses [Figs. S2(a) and S2(b)]; and the ODMR spectra and the central resonance frequencies after annealing ND14 and ND15 (Fig. S3). The ODMR signals are collected (a) and (b) at a laser power of 65 mW at various MW powers and (c) and (d) with a MW power of -20 dBm at various laser powers.

ACKNOWLEDGMENTS

The authors thank Professor S. Baran and Dr. Anna M. Majcher-Fitas from the Institute of Physics, and Dr. Anna M. Nowakowska from the Faculty of Chemistry, Jagiellonian University, Poland, for supporting this research by providing access to their x-ray diffraction, magnetic measurements, and Raman spectroscopy instrumentation facility. This work was supported by the Foundation for Polish Science TEAM-NET program co-financed by the EU under the European Regional Development Fund, Grant No. POIR.04.04.00-00-1644/18. Dr. Mona Jani would like to acknowledge funding support from the “Latvian Quantum Technologies Initiative” project under the European Union Recovery and Resilience Facility, Grant No. 2.3.1.1.i.0/1/22/1/CFLA/001.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Mona Jani: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Resources (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Zuzanna Orzechowska:** Formal analysis (equal); Methodology (equal); Resources (equal); Validation (equal); Writing – review & editing (equal). **Mariusz Mrózek:** Formal analysis (equal); Methodology (equal); Resources (equal); Validation (equal); Writing – review & editing (equal). **Marzena Mitura-Nowak:** Methodology (equal); Resources (equal). **Wojciech Gawlik:** Funding acquisition (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal). **Adam M. Wojciechowski:** Conceptualization (equal); Methodology

07 June 2024 15:30:55

(equal); Resources (equal); Validation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES

- ¹G.-Q. Liu, R.-B. Liu, and Q. Li, “Nanothermometry with enhanced sensitivity and enlarged working range using diamond sensors,” *Acc. Chem. Res.* **56**(2), 95–105 (2023).
- ²A. Sigaeva, H. Shirzad, F. P. Martinez, A. C. Nusantara, N. Mougios, M. Chipaux, and R. Schirhagl, “Diamond-based nanoscale quantum relaxometry for sensing free radical production in cells,” *Small* **18**(44), 2105750 (2022).
- ³M. Jani, P. Czarnecka, Z. Orzechowska, M. Mrózek, W. Gawlik, and A. M. Wojciechowski, “Sensing of magnetic-field gradients with nanodiamonds on optical glass-fiber facets,” *ACS Appl. Nano Mater.* **6**(13), 11077–11084 (2023).
- ⁴J. R. Maze, P. L. Stanwix, J. S. Hodges, S. Hong, J. M. Taylor, P. Cappellaro, L. Jiang, M. V. G. Dutt, E. Togan, A. S. Zibrov, A. Yacoby, R. L. Walsworth, and M. D. Lukin, “Nanoscale magnetic sensing with an individual electronic spin in diamond,” *Nature* **455**(7213), 644–647 (2008).
- ⁵R. Dou, G. Zhu, W.-H. Leong, X. Feng, Z. Li, C. Lin, S. Wang, and Q. Li, “In operando nanothermometry by nanodiamond based temperature sensing,” *Carbon* **203**, 534–541 (2023).
- ⁶G. Balasubramanian, I. Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, C. Shin, C. Kim, A. Wojcik, P. R. Hemmer, A. Krueger, T. Hanke, A. Leitenstorfer, R. Bratschkitsch, F. Jelezko, and J. Wrachtrup, “Nanoscale imaging magnetometry with diamond spins under ambient conditions,” *Nature* **455**(7213), 648–651 (2008).
- ⁷G. Kucsko, P. C. Maurer, N. Y. Yao, M. Kubo, H. J. Noh, P. K. Lo, H. Park, and M. D. Lukin, “Nanometre-scale thermometry in a living cell,” *Nature* **500**(7460), 54–58 (2013).
- ⁸K. Beha, A. Batalov, N. B. Manson, R. Bratschkitsch, and A. Leitenstorfer, “Optimum photoluminescence excitation and recharging cycle of single nitrogen-vacancy centers in ultrapure diamond,” *Phys. Rev. Lett.* **109**(9), 097404 (2012).
- ⁹M. W. Doherty, N. B. Manson, P. Delaney, F. Jelezko, J. Wrachtrup, and L. C. L. Hollenberg, “The nitrogen-vacancy colour centre in diamond,” *Phys. Rep.* **528**(1), 1–45 (2013).
- ¹⁰F. Dolde, H. Fedder, M. W. Doherty, T. Nöbauer, F. Rempp, G. Balasubramanian, T. Wolf, F. Reinhard, L. C. L. Hollenberg, F. Jelezko, and J. Wrachtrup, “Electric-field sensing using single diamond spins,” *Nat. Phys.* **7**(6), 459–463 (2011).
- ¹¹J. Teissier, A. Barfuss, P. Appel, E. Neu, and P. Maletinsky, “Strain coupling of a nitrogen-vacancy center spin to a diamond mechanical oscillator,” *Phys. Rev. Lett.* **113**(2), 020503 (2014).
- ¹²M. W. Doherty, V. M. Acosta, A. Jarmola, M. S. J. Barson, N. B. Manson, D. Budker, and L. C. L. Hollenberg, “Temperature shifts of the resonances of the NV-center in diamond,” *Phys. Rev. B* **90**(4), 041201 (2014).
- ¹³R. Schirhagl, K. Chang, M. Loretz, and C. L. Degen, “Nitrogen-vacancy centers in diamond: Nanoscale sensors for physics and biology,” *Annu. Rev. Phys. Chem.* **65**(1), 83–105 (2014).
- ¹⁴A. M. Wojciechowski, P. Nakonieczna, M. Mrózek, K. Sycz, A. Kruk, M. Ficek, M. Głowacki, R. Bogdanowicz, and W. Gawlik, “Optical magnetometry based on nanodiamonds with nitrogen-vacancy color centers,” *Materials* **12**(18), 2951 (2019).
- ¹⁵F. Camarero, J. Bocquel, J. Gallo, M. Bañobre-López, K. Berg-Sørensen, U. L. Andersen, A. Huck, and J. B. Nieder, “Magnetic field mapping around individual magnetic nanoparticle agglomerates using nitrogen-vacancy centers in diamond,” *Part. Part. Syst. Charact.* **38**(8), 2100011 (2021).
- ¹⁶F. Perona Martínez, A. C. Nusantara, M. Chipaux, S. K. Padamati, and R. Schirhagl, “Nanodiamond relaxometry-based detection of free-radical species when produced in chemical reactions in biologically relevant conditions,” *ACS Sens.* **5**(12), 3862–3869 (2020).
- ¹⁷S. Sotoma, C. P. Epperla, and H.-C. Chang, “Diamond nanothermometry,” *ChemNanoMat* **4**(1), 15–27 (2018).
- ¹⁸L. P. McGuinness, Y. Yan, A. Stacey, D. A. Simpson, L. T. Hall, D. Maclaurin, S. Prawer, P. Mulvaney, J. Wrachtrup, F. Caruso, R. E. Scholten, and L. C. L. Hollenberg, “Quantum measurement and orientation tracking of fluorescent nanodiamonds inside living cells,” *Nat. Nanotechnol.* **6**(6), 358–363 (2011).
- ¹⁹T. F. Segawa and R. Igarashi, “Nanoscale quantum sensing with nitrogen-vacancy centers in nanodiamonds—A magnetic resonance perspective,” *Prog. Nucl. Magn. Reson. Spectrosc.* **134–135**, 20–38 (2023).
- ²⁰D. Olivares-Postigo, F. Gorrini, V. Bitonto, J. Ackermann, R. Giri, A. Krueger, and A. Bifone, “Divergent effects of laser irradiation on ensembles of nitrogen-vacancy centers in bulk and nanodiamonds: Implications for biosensing,” *Nanoscale Res. Lett.* **17**(1), 95 (2022).
- ²¹T. Plakhotnik, M. W. Doherty, J. H. Cole, R. Chapman, and N. B. Manson, “All-optical thermometry and thermal properties of the optically detected spin resonances of the NV-center in nanodiamond,” *Nano Lett.* **14**(9), 4989–4996 (2014).
- ²²N. Aslam, H. Zhou, E. K. Urbach, M. J. Turner, R. L. Walsworth, M. D. Lukin, and H. Park, “Quantum sensors for biomedical applications,” *Nat. Rev. Phys.* **5**(3), 157–169 (2023).
- ²³J.-C. Arnault, T. Petit, H. A. Girard, C. Gesset, M. Combis-Schlumberger, M. Sennour, A. Koscheev, A. A. Khomich, I. Vlasov, and O. Shenderova, “Surface graphitization of ozone-treated detonation nanodiamonds,” *Phys. Status Solidi A* **211**(12), 2739–2743 (2014).
- ²⁴A. M. Panich, A. E. Aleksenskii, E. B. Yudina, and A. Y. Vul’, “Spatially resolved spin-lattice relaxation times and line widths in manganese-grafted detonation nanodiamonds,” *J. Phys. Chem. C* **126**(3), 1489–1495 (2022).
- ²⁵D. Bluvstein, Z. Zhang, and A. C. B. Jayich, “Identifying and mitigating charge instabilities in shallow diamond nitrogen-vacancy centers,” *Phys. Rev. Lett.* **122**(7), 076101 (2019).
- ²⁶R. Kumar, S. J. Yoon, K. G. Lee, P. Pal, R. P. Pant, C. K. Suman, S. R. Dhakate, R. Kumar, D. K. Avasthi, and D. K. Singh, “Purification method dependent fluorescence from nitrogen-vacancy (NV) centers of nano-diamonds,” *RSC Adv.* **6**(52), 47164–47173 (2016).
- ²⁷M. V. Hauf, B. Grotz, B. Naydenov, M. Dankerl, S. Pezzagna, J. Meijer, F. Jelezko, J. Wrachtrup, M. Stutzmann, F. Reinhard, and J. A. Garrido, “Chemical control of the charge state of nitrogen-vacancy centers in diamond,” *Phys. Rev. B* **83**(8), 081304 (2011).
- ²⁸Z. Yuan, M. Fitzpatrick, L. V. H. Rodgers, S. Sangtawesin, S. Srinivasan, and N. P. de Leon, “Charge state dynamics and optically detected electron spin resonance contrast of shallow nitrogen-vacancy centers in diamond,” *Phys. Rev. Res.* **2**(3), 033263 (2020).
- ²⁹K. Panda, J. J. Hyeok, J. Y. Park, K. J. Sankaran, S. Balakrishnan, and I.-N. Lin, “Nanoscale investigation of enhanced electron field emission for silver ion implanted/post-annealed ultrananocrystalline diamond films,” *Sci. Rep.* **7**(1), 16325 (2017).
- ³⁰B.-R. Lin, S. Kunuku, C.-H. Chen, T.-Y. Chen, T.-Y. Hsiao, H.-K. Yu, Y.-J. Chang, L.-C. Liao, H. Niu, and C.-P. Lee, “Fluorescent Fe embedded magnetic nanodiamonds made by Ion implantation,” *Sci. Rep.* **9**(1), 1297 (2019).
- ³¹M. Jani, M. Mrózek, A. M. Nowakowska, P. Leszczenko, W. Gawlik, and A. M. Wojciechowski, “Role of high nitrogen-vacancy concentration on the photoluminescence and Raman spectra of diamond,” *Phys. Status Solidi A* **220**(4), 2200299 (2023).
- ³²B. Rajchel, M. Drwiega, E. Lipińska, and M. Wierba, “Adaptation of the 70 kV INP ion implanter to the IBA technique,” *Nucl. Instrum. Methods Phys. Res., Sect. B* **89**(1), 342–345 (1994).
- ³³F. Ziegler and J. P. Biersack, “The stopping and range of ions in matter,” in *Treatise Heavy-Ion Science, Astrophysics, Chemistry, and Condensed Matter*, edited by D. A. Bromley (Springer US, Boston, MA, 1985), Vol. 6, pp. 93–129.
- ³⁴Z. Orzechowska, M. Mrózek, A. Filipkowski, D. Pysz, R. Stępień, M. Ficek, A. M. Wojciechowski, M. Klimczak, R. Bogdanowicz, and W. Gawlik, “Tellurite

