## **Nano-optical studies of silicon-vacancy color centers in thin polycrystalline diamond membranes**

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#### **Abstract**

<span id="page-3-0"></span>Quantum information and computing advancements are contingent on the efficacy of spin-photon interfaces, wherein atomic transitions are coupled to the resonant mode of an optical cavity, thereby enhancing the photon emission rate and augmenting the overall effciency of quantum networks. However, the substantial enhancement of the emission rate (Purcell effect) is only achievable when a quantum emitter interacts with a resonant optical antenna of specifc dimensions. Amidst the various semiconductor quantum emitters, silicon-vacancy [\(SiV\)](#page-14-0) color centers in diamond hold great promise for scalable operations, owing to their limited inhomogeneous broadening and room temperature stability. Nevertheless, their restricted out-coupling effciency due to the high refractive index of bulk diamonds presents a signifcant challenge. Addressing this limitation involves the manipulation of the local density of states [\(LDOS\)](#page-13-0) by altering the photonic environment through the integration of dielectric microstructures or plasmonic nanostructures.

To achieve resilient heterostructure devices, integrated quantum photonics, hybrid quantum systems, and other intricate functional materials, it is imperative that the single-color centers be embedded in thin, free-standing membranes with thicknesses ranging from a few micrometers to hundreds of nanometers. While the utilization of high-quality single-crystalline diamond [\(SCD\)](#page-14-1) seems intuitive, the technological intricacies involved in fabricating single-crystal diamond membranes present challenges, as they cannot be cultivated on a substrate other than diamond, and their physical and chemical properties lag behind advanced materials such as silicon technology.

Initially, a comprehensive examination of the optical properties of [SiV](#page-14-0) centers in polycrystalline diamond [\(PCD\)](#page-14-2) membranes of varying thickness was conducted. A combined study of microphotoluminescence measurements and electron microscopy on [PCD](#page-14-2) membranes housing [SiV](#page-14-0) color centers underscored the pivotal role of diamond grain size in the effective isolation of individual [SiV](#page-14-0) centers, mitigating background interference originating from grain boundaries [\(GBs](#page-13-1)). Additional depth-resolved elemental analysis using time-of-fight secondary ion mass spectrometer [\(TOF-SIMS\)](#page-15-0) conducted on both un-implanted and implanted [PCD](#page-14-2) membranes indicated that [PCD](#page-14-2) membranes with a thickness in the micrometer (µm) range hold potential for quantum optical applications, provided that the nano-crystalline regions are adequately removed, either through back thinning or the substantial enhancement of spatial resolution in optical excitation through near-feld or antenna-enhanced microscopy.

Subsequently, fnite-difference time-domain [\(FDTD\)](#page-13-2) calculations were employed to explore the design considerations for nanoantennas. The research suggested that a gold nano-cone with an aspect ratio of  $\approx 1$  yields a substantial enhancement in the Purcell factor (*F*) exceeding four orders of magnitude, accompanied by an antenna efficiency of 80% under effcient near-feld coupling with a quantum emitter. The fabrication process involved the creation of ultra-sharp gold nano-cones with dimensions of approximately 100 nm, boasting an aspect ratio of  $\approx$  1 through gold sputtering and focused ion beam [\(FIB\)](#page-13-3) milling procedures on commercially available scanning near-feld probes (atomic force microscope [\(AFM\)](#page-13-4) probes), thus enabling precise near-feld manipulation of quantum emitters. The optical studies on nano-cones showed that the localized surface plasmon resonance [\(LSPR\)](#page-14-3) linewidth is relatively narrow (around 30 – 50 nm) and spans the required near-infra-red [\(NIR\)](#page-14-4) spectral region, enabling them to implement near-feld coupling with [NIR](#page-14-4) quantum emitters. Since the [LSPR](#page-14-3) shift is proportional to the refractive index modifcation of the embedding medium, the optical response of the nano-cone [LSPR](#page-14-3) was fine-tuned by adjusting the aspect ratio of the nanostructure, ensuring a spectral matching with the quantum emitter.

To unravel this novel observation for the hybrid quantum system, we performed the nearfeld coupling with nanometer precision by utilizing [AFM](#page-13-4) integrated confocal microscopy. The controlled near-feld interaction of [SiV](#page-14-0) centers with gold nano-cones fabricated on commercial [AFM](#page-13-4) probes ensured a Purcell factor of  $F \approx 57$ . Discrepancies between theoretical predictions and experimental results primarily stem from two factors: spectral mismatch and random dipole orientations of [SiV](#page-14-0) color centers on [PCD](#page-14-2) membranes. The future objective focuses on precisely tailoring the dimensions of the nano-cones and the creation of [SiV](#page-14-0) color centers within high-quality [PCD](#page-14-2) membranes, thereby achieving perfect spectral matching and ideal dipole orientation. This, in turn, will effectively enhance the near-field coupling.

#### **Zusammenfassung**

<span id="page-5-0"></span>Fortschritte in der Quanteninformation und -informatik hängen von der Effzienz von Spin-Photonen-Schnittstellen ab, bei denen atomare Übergänge an die Resonanzmode eines optischen Resonator gekoppelt werden, wodurch die Photonen-Emissionsrate erhöht und die Gesamteffzienz von Quantennetzwerken gesteigert wird. Eine wesentliche Steigerung der Emissionsrate (Purcell-Effekt) ist jedoch nur dann möglich, wenn ein Quantenemitter mit einer resonanten optischen Antenne mit bestimmten Abmessungen wechselwirkt. Unter den verschiedenen Halbleiter-Quantenemittern sind die Silizium-Vakanzzentren [\(SiV\)](#page-14-0) in Diamant aufgrund ihrer begrenzten inhomogenen Verbreiterung und ihrer Stabilität bei Raumtemperatur sehr vielversprechend für skalierbare Funktionalitäten. Allerdings stellt ihre eingeschränkte Auskopplungseffzienz aufgrund des hohen Brechungsindexes von Diamanten eine große Herausforderung dar. Um diese Einschränkung zu überwinden, muss die lokale Zustandsdichte [\(LDOS\)](#page-13-0) manipuliert werden, indem die photonische Umgebung durch die Integration von dielektrischen Mikrostrukturen oder plasmonischen Nanostrukturen verändert wird.

Um robust Heterostruktur-Bauelemente, integrierte Quantenphotonik, hybride Quantensysteme und andere komplexe Funktionsmaterialien herzustellen, soltten die einfarbigen Zentren unbedingt in dünne, freistehende Membranen eingebettet werden, deren Dicke von einigen Mikrometern bis zu Hunderten von Nanometern reicht. Während die Verwendung von hochwertigem einkristallinem Diamant [\(SCD\)](#page-14-1) intuitiv erscheint, stellen die technologischen Feinheiten bei der Herstellung von einkristallinen Diamantmembranen eine Herausforderung dar, da sie nicht auf einem anderen Substrat als Diamant gewachsen werden können und ihre physikalischen und chemischen Eigenschaften hinter denen fortschrittlicher Materialien wie der Siliziumtechnologie zurückbleiben.

Zunächst wurde eine umfassende Untersuchung der optischen Eigenschaften von [SiV-](#page-14-0)Zentren in [PCD-](#page-14-2)Membranen unterschiedlicher Dicke durchgeführt. Eine kombinierte Studie von Mikrophotolumineszenzmessungen und Elektronenmikroskopie an [PCD-](#page-14-2)Membranen, die [SiV-](#page-14-0)Farbzentren beherbergen, unterstrich die zentrale Rolle der Diamantkorngröße bei der effektiven Isolierung einzelner [SiV-](#page-14-0)Zentren, wodurch Hintergrundstörungen, die von crystalline [\(GBs](#page-13-1)) ausgehen, abgeschwächt werden. Zusätzliche tiefenaufgelöste Elementanalysen mit Hilfe von Flugzeit-Sekundärionen-Massenspektrometern [\(TOF-SIMS\)](#page-15-0), die sowohl an nicht-implantierten als auch an implantierten [PCD-](#page-14-2)Membranen durchgeführt wurden, zeigten, dass [PCD-](#page-14-2)Membranen mit einer Dicke im Mikrometerbereich (µm) Potenzial für quantenoptische Anwendungen

haben, vorausgesetzt, dass die nanokristallinen Bereiche angemessen entfernt werden, entweder durch rückseitiges Ausdünnen oder durch eine wesentliche Verbesserung der räumlichen Aufösung bei optischer Anregung durch Nahfeld- oder antennenverstärkte Mikroskopie.

Anschließend wurden Berechnungen im Finite-Differenzen-Zeitbereich [\(FDTD\)](#page-13-2) durchgeführt, um die Designüberlegungen für Nanoantennen zu untersuchen. Die Untersuchungen ergaben, dass ein Gold-Nano-Kegel mit einem Seitenverhältnis von etwa 1 eine erhebliche Verbesserung des Purcell-Faktors (*F*) um mehr als vier Größenordnungen ermöglicht, begleitet von einer Antenneneffzienz von 80% bei effzienter Nahfeldkopplung mit einem Quantenemitter. Das Herstellungsverfahren umfasste die Erzeugung ultrascharfer Gold-Nano-Kegel mit Abmessungen von etwa 100 nm und einem Seitenverhältnis von etwa 1 durch Goldsputtern und fokussierte Ionenstrahl-Fräsverfahren [\(FIB\)](#page-13-3) auf handelsüblichen scannenden Nahfeldsonden [\(AFM-](#page-13-4)Sonden), was eine präzise Nahfeldmanipulation von Quantenemittern ermöglicht. Die optischen Untersuchungen an Nano-Kegel haben gezeigt, dass die Linienbreite der lokalisierten Oberfächenplasmonenresonanz [\(LSPR\)](#page-14-3) relativ schmal ist (ca. 30 - 50 nm) und den erforderlichen [NIR-](#page-14-4)Spektralbereich überspannt, so dass eine Nahfeldkopplung mit [NIR-](#page-14-4)Quantenemittern möglich ist. Da die [LSPR-](#page-14-3)Verschiebung proportional zur Änderung des Brechungsindex des Einbettungsmediums ist, wurde die optische Reaktion des Nano-Kegels [LSPR](#page-14-3) durch Anpassung des Seitenverhältnisses der Nanostruktur fein abgestimmt, um eine spektrale Anpassung an den Quantenstrahler zu gewährleisten.

Um diese neuartige Beobachtung für das hybride Quantensystem zu entschlüsseln, haben wir die Nahfeldkopplung mit Nanometerpräzision unter Verwendung der integrierten konfokalen Mikroskopie von [AFM](#page-13-4) durchgeführt. Die kontrollierte Nahfeldwechselwirkung von [SiV-](#page-14-0)Zentren mit Gold-Nano-Kegel, die auf handelsüblichen [AFM-](#page-13-4)Sonden hergestellt wurden, sorgte für einen Purcell-Faktor von *F* ≈ 57. Die Diskrepanzen zwischen den theoretischen Vorhersagen und den experimentellen Ergebnissen sind in erster Linie auf zwei Faktoren zurückzuführen: spektrale Fehlanpassung und zufällige Dipolausrichtungen der [SiV-](#page-14-0)Farbzentren auf [PCD-](#page-14-2)Membranen. Das künftige Ziel besteht darin, die Abmessungen der Nano-Kegel und die Bildung von [SiV-](#page-14-0)Zentren in hochwertigen [PCD-](#page-14-2)Membranen genau zu bestimmen, um so eine perfekte spektrale Anpassung und eine ideale Dipolausrichtung zu erreichen. Dies wiederum wird die Nahfeldkopplung effektiv verbessern.

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Last but certainly not least, I am grateful for the life I lead today and the person I have become. With deep reverence, I dedicate this dissertation to those who are captivated by the enchantment of science.

## **Declaration on oath**

<span id="page-9-0"></span>I, Haritha Kambalathmana, declare that this thesis and the work presented in it are my own and have been generated by me as the result of my own original scientific work. I confirm that, to the best of my knowledge, my thesis does not infringe upon anyone's copyright nor violate any proprietary rights.

Any ideas, techniques, quotations, or any other material from the work of other people included in my thesis, published or otherwise, are fully acknowledged in accordance with the standard referencing practices.

Siegen, 01-10-2024 **Author: Haritha Kambalathmana** 



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#### **Acronyms**

- <span id="page-13-5"></span><span id="page-13-4"></span>**AFM** Atomic Force Microscope
- **APD** Avalanche Photodiode
- **CQED** Cavity Quantum Electrodynamics
- <span id="page-13-9"></span>**CVD** Chemical Vapor Deposition
- **EBID** Electron Beam Induced Deposition
- **EBL** Electron Beam Lithography
- **EM-CCD** Electron Multiplying CCD
- <span id="page-13-7"></span>**FCC** Face Centered Lattice
- <span id="page-13-2"></span>**FDTD** Finite-Difference Time-Domain
- <span id="page-13-3"></span>**FIB** Focused Ion Beam
- <span id="page-13-1"></span>**GB** Grain Boundary
- **GC** Grain Center
- <span id="page-13-6"></span>**GeV** Germanium Vacancy
- **HBT** Hanbury-Brown and Twiss
- <span id="page-13-8"></span>**HPHT** High-Pressure High-Temperature
- **INFN** Italian National Institute of Nuclear Physics
- **IRF** Instrument Response Function
- <span id="page-13-0"></span>**LDOS** Local Photonic Density of States

#### Acronyms

- <span id="page-14-3"></span>**LSPR** Localized Surface Plasmon Resonance
- <span id="page-14-7"></span>**MPCVD** Microwave Plasma Chemical Vapor Deposition
- **NA** Numerical Aperture
- **NIL** Nanoimprint Lithography
- <span id="page-14-4"></span>**NIR** Near Infra-Red
- **NSL** Nanosphere Lithography
- <span id="page-14-5"></span>**NV** Nitrogen Vacancy
- <span id="page-14-2"></span>**PCD** Polycrystalline Diamond
- **PECVD** Plasma-Enhanced Chemical Vapor Deposition
- **PL** Photoluminescence
- **PML** Perfectly Matched Layer
- **RF** Radio Frequency
- **RIE** Reactive Ion Etching
- <span id="page-14-1"></span>**SCD** Single Crystalline Diamond
- **SCM** Scanning Confocal Microscope
- **SEM** Scanning Electron Microscope
- <span id="page-14-6"></span>**SERS** Surface-Enhanced Raman Spectroscopy
- <span id="page-14-0"></span>**SiV** Silicon Vacancy
- **SnV** Tin Vacancy
- **SPP** Surface Plasmon Polariton
- **SRIM** Stopping and Range of Ions in Matter
- **STEM** Scanning Transmission Electron Microscopy
- **TCSPC** Time-Correlated Single-Photon Counter
- **TEM** Transmission Electron Microscope
- **TERS** Tip-Enhanced Raman Spectroscopy
- <span id="page-15-0"></span>**TOF-SIMS** Time-of-Flight Secondary Ion Mass Spectrometry
- **UV-NIL** UV-Nanoimprint Lithography
- **VC** Carbon Vacancy
- <span id="page-15-1"></span>**ZPL** Zero Phonon Line

# **1**

## **INTRODUCTION**

<span id="page-18-0"></span>*"Light interacts with matter, creating the world around us. Without light, there would be no color, no beauty, no life"*

— Dr. Michio Kaku

#### <span id="page-18-1"></span>**1.1 Motivation**

The electromagnetic spectrum includes various forms of energy, but the light is most intriguing because it allows humans to understand their surroundings better. Despite the impressive capabilities of light, there are still limitations to what we can achieve with it. The interaction between light and matter is weak due to the signifcant size difference between the wavelength of visible light and the size of electrons, which are the components of matter that interact with light the most [\[1\]](#page-152-0). This size mismatch results in low probabilities of light absorption or emission, hindering the miniaturization of light sources and detectors and preventing low-power optical non-linearities needed for all-optical information processing. However, tiny quantum light sources are essential for both re-search and practical applications in the field of quantum science and technology [\[2,](#page-152-1) [3\]](#page-152-2). For example, in quantum information science, single-photon sources are used to generate the basic units of quantum information, "qubits". Single photons are ideal qubits because they can be easily manipulated, transmitted over long distances, and measured with high accuracy; hence they are essential for developing quantum computers and other quantum technologies [\[4\]](#page-152-3). Whereas in quantum cryptography, single-photon sources are used to create secure communication channels. Encoding information onto single photons makes it possible to send messages that cannot be intercepted without detection. In quantum metrology, single-photon sources are used for precision measurements of physical quantities such as time, frequency, and length. Single photons can be used to create highly stable reference standards and to measure tiny changes in physical systems. However, the deployment of ideal photo-stable, bright, and indistinguishable single-photon sources remains a challenge in quantum communication and cryptography applications [\[4\]](#page-152-3).

A series of experiments on solid-state atom-like emitters such as organic molecules, quantum dots, and color centers in diamonds have been proposed and verifed as potential

candidates for practical quantum optical devices [\[2,](#page-152-1) [3,](#page-152-2) [5\]](#page-152-4). There are several reasons why diamond-based single photon sources are regarded as ideal [\[6\]](#page-152-5). These reasons include their high purity level, ability to emit bright photons, long-term stability, capacity to operate both at room temperature and high temperatures, and potential for scalability [\[7,](#page-152-6) [8,](#page-152-7) [9\]](#page-153-0). Many defect centers in diamond have been explored, including nickel-based (NE8) centers [\[10\]](#page-153-1), chromium-related color centers [\[11,](#page-153-2) [12\]](#page-153-3) nitrogen-vacancy [\(NV\)](#page-14-5) centers [\[4,](#page-152-3) [13\]](#page-153-4) germanium-vacancy centers [\(GeV\)](#page-13-6) [\[14\]](#page-153-5) and silicon-vacancy [\(SiV\)](#page-14-0) centers [\[15,](#page-153-6) [16\]](#page-153-7).