glass rods with submicron-size diamonds as photonic magnetic field and temperature sensors," *Adv. Quantum Technol.* **5**(3), 2100128 (2022).

³⁵J. Koike, D. M. Parkin, and T. E. Mitchell, "Displacement threshold energy for type IIa diamond," *Appl. Phys. Lett.* **60**(12), 1450–1452 (1992).

³⁶S. P. Turaga, H. Jin, E. J. Teo, and A. A. Bettiol, "Cross-sectional hyperspectral imaging of proton implanted diamond," *Appl. Phys. Lett.* **115**(2), 021904 (2019).

³⁷V. Mochalin, S. Osswald, and Y. Gogotsi, "Contribution of functional groups to the Raman spectrum of nanodiamond powders," *Chem. Mater.* **21**(2), 273–279 (2009).

³⁸M. Yang, Q. Yuan, J. Gao, S. Shu, F. Chen, H. Sun, K. Nishimura, S. Wang, J. Yi, C.-T. Lin, and N. Jiang, "A diamond temperature sensor based on the energy level shift of nitrogen-vacancy color centers," *Nanomaterials* **9**(11), 1576 (2019).

³⁹X.-M. Zhang, S.-Y. Wang, Y.-B. Shi, H. Yuan, Z.-M. Ma, F. Wang, Z.-D. Lin, L. Qin, and J. Liu, "Quantitative analysis of spectral characteristics and concentration of ensembles of NV-centers in diamond," *Diamond Relat. Mater.* **76**, 21–26 (2017).

⁴⁰A. Savvin, A. Dormidonov, E. Smetanina, V. Mitrokhin, E. Lipatov, D. Genin, S. Potanin, A. Yeliseyev, and V. Vins, "NV-diamond laser," *Nat. Commun.* **12**(1), 7118 (2021).

⁴¹J. H. N. Loubser and J. A. van Wyk, "Electron spin resonance in the study of diamond," *Rep. Prog. Phys.* **41**(8), 1201 (1978).

⁴²J. R. Maze, A. Gali, E. Togan, Y. Chu, A. Trifonov, E. Kaxiras, and M. D. Lukin, "Properties of nitrogen-vacancy centers in diamond: The group theoretic approach," *New J. Phys.* **13**(2), 025025 (2011).

⁴³T. P. M. Alegre, C. Santori, G. Medeiros-Ribeiro, and R. G. Beausoleil, "Polarization-selective excitation of nitrogen vacancy centers in diamond," *Phys. Rev. B* **76**(16), 165205 (2007).

⁴⁴H. Zhang, C. Belvin, W. Li, J. Wang, J. Wainwright, R. Berg, and J. Bridger, "Little bits of diamond: Optically detected magnetic resonance of nitrogen-vacancy centers," *Am. J. Phys.* **86**(3), 225–236 (2018).

⁴⁵C. Chen, I. C. Cho, H.-S. Jian, and H. Niu, "Fe doped magnetic nanodiamonds made by ion implantation," *Sci. Rep.* **7**(1), 41938 (2017).

⁴⁶A. Dréau, M. Lesik, L. Rondin, P. Spinicelli, O. Arcizet, J.-F. Roch, and V. Jacques, "Avoiding power broadening in optically detected magnetic resonance of single NV defects for enhanced dc magnetic field sensitivity," *Phys. Rev. B* **84**(19), 195204 (2011).

⁴⁷K. Jensen, V. M. Acosta, A. Jarmola, and D. Budker, "Light narrowing of magnetic resonances in ensembles of nitrogen-vacancy centers in diamond," *Phys. Rev. B* **87**(1), 014115 (2013).

⁴⁸V. M. Acosta, E. Bauch, M. P. Ledbetter, A. Waxman, L.-S. Bouchard, and D. Budker, "Temperature dependence of the nitrogen-vacancy magnetic resonance in diamond," *Phys. Rev. Lett.* **104**(7), 070801 (2010).

⁴⁹V. M. Acosta, A. Jarmola, E. Bauch, and D. Budker, "Optical properties of the nitrogen-vacancy singlet levels in diamond," *Phys. Rev. B* **82**(20), 201202 (2010).

⁵⁰D. M. Toyli, D. J. Christle, A. Alkauskas, B. B. Buckley, C. G. Van de Walle, and D. D. Awschalom, "Measurement and control of single nitrogen-vacancy center spins above 600 K," *Phys. Rev. X* **2**(3), 031001 (2012).

Sensing of Magnetic-Field Gradients with Nanodiamonds on Optical Glass-Fiber Facets

Mona Jani,* Paulina Czarnecka, Zuzanna Orzechowska, Mariusz Mrózek, Wojciech Gawlik, and Adam M. Wojciechowski*



Cite This: *ACS Appl. Nano Mater.* 2023, 6, 11077–11084



Read Online

ACCESS |

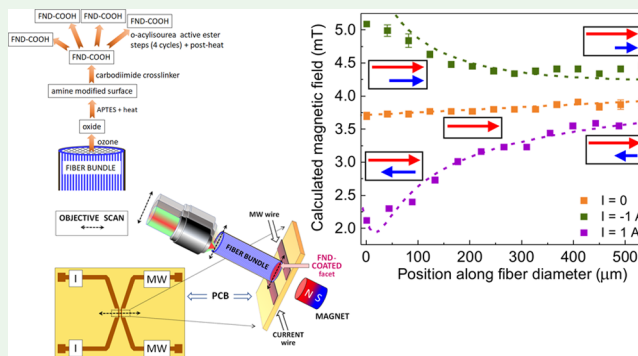
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: We demonstrate a photonic sensor of the magnetic field and its gradients with remote readout. The sensor is based on optically detected magnetic resonance (ODMR) in nanodiamonds with nitrogen-vacancy color centers that are covalently attached as a thin film on one facet of an optical fiber bundle. By measuring ODMR signals from a group of individual fibers in an ~ 0.5 -mm-wide imaging bundle, differences of local magnetic field strengths and magnetic field gradients are determined across the plane of the bundle facet. The measured gradients are created by direct electric currents flowing in a wire placed near the nanodiamond film. The measurement enabled the determination of the net magnetic field corresponding to various current directions and their corresponding magnetic field gradients. This demonstration opens up a perspective for compact fiber-based endoscopy, with additional avenues for remote and sensitive magnetic field detection with submicrometer spatial resolution under ambient conditions.