This thesis mainly focuses on the [SiV](#page-14-0) color centers among various other color centers studied so far. The [SiV](#page-14-0) color centers in a diamond are particularly suitable as most of the emission (>90%) is concentrated in a narrow zero-phonon line [\(ZPL\)](#page-15-1) with a linewidth of about 1 nm at room temperature and a short lifetime of 1 ns [\[9,](#page-153-0) [17\]](#page-153-8). The inversion symmetry of [SiV](#page-14-0) centers leads to high spectral stability, which allows the creation of single photons from separate emitters with good indistinguishability [\[18\]](#page-153-9). This color center exhibits single-photon emission in the MHz range [\[19\]](#page-154-0), with its polarized emission characteristics indicating high dipole purity. This attribute renders it apt for potential applications such as quantum cryptography [\[20\]](#page-154-1) and the quantum frequency conversion of individual photons [\[21\]](#page-154-2). Facilitating the advancement of robust heterostructure devices, integrated quantum photonics, hybrid quantum systems [\[22\]](#page-154-3), and other intricate functional materials necessitate the integration of single-color centers into thin, free-standing membranes spanning from a few micrometers to hundreds of nanometers in thickness. Although utilizing high-quality single-crystalline diamond [\(SCD\)](#page-14-1) appears straightforward, the technological hurdles in fabricating [SCD](#page-14-1) membranes stem from their inability to grow on substrates other than diamond. Moreover, their physical and chemical characteristics fall behind those of cutting-edge materials like silicon technology [\[23,](#page-154-4) [24,](#page-154-5) [25\]](#page-154-6). Conversely, free-standing polycrystalline diamond [\(PCD\)](#page-14-2) membranes can be readily obtained from nanocrystalline diamond seeds supported by a substrate that can be selectively wet-etched [\[26,](#page-154-7) [27\]](#page-154-8). However, the practical application of these membranes in quantum optics or integrated quantum photonics is currently constrained by elevated levels of radiative and non-radiative crystallographic defects, mainly within the non-diamond carbon phases of the host matrix [\[27\]](#page-154-8). Notably, the  $SP<sup>2</sup>$  carbon hybridized segments at grain centers and boundaries have a detrimental impact on the quantum efficiency of the emitter, while background photoluminescence poses challenges in selectively addressing single-color centers in [PCD](#page-14-2) membranes [\[28\]](#page-155-0).

For the realization of [SiV-](#page-14-0)based ultrafast, bright, and indistinguishable single-photon sources at room temperature, the generation of a single photon needs to be faster than the dephasing time. Nevertheless, the low quantum yield and light trapping due to the large refractive index of a diamond host limit their maximum photon count rate. There are methods to enhance the light-matter interaction, such as using an optical cavity or

<span id="page-20-0"></span>

**Figure 1.1.** A schematic representation of a hybrid quantum system. A [SiV](#page-14-0) color center in a [PCD](#page-14-2) nano-membrane is coupled with a gold nano-cone fabricated on scanning near-feld [AFM](#page-13-4) probe.

plasmonic nanostructures to confine light [\[29,](#page-155-1) [30,](#page-155-2) [31\]](#page-155-3). However, these methods have fundamental limitations that alternative strategies must address to unlock the full potential of strong light-matter interactions. The common approach is to manipulate the photon emission by a resonant structure that modifes its spontaneous emission rate, known as the "Purcell effect" [\[32\]](#page-155-4). A signifcant Purcell enhancement occurs only when a quantum emitter interacts with a high-quality factor resonant nanostructures of the desired dimension and optical properties [\[31\]](#page-155-3). Different techniques have been exploited for manipulating the quantum emitters, including photonic crystal structures [\[33\]](#page-155-5), solid-immersion lenses [\[34\]](#page-155-6), optical antennas [\[29,](#page-155-1) [32\]](#page-155-4), and scanning micro-cavities [\[30\]](#page-155-2). Several research studies show that plasmonic nanostructures have a great capacity to attain more than three orders of magnitude Purcell factors [\[35\]](#page-155-7), since they can support localized surface plasmon reso-nance [\(LSPR\)](#page-14-3) and can massively localize electromagnetic fields into a tiny mode volume, increasing the excitation rate of the quantum emitter. So far, various plasmonic optical antenna geometries and materials have been used to enhance the radiative decay rate of a single emitter [\[36,](#page-155-8) [37\]](#page-155-9). For example, planar antenna [\[38\]](#page-156-0), bow-tie antenna [\[39\]](#page-156-1), gold nanorods [\[31,](#page-155-3) [40\]](#page-156-2), spherical nanoparticles [\[41\]](#page-156-3) and so on. Most of the nanostructures require sophisticated nanofabrication techniques and complex experimental approaches. The main factor that is demanding is the requirement of controlled coupling between the emitter and the antenna [\[35,](#page-155-7) [42\]](#page-156-4). Besides, one cannot increase the Purcell factor [\[43\]](#page-156-5) without the expense of loss in the metal nanostructure, which is characterized by the antenna efficiency [\[36\]](#page-155-8).

In this thesis, a bottom-up approach is adopted to enable efficient yet controlled near-

feld coupling of two quantum systems resulting in enhanced spontaneous emission rate. One approach to address efficient near-field coupling is to create quantum emitters (here we chose [SiV](#page-14-0) color centers) in nanometer-thick dielectric material (we use about 50 nm thick [PCD](#page-14-2) membranes [see Figure [1.1\]](#page-20-0) [\[28,](#page-155-0) [44\]](#page-156-6). This method offers a way to enhance the near-feld coupling of quantum emitters with plasmonic nanostructures. Since the thickness of the diamond membrane is only a few hundred nanometers, the integration of the dielectric with photonic devices for emitter manipulation is fairly made easy [\[45,](#page-156-7) [46\]](#page-156-8). The optical nanoantenna used for the nanomanipulation is fabricated via a versatile, simple, and relatively fast fabrication approach by combining gold sputtering followed by focused ion beam [\(FIB\)](#page-13-3) milling on a commercially available atomic force microscopy [\(AFM\)](#page-13-4) cantilever. This method creates sharp plasmonic gold nano-cones on the tip apex of [AFM](#page-13-4) probes, enabling nanometer control over the near-feld coupling with [SiV](#page-14-0) centers in [PCD](#page-14-2) membranes. Ultra-sharp nanoantennas created on scanning near-feld probes (e.g., [AFM](#page-13-4) probes) demonstrated the ability to carefully manipulate the photo-physics of quantum emitters. Their unique dimension not only supports localized felds with tiny mode volumes but also allows significant antenna efficiency [\[36,](#page-155-8) [47\]](#page-157-0). In addition, we show that via controlled coupling of [SiV](#page-14-0) color centers to [AFM](#page-13-4) probe-based gold nano-cones, one could enhance the excited-state decay rate and achieve faster spontaneous emission rates [\[35\]](#page-155-7).

This thesis investigates the use of gold nano-cones as optical nanoantennas, which function as nanocavities with very small mode volumes, to manipulate the emission properties of [SiV](#page-14-0) color centers in thin [PCD](#page-14-2) membranes. By characterizing and quantifying the interaction between an ensemble of [SiV](#page-14-0) color centers and a gold nano-cone fabricated on [AFM](#page-13-4) probe, the study aims to unveil the possibility of creating a hybrid quantum system that supports ultrafast photon emission. The introduction frst discusses single photon sources and their applications, followed by a brief overview of optical cavities and their role in modifying the spontaneous emission rate of quantum emitters, and finally, the effect of nanoscale positioning and orientation control of an emitter relative to an optical nanoantenna on the interaction is discussed.

<span id="page-21-0"></span>The experiments presented in this research are classifed into three sections, namely, the creation and optical characterization of diamond-based single-photon sources in section [1.2,](#page-21-0) the investigation of a plasmonic nano-cone antenna as a nanoscale resonator for nearfeld light-matter interaction and manipulation in section [1.3,](#page-23-0) and fnally the plasmonassisted emission and manipulation of quantum emitters in section [1.4.](#page-25-0) In this chapter, we are briefy introducing each experimental section with its motivation, challenges, and outcomes.

#### **1.2 Diamond Based Single Photon Sources**

Single-photon sources based on color centers in diamond have emerged as one of the most promising platforms for a wide range of quantum technologies, including quantum communication, quantum cryptography, and quantum computing [\[2,](#page-152-1) [3,](#page-152-2) [5\]](#page-152-4). Diamond is a unique material with a range of optical and physical properties, making it an ideal candidate for quantum applications [\[48,](#page-157-1) [49\]](#page-157-2). These protocols rely on the ability to generate and manipulate single photons with high fidelity, which can be achieved with diamond color centers. Color centers in diamonds are defects in the crystal structure that result from the substitution of a carbon atom with a foreign atom, such as nitrogen or silicon [\[10\]](#page-153-1)-[\[16\]](#page-153-7). These defects give rise to a unique electronic and optical behavior that makes them useful for various applications [\[18\]](#page-153-9). One of the critical advantages of color centers in diamonds is their robustness and stability at room temperature, which allows for practical implementation in a wide range of environments. They also exhibit excellent coherence properties, which enable the implementation of high-fdelity quantum operations [\[10\]](#page-153-1). Moreover, diamond is a biocompatible material, making it a promising candidate for applications in biotechnology and medicine [\[50,](#page-157-3) [51\]](#page-157-4). It is also chemically inert and has a high refractive index, which makes it an ideal platform for integrated photonics [\[6\]](#page-152-5).

One of the most well-studied color centers in diamond is the [NV](#page-14-5) center, which has a long spin coherence time and high photoluminescence quantum efficiency [\[4,](#page-152-3) [13\]](#page-153-4). The [NV](#page-14-5) center in a diamond consists of a nitrogen atom located at a lattice site adjacent to a vacancy in the diamond crystal structure [\[52\]](#page-157-5). The [NV](#page-14-5) center emits photons with a well-defned energy and polarization state, making it an ideal candidate for single photon applications [\[34\]](#page-155-6). One of the key advantages of [NV](#page-14-5) centers in diamond as single-photon sources is their ability to operate at room temperature [\[53\]](#page-157-6). Unlike other single-photon sources that require cryogenic temperatures to operate, [NV](#page-14-5) centers can emit photons at room temperature with high efficiency and low noise. Other diamond color centers have also been investigated as single-photon sources, such as the [SiV](#page-14-0) center and the [GeV](#page-13-6) center [\[7,](#page-152-6) [14\]](#page-153-5). Recently, [SiV](#page-14-0) color centers have become popular for a wide range of applications [\[7,](#page-152-6) [16,](#page-153-7) [54\]](#page-157-7). The [SiV](#page-14-0) color centers in diamonds are especially promising due to their photo-stability, and ability to emit single photons within a narrow spectral range of about 1 nm at room temperature, and high brightness [\[7,](#page-152-6) [17\]](#page-153-8). These color centers have been shown to exhibit efficient and stable single photon emission, and their optical properties can be tuned through various means, such as strain engineering or chemical doping [\[55,](#page-157-8) [56\]](#page-157-9). Using diamond as a host material for single-photon sources also offers advantages in terms of scalability and integration with other technologies. Diamond color centers can be created and manipulated with high precision, allowing for the creation of large arrays of singlephoton sources with well-controlled properties. However, many important issues still need to be addressed through further basic research. For instance, producing color centers

in nanoscale diamonds needs to become more reliable, and scientists need to control better the photo-physics and single-photon emission characteristics of these quantum emitters. One efficient approach for manipulating the emission dynamics is integrating diamond color centers with other technologies, such as plasmonic nanostructures, to enhance their emission properties and enable near-feld coupling [\[38,](#page-156-0) [42\]](#page-156-4).

Recent studies have shown that creating [SiV](#page-14-0) color centers in thin [PCD](#page-14-2) membranes offers an excellent platform for creating quantum emitters in nanoscale dimensions that can be coupled to plasmonic nanostructures [\[28,](#page-155-0) [57\]](#page-158-0). For several reasons, color centers in [PCD](#page-14-2) membranes are chosen for near-feld coupling with plasmonic nanostructures instead of color centers in polycrystalline bulk diamonds [\[23\]](#page-154-4). Firstly, the [PCD](#page-14-2) membranes have a much smaller thickness than the [PCD](#page-14-2) bulk, which enables efficient near-field coupling between the color centers and plasmonic nanostructures. The smaller thickness of the diamond membrane allows the plasmonic feld to penetrate deep into the diamond, leading to a strong interaction between the color centers and the plasmonic feld. Secondly, the surface-area-to-volume ratio is large, which enhances the near-feld coupling between the color centers and the plasmonic field, leading to a stronger interaction and higher quantum effciency. Thirdly, [PCD](#page-14-2) membranes are relatively easier to fabricate than [SCD](#page-14-1) in bulk. The fabrication of [PCD](#page-14-2) involves using a sacrifcial layer selectively etched to release the diamond membrane. This technique allows for the creation of freestanding diamond membranes with a thickness of a few hundred nanometers, which can be easily integrated with plasmonic nanostructures [\[28\]](#page-155-0). This makes them ideal for single-photon applications, such as single-photon sources and quantum sensing [\[57\]](#page-158-0). By coupling [SiV](#page-14-0) centers to sharp nanostructures on scanning near-feld probes; for example, a gold nanocone fabricated on [AFM](#page-13-4) probe, the spontaneous emission decay rate of the quantum emitter can be manipulated [\[44,](#page-156-6) [58,](#page-158-1) [59,](#page-158-2) [60,](#page-158-3) [61\]](#page-158-4). The optical response of the nano-cone was optimized by tuning the aspect ratio of the nanostructure to achieve a spectral match between the emitter and nano-cone [\[47,](#page-157-0) [61\]](#page-158-4).

#### <span id="page-23-0"></span>**1.3 Optical Antenna: A Nano-scale Resonator**

The principle behind the operation of optical antennas as nano-scale resonators is the excitation of surface plasmons in metallic nanostructures [\[31,](#page-155-3) [61,](#page-158-4) [62\]](#page-158-5). When light interacts with a metallic nanoparticle or nanostructure, it can excite collective oscillations of free electrons, known as surface plasmons [\[63\]](#page-158-6). These plasmons can be strongly confned and amplifed in the vicinity of the metallic structure, leading to enhanced local electromagnetic felds [\[37\]](#page-155-9). This leads to the formation of a highly localized, nano-scale electromagnetic feld, which can interact with nearby emitters such as quantum dots, molecules, or color centers [\[42,](#page-156-4) [44,](#page-156-6) [61\]](#page-158-4). The presence of the optical antenna modifes the local density of states [\(LDOS\)](#page-13-0), which governs the rate at which an emitter emits photons [\[62,](#page-158-5) [58\]](#page-158-1). This leads to the enhancement or suppression of the emission rate of the emitter, depending on the nature of the coupling [\[42,](#page-156-4) [43\]](#page-156-5).

The working principle of optical antennas is highly dependent on the geometry and composition of the metallic nanostructure [\[32\]](#page-155-4). By controlling the size, shape, and composition of the optical antenna, it is possible to tune the resonance condition for surface plasmon excitation and tailor the strength of the coupling with nearby emitters [\[36,](#page-155-8) [37\]](#page-155-9). This makes optical antennas a versatile tool for enhancing and manipulating light-matter interactions at the nanoscale, with potential applications in nanophotonics, quantum information processing, and sensing [\[58,](#page-158-1) [64,](#page-158-7) [65\]](#page-158-8). The key properties of optical antennas include (i) Resonant wavelength: which is determined by its size, shape, and composition and is typically in the visible or near-infrared spectral range [\[46,](#page-156-8) [47\]](#page-157-0). By tuning the resonant wavelength, the antenna can be designed to interact with specific frequencies of light and emitters, (ii) Enhancement factor: optical antennas can enhance the local electromagnetic feld intensity by several orders of magnitude, leading to enhanced light-matter interactions and modifed emission properties of nearby emitters [\[44\]](#page-156-6). The enhancement factor is determined by the coupling strength between the emitter and the antenna, which depends on the antenna size, shape, and distance from the emitter, (iii) Directionality: the directionality of the emission from an optical antenna can be controlled by the geometry of the antenna [\[38,](#page-156-0) [55\]](#page-157-8). For example, bowtie-shaped antennas can emit light in a highly directional manner, while nanorods can emit light in a more isotropic manner [\[39\]](#page-156-1), (iv) Polarization: the polarization of the emission from an optical antenna can be controlled by the orientation of the antenna with respect to the incident light polarization [\[47\]](#page-157-0). This is because the plasmon resonances in the antenna are highly sensitive to the polarization of the incident light,  $(v)$  Quantum efficiency: the quantum efficiency of the emitter coupled to an optical antenna can be modifed by the presence of the antenna [\[36\]](#page-155-8). In general, the presence of the antenna can lead to both enhanced and suppressed emissions, depending on the nature of the coupling.

Figure [1.2](#page-25-1) illustrates various basic geometries of optical nanoantennas [\[66\]](#page-158-9); starting with the spherical dipole antenna, when two spheres come together, they form a nanodimer with a narrow gap (the feed gap) between them, creating a strong feld hotspot. Another design involves elongated ellipsoids, resembling dipole nanorod antennas. Aligning two nanorods closely creates a two-wire nanoantenna [\[40,](#page-156-2) [67\]](#page-159-0). Moreover, nanoparticles can form arrays, acting as linear nanorod antennas [\[68,](#page-159-1) [69\]](#page-159-2). A bowtie nanoantenna consists of two triangular shapes with tips forming a broad bandwidth feed gap [\[39,](#page-156-1) [70\]](#page-159-3). An optical Yagi-Uda nanoantenna combines a resonant nanorod antenna, a refector nanorod, and director nanorods [\[55,](#page-157-8) [71\]](#page-159-4). Optical antennas fnd widespread application across diverse felds, including nanophotonics, quantum information processing, sensing, and biomedical imaging [\[29,](#page-155-1) [68,](#page-159-1) [72,](#page-159-5) [73\]](#page-159-6). Notably, they play a pivotal role in plasmon-

<span id="page-25-1"></span>

**Figure 1.2.** A schematic representation of different types of experimental plasmonic nanoantennas

enhanced spectroscopy, where the optical antennas are used to enhance the sensitivity and resolution of various spectroscopy techniques, such as Raman spectroscopy and fuorescence spectroscopy [\[73\]](#page-159-6). By coupling an emitter, such as a molecule or a quantum dot, to an optical antenna, it is possible to enhance the emission rate and modify the spectral properties of the emitter [\[35,](#page-155-7) [46,](#page-156-8) [74\]](#page-159-7). Next, optical antennas can be used to enhance the emission rate and directional emission of single-photon sources, such as quantum dots or color centers [\[38,](#page-156-0) [42,](#page-156-4) [56\]](#page-157-9). Creating these single-photon sources with nanoantenna cavities requires essential prerequisites: fabricating resonant nanoantennas smaller than 200 nm, understanding the local near-feld distribution within the mode volume by imaging nanoantenna mode patterns, and lastly, achieving precise nanometerscale control over the positioning and orientation of individual emitters within the same volume [\[42,](#page-156-4) [47\]](#page-157-0). This precise mapping of coupling strength is essential to identify the optimal coupling position for the emitter within the nanoantenna mode, as close proximity can suppress fuorescence enhancement, potentially elevating non-radiative rates [\[37,](#page-155-9) [45,](#page-156-7) [75\]](#page-159-8).