KEYWORDS: nanodiamond, photonic sensor, ODMR, nitrogen-vacancy, fluorescence, magnetic field gradients



1. INTRODUCTION

Integration of fluorescent nanodiamonds (FNDs) containing negatively charged nitrogen-vacancy (NV) centers with optical glass fibers is a crucial area of research for remote nanoscale magnetometry^{1–4} and thermometry.^{5,6} Electronic spin states of NVs can be manipulated using microwave (MW) fields, and the change of their state can be read out using the optically detected magnetic resonance technique. As NV centers are sensitive to their environment, FNDs have been used to measure parameters such as local magnetic field,⁷ temperature,⁸ and concentration of: spin labels,⁹ ions in solution,¹⁰ and free radicals (iron-containing proteins).¹¹ They have also been useful for the development of relaxometry methods, e.g., ref 11. The use of optical fibers allows the development of a compact endoscopy approach, where NV centers can be excited and their emission can be collected along the same fiber from remote distances.^{2,4,12} Integration of FND with fibers has been demonstrated by coupling FNDs with single-mode fibers,¹³ photonic crystal fibers,¹⁴ and fiber tapers.¹⁵ To date, detection of local magnetic fields by side excitation and longitudinal collection has been performed using the ODMR technique with FND and microdiamonds doped in tellurite,^{2,16} and lead silicate glass fibers.¹⁷ In addition, an MW-free detection mode was demonstrated in ref 12 where it was shown with submicrometer diamond particles embedded in 60 cm long lead silicate glass fiber that the fluorescence level can

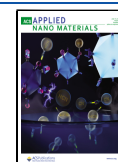
be related to the magnetic field value in a broad dynamic range of 0–35 mT. Furthermore, a multichannel fiber sensor capable of parallel-in-time mapping and instantaneous readout of individual pixels was demonstrated and allowed magnetic mapping with high spatial resolution using the FND-coated fiber facet.⁴ Despite these efforts, FND-fiber sensors have not yet reached the level of traditional optical platforms, and further development is needed to achieve sensitive measurements of magnetic field distributions with high spatial resolution and real-time readout over remote distances.

Here, we present our attempt to solve this task with a surface-chemical approach by covalently anchoring carboxylated FNDs in a thin film on a facet of a glass imaging fiber bundle (IFB) that is surface-functionalized with (3-aminopropyl)triethoxysilane (APTES), following Patoary et al. who prepared the nanodiamond thin films on plain-glass substrate.¹⁸ With this approach, we managed to procure robust FND thin films with high interface quality. NV fluorescence from the appropriately coated IFB front facet and its

Received: February 27, 2023

Accepted: May 30, 2023

Published: June 14, 2023



propagation through the IFB were detected using wide-field microscopy and confocal microscopy. Variations of the magnetic field strength occurring at one facet of the FND-anchored fiber are simultaneously read as the fluorescence variation through the other end facet of the same fiber. In our previous article,⁴ we reported observation of ODMR signals from FNDs through single cores of IFB, albeit with a low signal-to-noise ratio, which hindered practical magnetic field measurements. In a related work,¹⁹ it was observed that the ODMR signals became very noisy due to background fluorescence when the region of interest decreased. To mitigate such a problem, in this work, we applied an improved camera system and imaging protocol, which have resulted in great enhancement in the signal-to-noise ratio of the recorded ODMR signals, thus enabling precise detection of magnetic field gradients.

In the following, we describe an application of an IFB appropriately coated with FND for monitoring magnetic field variations. This proof-of-principle experiment demonstrates sensitive mapping with a high spatial resolution of the magnetic fields around a micrometer-thin current-conducting wire near the FND film. We hope that it enables a significant step toward the development of nanosensing technology by remote and instantaneous mapping of the magnetic field gradients under ambient conditions.

2. EXPERIMENTAL SECTION

2.1. Chemical Thin-Film Assembly of FNDs on the Facet of a Fiber Bundle. Conventional approaches for the integration of FNDs in optical fibers include embedding FNDs in molten glass during the direct fiber fabrication process,^{2,12,20,21} attaching them by fusing,²² gluing,²³ or depositing on the fiber facet.^{24,25} However, these standard methods limit the selection of applicable fiber types, hinder optical readout sensitivities, or are overly complex. An alternative approach, which we applied in this study, is the use of a silanization method, to covalently attach FNDs to the chosen glass fiber. We followed a deposition protocol laid out in ref 18, where the authors describe in detail the formation of a covalently bonded nanodiamond network, its spectroscopic characterizations, and surface morphology on glass substrates. We were able to form uniform and thin layers of FND having the Volmer–Weber type of growth over large surface areas on glass substrates and on fibers with very specific glass compositions.⁴ The silanization method used for covalently assembling FNDs on glass is sensitive to parameters such as concentrations, solvent quality, temperature, and reaction times. Variations in these parameters can negatively impact the adhesion of the film. A high-density silanization of the glass surface with APTES is crucial in the creation of the thin film because it determines the efficiency of the covalent bonding of the FNDs with the surface-terminating amino groups. APTES is currently one of the most widely used organosilane agents for the preparation of amino-functionalized organic thin films,²⁶ for the chemical incorporation of nanoparticles,²⁷ proteins,²⁸ and DNA²⁶ in substrates. Several studies suggested that heat treatments densify the modified APTES layers by horizontal heat-enhanced polymerization,^{29,30} reduce the thickness of an APTES film, and crosslink silane molecules on the surface by eliminating H₂O molecules, forming a more robust silane layer.³¹ Curing functionalized APTES substrates between 70 and 150 °C eliminates a substantial amount of loosely bound APTES containing protonated amino groups from the surface by evaporation or condensation.²⁹ Moreover, most ethoxy groups are removed, and the surface is covered with a new class of well-ordered neutral amino groups that are more reactive than the protonated buried and/or randomly oriented amino groups of the film before heat treatment. Furthermore, the amino-functionalized layer is more hydrolytically stable in an aqueous solution than the layers prior to curing and exhibits a strong antigen-binding capacity.³²

We modified our previous deposition protocol,⁴ which lacked heat treatments, by incorporating intermediate heating steps in the procedure to obtain an APTES monolayer coating at the glass interface that is chemically, mechanically, and hydrolytically stable in an aqueous solution with a high number of accessible reactive amino groups well ordered at the interface. The developed procedure resulted in a dense coverage with good homogeneity of the deposited thin films of FND on the optical glass-fiber facet (shown in Figure 3b in Section 3.1) relative to the simple drop-drying deposition of FNDs. Furthermore, whereas previously, the FNDs uniformly assembled on APTES-functionalized glass surfaces were very prone to detach; we noticed that heat treatments did not remove the physisorbed molecules, but enhanced the crosslinking reaction of the silane layer, thus improving the bond stability at the glass interface.^{29,33}

A suspension of carboxylated FNDs (FND-COOH) with a size of 140 nm and 1.5 ppm concentration of NV centers was obtained from Adamas Nanotechnologies. The spectroscopic properties of these FNDs have been previously characterized in ref 34. The imaging fiber bundle (IFB) had cladding made of soda-lime-silicate glass (SK222) with a refractive index of $n_d = 1.522$ and the cores were made of barium–zirconia–borosilicate glass (Zr3/XV) with $n_d = 1.611$.^{35,36} Individual pixels in the bundle had a diameter of 2.8 μm , while the entire bundle had core and clad diameters of 0.532 and 0.550 mm, respectively.

In our approach, IFB was first hydroxylated with ozone for 30 min (Ossila UV Ozone Cleaner) and then immediately immersed in a 0.01% (v/v) solution of APTES in toluene for 30 min. This resulted in covalent interactions between the hydroxyl groups present on the surface and the hydrolyzed silane molecules *via* hydrogen bonds. One end of IFB facet was then sonicated in toluene for 5 min to remove any physisorbed APTES molecules and heated at 150 °C for 10 min on a heating plate to evaporate excess molecules that were not bound to the surface. The procedure resulted in a well-anchored and stable cross-linked layer of APTES.