#### <span id="page-25-0"></span>**1.4 Plasmon Enhanced Single-Photon Emission**

In quantum mechanics, spontaneous emission is the process by which an excited quantum emitter (such as an atom, molecule, or quantum dot) emits a photon in a random direction without any external stimulation [\[45,](#page-156-7) [76,](#page-159-9) [77,](#page-159-10) [78\]](#page-160-0). This process is typically characterized by an exponentially decaying emission rate, which is determined by the intrinsic properties of the emitter. However, recent advances in nanophotonics have shown that the emission rate of quantum emitters can be signifcantly enhanced by coupling them to optical antennas [\[42,](#page-156-4) [44,](#page-156-6) [61\]](#page-158-4). Optical antennas have been extensively used to manipulate the photo-physics of quantum emitters, particularly in the context of controlling their radiative decay rates and spectral properties [\[42\]](#page-156-4). They can manipulate the photo-physics of quantum emitters, which refers to the various processes involved in the absorption, emission, and transfer of energy between the emitter and its surroundings [\[36\]](#page-155-8).

For example, suppose two emitters are placed in close proximity to each other. In that case, their excited states can interact through dipole-dipole coupling, leading to energy transfer and quenching of their fuorescence [\[75\]](#page-159-8). However, by placing an optical antenna between the two emitters, it is possible to create a resonant mode that mediates the energy transfer and enhances the overall fuorescence intensity [\[45\]](#page-156-7). These nanoscale structures are designed to efficiently convert free-space electromagnetic radiation into [LSPRs](#page-14-3), which can, in turn, enhance the emission rate of nearby quantum emitters [\[74\]](#page-159-7).

The key idea behind this enhancement mechanism is that the presence of the optical antenna modifes the [LDOS](#page-13-0) around the emitter [\[79\]](#page-160-1). The [LDOS](#page-13-0) describes the density of available photon states at a given frequency and location and is proportional to the spontaneous emission rate of the emitter. By carefully designing the geometry and material properties of the optical antenna, it is possible to create a resonant mode that matches the emission frequency of the quantum emitter and strongly enhances the [LDOS](#page-13-0) in its vicinity [\[32\]](#page-155-4). Hence, it is possible to preferentially enhance the radiative pathway and increase the overall fuorescence effciency of the emitter [\[42\]](#page-156-4). In practice, the coupling between the quantum emitter and the optical antenna is typically achieved by placing the emitter in close proximity to the antenna, either by direct deposition or by using nanofabrication techniques [\[58,](#page-158-1) [80\]](#page-160-2). The enhancement of the spontaneous emission rate can then be characterized by measuring the fuorescence intensity and lifetime of the emitter, which are directly related to the [LDOS](#page-13-0) [\[32,](#page-155-4) [58\]](#page-158-1). The use of optical antennas to manipulate the spontaneous emission rate of quantum emitters has numerous potential applications in felds such as quantum information processing, sensing, and nanophotonics [\[81\]](#page-160-3). For example, it can be used to enhance the efficiency of single-photon sources improve the sensitivity of fuorescence-based sensors, or increase the brightness of nanoscale light sources [\[82,](#page-160-4) [83,](#page-160-5) [84\]](#page-160-6).

One of the earliest studies on this topic was published in 2005 by Novotny et al. demonstrated that a gold nanoparticle antenna could be used to enhance the emission rate of a single molecule placed in its near-feld region [\[31,](#page-155-3) [85\]](#page-160-7). The enhancement was attributed to the Purcell effect, where the presence of the antenna increases the [LDOS](#page-13-0) at the emission

#### 1 Introduction

wavelength of the molecule, leading to an increased emission rate. Subsequently, several studies have investigated the use of plasmonic nanoantennas for controlling the emission properties of quantum dots [\[35,](#page-155-7) [42,](#page-156-4) [58,](#page-158-1) [78,](#page-160-0) [86,](#page-160-8) [87\]](#page-160-9). In one such study, A. G. Curto et al. demonstrated that a silver nanorod antenna could be used to control the directionality of the emission from a single quantum dot [\[88\]](#page-161-0). The directionality was controlled by the orientation of the nanorod with respect to the quantum dot, which affected the coupling strength between the two. Another study by Kuznetsov et al. used a gold nanoantenna to enhance the emission rate of a single quantum dot [\[89\]](#page-161-1). They showed that the antenna acted as a cavity resonator, with the quantum dot as the emitter inside the cavity. By tuning the resonant wavelength of the cavity, they enhanced the emission rate of the quantum dot by up to a factor of 20. Diamond color centers have also been shown to exhibit enhanced emission properties when coupled with plasmonic nanoantenna. Recently, A. M. Flatae et al. have shown suppression of 99% of the surface trap states and 1460-fold Purcell enhancement in the excitonic emission in a bare CdTe quantum dot via controlled coupling with gold nano-cone [\[42\]](#page-156-4). This paper showed a versatile approach where a single quantum dot was functionalized onto the tip apex of an [AFM](#page-13-4) probe. Utilizing the [AFM,](#page-13-4) the quantum emitter coupled to a sharp gold nano-cone in nanometer precision. By optimizing the coupling strength, the emission dynamics of the quantum dot are manipulated [\[42\]](#page-156-4). However, the near-field coupling between the two hybrid quantum systems in this technique demands a more sophisticated approach. Similarly, a 1000-fold modifcation in the radiative decay rate on an ensemble of emitters via coupling to the nanoscale gap between a silver nanowire and a silver substrate was reported by K. J. Russell et al. [\[90\]](#page-161-2).

Optical antennas have shown great promise in this regard, but several limitations must be addressed. One limitation of using optical antennas to manipulate the spontaneous emission rate of quantum emitters is the issue of reproducibility. Fabricating reliable and reproducible optical antennas with well-defned geometries and resonant properties is a significant challenge. Minor variations in the fabrication process can lead to significant variations in the antenna's properties, making it difficult to achieve consistent results. A study by A. Cvitkovic et al. showed that the performance of plasmonic antennas for surface-enhanced infrared absorption spectroscopy was sensitive to variations in the geometry of the antennas, highlighting the importance of precise fabrication [\[91\]](#page-161-3). Another limitation is the effect of the surrounding environment on the performance of the optical antenna. The presence of nearby objects, such as other emitters or metallic structures, can interfere with the coupling between the emitter and the antenna, leading to a reduction in the enhancement of the spontaneous emission rate. A study by C. H. Lee et al. showed that the performance of a plasmonic antenna for surface-enhanced Raman spectroscopy [\(SERS\)](#page-14-6) could be affected by changes in the surrounding environment, limiting the reproducibility and reliability of the optical antennas [\[92\]](#page-161-4).

Additionally, the use of optical antennas may lead to increased non-radiative decay rates, resulting in a reduction in the overall quantum efficiency of the system [\[43\]](#page-156-5). This is because the strong coupling between the emitter and the antenna can lead to the transfer of energy from the emitter to the antenna, resulting in an increased probability of non-radiative decay channels [\[79\]](#page-160-1). Losses in the plasmonic materials used in optical antennas can also limit the enhancement of the spontaneous emission rate. Moreover, the enhancement of the spontaneous emission rate using optical antennas is limited to a certain range, since the enhancement could also saturate owing to the dominant non-radiative decay processes. The spontaneous emission rate enhancement is limited by the efficient coupling between the quantum emitter and the optical antenna [\[36\]](#page-155-8).

In conclusion, optical antennas have shown great promise for manipulating the spontaneous emission rate of quantum emitters, but several limitations must be considered. Future research should address these limitations and develop new ways to exploit the unique properties of optical antennas for various scientifc and technological challenges.

In the context of this thesis work, a sharp conical antenna on commercial [AFM](#page-13-4) probe is fabricated, characterized, and carefully optimized for the near-feld manipulation of [SiV](#page-14-0) color centers in thin [PCD](#page-14-2) membranes. A detailed study is discussed in chapter [4](#page-88-0) and chapter [6.](#page-130-0)

#### <span id="page-28-0"></span>**1.5 Thesis Outline**

The main objective of this thesis is to perform a systematic investigation of the infuence of plasmonic nanostructures in manipulating the emission photodynamics of quantum emitters. Initially, we aimed to enhance the optical properties of [SiV](#page-14-0) centers in ultrathin [PCD](#page-14-2) membranes through ion implantation and material processing to gain a better understanding of their characteristics. Next, through theoretical simulation, the parameters for the nanofabrication of plasmonic gold nano-cones were optimized. After the fabrication, the nanostructures were characterized by utilizing dark-feld microscopy. The controlled near-feld coupling of [SiV](#page-14-0) centers with nano-cone antennas enabled the achievement of a remarkable improvement in the spontaneous emission rate. This hybrid-quantum system generating enhanced photon emission at room temperature would facilitate the generation of lifetime-limited indistinguishable photons, which is a prerequisite for quantum optical applications such as linear-optical quantum computation [\[93,](#page-161-5) [94\]](#page-161-6) and Boson sampling [\[95,](#page-161-7) [96\]](#page-161-8). The narrow inhomogeneous distribution, strong [ZPL](#page-15-1) transition, and spectral stability of [SiV](#page-14-0) color centers in conjunction with the enhanced emission rate achieved through the nanoantenna[-SiV](#page-14-0) structure make them a promising foundation for further research in the feld of nano-quantum optics and a potential platform for quantum networks, optical quantum computing, sensing, and metrology [\[93,](#page-161-5) [95,](#page-161-7) [97,](#page-161-9) [98\]](#page-161-10).

An overview of the structure of the thesis is described here. The fundamental concepts required to follow this thesis are provided in chapter [2.](#page-30-0) The chapter starts with a brief description of a versatile semiconductor, "Diamond,": its material properties, growth, and physical classifcations, are discussed in section [2.1.](#page-30-1) In section [2.2,](#page-40-0) various methods for creating color centers, the optical properties of [SiV](#page-14-0) color centers, and also the optical characterization of [SiV](#page-14-0) color centers are explained. The section [2.3](#page-57-0) illustrates the design consideration and how the spontaneous emission rate can be modifed through discrete cavity nanostructures.

In chapter [3,](#page-78-0) the theoretical modeling of plasmonic gold nano-cones is discussed. The fnite-difference time-domain [\(FDTD\)](#page-13-2) calculation provides the desired parameters for fabricating the gold nano-cones. From the theoretical study, the exact location of the [LSPR](#page-14-3) is determined [see section [3.2.1\]](#page-79-1). The section [3.2.2,](#page-80-0) discusses the [FDTD](#page-13-2) calculations on how the Purcell factor and antenna efficiency are modified under a controlled near-field coupling of gold nano-cone with the single quantum emitter.

In chapter [4,](#page-88-0) the fabrication and optical characterization of sharp plasmonic gold nanocones are discussed. The nano-cones are fabricated through gold sputtering on commercial [AFM](#page-13-4) probes followed by the [FIB](#page-13-3) milling technique [see section [4.2\]](#page-91-0). The optical properties of the nano-cones are studied by using an inverted dark-feld spectroscopy system combined with [AFM.](#page-13-4) In section [4.3,](#page-98-0) the spectroscopy and theoretical simulation of the nano-cones are explained.

In chapter [5,](#page-110-0) the investigation of the properties of [PCD](#page-14-2) membranes containing [SiV](#page-14-0) centers are described. The ultimate focus of this study is to identify a method that eventually would allow addressing single emitters within the grain center of a [PCD](#page-14-2) membranes, hence reducing the unwanted background signals from the desired quantum emitter fuorescence signal. The section [5.2](#page-111-0) describes the growth of [PCD](#page-14-2) membrane. In section [5.3,](#page-113-0) a detailed description of creating the [SiV](#page-14-0) color centers on the [PCD](#page-14-2) membranes, the grain size evolution on [PCD](#page-14-2) membranes, and the optical characterization of [SiV](#page-14-0) color centers on [PCD](#page-14-2) membranes are shown.

In chapter [6,](#page-130-0) the manipulation of the emission photo-physics of an ensemble of [SiV](#page-14-0) color centers in thin [PCD](#page-14-2) membrane via plasmonic near-feld coupling is described. In section [6.2,](#page-132-0) the fabrication, characterization, and near-feld coupling of the hybrid quantum system are described in detail. The near-feld coupling scheme and the fnal remarks on the hybrid-quantum system are given in the section [6.3.](#page-139-0)

Finally, in chapter [7,](#page-144-0) a summary of the research work performed in this thesis and the outlook of ongoing and prospective projects to continue the work are presented.

## **2**

## <span id="page-30-0"></span>**FUNDAMENTAL CONCEPTS OF COLOR CENTERS IN DIAMOND AND OPTICAL ANTENNAS**

This chapter overviews the fundamental concepts necessary to understand the experimental, theoretical, and numerical methods used in this thesis. Additional details on the concepts discussed in this chapter are available in standard textbooks [\[48,](#page-157-1) [49,](#page-157-2) [99,](#page-162-0) [100,](#page-162-1) [101,](#page-162-2) [102,](#page-162-3) [103\]](#page-162-4).

#### <span id="page-30-1"></span>**2.1 Diamond**

Carbon is a versatile element whose electronic confguration allows it to form a wide variety of structures, such as fullerenes, carbon nanotubes, diamonds, and graphites. Besides various other allotropes of carbon, the most prominent comparison is between diamond and graphite. A diamond has  $SP<sup>3</sup>$  hybridized orbitals with covalently bonded carbon atom arrangements, whereas graphite is formed of carbon sheets with  $SP<sup>2</sup>$  hybridized orbitals. The carbon sheets in graphite are held together by a weak van der waals bonding. This signifcant difference in the structure of these allotropes explains why diamond is much harder than graphite and why graphite is an electrical conductor and diamond is an insulator. The thermodynamically stable carbon allotrope is graphite [\[100\]](#page-162-1). Due to the large activation energy barrier, diamond does not undergo a phase change to graphite; it is in a metastable form. Hence, diamond can be synthesized under conditions where it is in a thermodynamically stable phase. As long as the conditions change fast enough, the diamond will not revert to graphite as it cools [\[48,](#page-157-1) [100\]](#page-162-1).

#### <span id="page-30-2"></span>**2.1.1 Material and Optical Properties**

Diamonds are a unique semiconductor structure among different forms of carbon endowed with extraordinary mechanical, thermal, electrical, and optical properties that make them valuable for the scientifc community [\[49\]](#page-157-2). Table [1](#page-32-1) summarizes the main physical and optical properties of the diamond. The general properties of diamonds are as follows: pure diamond is composed only of the element "carbon". The diamond lattice is a face-centered

#### 2 Fundamental Concepts of Color Centers in Diamond and Optical Antennas

<span id="page-31-0"></span>

**Figure 2.1.** Transmission spectrum for a Type IIa diamond window [\[104\]](#page-162-5).

cubic [\(FCC\)](#page-13-7) lattice with two atom basis, where the frst lattice has its origin in (0,0,0) and the second one in  $(\frac{1}{4}, \frac{1}{4})$  $\frac{1}{4}$ ,  $\frac{1}{4}$  $\frac{1}{4}$ ) with a lattice constant of  $a_0$  = 0.357 nm. In a diamond lattice, each carbon atom is surrounded by four neighboring carbon atoms, and the crystal structure is in a tetrahedral arrangement associated with  $SP<sup>3</sup>$  hybridization. The bond length to the neighboring carbon atom is 1.54 Å, and the dimension of the unit cell is 3.567Åin a 109.284◦ angle and a binding energy of 711 kJ/mol. Each unit cell comprises eight atoms and 1.77  $\times$  10<sup>23</sup> atoms/cm<sup>3</sup>, which is the highest atomic density of any terrestrial material. Such properties are responsible for the extreme hardness of diamonds (with the highest Young's modulus  $\approx 1$  TPa). Apart from that, it has a high atomic density (3.5 g/cm<sup>3</sup>), a wide band gap (5.5 eV at room temperature), and is biocompatible. Moreover, diamond has the highest hardness, thermal conductivity, and lowest compressibility compared to different materials. Diamond is extremely chemically inert except for two main situations: at high temperatures, diamond is susceptible to oxidizing agents and when subjected to chemical attack by certain metals. Even though the properties of diamonds are superlative, they are not considered to be the best material due to the above-mentioned reasons [\[49\]](#page-157-2). Regarding the optical properties of diamond, it has a large transmission window ranging from near UV to far IR, thanks to its wide indirect band gap of 5.5 eV [see Figure [2.1\]](#page-31-0) [\[48,](#page-157-1) [49\]](#page-157-2). Since a diamond has covalent bonding, the dipole moment is zero for a pure diamond; hence there is no infrared absorption in the long-wavelength limit. However, diamond lacks frst-order infrared absorption, which makes it one of the most broadly transmitting solid materials with signifcantly less absorption in the visible region. As observed in the transmission spectrum in Figure [2.1,](#page-31-0) between 2.5 µm and 6.7 µm wavelength region, a weak intrinsic absorption exists due to the infrared lattice absorption or multi-photon absorption. The UV absorption edge begins for wavelengths slightly longer than the lowest energy gap at

<span id="page-32-1"></span>

Density	$3.5$ g/cm <sup>3</sup>
Crystal system	Cubic (two FCC shifted by
	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
Lattice parameter	$3.57\AA$
Thermal conductivity	$2 \times 10^3$ W/mK
Dielectric constant	5.7
Refractive index	$\approx 2.4$
Young's Modulus	$\approx$ 1 TPa
First Raman line	1332 cm <sup><math>-1</math></sup>
Band gap	$5.5 \text{ eV}$

**Table 1.** Physical and optical properties of Diamond [\[49\]](#page-157-2).

227 nm, i.e., 5.5 eV. Also, the absorption near the UV edge is a three-body interaction as a result of the indirect band gap of the diamond. A. T. Collins et al. and R. P. Mildren et al. found that the presence of impurities can appreciably alter the absorption, for example, an increment in the level of SP<sup>2</sup> carbon or the level of impurity can increase the absorption in diamond [\[49,](#page-157-2) [105\]](#page-162-6). Apart from that, various types of impurities can also modify the color of the diamond and even cause the diamond to become opaque [\[100\]](#page-162-1). Diamond has a large refractive index of  $\approx$  2.4, hence, exhibiting a large reflection coefficient and a small angle for total internal refection [\[49\]](#page-157-2).

#### <span id="page-32-0"></span>**2.1.2 Diamond Synthesis and Growth**

There are primarily three main ways to synthesize diamonds, such as the high-pressure high-temperature [\(HPHT\)](#page-13-8) method, chemical vapor deposition [\(CVD\)](#page-13-9) method, and the detonation of diamonds [\[100\]](#page-162-1). One of the earliest methods for diamond synthesis was to process graphite to conditions of  $\approx$  55,000 atmospheres and temperatures of  $\approx$  2000°C, known as the [HPHT](#page-13-8) synthesizing method. It is also possible that diamond can be naturally extracted from the lithospheric mantle below the earth's surface, where the [HPHT](#page-13-8) conditions are present. The creation of synthetic diamonds was frst discovered by the General Electric group, including Bundy, Hall, Strong, and Wentorf, in 1955 in the middle of the 20<sup>th</sup> century [\[104\]](#page-162-5). However, this process has several limitations, which can result in a high impurity content in the diamond. For example, contamination can be incorporated from the impure precursor and the reaction vessel. Moreover, the HPHT method is complicated and requires high-cost maintenance equipment [\[49,](#page-157-2) [100\]](#page-162-1). An alternative approach for diamond synthesis is [CVD](#page-13-9) and detonation of nanodiamonds. Both [CVD](#page-13-9) and detonation methods are relatively simple to implement, fexible, and offer excellent control over the incorporation of impurities compared with [HPHT](#page-13-8) method [\[100\]](#page-162-1).

In the diamond growth process, the metastable phase can be achieved from the precursors with high free energy, provided the activation barriers to more stable phases are sufficiently

<span id="page-33-0"></span>

Figure 2.2. Phase diagram of carbon. Diamond is the stable form at sufficiently high temperatures and pressures, whereas graphite is the stable form of carbon at lower temperatures and pressures [\[104\]](#page-162-5).

larger [\[104\]](#page-162-5). However, the formation of the metastable phase is totally dependent on determining the growth conditions at which the rates of competing processes of undesired products are low. Such competing processes over the diamond growth are the spontaneous graphitization of the diamond surface, the nucleation process, and the growth of graphitic deposits. As shown in Figure [2.2,](#page-33-0) graphite exhibits a stable form at lower temperatures and pressures, whereas diamond is in the metastable form at room temperature for pressure around 1 atm. Since the energy state is not the minimum energy state, the diamond does not spontaneously transform into graphite. In diamond growth processes, methane  $(CH_4)$ is used as the source of carbon, while hydrogen  $(H<sub>2</sub>)$  is responsible for terminating the dangling carbon bonds on the growth surface, hence preventing the formation of graphite structure. To prevent the graphitization from dominating over the diamond growth, a higher fraction of  $H_2$  to CH<sub>4</sub> precursor gas ratio is used (generally 96:4). Figure [2.2](#page-33-0) gives an overview of the approximate temperature and pressure conditions to achieve diamond growth. The black circle in Figure [2.2](#page-33-0) represents an approximate region for diamond creation via [HPHT](#page-13-8) method, and the solid black line indicates the region where [CVD](#page-13-9) diamond growth is favorable [\[104\]](#page-162-5).

The general [CVD](#page-13-9) growth process has few variations, such as; microwave plasma [CVD](#page-13-9) [\(MPCVD\)](#page-14-7), hot flament [CVD,](#page-13-9) cathode arc discharge and welding [CVD](#page-13-9) respectively. Since the diamond samples used in this thesis research are fabricated via [MPCVD](#page-14-7) growth technique, only this growth process will be discussed in detail in the following subsection.

#### **Diamond Growth via [MPCVD](#page-14-7)**

The diamond growth process is complex, and a complete understanding of the reaction mechanism is not yet attained [\[104\]](#page-162-5). Figure [2.3\(](#page-35-0)a) is a schematic representation of the diamond growth process via [MPCVD](#page-14-7) method. The primary role of the microwave plasmaassisted machine is to enable the optimal chemical/thermal environment for diamond deposition. The growth process takes two steps; initially, the substrate surface treatment or the nucleation takes place, then the diamond growth. The crucial role of microwave plasma is to create radical species to promote diamond growth, mainly atomic hydrogen and carbon-containing radicals [\[106,](#page-162-7) [107\]](#page-162-8).

In the case of diamond growth by commonly preferred precursor gas mixture methane  $(CH<sub>4</sub>)$  and hydrogen  $(H<sub>2</sub>)$ , the formation of atomic hydrogen and carbon radicals plays a significant role. Primarily,  $CH_4$  and  $H_2$  precursor gas mixture enters a high-temperature energetic region where the plasma ionizes the gases. Then, the ionized species are transported via diffusion or convection throughout the chamber and deposited on the diamond surface. As the surface is stabilized and the graphitic formation is terminated by atomic hydrogen, the atoms form carbon-containing free radicals. Here the molecular hydrogen dissociates into atomic hydrogen, and methane molecules dissociate into  $CH<sub>3</sub>$  and possibly other radicals such as  $CH<sub>2</sub>$  and CH [see Figure [2.3\(](#page-35-0)a)]. Once a vapor phase with enough atomic hydrogen and carbon-containing radicals is formed in the temperature-regulated substrate, the growth process can occur. At last, any remnants of the SP $^3$  and SP $^2$  carbon on the surface will react with the gaseous species creating  $SP<sup>3</sup>$  hybridized carbon. Several factors can affect the uniformity of the deposition, such as the uniformity of the substrate temperature profle and the uniformity of the discharge located adjacent to the substrate [\[106,](#page-162-7) [107\]](#page-162-8).

The environment for a general  $H_2$ -CH<sub>4</sub> deposition process depends on several parameters, such as the substrate temperature, atomic hydrogen fux, carbon-containing radicals flux and composition, the deposition uniformity, and finally, other impurity species flux. Generally, for the [MPCVD](#page-14-7) growth process, microwave radiation at a frequency of 2.45 GHz and temperatures in the range of 800 -  $1100^{\circ}$ C is used [\[106\]](#page-162-7). However, if the substrate temperature is kept too high, the diamond converts to graphite; hence obtaining the correct substrate temperature is critical. The favorable growth condition of diamond deposition via [MPCVD](#page-14-7) is the following: substrate temperature in the range of 1100 - 1500◦C to above 3000◦C, and pressure ranging from 1 to 200 torr. Under this condition, various surface phenomena can occur, like adsorption, desorption, and abstraction reactions necessary for diamond growth [\[107\]](#page-162-8).

<span id="page-35-0"></span>

**Figure 2.3.** (a) Schematic illustration of the chemical processes involved in a diamond [MPCVD](#page-14-7) growth process. The reactant gases are ionized, and radicals are formed. Through various transport mechanisms, the species are transported to the surface and build the diamond structure. (b) Raman spectra of different forms of  $SP<sup>2</sup>$  and  $SP<sup>3</sup>$  bonded carbon [\[48\]](#page-157-1).

There are several characterization tools for [CVD](#page-13-9) diamond, but the most commonly emerged tool is Raman spectroscopy [\[108\]](#page-163-0). Raman spectroscopy provides well-defned spectra corresponding to different carbonaceous compounds, such as graphite, glassy carbon, and amorphous diamond-like carbon [\[108,](#page-163-0) [109,](#page-163-1) [110\]](#page-163-2). By analyzing the spectral peak position and spectral peak width, it is possible to determine phase purity and crystalline perfection. Figure [2.3](#page-35-0) (b) shows the Raman spectra for different forms of  $SP<sup>2</sup>$  and  $SP<sup>3</sup>$ hybridized carbon. A sharp peak centered at a Raman shift from 1331 cm $^{-1}$  to 1335 cm $^{-1}$ at room temperature shown in Figure [2.3\(](#page-35-0)b) corresponds to diamond, while the Raman line corresponding to graphite indicates much broader spectra, with a broad band centered from 1565 cm<sup>-1</sup> to 1585 cm<sup>-1</sup>. When internal compressive stress is applied, the peak frequency up-shifts, while in correlation with temperature, there will be a corresponding downshift in the peak frequency. The reasons for band broadening can be related to internal stress, thermoelastic stress, pure thermal effects, or due to the density of defects in the crystal as well as the crystallite size. Much stronger features appear in regards to microcrystalline graphite at 1350 cm $^{-1}$ , and the peak at 1580 cm $^{-1}$  shifts to lower wave
numbers with decreasing crystalline size [\[108,](#page-163-0) [111,](#page-163-1) [109,](#page-163-2) [110\]](#page-163-3).

In general, the growth conditions used in [MPCVD](#page-14-0) can be adjusted to control the crystallinity of the diamond film. Higher temperatures, lower pressures, and lower  $CH<sub>4</sub>$ concentrations favor the growth of [SCD,](#page-14-1) while lower temperatures, higher pressures, and higher CH<sup>4</sup> concentrations favor the growth of [PCD](#page-14-2) [\[28,](#page-155-0) [112\]](#page-163-4). The following section describes [SCD](#page-14-1) and [PCD](#page-14-2) in detail and how to differentiate them via optical characterization tools.

### **Single Crystalline Diamond (SCD) and Polycrystalline Diamond (PCD)**

There are two main types of diamonds such as: [SCD](#page-14-1) and [PCD](#page-14-2) [\[106,](#page-162-0) [112\]](#page-163-4). A [SCD](#page-14-1) comprises a single, continuous crystal lattice, which is very rare and highly prized for its exceptional hardness, thermal conductivity, and optical properties. [SCD](#page-14-1) is typically grown through [CVD](#page-13-0) method, in which a diamond seed crystal is exposed to a gas containing carbon atoms. The carbon atoms then attach themselves to the surface of the diamond seed crystal, gradually building up the diamond crystal structure until it is large enough to be harvested and cut into gemstones or used in industrial applications. While a [PCD](#page-14-2) is made up of many smaller diamond crystals that have grown together. This type of diamond is much more common than [SCD,](#page-14-1) and is used extensively in industrial applications such as cutting tools, drill bits, and abrasives.

A [PCD](#page-14-2) is typically made by subjecting a mixture of diamond crystals and metal powder to high temperatures and pressures, causing the diamond crystals to bond together and form a dense, hard material. However, the quality of both [SCD](#page-14-1) and [PCD](#page-14-2) diamonds varies signifcantly for both natural and synthetic diamonds since they are incorporated with impurities and defects. The quality can be defned based on several parameters, such as the number of incorporated defects and the Raman signal. A high-quality diamond is created when the fux of atomic hydrogen exceeds the carbon species concentration (such as the  $CH_4/H_2$  ratio). Since the diamond quality is in correlation with the intended application, a simple way of defning diamond quality would be based on the diamond crystal quality. A well-defned diamond crystal indicates a higher-quality deposition regime, whereas poorly defned crystals regard a lower-quality regime [\[112\]](#page-163-4).

The Raman spectra of these two types of diamonds can differ significantly due to their different crystal structures and grain orientations [\[108\]](#page-163-0). A [SCD](#page-14-1) has a highly ordered atomic structure, which gives rise to a sharp and intense Raman peak known as the diamond peak; arises due to the stretching vibration of the carbon-carbon bond in the diamond lattice. The Raman spectrum of [SCD](#page-14-1) typically shows a single, strong diamond peak with little to no peak broadening [\[28,](#page-155-0) [113\]](#page-163-5). The [PCD](#page-14-2) on the other hand, are made up of multiple diamond grains with different crystal orientations. Hence, the Raman

<span id="page-37-0"></span>

**Figure 2.4.** (a) A schematic diagram illustrating the growth of a [PCD](#page-14-2) membrane and the progression of grain structure from the nucleation layer towards the top layer. The [TEM](#page-15-0) image shows the crosssectional view of the [PCD](#page-14-2) growth, with nucleation layer and crystal growth. (b) Raman spectra of a microcrystalline diamond thin film. The figure depicts the outcomes of Raman spectroscopy conducted at an ambient temperature of an as-grown diamond thin flm, exhibiting a prominent peak characteristic of diamond material at 1332 cm<sup>-1</sup> [\[61\]](#page-158-0).

spectrum of [PCD](#page-14-2) shows multiple diamond peaks due to the different orientations of the diamond grains [\[106,](#page-162-0) [112\]](#page-163-4). The number and position of the diamond peaks depend on the orientation of the grains and their interaction with the incident laser. In general, the diamond peaks in [PCD](#page-14-2) are broader and less intense than those in [SCD](#page-14-1) flms due to the random orientation of the grains [\[28,](#page-155-0) [113\]](#page-163-5). Another characteristic feature of [PCD](#page-14-2) in the Raman spectroscopy is the presence of a broad peak known as the graphitic peak. This peak arises due to the presence of graphitic carbon, which is more prevalent in [PCD](#page-14-2) flms due to their disordered atomic structure. The graphitic peak typically appears at around 1580 cm−<sup>1</sup> and is broader and less intense than the diamond peak [\[28\]](#page-155-0). Apart from the [SCD](#page-14-1) and [PCD](#page-14-2) bulk diamond samples, it is also possible to create [PCD](#page-14-2) membranes. Figure [2.4\(](#page-37-0)a) is a schematic representation of the [PCD](#page-14-2) membrane growth and how the grain size evolves from the nucleation layer towards the top layer of the diamond membrane. The [PCD](#page-14-2) membranes are grown from diamond seeds via [MPCVD](#page-14-0) growth process. In this process, a diamond seed is placed on a substrate of our choice, which is then placed in the [CVD](#page-13-0) reaction chamber. A gas mixture containing  $H_2$  and a small amount of  $CH_4$  is introduced into the reaction chamber, and a microwave feld is applied to the gas mixture to create a plasma. The plasma dissociates the  $CH<sub>4</sub>$  molecules into carbon and hydrogen atoms, depositing the carbon atoms on the surface of the diamond seed forming a new layer of a diamond crystal. As the deposition continues, the diamond crystal grows vertically, away from the diamond seed, creating a [PCD](#page-14-2) membrane. The growth process can be controlled by adjusting the concentration of  $CH_4$  in the gas mixture, the pressure, temperature, and the microwave power. By optimizing these parameters, it is possible to grow [PCD](#page-14-2) membranes with high quality and uniformity [\[28\]](#page-155-0).

The grain size of a [PCD](#page-14-2) membrane grown from diamond seeds depends on several factors, including the size of the diamond seeds, the growth conditions, and the growth time [\[28,](#page-155-0) [112,](#page-163-4) [114\]](#page-163-6). Initially, when the diamond seeds are frst deposited on the substrate, and the growth process begins, the diamond crystals are typically small and irregularly shaped, with a wide distribution of sizes. As the deposition continues, the diamond crystals grow and begin to merge, forming larger and more uniform [PCD](#page-14-2) membranes. The grain size of the diamond crystals within the membrane is infuenced by the growth conditions, such as temperature, pressure, gas composition, and the type of plasma used in the growth process. Increasing the temperature and reducing the pressure during the growth process can lead to larger grain sizes while reducing the growth time results in smaller grain sizes [\[28\]](#page-155-0).

In general, [PCD](#page-14-2) membranes grown using [MPCVD](#page-14-0) techniques have grain sizes ranging from several micrometers to tens of micrometers [\[28\]](#page-155-0). The grain size distribution can be characterized using techniques such as scanning electron microscopy [\(SEM\)](#page-14-3) and X-ray diffraction (XRD) analysis. As depicted in Figure [2.4](#page-37-0) (a), the grain size is relatively smaller near the nucleation layer compared to the top surface layer of an [PCD](#page-14-2) membrane. The [TEM](#page-15-0) image shown in Figure [2.4](#page-37-0) (a) clearly shows the evolution of the grain size for a 5 µm [PCD](#page-14-2) membrane grown by [MPCVD](#page-14-0) method. The regulation of grain size in [PCD](#page-14-2) membranes is crucial for enhancing not just their mechanical, thermal, and electrical characteristics but also for tailoring them to suit particular applications that utilize the membranes featuring individual quantum emitters and their close-proximity light-matter interactions.

In a Raman spectrum of diamond, there are several characteristic peaks or lines that provide information about the diamond crystal structure, defects, and impurities [\[108,](#page-163-0) [115\]](#page-163-7). Figure [2.4\(](#page-37-0)b) shows the Raman spectra of a microcrystalline diamond thin flm showing the prominent Raman lines in the Raman spectrum [\[61\]](#page-158-0). The most prominent Raman line in diamonds is the so-called "diamond peak" or "first-order Raman peak," which appears at around 1332 cm $^{-1}$  in the Raman spectrum. This peak results from the inelastic scattering of light by the diamond lattice vibrations and is sensitive to changes in the crystal structure, such as lattice strain and defects. Other Raman lines in diamond include the "carbon peak" or "D peak," which appears at around 1500  $cm^{-1}$  and is related to the presence of SP<sup>2</sup>-hybridized carbon atoms in the diamond lattice, and finally the "G peak," which appears at around 1600 cm<sup>-1</sup> and is associated with the graphitic content in the diamond. However, there are some Raman features in a diamond that appears in the range between  $1000\ \mathrm{cm^{-1}}$  and  $1200\ \mathrm{cm^{-1}}$  related to the lattice vibrations of the diamond

and is referred to as the "diamond lattice modes." These diamond lattice modes are a series of weak Raman peaks or broad bands that are observed in the low-frequency region of the Raman spectrum. The exact position and intensity of these modes depend on the crystal structure and defects present in the diamond sample. As shown here, in Figure [2.4\(](#page-37-0)b), in some cases, a weak Raman peak may be observed around 1150 cm $^{-1}$ , which is sometimes referred to as the "G-prime" peak or "carbon-related peak." This peak is related to the presence of  $SP^2$ -bonded carbon impurities or defects in the diamond lattice [\[110\]](#page-163-3). However, this peak is not a well-defned feature, and its exact position and intensity can vary depending on the sample and experimental conditions [\[110\]](#page-163-3). Hence, by analyzing the intensity, width, and shape of these Raman lines, it is possible to extract valuable information about the crystal quality, defects, impurities, and stress in diamond materials.