Separately, an amine-reactive *O*-acylisourea solution of FND-COOH was prepared by mixing 1 mg/mL FND-COOH in a 1:1 ratio (v/v) with 0.3 mg/mL 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride in a buffer solution of 2 mM potassium chloride (pH 6.5). The APTES-functionalized IFB facet was then immersed in this solution for 30 min to complete the first cycle of formation of a thin layer of FNDs on the glass surface. Four additional cycles of regeneration were carried out using a cyclic procedure involving ethylenediamine followed by amine-reactive *O*-acylisourea steps to increase the density of the FND thin-film layers. The resulting covalently thin-film assembled FND on the IFB facet was then rinsed with deionized water, naturally dried, and post-heated at 150 °C for 15 min. Post-heating provided a great improvement in the anchoring and bond strength of the FND film on glass surfaces, including its robustness and quality. The FND thin film was stable in general handling throughout our experiments and, in particular, remained less scratched compared to the physically deposited FNDs in our previous attempts.³⁷ Finally, we washed the formed FND film with deionized water and dried it in argon. In Figure 1, we illustrate schematically the applied chemical technology. As not all diamonds had equal sizes and shapes,³⁸ FNDs were not uniformly attached to the silanized surface, and therefore it was not easy to obtain quantitative information on the attachment strength of FNDs. However, we could observe that the thin film of FNDs attached on the IFB was stable and resistant to scratches. In particular, it worked efficiently for more than 5 months despite frequent contacts with the antenna board.

2.2. Fluorescence Microscopy and ODMR Setups. In our work, two imaging methods have been used: wide-field microscopy and confocal fluorescence microscopy. They are based on two separate but complementary setups that work in the epifluorescence mode. Although the confocal fluorescence setup has a high resolution and a different technique for excitation than the wide-field technique, the latter is very suitable for imaging large areas.

The wide-field fluorescence microscopy images were acquired using a Motic BA210E microscope operating in the epifluorescence mode. A green LED light source was used to excite the FNDs assembled on

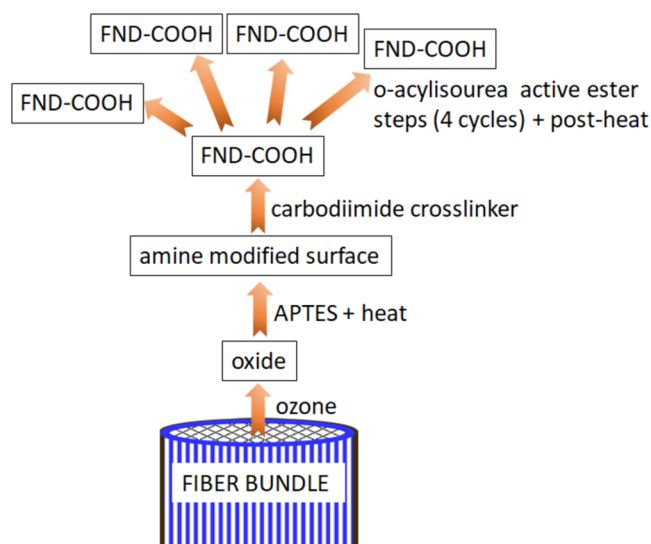


Figure 1. Schematic diagram to show steps followed to covalently anchoring carboxylated FNDs in a thin film on a facet of a glass imaging fiber bundle (IFB) that is surface-functionalized with (3-aminopropyl)triethoxysilane (APTES).

the fiber facet, and the images were taken with 40 $\times$ /0.65 (LUCPLFN, Olympus) objective captured with a digital camera (Moticam3+).

The confocal images were acquired using a home-built microscopy setup with an oil-immersion objective (100 $\times$ /1.3, UPLFN Olympus) and a 532 nm laser (Sprout G, Lighthouse Photonics, attenuated to $\sim$ 1 mW). After laser excitation of FNDs, their backward-emitted fluorescence was separated by a dichroic mirror and filtered spatially and spectrally (FELH600, Thorlabs) before being detected by a single-photon counting module (SPCM-AQRH-14-FC, Excelitas Technologies) and the images were collected by scanning the sample above the objective using a piezo-nano-positioning stage (Nano-LP200, Mad City Labs) controlled by a PC with Qudi software.³⁹

The arrangement to collect the ODMR signals through IFB comprises a home-built, wide-field microscopy setup and is shown schematically in Figure 2. Approximately 65 mW of the green laser

power was focused on the back-focal plane of the 40 $\times$ /0.6 objective (LUCPLFN, Olympus) and transmitted through IFB from its uncoated facet to the one coated with FND. The coated facet of IFB was centered between two parallel copper striplines (34 μ m-high, 170 μ m-wide, and 2.4 mm-long) on a printed circuit board, for brevity called the “antenna”,⁴⁰ and was placed 0.2 mm above the antenna. The NV fluorescence excited in FND was transmitted backward through IFB and the objective and was detected by a camera.

One of the antenna striplines transmitted the MW signal to manipulate the ground-level spin states of the NV centers. Another stripline, separated by 320 μ m, conducted a direct electric current from a stable current source to create a given spatial magnetic field distribution. An additional and stronger bias field of $B_0 = 3.8$ mT was applied using a permanent magnet to lift the degeneracy of the $m_s = \pm 1$ states and had a normal direction to the antenna board. The continuous-wave MW field was generated by a signal generator (SG386, Stanford Research Systems), and its frequency was swept around the resonance frequency of the $m_s = 0 - m_s = \pm 1$ transition at 2870 MHz with steps of 0.5 MHz. The red fluorescence (ca. 600–800 nm) transmitted through the fiber bundle was captured by the microscope objective, filtered, and projected onto the sCMOS camera (Andor Zyla 5.5). ODMR data collection was performed in LabView software, which controlled the camera, signal generator, and digital pattern generator (Pulse Streamer 8/2, Swabian Instruments). During continuous light illumination, two images were captured with MWs turned on and off for every frequency to subtract the background and calculate the normalized fluorescence contrast, which helped to reduce fluorescence intensity variations due to laser power drifts and improved the overall signal-to-noise ratio.

Images given by the central 704 $\times$ 594 pixels were acquired, corresponding to a full frame (FF) field of view of 205 μ m $\times$ 173 μ m and an effective pixel size of $\sim$ (0.55 μ m)². To achieve a high spatial resolution while maintaining a sufficient signal-to-noise ratio, fluorescence from smaller areas of interest (AOIs) was acquired. Each AOI had dimensions of $\sim$ 15.6 μ m $\times$ 15.6 μ m, equivalent to 22 individual fibers in the IFB. The fluorescence collected within each AOI was integrated and ascribed to a given position r between the antenna wires. Figure S1 illustrates the selection of individual AOIs and their application to map of the magnetic field distribution near the current-conducting wire along the entire width of the IFB. The dependence of integrated fluorescence intensity on the distance r from the current wire enabled the determination of the spatial distribution of the magnetic field.

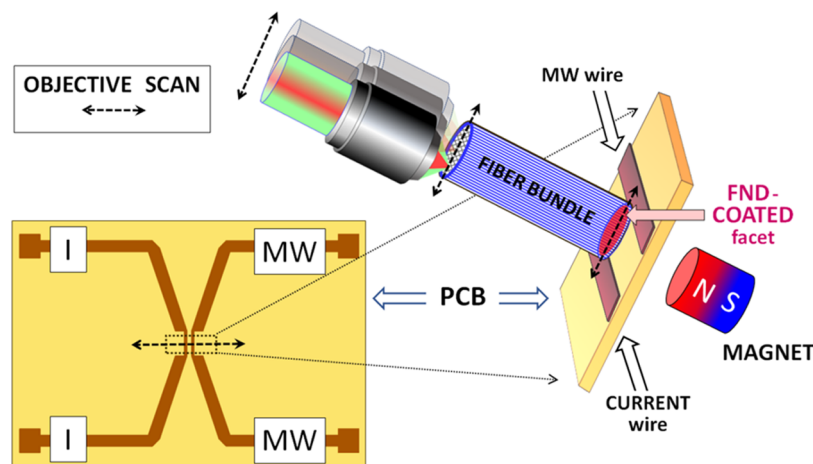


Figure 2. Schematics of the ODMR setup showing the fiber bundle (IFB) with its coated and uncoated facets, the microscope objective, the permanent magnet creating the bias field, and the antenna with two striplines: the MW and current (I) wire. The laser light illuminates the uncoated facet and excites NV centers in FNDs placed on the coated facet. The emitted NV fluorescence, which depends on the local MW and magnetic field strengths, is collected through the fiber bundle and transmitted backward by IFB toward the objective to be detected and yields the ODMR signal. Dashed double-ended arrows indicate the scan direction of: the moving objective, the laser beam focused on the uncoated IFB facet, and the scanned laser beam over the specific spot on the coated IFB surface between the striplines.

3. RESULTS AND DISCUSSION

3.1. Imaging Fluorescence of an FND Film. As described in Section 2.1, to achieve sufficiently dense and uniform films with covalent assemblies of FNDs on an end facet of IFB, four coating cycles followed by thermal treatments were performed. Figure 3a shows the wide-field

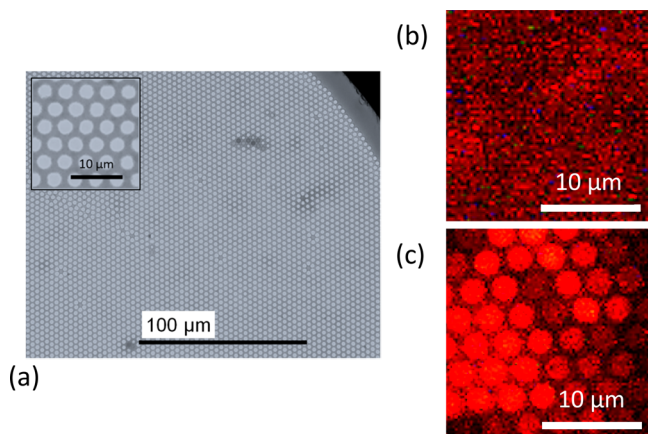


Figure 3. Wide-field microscope images of IFB: (a) fiber structure with individual pixels of $2.8\ \mu\text{m}$ diameter; (b) red fluorescence of the IFB facet coated with FND excited by green light; (c) red fluorescence of FNDs seen from the uncoated side of IFB, excited by green light.

microscope image of the clean IFB facet before FND deposition. Individual fibers of the IFB with $2.8\ \mu\text{m}$ diameter are easily visible as bright spots due to a relatively high-refractive-index contrast between the fiber core and the fiber cladding that eliminates optical crosstalk between individual fibers. The IFB had a sufficiently high numerical aperture ($\text{NA} > 0.5$) to allow efficient observation of the fluorescence emitted from its coated facet and allow its transmission throughout the bundle. Figure 3b,c presents fluorescence images from an epifluorescence microscope that displays the coated and the uncoated facets of the IFB, respectively. In Figure 3b, the red fluorescence is emitted by the NV centers deposited on the coated IFB surface and shows that the FND film obtained is relatively homogeneous and exhibits a high degree of coverage. When the IFB ends were interchanged to observe the uncoated side, as shown in Figure 3c, each core appeared much brighter than the cladding, due to efficient fluorescence guidance in the individual IFB cores.

To confirm the excitation and distribution of FNDs on the coated IFB facet and efficient propagation of NV fluorescence through the IFB, we have used scanning confocal fluorescence microscopy as schematized in Figure 4 (left). Typical images with confocal fluorescence intensity maps of the $200\ \mu\text{m} \times 200\ \mu\text{m}$ region are shown in the top image for the FND-coated IFB facet and in the lower image for the uncoated side. The direct NV emission from the coated facet appears with a higher fluorescence photon count rate of about 250 kc/s, while collecting photons through the other end resulted in lower photon counts of about 65 kc/s. Confocal scanning maps confirm that FNDs are uniformly distributed over the entire fiber facet and show that the NV emission efficiently couples to the guided optical modes of the IFB.

3.2. Detection of Magnetic Field Gradients through the IFB. **3.2.1. ODMR Spectra.** NV magnetometry is a very

successful method of studying bulk diamonds. As shown in our earlier work,³⁷ ODMR can also be very useful with ensembles of arbitrary-oriented FNDs with NV. When there is no magnetic field, the ODMR spectrum exhibits a standard resonance centered at 2870 MHz, as illustrated in Figure 5a. When a sufficiently strong magnetic field is applied, the ODMR resonance in FNDs broadens and loses its contrast, due to averaging over arbitrary orientations of the projections of NV axes of individual particles. Importantly, this broadening is approximately proportional to the magnetic field strength and enables its determination. However, to observe and quantify any sizeable broadening and exploit it for magnetometry, the external field must be sufficiently strong ($\gtrsim 1\ \text{mT}$), as for very weak fields, interactions between $m_s = \pm 1$ spin states due to off-axis strain hinder the observation of any changes in the ODMR spectrum.⁴¹

In the present work, we wanted to obtain the ODMR signals from arbitrary-oriented FND to demonstrate the magnetic sensing capabilities of very small changes δB of the magnetic field, such as those created by electric currents. For this purpose, we used one wire on the described antenna board that carried currents up to $\pm 1\ \text{A}$ placed close to the FND-coated IFB. The current-induced magnetic fields are strongly inhomogeneous and change their intensity with distance r from the wire according to the Biot–Savart law.

Figure 5b depicts the acquired FF field-of-view ODMR spectra of the FND film recorded through the other end of the IFB at three positions between the antenna wires along the diameter of the IFB (double-ended dashed arrow shown in Figure 2) and three applied intensities of the current flowing through the antenna wire: 0, +1 A, and −1 A (negative currents mean a reversal of the polarity of the current source). The plots clearly show that the application of current-created δB indeed shifts the edges of the broadened resonances and enables quantification of this effect for magnetometric purposes. ODMR spectra collected near the current-carrying wire are visibly broader for one current direction ($I = -1\ \text{A}$), which corresponds to a higher value of the net magnetic field $B_0 + \delta B$ than for the reverse direction ($I = +1\ \text{A}$), where δB opposed the bias field and decreased its net strength to $B_0 - \delta B$. The dependence of $\delta B(r)$ on distance r from the current wire is reflected in the curves depicted by various colors in Figure 5b that correspond to different spatial locations. The observed dependences become more pronounced when the signal derivatives are plotted as in Figure 5c rather than the fluorescence intensity.³⁷ Consequently, the ODMR signals presented in Figure 5 illustrate that the NV centers and the IFB can be used successfully to remote sensing the magnetic field distributions.

3.2.2. Demonstration of the Gradiometric Magnetic Field Sensing on Micrometer Scales. To demonstrate in more detail the feasibility of detecting spatial variations in the magnetic field generated by a current-carrying wire with an applied bias field of $B_0 = 3.8\ \text{mT}$, the microscope objective was moved transversely to the IFB and antenna wires. In this way, the distance r of the imaged AOI from the current wire was scanned in small steps moving away from the current wire. For each step, the microscope was refocused on the uncoated IFB facet to correct for residual unevenness of the facet's surface. This allowed us to improve fluorescence collection and record better ODMR signals from individual AOI, and associate them with position r . Figure S1 shows a stitched camera image (as seen from the objective) of the entire diameter of the uncoated