# **2.1.3 Physical Classifcation of Diamond**

In natural diamonds, the point defects are categorized based on the foreign atoms and vacancies incorporated during the crystal formation. The physical classifcation of diamonds is strictly based on the optical absorption of nitrogen, boron, and hydrogen-related defects and the paramagnetic absorption of single substitutional nitrogen. Diamond is classifed primarily into type I and type II, determined by the peculiarities of their optical absorption.

# **Type I**

In the type I diamond, the impurity-related optical absorption is dominated by nitrogen defects. The nitrogen content in type I natural diamond is not distributed uniformly; instead, it creates clusters of about 10 atoms in some areas. The type I diamond is again divided into three subdivisions: type Ia, type Ib, and type Ic respectively. Type I diamonds do not show absorption due to substitutional nitrogen atoms. The nitrogen concentration in type Ia is about 500 ppm - 3000 ppm. A pure type Ia diamond should only contain single substitutional nitrogen atoms in concentrations below  $10^{16}$  cm<sup>-3</sup>. Compared with type Ia diamonds, type Ib diamonds contain paramagnetic single substitutional nitrogen atoms as the dominating defects [\[116\]](#page-163-8). Most synthetic diamonds having nitrogen fall into the type Ib category; however, only 1 in 1000 natural diamonds are of this type. The characteristic features of type Ib diamonds are the following: the absorption continuum is at wavelengths below 500 nm, and the absorption peak is at  $2.5 \mu m$ ,  $0.37 \mu m$ ,  $7.4 \mu m$ , 8.8 µm, and 9.1 µm respectively. In a type Ic diamond, a high concentration of dislocation is present. This type of diamond is not related to nitrogen. The absorption continuum of type Ic is at wavelengths below 900 nm, and the characteristic IR absorption is visible at 560 nm.

### **Type II**

A type II diamond shows no optical absorption and paramagnetic absorption related to nitrogen defects. A pure type II diamond should only contain nitrogen content below  $10^{17}$ cm−<sup>3</sup> . Similar to type I diamonds, type II diamond is also sub-categorized into type IIa, type IIb, and type IIc. Type IIa diamonds do not show specific IR optical absorption due to boron and hydrogen impurities in the one-phonon region. Moreover, they usually contain nitrogen content of less than  $10^{18}$  cm<sup>-3</sup>. In type IIb, they show the optical absorption spectrum due to the boron impurities. The characteristic difference between type IIa and type IIb is the absorption tail [the strength of absorption tail is of few  $\text{cm}^{-1}]$  spreading from about 1 eV up to the fundamental band-gap energy of 5.5 eV. When diamonds exhibit dominating hydrogen-related absorption at around 2900 cm $^{-1}$ , they fall into the type IIc category.

### **2.2 Color centers in Diamond**

Color centers in diamond are atomic-scale structural defects or impurities within the diamond crystal lattice that cause the diamond to absorb and refect light in a way that produces colors. These defects occur when an atom or group of atoms within the lattice is missing, replaced, or has an extra atom added, leading to changes in the electronic and optical properties of the diamond. Color centers in diamond are fascinating quantum emitters owing to their extraordinary optical, electronic, and quantum properties that make them useful for a wide range of scientific and technological applications [\[7,](#page-152-0) [18\]](#page-153-0). In this section, we discuss the properties of color centers in section [2.2.1,](#page-40-0) different methods for creating color centers in section [2.2.2,](#page-46-0) explaining briefy on the [SiV](#page-14-4) color centers in section [2.2.3,](#page-51-0) and finally the optical study of [SiV](#page-14-4) color centers are given in section [2.2.4.](#page-54-0)

### <span id="page-40-0"></span>**2.2.1 Properties and Types of Color Centers**

A crystal lattice is a periodic structure of atoms or molecules arranged in a unique manner. Each crystal is made of unit cells with few basis atoms, which repeat themselves throughout the crystal structure. An ideal crystal structure is free of impurities and vacancies; however, a natural crystal is incorporated with different kinds of defects such as vacancies, foreign atoms at lattice sites, interstitial (zero dimension), chains of point defects, dislocations (one dimension), stacking faults, grain boundaries, domain walls (two dimensions), finally the incorporation of macroscopic impurities (three dimensions) [see Figure [2.5\]](#page-41-0) [\[101,](#page-162-1) [115\]](#page-163-7). Figure [2.5](#page-41-0) is a schematic representation of the point defects in a crystal lattice [\[101\]](#page-162-1). The crystalline defects can be classifed mainly into three types, (a) Interstitial atoms: these are the occupation of a position between the equilibrium positions of the ideal lattice atoms, they can also be an impurity atom [see Figure [2.5\(](#page-41-0)a)] (b) Vacancies: they are the missing atoms in the lattice [see Figure [2.5\(](#page-41-0)b)] (c) Substitutional impurities: which are the

<span id="page-41-0"></span>

**Figure 2.5.** Schematic representation of the point defects that can occur in a crystal lattice. (a) Interstitial atom. (b) Vacancy. (c) Substitutional atom [\[101\]](#page-162-1).

replacement of atoms in the host lattice site [see Figure [2.5\(](#page-41-0)c)] respectively [\[101\]](#page-162-1).

The wide band gap ( $\approx$  5.5 eV) material "diamond" is a fascinating crystal structure for the quantum optics community, owing to their ability to host more than 500 optically active point defects, color centers with fuorescence signals ranging from deep ultraviolet (UV) to infrared (IR). Most diamond hosts possess crystal lattice defects of various types, such as anthropogenic or natural, epigenetic or syngenetic [\[101,](#page-162-1) [117\]](#page-163-9). The consequence of these optically active defects on the diamond is that the material properties of the diamond are modifed, and based on that, the diamond is classifed. The most obvious effect is the variation of the diamond's color and semiconductivity, as explained by the band theory.

Figure [2.6](#page-42-0) depicts the electronic states inside the diamond crystal band gap. The radiative electronic transitions inside the diamond band gap give different color appearances to the diamond. As shown in Figure [2.6\(](#page-42-0)a), and Figure 2.6(b), the superposition of  $SP<sup>3</sup>$  orbitals of isolated carbon (C) atom gives rise to the band structure of an infinite solid. The bonding and anti-bonding states are broken down into the valence bands and conduction bands, which are formed via the overlap of the orbitals. A vacancy is created as a result of a missing carbon atom. The four orbitals on the surrounding atoms interact with each other in the tetrahedral environment giving rise to states with  $a_1$  and  $t_2$  symmetry [see Figure [2.6\(](#page-42-0)c)]. Since the interaction between the orbitals is weaker than the C-C interaction, the electronic states related to the defects lie within the band gap of the semiconductor. Figure [2.6](#page-42-0) (d) indicates the incorporation of a nitrogen atom on one of the sites around the vacancy, which further splits the  $t_2$  states [\[115,](#page-163-7) [118\]](#page-164-0).

A vacancy in the diamond corresponds to an empty position in the crystal lattice. They can be created by knocking off a carbon atom via radiation damage. When these vacancies interact with interstitial atoms, they absorb visible light and act as color centers, exhibiting

<span id="page-42-0"></span>

**Figure 2.6.** Schematic representation of the electronic structure of a point defect in diamond. (a) The electronic states correspond to the  $SP<sup>3</sup>$  orbitals on an isolated C atom. (b) The superposition of the orbitals forms the band structure of an infinite solid. (c) A vacancy is created by removing a carbon atom. (d), The electronic states split the  $t_2$  states when an impurity atom such as nitrogen is introduced. [\[118\]](#page-164-0)

green or blue color corresponding to type I diamonds and brown color for type IIa diamonds. Vacancies can be detected by ultraviolet fuorescence and by observing the characteristic absorption lines. The absorption line at 741.2 nm, is known as neutral vacancy or the "GR1" center [\[108,](#page-163-0) [119\]](#page-164-1). As the diamond is annealed above 400◦C, the vacancy migrates and couples with other impurities in the diamond, creating compound defects with other vacancies and interstitial atoms; hence the "GR1" center disappears [\[119\]](#page-164-1). The newly formed compound defects are optically active, and the corresponding color is dependent on the annealing time and the pre-existing defect type. Vacancies can also be created or modifed via various other methods; for example, ion implantation and in-situ doping [a detailed discussion on the creation of color centers is given in section [2.2.2\]](#page-46-0).

### **Properties of Color centers**

The fascinating properties of color centers are discussed below:

(a) **Optical Properties:** Color centers in diamond can absorb and emit light at specifc

### 2 Fundamental Concepts of Color Centers in Diamond and Optical Antennas

wavelengths, leading to their characteristic colors. The absorption and emission spectra of color centers can be measured and analyzed to determine their energy levels and electronic transitions. Various spectroscopic techniques such as absorption spectroscopy and photoluminescence spectroscopy are commonly used to study the optical properties of color centers in diamond. Numerous scientifc studies have employed these techniques to investigate the absorption and emission characteristics of various color centers. For example, references [\[52\]](#page-157-0) and [\[120\]](#page-164-2) provide detailed experimental evidence for the optical properties of NV centers in diamonds.

- (b) **Electronic properties:** Many color centers in diamond possess unpaired electron spins, making them suitable for spin-based applications and quantum information processing. The spin states of color centers can be manipulated and detected using techniques such as electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR). The electronic properties of color centers make them useful for a range of applications in electronics and photonics. For example, [NV](#page-14-5) centers in a diamond can be used as single-photon sources and qubits for quantum information processing [\[52\]](#page-157-0). In 2008, J.R. Maze et al. showed that the electronic structure of the [NV](#page-14-5) center, which includes an unpaired electron spin, makes it an attractive candidate for quantum information processing and sensing applications [\[121\]](#page-164-3).
- (c) **Sensitivity to temperature and pressure:** Certain color centers in diamond exhibit sensitivity to external factors such as temperature, magnetic felds, and strain, enabling their use as sensors or probes for applications in geophysics, material science, and environmental monitoring [\[36\]](#page-155-1). The changes in the optical or spin properties of color centers can be correlated with the environmental conditions they are exposed to, enabling sensitive measurements. In 2020, A. Kuwahata et. al. reported that the [NV](#page-14-5) centers in a bulk diamond can be used as a magnetometer for detecting magnetic nanoparticles in biomedical applications [\[50\]](#page-157-1). Similarly, in 2018, S. Lindner et al. reported that [SiV](#page-14-4) color centers in nanodiamonds exhibit a strongly inhomogeneous distribution with regard to the center wavelengths and linewidths of the [ZPL](#page-15-1) emission at room temperature. Moreover, they do exhibit sensitivity to pressure changes, making them useful for pressure sensing applications [\[122\]](#page-164-4).
- (d) **Stability:** The stability and dynamics of color centers play a crucial role in their optical and spin properties and determine their suitability for different applications. Diamond is a very stable material, and color centers in diamond are generally stable at room temperature and do not degrade over time. This makes them attractive for long-term applications, such as sensing and imaging. For example, boron-doped diamond has been used as a stable electrochemical electrode for sensing applications [\[123\]](#page-164-5). Understanding the stability of color centers and their response to external perturbations is important for their practical utilization.
- (e) **Quantum properties:** Finally, color centers in diamond exhibit quantum properties,

<span id="page-44-0"></span>

**Figure 2.7.** Schematic representation of the crystal lattice structure of color centers in diamond. (a) Atomic structure of a nitrogen-vacancy [\(NV\)](#page-14-5) center in diamond. (b) Atomic structure of germanium vacancy [\(GeV\)](#page-13-1) color center. (c) Atomic structure of tin vacancy [\(SnV\)](#page-14-6) color center [\[52,](#page-157-0) [127,](#page-165-0) [128\]](#page-165-1)

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such as long spin coherence times [\[52\]](#page-157-0) and entanglement [\[124\]](#page-164-6), that make them useful for quantum sensing and quantum computing applications [\[53,](#page-157-2) [93,](#page-161-0) [97\]](#page-161-1). For example, L. Childress et al. and R. Hanson et al. showed that [NV](#page-14-5) centers in diamond had been used to demonstrate high-fidelity quantum operations and entanglement generation [\[125\]](#page-164-7). Similarly, the [SiV](#page-14-4) center in a diamond had been shown to exhibit coherent spin manipulation and entanglement with nearby spins achieving 89% fidelity [\[126\]](#page-164-8).

#### **Types of Color Centers**

The presence of color centers in diamond, which are atomic-scale defects or impurities, can give rise to a variety of colors and optical properties [\[6,](#page-152-1) [49\]](#page-157-3). There are more than 500 color centers in diamond discovered so far, but, only a few have been recognized as potential candidates for various applications. In the following section, we will examine some of the major color centers that have been extensively studied in recent years.

### **Nitrogen-Vacancy [\(NV\)](#page-14-5) Centers**

The [NV](#page-14-5) center is one of the most well-studied color centers in diamond, and it has attracted signifcant attention due to its unique combination of long spin coherence times and optical stability at room temperature [\[52\]](#page-157-0). The [NV](#page-14-5) center is created when a nitrogen atom substitutes for a carbon atom, and an adjacent carbon vacancy [\(VC\)](#page-15-2) is formed [see

Figure [2.7\(](#page-44-0)a)]. The [NV](#page-14-5) center exhibits a spin-triplet ground state, with a spin-1 electronic ground state and a spin-1 excited state. The ground state can be optically polarized and read out using green laser light, while the excited state can be accessed using red or near-infra-red [\(NIR\)](#page-14-7) light. The [NV](#page-14-5) center has emerged as a promising candidate for a range of applications, including sensing, imaging, and quantum information processing [\[22,](#page-154-0) [53,](#page-157-2) [120\]](#page-164-2). One of the most notable properties of the [NV](#page-14-5) center is its ability to sense magnetic felds with high sensitivity at room temperature. This makes the [NV](#page-14-5) center a promising candidate for magnetic feld sensing in a wide range of applications, including materials science, geology, and biomedical imaging [\[129\]](#page-165-2). The [NV](#page-14-5) center has also been used as a single-photon source, which is a critical component for quantum information processing applications. Single-photon sources based on [NV](#page-14-5) centers have demonstrated high photon purity, indistinguishability, and stability, which are essential for quantum applications [\[5\]](#page-152-2).

In addition to sensing and quantum applications, the [NV](#page-14-5) center has also been used for imaging applications, including fuorescence microscopy and magnetic resonance imaging (MRI). The [NV](#page-14-5) center's unique properties allow for high-resolution imaging of biological systems with sub-cellular resolution [\[51\]](#page-157-4). Despite the promising properties of the [NV](#page-14-5) center, some challenges still need to be addressed. For example, the [NV](#page-14-5) center's emission in the visible region is limited by its broad [ZPL](#page-15-1) emission [\[52\]](#page-157-0). Efforts are currently underway to develop techniques for efficiently collecting and detecting the [NV](#page-14-5) center's optical emission [\[52\]](#page-157-0).

# **Germanium Vacancy [\(GeV\)](#page-13-1) Centers**

Germanium vacancy [\(GeV\)](#page-13-1) centers are one of the recently discovered color centers in diamond exhibiting long spin coherence times and optical stability at room temperature [\[14\]](#page-153-1). The electronic and optical properties of [GeV](#page-13-1) centers make them attractive candidates for quantum information processing, sensing, and optoelectronics applications [\[127\]](#page-165-0). The [GeV](#page-13-1) center is created by substituting a germanium atom for a carbon atom in the diamond lattice and inducing a nearby [VC,](#page-15-2) as shown in Figure [2.7\(](#page-44-0)b). These centers have a spintriplet ground state and are characterized by strong absorption in the ultraviolet (UV) region and narrow emission lines in the visible and [NIR](#page-14-7) regions of the spectrum which are attributed to [ZPLs](#page-15-1) and phonon sidebands. The [ZPLs](#page-15-1) are narrow spectral peaks that arise from the radiative recombination of excited electron-hole pairs, while the phonon sidebands are broad features that arise from coupling between the excited electron and lattice vibrations.

Furthermore, the [GeV](#page-13-1) center has unique optical properties that make it useful for imaging applications. For instance, the [GeV](#page-13-1) center emits light in the [NIR](#page-14-7) region of the spectrum, which is ideal for imaging deep inside biological tissues.

### **Tin-Vacancy [\(SnV\)](#page-14-6) Centers**

Tin-vacancy [\(SnV\)](#page-14-6) color centers are another type of atomic-scale defect in a diamond that exhibits interesting optical and electronic properties [\[128\]](#page-165-1). As shown in Figure [2.7\(](#page-44-0)c), the [SnV](#page-14-6) centers are created when a tin atom substitutes for a carbon atom in the diamond lattice and an adjacent carbon atom is missing, creating a vacancy. [SnV](#page-14-6) centers exhibit a unique optical absorption spectrum, with peaks in the visible and [NIR](#page-14-7) regions of the spectrum. The electronic structure of [SnV](#page-14-6) centers is characterized by a ground state with a spin-1/2 electronic spin and a frst excited state with a spin-1/2 electronic spin. The excited state is located at an energy of around 1.3 eV above the ground state, making it accessible by visible light. The spin coherence times of [SnV](#page-14-6) centers are relatively long, with values of up to 200 us measured experimentally [\[130\]](#page-165-3).

Similar to other color centers in diamond, [SnV](#page-14-6) centers exhibit a unique combination of long spin coherence times and optical stability at room temperature, making them promising candidates for various applications in quantum technology [\[128,](#page-165-1) [130\]](#page-165-3). They also exhibit a strong coupling to the vibrational modes of the diamond lattice, which can be used to control their electronic spin states. One of the most important properties of [SnV](#page-14-6) centers is their optical transitions, which allow for their manipulation and readout using laser light. The [SnV](#page-14-6) centers exhibit optical transitions in the visible and [NIR](#page-14-7) spectral ranges, which can be used for spin initialization, manipulation, and readout. For example, the groundstate spin can be optically initialized using green laser light, and the excited-state spin can be read out using red or [NIR](#page-14-7) light. The optical transitions of [SnV](#page-14-6) centers have been experimentally studied and modeled using various techniques, including time-resolved photoluminescence and coherent control measurements [\[131\]](#page-165-4). In addition, [SnV](#page-14-6) centers have been used for sensing applications, including the detection of magnetic felds and temperature [\[128\]](#page-165-1). Overall, [SnV](#page-14-6) centers in diamond offer a unique combination of optical and electronic properties that make them promising candidates for a range of applications in quantum information processing, sensing, and optoelectronics.