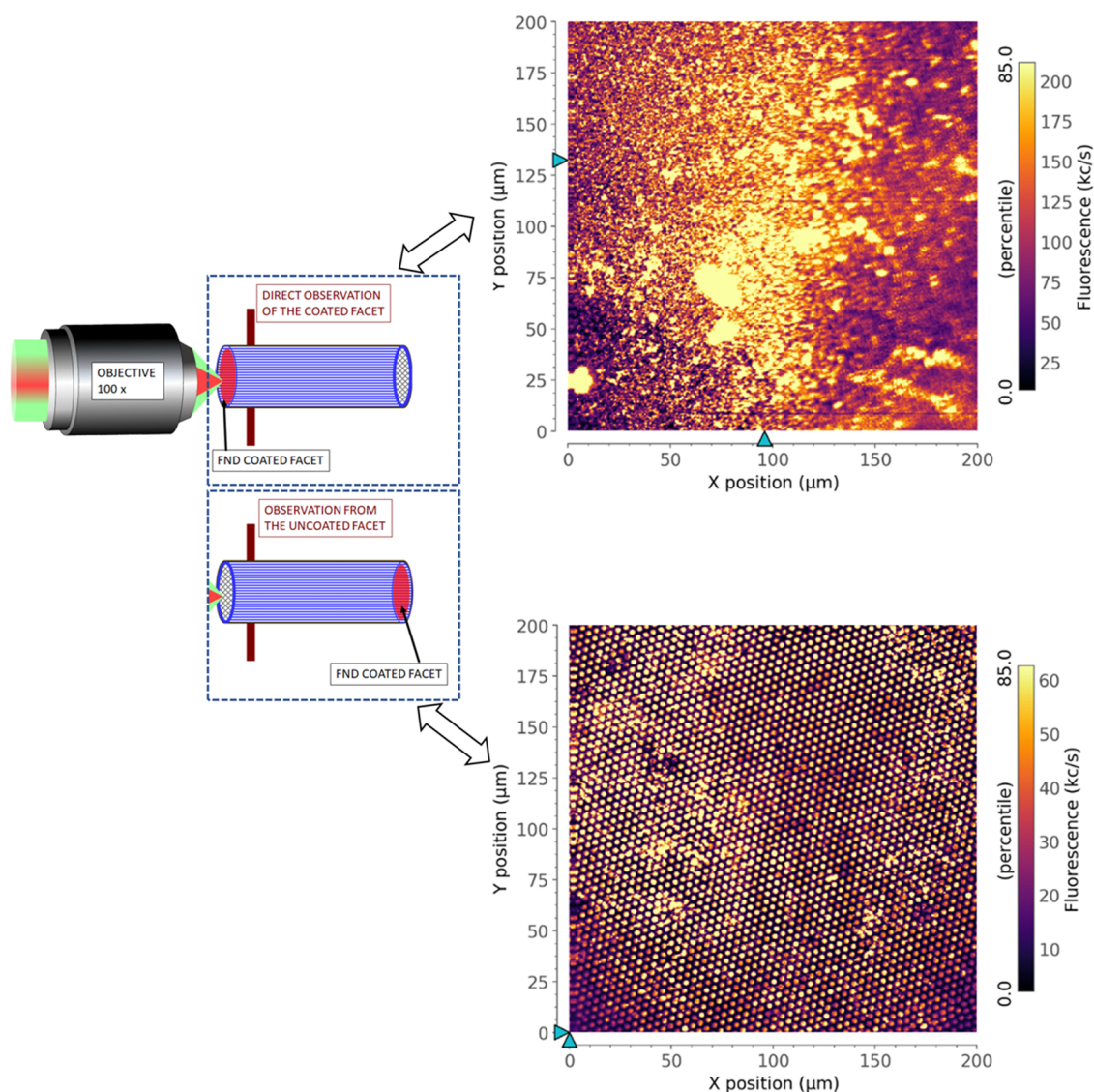


Figure 4. Schematics of confocal microscopy observation of both facets of IFB (left) and confocal maps showing fluorescence from the FND film obtained with four regeneration cycles: the top image directly shows the coated facet, and the lower image shows fluorescence recorded through the IFB, i.e., from the uncoated side.

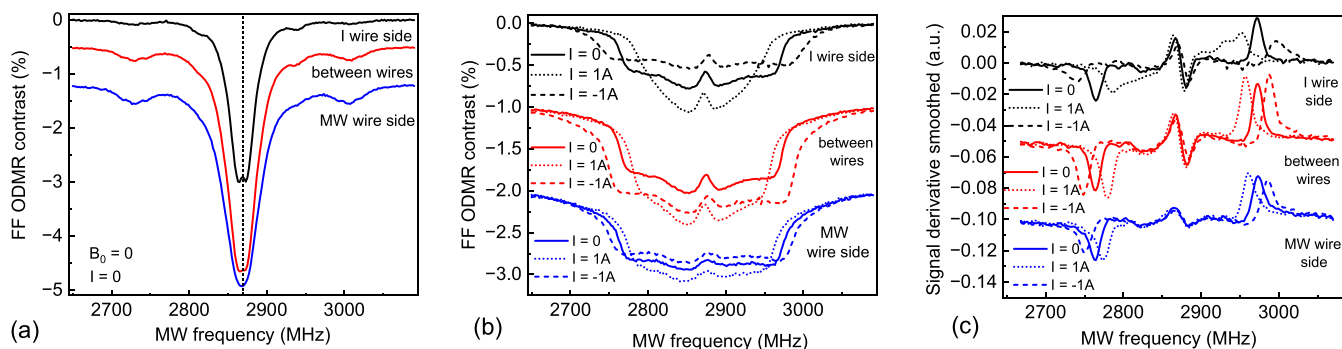


Figure 5. ODMR signals collected through the IFB at different positions between antenna wires along the fiber diameter [direction indicated in Figure 2 by the double-arrowed dashed line]. (a) Zero magnetic field, zero current. At $B_0 = 3.8$ mT for different current intensities: (b) regular ODMR signals and (c) derivatives of ODMR signals. The outer peaks in (b, c) correspond to the edges of the ODMR spectrum and clearly shift with magnetic field changes. Only the top curves correspond to the left scales, the other curves are vertically offset to avoid their overlap.

side of the IFB facet positioned between the MW and the current wires over the entire widths of IFB.

Three different current values were applied, $I = 0, \pm 1$ A, and ODMR spectra were acquired from AOIs. Figure 6a–c shows the resulting ODMR resonances recorded for each current

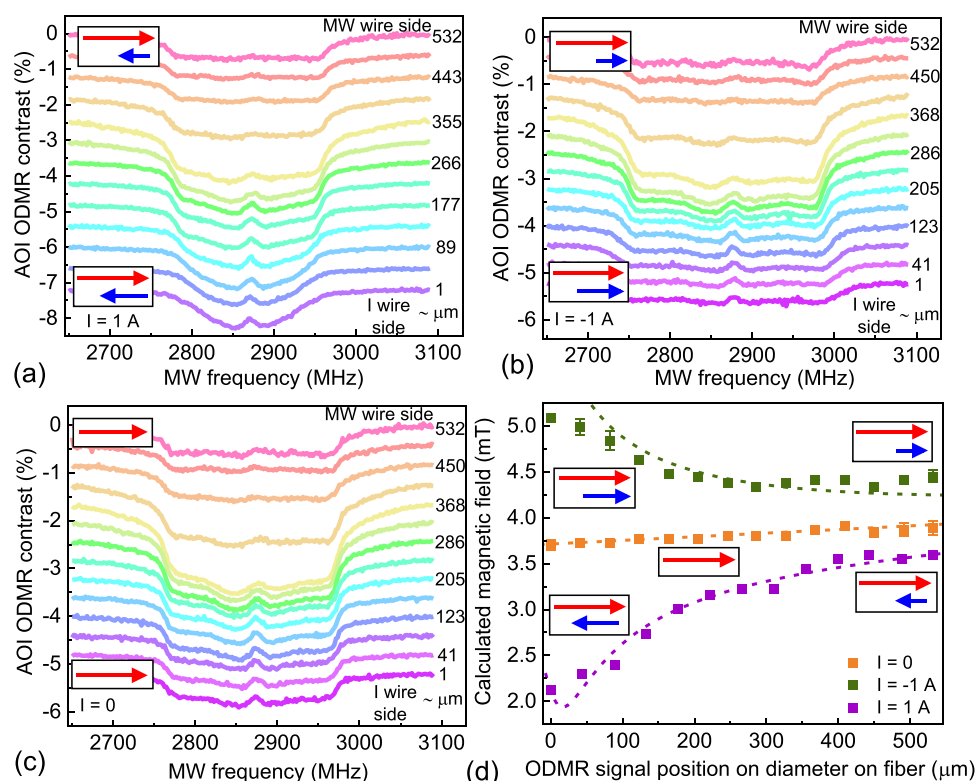


Figure 6. Spatial dependence of ODMR spectra caused by the magnetic field of a current-carrying wire: (a) +1 A current, (b) reversed current direction, −1 A, (c) zero current. For a zero applied current, only a fluorescence contrast value changes spatially due to the distance from the MW line, while the width of the spectrum remains constant and is set by the uniform bias field. Spectra with applied current show gradual narrowing (a) and broadening (b) as a result of vector addition of bias and created fields; (d) calculated magnetic field versus distance from the current-carrying wire. The dashed lines are the simulations for an infinite wire model. In the insets, the red arrows represent the bias magnetic field while the blue arrows show the magnitude and relative orientation of the current-generated field. The length of the arrows indicates the opposing or adding of field from current wire to bias field.

value and a range of distances r , associated with a gradual change in magnetic field strength $\delta B(r)$, averaged over selected AOIs. For one direction of the applied current, $I = +1$ A, the ODMR peak appeared to be broadened and its contrast was reduced when the distance r from the current wire toward the MW wire increased, while for the reverse current direction, $I = -1$ A, the opposite behavior was observed, due to the vector addition of bias B_0 and wire-created δB , as marked schematically in Figure 6d. No substantial changes of spectra were observed with zero applied current; only the fluorescence contrast decreased with increasing r due to a weakening of the MW strength (Figure 6c). The dependences shown in Figure 6a–c enabled systematic determination of the spatial distribution of the magnetic field by analyzing the positions of external edges in the ODMR spectra.³⁷

Figure 6d presents the main result of this work, the spatial dependences of the net magnetic field $B_0 + \delta B$ (colored points) on the position between the wire for different currents, and compares them with the modeling (dashed lines) based on the Biot–Savart law. For the modeling, we took the wire dimensions: 34 μm height, 170 μm width, but instead of a real length of 2.4 mm, we extended it to infinity to simplify the modeling. The static bias field value of 3.68 mT (at $r = 0$) with an additional small gradient of 0.4 mT/mm was used. As shown, we have a very good accuracy of the two dependencies for most of the scanned distances. The accuracy of the fit is slightly reduced near the edge of the current wire ($r = 0$), due to our simplification of the infinite length of the wire. An

extension of the model to include the exact dimensions of the antenna structure is fairly straightforward; however, more interesting is to note that the good match with the measurements was obtained for a specific, finite height of the NV layer in the FND film: 20 μm above the antenna plane. This finding demonstrates that the described method enables a high-resolution precision mapping of inhomogeneous magnetic fields and extending beyond a simple two-dimensional (2D) information.

The magnetic sensitivity of such mapping with FND-coated IFB is proportional to the slope (S) at the edge of the ODMR spectrum and inversely proportional to the square root of the photon number (N).⁴² The value of N can be obtained from a single fluorescence image, while S can be derived from the spectra in Figure 6. On the basis of available experimental data, we estimate that the projected magnetic sensitivity for the fiber probes discussed in this work is around $1.6 \mu\text{T}/\sqrt{\text{Hz}}$.