<span id="page-46-0"></span>Other types of color centers in diamonds include the nitrogen-vacancy-nitrogen (NVN) center, the nitrogen-vacancy-silicon (NVS) center, and the [SiV](#page-14-4) center, etc [\[6,](#page-152-1) [15\]](#page-153-2). These color centers exhibit a range of optical and spin properties, making them useful for various applications. The most well-studied color centers in diamonds include the [NV](#page-14-5) center and the [SiV](#page-14-4) center. Each type of color center has unique properties and potential applications in sensing, imaging, and quantum information processing, among other research areas. Further exploration of the properties of color centers in diamond is expected to lead to new discoveries and applications in various felds. A detailed study on the [SiV](#page-14-4) color center is given in section [2.2.3](#page-51-0) and in section [2.2.4.](#page-54-0)

# **2.2.2 Creation of Color Centers**

Color centers can be found naturally or can be created via synthetic methods. However, for high-quality samples, the defect concentration is  $< 1$  ppm, which is too low for many of the intended applications. Moreover, a controlled creation of color centers is a prerequisite for many applications. This section focuses on two general methods for creating defect centers in diamonds: "ion implantation" with the required ion and "in-situ doping" with a dopant from a solid or gaseous source during the diamond growth. Each method has its pros and cons, and not all methods suit every application. The synthetic methods for creating color centers in diamond depend on various factors, such as the annealing temperature, vacancy density, and local charge environment [\[132,](#page-165-5) [133,](#page-165-6) [134\]](#page-165-7).

### **In-situ Doping**

Defect centers formed by activating incorporated ions in grown diamonds are known as "in-situ doping" method [\[115,](#page-163-7) [135,](#page-165-8) [136\]](#page-165-9). In this process, defect centers are formed by creating additional vacancies in doped diamonds by irradiation with energetic neutrons, electrons, or ions, followed by thermal annealing above 600◦ C. Here, the newly created vacancies are combined with the ions already present in the diamond lattice. Color centers created via this method are often randomly distributed because controlling the creation depth relative to the surface is quite challenging, while defects are created along the path of the particle in the lattice, and the scattering cross section varies for every species.

The physics behind the doping process is relatively straightforward, as it incorporates donor or acceptor atoms in the semiconductor material, resulting in a p-type or n-type semiconductor. As a result, the conductivity of the diamond is affected by the incorporation of foreign atoms like boron or phosphorous. P-type doping can be performed in a natural diamond via incorporating boron during the [CVD](#page-13-0) growth process. However, to achieve effcient p-type doping, the nitrogen concentration in the diamond should be sufficiently low [\[137\]](#page-166-0). In the case of an n-type semiconductor, phosphorous serves as an electron donor, providing additional electrons to create the abundance of electrons required for n-type semiconductors [\[115,](#page-163-7) [135,](#page-165-8) [136\]](#page-165-9).

For the creation of [NV](#page-14-5) centers, no additional dopant source is often necessary because nitrogen is an abundant component in the atmosphere and can be naturally found in a diamond. The diamond growth at low pressures always results in residual nitrogen in the chamber, which can be incorporated into the diamond during growth. It is also possible to create individual [NV](#page-14-5) centers in isolated diamond nanocrystals, but the reproducibility is low. Other color centers like the [SiV](#page-14-4) center or Cr-related single photon emitters were created by choosing an appropriate substrate: silicon, silicon dioxide, and sapphire. Figure [2.8](#page-48-0) is a schematic representation of the "in-situ doping" of [SiV](#page-14-4) centers on a diamond

<span id="page-48-0"></span>

**Figure 2.8.** Schematic representation of "in-situ doping" of [SiV](#page-14-4) centers on a diamond membrane (a) Diamond membrane grown on top of a silicon substrate via [MPCVD](#page-14-0) growth process. (b) Doping process: silicon atoms are incorporated into the diamond during the [MPCVD](#page-14-0) growth. (b) Creation of free-standing diamond membrane supported by silicon frame. The incorporated silicon converted into [SiV](#page-14-4) upon thermal annealing process.

membrane during the [MPCVD](#page-14-0) diamond growth process [\[28\]](#page-155-0). The diamond membrane is grown on a silicon substrate via [MPCVD](#page-14-0) growth technique, where the silicon substrate is seeded with diamond nanoparticles for high nucleation densities [see Figure [2.8\(](#page-48-0)a)]. Since the diamond growth happens at elevated temperatures, silicon atoms diffuse from the substrate and are incorporated into the diamond membrane, depicted in Figure [2.8\(](#page-48-0)b). Finally, a free-standing diamond membrane with diffused silicon ions is created by removing the silicon substrate using the deep [RIE](#page-14-8) process, which is shown in Figure [2.8\(](#page-48-0)c). To activate the diffused ions and to form active [SiV](#page-14-4) color centers, the membrane is thermally annealed at temperatures above 1500◦C [\[28\]](#page-155-0).

An alternative method in "in-situ doping" is to place, e.g., small pieces of silicon alongside the sample, which is not affected by the diamond growth process [\[138\]](#page-166-1). For precise control of the dopant amount, it is better to choose a gaseous component like silanes or nickelocenes or even additional nitrogen or nitrogen-containing gas species. Turning the source of the dopant on and off makes it possible to control the thickness of the layer with incorporated impurities and depth [\[115,](#page-163-7) [135\]](#page-165-8). Consequently, it is possible to generate a very thin and shallow layer of color centers in a diamond flm with the possibility to structure the diamond film afterward to create confinement around the incorporated color centers. An alternative way of controlling the depth of color centers relative to the diamond surface is via delta doping [\[138\]](#page-166-1). The delta doping method was primarily demonstrated for creating [NV](#page-14-5)<sup>−</sup> and the [SiV](#page-14-4)<sup>−</sup> color centers. The delta doping process for creating [NV](#page-14-5) is as follows:  $N_2$  gas is introduced during the plasma-enhanced chemical vapor deposition [\(PECVD\)](#page-14-9) diamond growth, and as a result, a nanometer-thick nitrogendoped layer was formed to create [NV](#page-14-5) centers. Similarly, [SiV](#page-14-4) color centers are created by controlling the silicon concentration during the growth, giving control of the concentration over two orders of magnitude.

<span id="page-49-0"></span>

**Figure 2.9.** (a) Image of a bare diamond sample covered by aluminum foils after implantation. The metal degraders help to control the depth of ion implantation. (b) Ion distribution, in terms of ions, stopped per nanometer per ion implanted for 8, 9, 9.5, 10, 11.2 MeV energy, as calculated by [SRIM](#page-14-10) calculations [\[133\]](#page-165-6).

#### **Ion Implantation and Annealing**

One of the most commonly used techniques to modify a material's physical, chemical, and optical properties is ion implantation, where external impurities are introduced into the matrix. In this method, atoms are ionized, accelerated with an electric feld, and bombarded into the target material. The critical factor determining the range of implanted ions is the acceleration energy, which ranges from a few keV to MeV. Due to the introduction of external atoms or impurities via bombardment with high-energy ions, the crystal gets damaged. Subsequent thermal annealing above 600◦C under vacuum conditions is a vital method to recover the crystal lattice and hence activate the defect centers into their favorable locations. A combination of ion implantation with thermal annealing for activating the dopant or to remove defects is a technologically essential and routinely employed process in the semiconductor industry. Using Monte Carlo modeling "stopping and range of ions in matter [\(SRIM\)](#page-14-10)" calculations, it is feasible to forecast the implantation profile by selecting various parameters such as ion species, acceleration energy, mass (if isotopes are involved), angle of incidence, different types of target materials (including elements, compositions, or dielectrics), layer thicknesses, and the number of layers [\[133\]](#page-165-6). The output data includes the ion range (depth), distribution, and the number of vacancies produced. By considering the density and lattice spacing, the software estimates different probabilities of collisions among the implanted ions. Additionally, information is provided on the number of generated vacancies and their distribution in the crystal, the stopping range of the implanted ions and their distribution, damage events, and the concentration of the created vacancies.

A [FIB](#page-13-2) is utilized in ion implantation to enable fne control over the number of implanted

ions to introduce the ions in the desired position along the three directions. The average number of ions can be fne-tuned to even a single ion per bunch; hence deterministic implantation of a specific number of ions in the desired position is possible in this method. Moreover, by controlling the energy of the ions, the depth of ion implantation can be controlled. As shown in Figure [2.9\(](#page-49-0)a), a bulk diamond sample is partially covered with 1-2 aluminum foils; they are used as energy degraders during silicon ion implantation to create [SiV](#page-14-4) color centers. The thickness of the aluminum energy degraders has already been taken into account during the [SRIM](#page-14-10) simulations to calculate the required ion energy and the range of the silicon ions in a diamond. Figure [2.9\(](#page-49-0)b) represents the ion distribution calculated by the [SRIM](#page-14-10) simulation for creating [SiV](#page-14-4) color centers via silicon ion implantation. The simulation was performed for 5 different energies, 8, 9, 9.5, 10, and 11.2 MeV, respectively. When the energy is lower, say at 8 MeV with the presence of 2 aluminum foils, the silicon ion depth range inside the diamond is 80 nm, with the distribution peak inside aluminum, and only the extreme Bragg peak tail lying inside the diamond material. Under such conditions, ion transmission in diamond is only 1.4%. When working at the highest energy (11.2 MeV), the silicon ion depth range inside the diamond extends up to 600 nm, with the distribution peak at about 100 nm from the diamond surface, which corresponds to a transmission of about 70% [\[113,](#page-163-5) [133\]](#page-165-6). The silicon ion implantation caused damage to the crystal lattice structure of the diamond; hence the recovery of the crystal lattice is achieved via thermal annealing. To activate the [SiV](#page-14-4) color centers, a thermal annealing process is performed in the range of  $1000 - 1200 °C$  [\[133\]](#page-165-6).

Recently, L. Hunold et al. presented an implantation technique that enabled the controlled creation of [SiV](#page-14-4) color centers in a matrix implantation fashion [\[113\]](#page-163-5). The beam was prealigned on the sapphire substrate, and the sample was mounted in a way that it could be moved later on to the beam position. This procedure also enabled the acquisition of information about the size of the beam spot. Figure [2.10\(](#page-51-1)a), Figure [2.10\(](#page-51-1)b) represents a diagram illustrating the setup employed for this process. Then, the silicon ion beam was accelerated and directed towards the pinhole [see Figure [2.10\(](#page-51-1)b)]. The beam then passes through the pinhole and reaches the sample holder, which was equipped with an aperture covered by the sapphire substrate. When the energetic ions interact with the substrate, they cause the emission of photoluminescent light from the targeted location. Hence, this implantation technique offers great control over both lateral and horizontal positions via utilizing a 1 µm aperture pinhole, enabling the creation of [SiV](#page-14-4) color centers in a matrix fashion, as displayed in Figure [2.10\(](#page-51-1)c). Employing aluminum retarders, the depth, and fuence of the implantation were precisely controlled down to a single emitter level. Figure [2.10\(](#page-51-1)c) is a confocal scan of [SiV](#page-14-4) color centers in a [SCD](#page-14-1) sample created by the ion implantation technique mentioned above. However, the scattering ions created from the pinhole proposed certain limitations in terms of unwanted background signals and the uncontrolled creation of emitters [\[113\]](#page-163-5).

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<span id="page-51-1"></span>

**Figure 2.10.** (a) Schematic of the beam imaging system. (b) The beam enters the setup from the left side and travels through a pinhole before reaching the sapphire plate. A piezo stage is mounted for holding the components, and a longitudinal micrometer stage for adjusting the camera position. (c) Confocal scan of [SiV](#page-14-4) color centers created in matrix form using precise ion implantation [\[113\]](#page-163-5).

The main drawback of the ion implantation technique is the generation of a relatively high number of structural defects (vacancies), random activation and orientation of the centers, and the uncertain activation yield of the implanted centers of either as low as few percent [in the case of [SiV](#page-14-4) centers] or as high as 80% [for [NV](#page-14-5) in diamond]. Moreover, in the case of complex color centers, the presence of structural defects affects the activation of color centers. Hence to improve the activation yield of the color centers, femtosecond laser micro-machining followed by proper annealing has emerged as a promising technique, where the amount of defects created is controlled via damaging the lattice with carbon or proton [\[132,](#page-165-5) [133\]](#page-165-6).

<span id="page-51-0"></span>In this thesis, we are focusing mainly on the [SiV](#page-14-4) color centers in thin [PCD](#page-14-2) diamond created via ion implantation. The section [2.2.3](#page-51-0) discusses more on the creation of [SiV](#page-14-4) on diamond samples in general.

<span id="page-52-0"></span>

**Figure 2.11.** Introduction to the [SiV](#page-14-4)<sup>−</sup> centre. (a) Illustrates the split ground and excited states of the [SiV](#page-14-4)<sup>−</sup> center, resulting in four optical transitions labeled A through D. (b) Displays the fuorescence spectrum of [SiV](#page-14-4)<sup>-</sup> ensemble in [001]-oriented bulk diamond at 4 K, generated through non-resonant excitation at 700 nm. The dominant transitions from the <sup>28</sup>Si isotope are labeled A through D as two doublets, while the weaker, red-shifted transitions come from  $29$ Si and  $30$ Si. The inset shows the atomic structure of the [SiV](#page-14-4)<sup>−</sup> center, with the silicon atom (blue) in a split-vacancy confguration between the unoccupied lattice sites (dashed circles) and the nearest neighbor carbon atoms (grey) [\[115\]](#page-163-7).

### **2.2.3 The Silicon-Vacancy Color Centers**

The negatively charged [SiV](#page-14-4) center is a promising color center in diamond for quantum information processing and sensing applications. The crystal structure of a [SiV](#page-14-4)<sup>−</sup> center can be described as follows: a silicon atom lying between adjacent vacancies in a diamond lattice. The silicon atom in the [SiV](#page-14-4) color center is not located on the carbon lattice site; instead, it moves along the  $< 111 >$  direction of the diamond lattice toward the neighboring vacancy creating the split-vacancy site. The symmetry class of [SiV](#page-14-4) center is  $D_{3d}$ . In the defned lattice system, the silicon atom is surrounded by six neighboring carbon atoms, three on each vacant side. The bonds between those atoms are mainly responsible for the optical properties of the color center. Here, the Si-C bond is larger than the common C-C bond in the diamond. An [SiV](#page-14-4) can exist in both neutral as well as in a negatively charged state. An [SiV](#page-14-4)<sup>−</sup> center is more commonly pronounced in diamond [\[115\]](#page-163-7).

Since the silicon atom sits interstitially in the center of the split-vacancy, it does not couple strongly with the diamond phonons, resulting in strong [ZPL](#page-15-1) with weak phonon side bands. An [SiV](#page-14-4)<sup>−</sup> has a strong [ZPL](#page-15-1) at around 740 nm with a narrow linewidth ranging from 0.7 - 5 nm at room temperature [\[7\]](#page-152-0). Moreover, at room temperature, 70% of the [SiV](#page-14-4) fuorescence is concentrated in the sharp [ZPL](#page-15-1) [\[7\]](#page-152-0). Hence the Debey-Waller factor (DW) is quite significant compared to an [NV](#page-14-5) color center in diamond. This strong [ZPL](#page-15-1) emission arises from the transition between the upper excited state  $(E_u)$  to the lower ground state (*Eg*), marked as transition "A" in Figure [2.11\(](#page-52-0)a). Since the [SiV](#page-14-4)<sup>−</sup> is a spin 1/2

system containing ground and excited state, at lower temperatures ( $\approx$  4K), both energy states split up in two branches by the orientation of the spin (creating the fine structure) [\[139\]](#page-166-2). Figure [2.11\(](#page-52-0)b) shows the fuorescence spectrum of the [SiV](#page-14-4) center exhibiting four major peaks (labeled as A, B, C, and D) at a lower temperature of 4K. The inset in Figure [2.11\(](#page-52-0)b) indicates the lattice structure of the [SiV](#page-14-4)<sup>−</sup> color center. As shown in Figure [2.11\(](#page-52-0)a), the lower intensity of the frst two peaks in Figure [2.11\(](#page-52-0)b) is presumably based on the fact that they refer to transitions originating from the upper branch of the excited state (A and B). However, transitions C and D appear more intense since they are associated with the transitions directly from the lower excited state to the lower ground state. In this case, the selection rules for fne structure and spin-orbit coupling involve changes in the total angular momentum quantum number (J) and the magnetic quantum number (*M*<sub>*I*</sub>). The selection rule says that:  $\Delta J = 0, \pm 1$  and  $\Delta M_I = 0, \pm 1$ . Since transitions C and D involve changes in J and are consistent with the allowed values of ∆*J* and ∆*M<sup>J</sup>* results those transitions to be more probable and intense, as shown in Figure [2.11\(](#page-52-0)b). The larger separation of the two middle peaks is due to the larger fne splitting of the excited state (fve times the ground state splitting) [\[139\]](#page-166-2). Apart from the very narrow strong [ZPL](#page-15-1) emission, [SiV](#page-14-4)<sup>−</sup> has a very short photoluminescence lifetime of 1 - 4 ns [\[44\]](#page-156-0).

#### **Creation of SiV color center via Ion Implantation**

The [SiV](#page-14-4) color centers are not naturally found in diamond, whereas they are very commonly visible in a synthetic diamond as a result of doping with silicon during the diamond growth [due to the etching of silicon substrates, quartz reactor walls, or windows in the [CVD](#page-13-0) growth plasma] [\[28\]](#page-155-0). The main two approaches to create [SiV](#page-14-4) are in-situ doping and ion implantation. Generally, silicon atoms are already present in most of the [CVD](#page-13-0) fabricated diamond flms via diffusion from a silicon-containing substrate and/or from the silica reactor windows [\[135\]](#page-165-8). This process creates [SiV](#page-14-4) centers without further annealing and ion implantation procedures [\[115\]](#page-163-7). By balancing a dopant source, the depth of impurities can be controlled in this method. It is also possible to ensure that up to one [SiV](#page-14-4) center appears per grain, provided the growth rate is known. However, this method does not have lateral control of the [SiV](#page-14-4) creation and leads to the clustering formation of [SiV](#page-14-4) centers [\[136\]](#page-165-9).