4. CONCLUSIONS

In conclusion, we used the silanization method with intermediate heat treatments to covalently form a robust and uniform thin-film assembly of FNDs on a facet of IFB. Fluorescence wide-field microscopy images and confocal scanning maps confirm that NV fluorescence can be efficiently guided through the individual fiber cores of 2.8 μm in diameter in the IFB, allowing remote detection of optical signals. Moreover, each core conveys fluorescence information independently, i.e., from the specific FNDs that cover its

surface, which allows for spatially resolved detection of NV ODMR signals.

From changes of the resonance width in the observed ODMR spectra, we retrieved information on the local magnetic field. With the FND-coated IFB facets acting as a remote sensor and IFB as an image relay, we have detected magnetic field gradients near the current-carrying structure on a scale of a few tens of micrometers. Importantly, the use of the fiber piece allowed us to move the microscope objective away from the location where the magnetic field was measured, thus removing the influence of the objective on the measurement. The improved camera system and imaging protocol allowed us to greatly enhance the signal-to-noise ratio and enabled us to reach the magnetometric sensitivity of $1.6 \mu\text{T}/\sqrt{\text{Hz}}$. The very good agreement of the measured and simulated values demonstrated that the nanodiamond films with NV centers and image-transmitting fiber links can be successfully used in remote sensing of three-dimensional magnetic field distributions. This study enables future applications in remote magnetic field sensing and imaging, which require a high spatial resolution. We anticipate that such integrated photonic sensors can be beneficial for high-sensitivity magnetic endoscopy in bio-diagnostics and inspection of integrated electronic circuits.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.3c00887>.

Entire fiber facet and exact positions of the selected AOIs relative to the current and microwave wires (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Mona Jani – Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland;
orcid.org/0000-0001-8289-2804; Email: mona.jani@uj.edu.pl

Adam M. Wojciechowski – Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland;
orcid.org/0000-0003-1805-6718;
Email: a.wojciechowski@uj.edu.pl

Authors

Paulina Czarnecka – Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland

Zuzanna Orzechowska – Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland;
orcid.org/0000-0003-0103-757X

Mariusz Mrózek – Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland

Wojciech Gawlik – Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Kraków, Poland

Complete contact information is available at:
<https://pubs.acs.org/doi/10.1021/acsanm.3c00887>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Foundation for Polish Science TEAM-NET Programme co-financed by the EU under the

European Regional Development Fund, grant no. POIR.04.04.00-00-1644/18.

■ REFERENCES

- (1) Fedotov, I. V.; Doronina-Amitonova, L. V.; Sidorov-Biryukov, D. A.; Safronov, N. A.; Levchenko, A. O.; Zibrov, S. A.; Blakley, S.; Perez, H.; Akimov, A. V.; Fedotov, A. B.; Hemmer, P.; Sakoda, K.; Velichansky, V. L.; Scully, M. O.; Zheltikov, A. M. Fiber-Optic Magnetometry with Randomly Oriented Spins. *Opt. Lett.* **2014**, *39*, 6755–6758.
- (2) Ruan, Y.; Simpson, D. A.; Jeske, J.; Ebdorff-Heidepriem, H.; Lau, D. W. M.; Ji, H.; Johnson, B. C.; Ohshima, T.; Afshar V, S.; Hollenberg, L.; Greentree, A. D.; Monro, T. M.; Gibson, B. C. Magnetically Sensitive Nanodiamond-Doped Tellurite Glass Fibers. *Sci. Rep.* **2018**, *8*, No. 1268.
- (3) Blakley, S. M.; Fedotov, I. V.; Kilin, S. Y.; Zheltikov, A. M. Room-Temperature Magnetic Gradiometry with Fiber-Coupled Nitrogen-Vacancy Centers in Diamond. *Opt. Lett.* **2015**, *40*, 3727–3730.
- (4) Czarnecka, P.; Jani, M.; Sengottuvel, S.; Mrózek, M.; Dąbczyński, P.; Filipkowski, A.; Kujawa, I.; Pysz, D.; Gawlik, W.; Wojciechowski, A. M. Magnetically-Sensitive Nanodiamond Thin-Films on Glass Fibers. *Opt. Mater. Express* **2022**, *12*, 444–457.
- (5) Fedotov, I. V.; Blakley, S.; Serebryannikov, E. E.; Safronov, N. A.; Velichansky, V. L.; Scully, M. O.; Zheltikov, A. M. Fiber-Based Thermometry Using Optically Detected Magnetic Resonance. *Appl. Phys. Lett.* **2014**, *105*, No. 261109.
- (6) Kucsko, G.; Maurer, P. C.; Yao, N. Y.; Kubo, M.; Noh, H. J.; Lo, P. K.; Park, H.; Lukin, M. D. Nanometre-Scale Thermometry in a Living Cell. *Nature* **2013**, *500*, 54–58.
- (7) Tsukamoto, M.; Ito, S.; Ogawa, K.; Ashida, Y.; Sasaki, K.; Kobayashi, K. Accurate Magnetic Field Imaging Using Nanodiamond Quantum Sensors Enhanced by Machine Learning. *Sci. Rep.* **2022**, *12*, No. 13942.
- (8) Wu, Y.; Alam, M. N. A.; Balasubramanian, P.; Ermakova, A.; Fischer, S.; Barth, H.; Wagner, M.; Raabe, M.; Jelezko, F.; Weil, T. Nanodiamond Theranostic for Light-Controlled Intracellular Heating and Nanoscale Temperature Sensing. *Nano Lett.* **2021**, *21*, 3780–3788.
- (9) Vavra, J.; Rehor, I.; Rendler, T.; Jani, M.; Bednar, J.; Baksh, M. M.; Zappe, A.; Wrachtrup, J.; Cigler, P. Supported Lipid Bilayers on Fluorescent Nanodiamonds: A Structurally Defined and Versatile Coating for Bioapplications. *Adv. Funct. Mater.* **2018**, *28*, No. 1803406.
- (10) Gorrini, F.; Giri, R.; Avalos, C. E.; Tambalo, S.; Mannucci, S.; Basso, L.; Bazzanella, N.; Dorigoni, C.; Cazzanelli, M.; Marzola, P.; Miotello, A.; Bifone, A. Fast and Sensitive Detection of Paramagnetic Species Using Coupled Charge and Spin Dynamics in Strongly Fluorescent Nanodiamonds. *ACS Appl. Mater. Interfaces* **2019**, *11*, 24412–24422.
- (11) Martínez, F. P.; Nusantara, A. C.; Chipaux, M.; Padamati, S. K.; Schirhagl, R. Nanodiamond Relaxometry-Based Detection of Free-Radical Species When Produced in Chemical Reactions in Biologically Relevant Conditions. *ACS Sens.* **2020**, *5*, 3862–3869.
- (12) Filipkowski, A.; Mrózek, M.; Stepniewski, G.; Kierdaszuk, J.; Drabińska, A.; Karpate, T.; Głowacki, M.; Ficek, M.; Gawlik, W.; Buczyński, R.; Wojciechowski, A.; Bogdanowicz, R.; Klimczak, M. Volumetric Incorporation of NV Diamond Emitters in Nano-structured F2 Glass Magneto-Optical Fiber Probes. *Carbon* **2022**, *196*, 10–19.
- (13) Patel, R. N.; Schröder, T.; Wan, N.; Li, L.; Mouradian, S. L.; Chen, E. H.; Englund, D. R. Efficient Photon Coupling from a Diamond Nitrogen Vacancy Center by Integration with Silica Fiber. *Light Sci. Appl.* **2016**, *5*, e16032.
- (14) Fedotov, I. V.; Safronov, N. A.; Shandarov, Y. A.; Tashchilina, A. Y.; Fedotov, A. B.; Nizovtsev, A. P.; Pustakhod, D. I.; Chizevski, V. N.; Matveeva, T. V.; Sakoda, K.; Kilin, S. Y.; Zheltikov, A. M. Photonic-Crystal-Fiber-Coupled Photoluminescence Interrogation of

Nitrogen Vacancies in Diamond Nanoparticles. *Laser Phys. Lett.* **2012**, *9*, 151–154.

(15) Schröder, T.; Fujiwara, M.; Noda, T.; Zhao, H.-Q.; Benson, O.; Takeuchi, S. A Nanodiamond-Tapered Fiber System with High Single-Mode Coupling Efficiency. *Opt. Express* **2012**, *20*, 10490–10497.

(16) Ruan, Y.; Ji, H.; Johnson, B. C.; Ohshima, T.; Greentree, A. D.; Gibson, B. C.; Monro, T. M.; Ebendorff-Heidepriem, H. Nanodiamond in Tellurite Glass Part II: Practical Nanodiamond-Doped Fibers. *Opt. Mater. Express* **2015**, *5*, 73–87.