Using [FIB,](#page-13-2) it is possible to implant the ions in the desired position with fne control over the number of ions implanted [\[16,](#page-153-3) [133,](#page-165-6) [140\]](#page-166-3). However, it results in structural damage to the crystal in terms of changes in the bonding confguration, thereby affecting the chemical and physical properties of the material [\[141\]](#page-166-4). Hence, restoring the diamond lattice after implantation is necessary by promoting both vacancy-interstitial and siliconvacancy recombination via thermal activation of vacancy diffusion in a high vacuum chamber (thermal annealing). The controlled positioning of the vacancy centers on the sample is the leverage of this technique, however, at the expense of random activation and orientation of the centers. A further advantage is probing the changes that occurred

due to ion implantation via detecting the presence of the  $SP<sup>2</sup>$  graphitic phase at ambient conditions, where the  $SP<sup>3</sup>$  phase of the diamond is metastable at ambient conditions and  $SP<sup>2</sup>$  graphitic binding is stable.

In this work, [SiV](#page-14-4) color centers were created via shallow ion implantation on nanometerthick [PCD](#page-14-2) membranes at our recently developed facility. The facility consists of a High Voltage Tandem accelerator (3 MeV) along with a Negative sputter ion source (HVEE 860), shown in Figure [2.10\(](#page-51-1)a). A pulsed ion beam was generated by the electrostatic defector facility DEFEL (Electrostatic DEFlector) at the INFN LABEC laboratory in Florence [\[142\]](#page-166-5). We were thus able to implant  $Si^{3+}$  ions accelerated in the range of 0.2 - 15 MeV [according to the accelerating voltage and the state of charge of the selected ions] with a broad range of fluences, from  $10^8$  to  $10^{15}$  cm<sup>-2</sup> [see Figure [2.9\(](#page-49-0)a)]. Moreover, using aluminum foils, we controlled the implantation depth by degrading the ion energy down to a few tens of keV, as shown in Figure [2.9\(](#page-49-0)b) [\[133,](#page-165-6) [132\]](#page-165-5). To activate [SiV](#page-14-4) color centers in the [PCD](#page-14-2) membranes, we performed an annealing step in an alumina oven at high vacuum conditions. The heating ramp starts from 20◦*C* to reach 1150◦*C* in 2 hours to maintain the low pressure of the gases desorbed during heating, and the temperature stays at 1150◦*C* for 1 hour.

# <span id="page-54-0"></span>**2.2.4 Optical Study of Silicon Vacancy Centers**

This section provides a comprehensive examination of the nuanced disparities in the optical properties of [SiV](#page-14-4) color centers, exploring the variations observed in two distinct environments: bulk diamond and [PCD](#page-14-2) membranes. [SiV](#page-14-4) color centers, renowned for their pivotal role in quantum optics and emerging quantum technologies, exhibit intricate variations in their optical characteristics contingent upon their local surroundings. These distinctions encompass a spectrum of optical parameters, emission spectra, quantum yields, radiative decay rates, and more, offering a multifaceted view of the differences in their behavior.

Understanding these discrepancies is instrumental in tailoring the deployment of [SiV](#page-14-4) color centers in various felds, including quantum information processing, quantum communication, and sensing applications. While bulk diamond represents the pristine environment, [PCD](#page-14-2) membranes introduce complexity through their unique structural characteristics. The discussion delves into the underlying factors responsible for these differences, emphasizing the infuence of crystallographic variations and the impact of defects or grain boundaries. These intricacies highlight the signifcance of the local environment in shaping the optical properties of [SiV](#page-14-4) color centers. Numerous studies have contributed significant insights into these variations. For example, the work of C. Dawedeit et al. highlighted the infuence of grain boundaries in [PCD](#page-14-2) membranes on [SiV](#page-14-4) color center properties, providing a deeper understanding of the role played by crystallographic defects [\[114\]](#page-163-6). Moreover, modifcations were observed in the emission spectra of [SiV](#page-14-4) centers within [PCD](#page-14-2) membranes, shedding light on the spectral alterations arising from the distinctive environmental conditions in these structures [\[143\]](#page-166-6).

In general, the characterization of the [SiV](#page-14-4) color center in diamond was performed using a home-built temporal and spectrally resolved confocal-microscope setup with a Hanbury-Brown and Twiss [\(HBT\)](#page-13-3) interferometer [\[133\]](#page-165-6). To image individual color centers, a widefeld illumination system can be used to excite the sample, and the fuorescence image of the emitters is captured by an electron multiplying CCD [\(EM-CCD\)](#page-13-4) camera. Figure [2.12\(](#page-56-0)a) shows the confocal scanning image of [SiV](#page-14-4) color centers in a 3  $\mu$ m thick diamond membrane. The emitters can be excited by a coherent monochromatic laser. Using a high numerical aperture [\(NA\)](#page-14-11), coverslip corrected oil immersion objective, both excitation and collection of the signal from the quantum emitters can be performed. The photoluminescence [\(PL\)](#page-14-12) spectra of the emitters are analyzed utilizing a spectrometer. A high [NA](#page-14-11) objective can be utilized for both excitation and collection of fuorescence signal from the [SiV](#page-14-4) centers for lifetime studies. Moreover, the single photon purity of a single [SiV](#page-14-4) color center can be monitored via a second-order intensity autocorrelation function using the [HBT](#page-13-3) interferometer setup. In a [HBT](#page-13-3) system, the laser excites [SiV](#page-14-4) centers, and the corresponding [PL](#page-14-12) signal from the sample is spectrally fltered to suppress the laser line. A 50/50 non-polarizing beam splitter sends the emitted photons to two [APDs](#page-13-5). These detectors are connected to the start-stop time-interval analyzer of a time-correlated single photon counter [\(TCSPC\)](#page-15-3) and the delay between the arrival times of two emitted photons is repeatedly measured and cretaed the histogramm with picosecond time resolution. To avoid cross-talk between the two APDs, a band-pass flter can be placed in front of the [APDs](#page-13-5).

The [PL](#page-14-12) spectra of [SiV](#page-14-4) color centers in the diamond membranes have a spectral range of 738 - 740 nm at room temperature, having a line width of 6 - 10 nm. Figure [2.12\(](#page-56-0)b) shows the comparison of [PL](#page-14-12) spectra of [SiV](#page-14-4) color centers in a bulk diamond sample as well as in [PCD](#page-14-2) membranes of various thicknesses ranging from 55 nm, 100 nm, and 3  $\mu$ m. The [PCD](#page-14-2) membranes are silicon ions implanted with an ion fluence of the order  $10^8$  to  $10^{15}$  cm<sup>-2</sup>. Here, the diamond membranes utilized are fabricated on a silicon substrate using [MPCVD](#page-14-0) followed by a [RIE](#page-14-8) method. The existence of contamination from the silicon substrate on the diamond membrane induces a high background in the [PL](#page-14-12) spectra of [SiV](#page-14-4) color centers in a diamond membrane, compared to those of [SiV](#page-14-4) centers in bulk diamond, is visible in the Figure [2.12\(](#page-56-0)b). The additional peak appeared at  $\approx$  720 nm in the [PL](#page-14-12) spectra of [SiV](#page-14-4) center in diamond membranes corresponding to the Raman "G" line [\[144\]](#page-166-7) of amorphous graphite at 1580 cm<sup>-1</sup>. The inset in Figure [2.12\(](#page-56-0)b) clearly shows the variation in the line-width of the [ZPL](#page-15-1) of [SiV](#page-14-4) color centers in bulk as well as in [PCD](#page-14-2) membranes. The excited state lifetime of the [SiV](#page-14-4) emitters has been measured in the range of 0.6 - 1 ns in

<span id="page-56-0"></span>

**Figure 2.12.** Silicon vacancy color centers in diamond. (a) fuorescence confocal image of [SiV](#page-14-4) emitters in a 3 µm diamond membrane implanted at a fluence of  $10^8$  cm<sup>-2</sup>. (b) Comparison of [SiV](#page-14-4) color center [PL](#page-14-12) spectra in bulk diamond and [PCD](#page-14-2) membrane. A strong [ZPL](#page-15-1) at  $\approx$  738 nm with a narrow linewidth of  $5 - 10$  nm. (c) Lifetime comparison of [SCD](#page-14-1) bulk (black) with  $3 \mu$ m (red) and 130 nm thickness [PCD](#page-14-2) (blue) membranes.

a [PCD](#page-14-2) membranes. The lifetime curves in Figure [2.12\(](#page-56-0)c) are ftted using single exponential fits, and the corresponding fitted lifetimes are explained in the text. [SiV](#page-14-4) centers in the bulk diamond samples show a longer lifetime of 1 ns compared to 0.6 ns in a 3 µm diamond membrane [see Figure [2.12\(](#page-56-0)c)].

The shorter lifetime of [SiV](#page-14-4) color centers in diamond membranes, as compared to bulk diamond, can be attributed to a range of factors related to the crystal quality and growth parameters of the diamond. In diamond membranes, [SiV](#page-14-4) centers experience enhancement in the nonradiative decay rate due to the poor crystal quality and the presence of graphitic phases of carbon, which in turn results in faster radiative decay rates and shorter lifetimes [\[28,](#page-155-0) [44\]](#page-156-0). The higher surface-to-volume ratio in diamond membranes exposes [SiV](#page-14-4) centers to surface effects and defects, which introduces the non-radiative recombination pathways. The lattice mismatch or strain introduced during the growth of diamond membranes on different substrates can affect the electronic structure and optical properties of [SiV](#page-14-4) centers, increasing non-radiative decay rates and reducing their lifetime [\[56,](#page-157-5) [112\]](#page-163-4). Additionally, the local environment within diamond membranes, including variations in strain, temperature, and the presence of other defects, can infuence [SiV](#page-14-4) center lifetimes [\[145\]](#page-166-8). Finally, fabrication techniques such as ion implantation and etching can introduce imperfections and crystal structure damage, creating additional non-radiative recombination centers. These combined factors contribute to the shorter lifetimes of [SiV](#page-14-4) color centers in diamond membranes when compared to their counterparts in bulk diamond [\[55,](#page-157-6) [56\]](#page-157-5).

In summary, the comprehensive exploration of these optical disparities enhances our understanding of the behavior of [SiV](#page-14-4) color centers in different diamond environments, which is crucial for tailoring their applications in various fields, such as quantum information processing, quantum communication, and sensing. Furthermore, these insights are pivotal for advancing quantum photonics and the development of diamond-based quantum technologies.

# **2.3 Optical Antennas**

Light is controlled by redirecting the wavefronts of propagating radiation through lenses, mirrors, and various diffractive elements in most optical science and engineering applications. However, manipulating light on a sub-wavelength scale is not possible owing to the wave nature of electromagnetic felds. Here comes the use of optical antennas; they operate similarly to radio wave and microwave antennas but at higher frequencies. Also, an optical nanoantenna bridges the size and impedance mismatch between the nanoemitters and free space radiation and enables the manipulation of light on a scale smaller than the wavelength of light [\[31,](#page-155-2) [103\]](#page-162-2). The term "antenna" was first used only casually in English, and establishing that word in the scientifc community took almost a decade. The frst document that used the word "antenna" to interpret an electromagnetic transmitter is a paper by André-Eugéne Blondel titled "Sur la théorie des antennes dans la télégraphie sans fil," presented in 1898 at a meeting of the Association Française pour l'Avancement des Sciences [\[31\]](#page-155-2). An antenna has a dimension of the order of the wavelength of light; hence, its fabrication requires extreme precision in both top-down and bottom-up nanofabrication methods.

A radio antenna was developed to solve the issues related to communication, while the critical focus of inventing an optical antenna was to uplift the microscopy research areas. It is a device designed to convert free propagating optical radiation into localized energy and vice versa. In microscopy, an optical antenna can replace conventional focusing optics like an objective lens, where it concentrates the laser radiation into a dimension way smaller than the diffraction limit. Since the diffraction limits the confnement of propagating radiation to roughly half a wavelength, the length scales over which optical felds can be manipulated traditionally lie outside the size range of interest to optical nanoantennas.

<span id="page-58-0"></span>

**Figure 2.13.** Schematic representation of a receiver or transmitter such as an atom, ion, or molecule interacting with free optical radiation via an optical antenna [\[31\]](#page-155-2).

### **2.3.1 Optical Antenna: A Nanoscale Resonator**

The crucial difference between the radio frequency [\(RF\)](#page-14-13) and microwave counterparts of an optical antenna lies in their physical properties and scaling behavior [\[103\]](#page-162-2). Since metals are not perfect conductors at optical frequencies, they are strongly correlated plasma, known as the free electron gas, which results in most of the difference between [RF](#page-14-13) and optical antennas. Nonetheless, an optical antenna can take various forms (sharp tips and/or nanoparticles); hence their property is also dependent on the shape and material due to the surface plasmon resonances [\[103\]](#page-162-2).

In the depicted schematic representation in Figure [2.13,](#page-58-0) the focus is on elucidating the intricate dynamics between a receiver or transmitter entity, exemplifed by an atom, ion, or molecule, and free optical radiation. The essential interaction occurs through the mediation of an optical antenna, a nanostructured device designed to facilitate and enhance the coupling of electromagnetic radiation in the optical range with the target entity [\[103\]](#page-162-2). This interaction is pivotal in the context of understanding and manipulating quantum states, where the optical antenna serves as a conduit for the exchange of energy between the atom, ion, or molecule and incident optical radiation. The optical antenna, acting as a bridge between the microscopic world and electromagnetic waves, plays a crucial role in concentrating and directing the radiation, thereby infuencing the absorption, emission, or scattering processes of the receiver or transmitter. This schematic representation provides a visual abstraction, offering a conceptual framework for comprehending the fundamental mechanisms underlying the interaction of matter with free optical radiation in the presence

of an optical antenna, which has implications for various scientifc disciplines, including quantum optics and nanophotonics [\[103\]](#page-162-2).

The antenna controls the light-matter interaction on the level of a single quantum system between the emitter or absorber and the radiation field. The presence of the antenna modifes the transmission rates and energy level structure (in the case of strong interaction) of the quantum system. Since metals are not perfect conductors, their optical properties are strongly affected by the existence of surface plasmon polariton [\(SPP\)](#page-14-14) resonances. These modes can be tightly confined into a tiny mode volume at the nanoscale by shaping metals using state-of-the-art nanofabrication. Hence, the properties of the antenna interconnect with the properties of the receiver/transmitter; thus, the two systems are considered as a coupled system, where the efficiency of the interaction is expressed in terms of the antenna gain, efficiency, impedance, and directivity [\[103\]](#page-162-2).

An optical nanoantenna, upon far-feld excitation, confnes or tightly focuses light at subwavelength volumes inside which the electromagnetic feld becomes highly structured [\[47\]](#page-157-7). This field has a vectorial field distribution, where the strength of the 3D structure in space is highly position-dependent. Hence, positioning a single photon emitter, such as a molecule close to the optical antenna, becomes critical in achieving optimum coupling [\[37,](#page-155-3) [103\]](#page-162-2). Additionally, the interaction efficiency for the excitation rate is correlated with the overlap between the absorption dipole moment of the emitter and the interacting optical field. Under dipole approximation, the excitation rate  $\Gamma_{\text{exc}}$  is directly proportional to the square of the exciting electric feld along the direction of the molecule's absorption dipole moment "P", which can be written as follows [\[103\]](#page-162-2):

$$
\Gamma_{\text{exc}} \propto |P.E(\omega_0, r)|^2 \tag{2.1}
$$

Here  $\omega_0$  represents the excitation frequency and *r* is the position of the emitter in space. A molecule's interaction with the optical feld can lie in two interaction regimes: such as weak-field interaction and strong-field interaction respectively.

At the more fundamental level, an optical antenna enhances the radiation properties of the quantum emitters. The ability of an optical antenna to strongly confne electromagnetic radiation into a localized field in the nanoscale emerged in a wide variety of applications: in super-resolution microscopy, enhanced weak Raman scattering, spectroscopy, biosensing and imaging, nonlinear processes, and nanoantenna-based efficient photodetectors [\[32,](#page-155-4) [73,](#page-159-0) [84,](#page-160-0) [103\]](#page-162-2). To gain complete insight into the spontaneous emission enhancement rate with minimal losses caused by absorption in a real metal, we will discuss several empirical rules to engineer an optical antenna in section [2.3.2,](#page-60-0). In section [2.3.4,](#page-67-0) optical antenna designs [where the effects related to the antenna composition and shape are taken into

<span id="page-60-0"></span>account] compatible with the state-of-the-art nanofabrication techniques are discussed.

### **2.3.2 Enhancement and Quenching of Fluorescence**

The localized felds created by an optical antenna open up new interaction mechanisms between light and matter, such as the higher-order multipole transitions and the momentumforbidden transitions. In free space, these interactions are inaccessible, while the photon momentum is much lower than the momentum of an unbound electron with the same energy. However, near an optical antenna, the photon momentum is no longer defined by the free space; instead, it is defned by the spatial confnement [here, the localized optical felds are associated with a photon momentum]. Thus, in near-feld optical interactions, the momentum of photons can be signifcantly enhanced to a level comparable to that of electrons, particularly in materials with low effective mass. Therefore, the presence of localized optical fields can induce "diagonal" transitions in the electronic band structure, leading to an overall increase in absorption strength. The matter excitations are associated with the oscillations of the surface charge density at the interface between the metal and the dielectric medium. When a quantum emitter is coupled to an optical antenna, the exciting factors determining the coupling effects between the light-matter interaction are the feld enhancement, the spontaneous emission rate, the quantum yield, and the radiation pattern. In this section [2.3.2,](#page-60-0) we discuss all the relevant parameters that determine the enhancement of the near-feld light-matter interactions.

### a) **Field Enhancement and Quenching**

Optical antennas can be tailored to serve different purposes by adopting specifc designs [\[103\]](#page-162-2). Linear antennas can be used for dipolar emission,  $\frac{\lambda}{4}$  antennas for emitting light in all directions, Yagi-Uda antennas [\[38,](#page-156-1) [55\]](#page-157-6) for directional emission, patch antennas, or parabolic-shaped nanocups [\[103\]](#page-162-2) that bend light similar to parabolic antennas. The specific emission properties of the antennas originate from the excitation of particular electromagnetic modes within the nanostructure. Early studies employing polarizability models identifed the [SPP](#page-14-14) resonance and the lightning rod effect as the two principal mechanisms responsible for electromagnetic enhancement. Since the strength of the near-feld is directly proportional to the surface charge density '*σ*', nanoparticles with sharp tips typically exhibit more substantial enhancements compared to nanospheres. Additional strategies to enhance the near field's intensity include utilizing nanoscale gaps between two nanoparticles, minimizing radiative broadening, and selecting different types of metals [\[36,](#page-155-1) [103\]](#page-162-2).