(17) Bai, D.; Huynh, M. H.; Simpson, D. A.; Reineck, P.; Vahid, S. A.; Greentree, A. D.; Foster, S.; Ebendorff-Heidepriem, H.; Gibson, B. C. Fluorescent Diamond Microparticle Doped Glass Fiber for Magnetic Field Sensing. *APL Mater.* **2020**, *8*, No. 081102.

(18) Patoary, N. H.; Rai, A.; Patel, K. P.; Rebecca, A.; Zhang, W.; Ulrich, A. J.; Galib, M.; Desai, T.; Zivanovic, S.; Yousufuddin, M.; Moore, A. L.; Radadia, A. D. Directed Covalent Assembly of Nanodiamonds into Thin Films. *Diamond Relat. Mater.* **2020**, *101*, No. 107605.

(19) Nishimura, Y.; Oshimi, K.; Umehara, Y.; Kumon, Y.; Miyaji, K.; Yukawa, H.; Shikano, Y.; Matsubara, T.; Fujiwara, M.; Baba, Y.; Teki, Y. Wide-Field Fluorescent Nanodiamond Spin Measurements toward Real-Time Large-Area Intracellular Thermometry. *Sci. Rep.* **2021**, *11*, No. 4248.

(20) Liu, X.; Cui, J.; Sun, F.; Song, X.; Feng, F.; Wang, J.; Zhu, W.; Lou, L.; Wang, G. Fiber-Integrated Diamond-Based Magnetometer. *Appl. Phys. Lett.* **2013**, *103*, No. 143105.

(21) Henderson, M. R.; Gibson, B. C.; Ebendorff-Heidepriem, H.; Kuan, K.; Afshar V, S.; Orwa, J. O.; Aharonovich, I.; Tomljenovic-Hanic, S.; Greentree, A. D.; Prawer, S.; Monro, T. M. Diamond in Tellurite Glass: A New Medium for Quantum Information. *Adv. Mater.* **2011**, *23*, 2806–2810.

(22) Filipkowski, A.; Mrózek, M.; Stępniewski, G.; Glowacki, M.; Pysz, D.; Gawlik, W.; Buczyński, R.; Klimczak, M.; Wojciechowski, A. Magnetically Sensitive Fiber Probe with Nitrogen-Vacancy Center Nanodiamonds Integrated in a Suspended Core. *Opt. Express* **2022**, *30*, 19573–19581.

(23) Bian, C.; Li, M.; Cao, W.; Hu, M.; Chu, Z.; Wang, R. Robust Integration of Nitrogen-Vacancy Centers in Nanodiamonds to Optical Fiber and Its Application in All-Optical Thermometry. *Chin. Opt. Lett.* **2021**, *19*, No. 120601.

(24) Rabreau, J. R.; Huntington, S. T.; Greentree, A. D.; Prawer, S. Diamond Chemical-Vapor Deposition on Optical Fibers for Fluorescence Waveguiding. *Appl. Phys. Lett.* **2005**, *86*, No. 134104.

(25) Schröder, T.; Schell, A. W.; Kewes, G.; Aichele, T.; Benson, O. Fiber-Integrated Diamond-Based Single Photon Source. *Nano Lett.* **2011**, *11*, 198–202.

(26) Briand, E.; Humblot, V.; Landoulsi, J.; Petronis, S.; Pradier, C.-M.; Kasemo, B.; Svedhem, S. Chemical Modifications of Au/SiO₂ Template Substrates for Patterned Biofunctional Surfaces. *Langmuir* **2011**, *27*, 678–685.

(27) Klimpovuz, C. R.; Oliveira, M. M. 3-Aminopropyltriethoxysilane (APTES) and Heat Treatment: A Novel and Simple Route for Gold Nanoparticles Anchored on Silica Substrate. *Chem. Pap.* **2021**, *75*, 2639–2646.

(28) Kim, J.; Cho, J.; Seidler, P. M.; Kurland, N. E.; Yadavalli, V. K. Investigations of Chemical Modifications of Amino-Terminated Organic Films on Silicon Substrates and Controlled Protein Immobilization. *Langmuir* **2010**, *26*, 2599–2608.

(29) Kim, J.; Holinga, G. J.; Somorjai, G. A. Curing Induced Structural Reorganization and Enhanced Reactivity of Amino-Terminated Organic Thin Films on Solid Substrates: Observations of Two Types of Chemically and Structurally Unique Amino Groups on the Surface. *Langmuir* **2011**, *27*, 5171–5175.

(30) Aissaoui, N.; Bergaoui, L.; Landoulsi, J.; Lambert, J.-F.; Boujday, S. Silane Layers on Silicon Surfaces: Mechanism of Interaction, Stability, and Influence on Protein Adsorption. *Langmuir* **2012**, *28*, 656–665.

(31) Metwalli, E.; Haines, D.; Becker, O.; Conzone, S.; Pantano, C. G. Surface Characterizations of Mono-, Di-, and Tri-Aminosilane Treated Glass Substrates. *J. Colloid Interface Sci.* **2006**, *298*, 825–831.

(32) Kim, J.; Seidler, P.; Fill, C.; Wan, L. S. Investigations of the Effect of Curing Conditions on the Structure and Stability of Amino-Functionalized Organic Films on Silicon Substrates by Fourier Transform Infrared Spectroscopy, Ellipsometry, and Fluorescence Microscopy. *Surf. Sci.* **2008**, *602*, 3323–3330.

(33) Silva, E. A.; Trindade, F. Z.; Reskalla, H. N. J. F.; de Queiroz, J. R. C. Heat Treatment Following Surface Silanization in Rebonded Tribochemical Silica-Coated Ceramic Brackets: Shear Bond Strength Analysis. *J. Appl. Oral Sci.* **2013**, *21*, 335–340.

(34) Jani, M.; Mrózek, M.; Nowakowska, A. M.; Leszczenko, P.; Gawlik, W.; Wojciechowski, A. M. Role of High Nitrogen-Vacancy Concentration on the Photoluminescence and Raman Spectra of Diamond. *Phys. Status Solidi (a)* **2023**, *220*, No. 2200299.

(35) Stepien, R.; Cimek, J.; Pysz, D.; Kujawa, I.; Klimczak, M.; Buczyński, R. Soft Glasses for Photonic Crystal Fibers and Microstructured Optical Components. *Opt. Eng.* **2014**, *53*, No. 071815.

(36) Morova, B.; Bavili, N.; Yaman, O.; Yigit, B.; Zeybel, M.; Aydin, M.; Dogan, B.; Kasztelan, R.; Pysz, D.; Buczyński, R.; Kiraz, A. Fabrication and Characterization of Large Numerical Aperture, High-Resolution Optical Fiber Bundles Based on High-Contrast Pairs of Soft Glasses for Fluorescence Imaging. *Opt. Express* **2019**, *27*, 9502–9515.

(37) Wojciechowski, A. M.; Mrózek, P. N. M.; Sycz, K.; Kruk, A.; Ficek, M.; Glowacki, M.; Bogdanowicz, R.; Gawlik, W. Optical Magnetometry Based on Nanodiamonds with Nitrogen-Vacancy Color Centers. *Materials* **2019**, *12*, No. E2951.

(38) Reineck, P.; Trindade, L. F.; Havlik, J.; Stursa, J.; Heffernan, A.; Elbourne, A.; Orth, A.; Capelli, M.; Cigler, P.; Simpson, D. A.; Gibson, B. C. Not All Fluorescent Nanodiamonds Are Created Equal: A Comparative Study. *Part. Part. Syst. Charact.* **2019**, *36*, No. 1900009.

(39) Binder, J. M.; Stark, A.; Tomek, N.; Scheuer, J.; Frank, F.; Jahnke, K. D.; Müller, C.; Schmitt, S.; Metsch, M. H.; Unden, T.; Gehring, T.; Huck, A.; Andersen, U. L.; Rogers, L. J.; Jelezko, F. Qudi: A Modular Python Suite for Experiment Control and Data Processing. *SoftwareX* **2017**, *6*, 85–90.

(40) Mrózek, M.; Mlynarczyk, J.; Rudnicki, D. S.; Gawlik, W. Circularly Polarized Microwaves for Magnetic Resonance Study in the GHz Range: Application to Nitrogen-Vacancy in Diamonds. *Appl. Phys. Lett.* **2015**, *107*, No. 013505.

(41) Rondin, L.; Tetienne, J.-P.; Hingant, T.; Roch, J.-F.; Maletinsky, P.; Jacques, V. Magnetometry with Nitrogen-Vacancy Defects in Diamond. *Rep. Prog. Phys.* **2014**, *77*, No. 056503.

(42) Dréau, A.; Lesik, M.; Rondin, L.; Spinicelli, P.; Arcizet, O.; Roch, J.-F.; Jacques, V. Avoiding Power Broadening in Optically Detected Magnetic Resonance of Single NV Defects for Enhanced DC Magnetic Field Sensitivity. *Phys. Rev. B* **2011**, *84*, No. 195204.