However, it is essential to consider not only the emission properties of the antenna but also the localization strength of the optical fields in the context of spectroscopy. By calculating the ratio between the amplitude of the local field at that particular position  $|\vec{E}_{loc}(\vec{r})|$  and the amplitude of the incoming field  $|\vec{E}_0(\vec{r})|$ , the electromagnetic

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field enhancement at a position  $\vec{r}$  can be determined [\[36,](#page-155-1) [102\]](#page-162-3). The local field enhancement can then be written as:

$$
f = f(\vec{r}) = \frac{|\vec{E}_{loc}(\vec{r})|}{|\vec{E}_0(\vec{r})|}
$$
(2.2)

Since the near feld and the emission properties of an antenna are not independent, the field at any point of evaluation  $\vec{r_0}$  excited by a dipolar source  $\vec{p}$  in a position of space⃗*r* in any dielectric environment is related to the felds obtained after exchanging the positions of excitation and evaluation. Thus the far-feld radiation from an emitter-antenna interaction can be realized in terms of the feld enhancement produced at the position of the emitter as a response to the incoming feld. Hence, understanding the feld enhancement of an emitter at close proximity to an optical antenna is the origin of an enhanced spectroscopic signal in the near-feld and its detection in the far-field [\[36\]](#page-155-1).

Upon weak resonant excitation, the fluorescence signal is defined as [\[36\]](#page-155-1):

$$
S_0 = \kappa \eta_0 |E_0.d|^2 \tag{2.3}
$$

where  $\kappa$  represents the collection efficiency,  $\eta_0$  is the quantum yield, *d* indicates the transition electric dipole moment, and  $E_0$  is the electric field at the emitter position respectively [\[36\]](#page-155-1).

#### b) **Decay Rate**

Spontaneous emission (SE) rate is not solely determined by the inherent characteristics of the emitter; it is also infuenced by the specifc electromagnetic surroundings in which it is placed. Moreover, the rate of spontaneous decay is directly linked to the [LDOS,](#page-13-6) which, in turn, relies on the transition dipole moment (*d*) associated with the atomic states engaged in the transition. It's worth noting that this substitution of the partial local density of states with the total local density of states is only applicable in homogeneous environments. This elucidates how alterations in environmental conditions can lead to fuctuations in the spontaneous decay rate. This modifcation in the spontaneous decay rate can be achieved by evaluating the radiative power emitted when a classical dipole is positioned near an optical antenna.

Consider an undriven harmonically oscillating dipole, as the dipole oscillates, it radiates energy. Thus, the dipole dissipates its energy into radiation and its dipole moment decreases. The term  $\tau_0$  defines the lifetime of the oscillator, which is the time for which the energy decayed to  $\frac{1}{e}$  of its initial value at  $t = 0$  [\[102\]](#page-162-3).

$$
\tau_0 = \frac{1}{\Gamma_{\text{(tot,0)}}} \tag{2.4}
$$

where,  $\Gamma_{\rm (tot,0)}$  is the classical expression for the atomic decay rate in free space. For energy conservation, the decrease in oscillator energy must be equal to the energy losses, i.e. when the intrinsic quantum yield,  $\eta_0 = 1$ , the entire energy dissipated by the oscillator is converted into radiation.

We can write the classical picture of spontaneous decay rate for an undriven harmonically oscillating dipole in a homogeneous medium ( i.e. free space, refractive index,  $n = 1$ ) as follows [\[102\]](#page-162-3):

<span id="page-62-0"></span>
$$
\Gamma_{\text{(tot,0)}} = \eta_0 \frac{1}{4\pi\epsilon_0} \frac{2q^2 \omega_0^2}{3\text{mc}^3} \tag{2.5}
$$

Here,  $\Gamma_{(tot,0)}$  depends on the oscillation frequency ( $\omega_0$ ), mass (m), and charge (q) of the particle.

The higher the index of refraction of the surrounding medium, the shorter the lifetime of the oscillator. Hence, if an atom is placed in a dielectric medium, two corrections in Equation [2.5](#page-62-0) have to be implemented: frstly, the impact of bulk dielectric properties should be considered using a dielectric constant, and secondly, the local field at the dipole's location needs to be adjusted.

In an inhomogeneous environment, a dipole that oscillates harmonically and is isolated will encounter a driving force generated by its own feld. This driving feld is the feld that returns to the oscillator after it has interacted with the surrounding environment. The interaction with the the secondary local feld, *E<sup>s</sup>* results in the resonance frequency shift and modification of the decay rate.

By assuming the interaction with the local field  $E_s$  is weak, we can describe the (normalized) spontaneous emission rate of a quantum system in an inhomogeneous environment ( $n \neq 1$ ) as follows [\[102\]](#page-162-3):

<span id="page-62-1"></span>
$$
\frac{\Gamma'_{\text{tot}}}{\Gamma_{\text{(tot,0)}}} = 1 + \eta_0 \frac{6\pi\epsilon_0}{|\mu_0|^2} \frac{1}{k^3} \operatorname{Im}(\mu_0^* E_s(r_0))
$$
\n(2.6)

In Equation [2.6,](#page-62-1)  $\Gamma_{\text{tot}}'$  indicates the total radiative decay rate of a classical dipole near an optical antenna, and it is normalized with respect to normalized decay rate  $(\Gamma_{diel})$ in the dielectric substrate, to consider the actual experimental conditions.

Since the local driving field  $E_s$  is proportional to the electric dipole moment  $\mu_0$ , the dependence on the magnitude of the dipole moment cancels out. Besides, the rate of energy dissipation in inhomogeneous environments (eg. atom in a cavity) is given as  $P_r/P_0$ . Where  $P_r$  and  $P_o$  indicate the power radiated by a classical dipole near an optical antenna and in free space respectively. Hence, for intrinsic quantum yield *η*<sup>0</sup> = 1, we can write [\[36,](#page-155-1) [102\]](#page-162-3),

$$
\frac{\Gamma_{\text{rad}}}{\Gamma_{(\text{rad},0)}} = \frac{P_r}{P_0} \tag{2.7}
$$

where  $\Gamma_{rad}$  indicates the radiative decay rate of a classical dipole near an optical antenna. When  $\eta_0 = 1$ ,  $\Gamma_{(rad,0)} = \Gamma_{(tot,0)}$ . So, in Equation [2.10,](#page-64-0)  $\Gamma_{(rad,0)}$  can be replaced by  $\Gamma_{\text{(tot,0)}}$ .

Due to the absorption of emitted power by metal losses, a comprehensive system

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analysis necessitates the computation of both radiative  $[\Gamma_{(\rm rad,0)}]$  and non-radiative  $[\Gamma_{(nrad,0)}]$  decay rates. Therefore, the total decay rate  $[\Gamma_{tot}]$  can be expressed as the sum of Γ<sub>rad</sub>, Γ<sub>nrad</sub> [indicates the non-radiative decay rate of a classical dipole near an optical antenna], and  $\Gamma_{\rm (nrad)}^0$  [intrinsic non-radiative decay rate] [\[36\]](#page-155-1). Classical counterparts of these quantities can be readily deduced using the Poynting theorem, which results in [\[36\]](#page-155-1),

$$
\frac{\Gamma_{\text{rad}} + \Gamma_{\text{nrad}}}{\Gamma_{\text{(rad,0)}}} = \frac{P_t}{P_0}
$$
\n(2.8)

where  $P_t$  is the total power dissipated by the dipole and  $\Gamma_{\rm rad}$  is the radiative decay rate under near-feld coupling

### c) **Quantum Yield**

The energy acquired by a quantum system can be dissipated through two primary mechanisms: radiative relaxation, which involves photon emission, and non-radiative relaxation, which encompasses various processes like coupling to vibrations, energy transfer to the surroundings, or quenching by other molecules [\[36\]](#page-155-1). In many cases, there is an interest in creating conditions that optimize the radiative emissions of a quantum system. A valuable metric for quantifying this emission is the quantum yield, which is defned as follows:

$$
Q = \frac{\Gamma_{(\text{rad},0)}}{\Gamma_{(\text{rad},0)} + \Gamma_{(\text{nrad},0)}}
$$
(2.9)

where  $\Gamma_{\rm (rad,0)}$  and  $\Gamma_{\rm (nrad,0)}$  represent the radiative, and non-radiative decay rates in free space, respectively. Whereas the total decay rate in free space is given by the sum of both radiative and non-radiative parts,  $\Gamma_{\rm (tot,0)}=\Gamma_{\rm (rad,0)}+\Gamma_{\rm (nrad,0)}$  [\[36\]](#page-155-1). In a homogeneous environment, *Q* is identical to the intrinsic quantum yield *η*0. Nevertheless,  $\Gamma_{\text{(rad,0)}}$  and  $\Gamma_{\text{(nrad,0)}}$  depend on the specific local surroundings and, as a result, can be infuenced by non-uniformities in the environment [\[103\]](#page-162-2). The quantum yield *Q* can be either enhanced or diminished by a specifc environmental condition. To ascertain the quantum yield within a given environment, it is essential to segregate the total decay rate into both radiative and non-radiative components. Thus, the combination of these factors can be assessed by evaluating the equilibrium between radiative emission directed to the far-feld and radiation absorbed by the environment  $(P_{\text{abs}})$ . For instance, in the vicinity of a noble metal surface, the quantum yield of a typically low-fuorescent molecule can be either enhanced or quenched, depending upon the coupling distance between the molecule and the metal surface. When the distance exceeds  $\approx$  5 nm, the presence of the metal surface generally increases  $\Gamma_{(rad,0)}$ , while at shorter distances, the molecule will release its excitation energy non-radiatively to the metal, thereby enhancing the  $\Gamma_{(nrad,0)}$ through fuorescence quenching [\[102,](#page-162-3) [103\]](#page-162-2).

d) **Antenna Effciency**

The antenna efficiency  $(\eta_a)$  is defined as the ratio between the radiated power and the total power transferred from the load to the antenna. For quantum loads (atoms or molecules),  $\eta_a$  can be expressed as  $\eta_a = \frac{\Gamma_{\rm rad}}{\Gamma_{\rm rad} + \Gamma}$  $\frac{1 \text{ rad}}{\Gamma_{\text{rad}} + \Gamma_{\text{nrad}}}$  [\[62,](#page-158-1) [146\]](#page-166-9). The modified quantum yield (*η*) is characterized by the following equation [\[36,](#page-155-1) [102,](#page-162-3) [147\]](#page-166-10):

<span id="page-64-0"></span>
$$
\eta = \frac{\eta_0}{(1 - \eta_0) \frac{\Gamma_{\text{(rad,0)}}}{\Gamma_{\text{rad}}} + \frac{\eta_0}{\eta_a}}
$$
(2.10)

As the quantum emitter approaches the metal surface,  $\Gamma_{\text{nrad}}$  becomes dominant over  $\Gamma_{rad}$  because the source field becomes increasingly inhomogeneous across the antenna. This leads to a more efficient excitation of multipoles [\[88\]](#page-161-2). It's essential to recognize a trade-off between intensity enhancement (often represented as *K*) and *ηa*. While radiative effects may decrease the near-field's strength, they often result in an increase in  $\eta_a$  [\[62\]](#page-158-1). Consequently, achieving a significant increase in the spontaneous emission rate without compromising *η<sup>a</sup>* poses a formidable challenge in this feld.

Our recent work has shown the fabrication and characterization of gold nano-cones having sharp tips with resonance in the near infra-red [NIR](#page-14-7) range [\[47\]](#page-157-7), in which we have discussed that these structures are suitable for enhancing the total radiative decay rate ( $\Gamma_{(tot,0)}$ ) of a quantum emitter by more than two orders of magnitude without the expense of antenna efficiency.

On the other hand, utilizing planar Yagi-Uda antenna [\[38,](#page-156-1) [55\]](#page-157-6), we have recently proved that the count rate of [SiV](#page-14-4) color centers in a diamond can be largely improved [\[56\]](#page-157-5).

# **2.3.3 Fabrication Methods**

Plasmonic nanostructures are widely used in various applications, including sensing, imaging, and energy harvesting, due to their unique optical properties. There are different fabrication methods for plasmonic nanostructures, each with its advantages and disadvantages [\[148\]](#page-167-0). Fabrication of plasmonic nanostructures requires precise control over size, shape, and composition [\[102,](#page-162-3) [103,](#page-162-2) [148,](#page-167-0) [149\]](#page-167-1). In this section, we will discuss some commonly used fabrication methods for plasmonic nanostructures.

In general, there are two main fabrication approaches: "top-down fabrication methods" and "bottom-up fabrication methods [\[149\]](#page-167-1)."

# **Top-down fabrication methods:**

Top-down fabrication methods involve using lithography techniques to pattern metallic flms and create plasmonic nanostructures. Some of the top-down fabrication methods include:

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- i) Electron beam lithography [\(EBL\)](#page-13-7) and sputter deposition: [EBL](#page-13-7) followed by sputtering is a precise technique for fabricating plasmonic nanostructures with high resolution [\[47,](#page-157-7) [147,](#page-166-10) [150\]](#page-167-2). It involves using an electron beam to pattern a resist layer on a substrate. The resist layer is then etched to form the desired plasmonic nanostructure. The resolution of [EBL](#page-13-7) can reach sub-10 nm, making it a suitable technique for fabricating plasmonic nanostructures, such as nanorods and nanoholes with high aspect ratios [\[151\]](#page-167-3). Moreover, the [EBL](#page-13-7) technique enables the fabrication of arbitrary shapes of plasmonic nanostructures with high precision.
- ii) UV lithography: UV lithography is a widely used technique for the fabrication of plasmonic nanostructures due to its simplicity and cost-effectiveness. This technique involves the use of a photomask to pattern a photoresist layer on a substrate, followed by UV light exposure to transfer the pattern onto the substrate. The exposed photoresist is then developed to create the desired plasmonic nanostructure. The UV lithography process can be divided into four main steps: (1) substrate preparation, (2) photoresist coating, (3) exposure and development, and (4) etching. UV lithography has been used to fabricate various plasmonic nanostructures, such as nanorings, nanoholes, and nanodisks [\[152\]](#page-167-4). For instance, researchers have used UV lithography to fabricate arrays of gold nanorings with diameters ranging from 200 nm to 1 µm. The plasmonic resonance of the nanorings was tuned by changing the diameter and thickness of the rings, and the arrays exhibited a high sensitivity to changes in refractive index.
- iii) Focused ion beam [\(FIB\)](#page-13-2): [FIB](#page-13-2) is a technique used to fabricate plasmonic nanostructures with high precision [\[78,](#page-160-1) [153\]](#page-167-5). It involves using a focused ion beam to remove material from a substrate to create the desired plasmonic nanostructure. [FIB](#page-13-2) can be used to create plasmonic nanostructures with complex shapes, such as nanocubes and nanotriangles. Moreover, [FIB](#page-13-2) can be used to fabricate plasmonic nanostructures on non-planar surfaces such as optical fbers and microspheres [\[154\]](#page-167-6). For example, [FIB](#page-13-2) techniques are employed to fabricate gold nanocubes for plasmonic sensing applications. The nanocubes were designed to have a size of 200 nm and exhibited a plasmonic resonance at a wavelength of 720 nm [\[86\]](#page-160-2).

### **Bottom-up fabrication methods:**

Bottom-up fabrication methods involve the self-assembly of metallic nanoparticles to create plasmonic nanostructures. Some of the bottom-up fabrication methods include:

i) Chemical synthesis: The chemical synthesis involves the reduction of metallic salts in the presence of a reducing agent and a stabilizing agent. The chemical synthesis approach provides excellent control over the size and shape of nanoparticles; hence the metallic nanoparticles can then be assembled to create plasmonic nanostructures [\[155\]](#page-167-7). This is a popular method for the fabrication of plasmonic nanostructures with

specific optical properties. One of the commonly used chemical synthesis methods for fabricating plasmonic nanostructures is the seed-mediated growth method. This method involves using small metal nanoparticles as seeds to initiate the growth of larger nanoparticles. The seed-mediated growth method can be used to synthesize various shapes of plasmonic nanoparticles, such as spheres, rods, and triangles. For example, a study by Sun et al. used the seed-mediated growth method to synthesize gold nanorods with tunable aspect ratios and plasmon resonances in the near-infrared region [\[155\]](#page-167-7). Another popular method for synthesizing plasmonic nanostructures is the polyol method, which involves the reduction of metal salts in a polyol solvent at high temperatures. The polyol method is a simple and scalable approach for synthesizing plasmonic nanoparticles with high monodispersity and stability. This method provides a synthesis of silver nanoparticles with a tunable size and shape, which exhibited plasmonic properties suitable for [SERS](#page-14-15) [\[156,](#page-167-8) [157\]](#page-167-9). These methods provide a high degree of control over the size, shape, and composition of nanoparticles, making them suitable for various applications in plasmonics and nanophotonics.

ii) Template-assisted synthesis: Template-assisted synthesis is a versatile method for fabricating plasmonic nanostructures with high precision and control over their size, shape, and composition. This method uses a template to guide the growth of plasmonic materials, such as gold, silver, and copper, into nanoscale structures [\[158,](#page-168-0) [159\]](#page-168-1). The template can be a biological molecule, such as DNA, a polymer, or a porous material, such as alumina or silica. The template-assisted synthesis process typically involves several steps, including template preparation, deposition of plasmonic materials onto the template, and removal of the template to obtain the final plasmonic nanostructures.

### **Hybrid fabrication methods:**

Hybrid fabrication methods involve the combination of top-down and bottom-up fabrication methods. Some of the hybrid fabrication methods include:

i) Nanoimprint lithography [\(NIL\)](#page-14-16): The [NIL](#page-14-16) involves the use of a template to pattern a resist-coated substrate. The metallic flm is then deposited on the patterned substrate, and the resist is removed to create plasmonic nanostructures [\[160\]](#page-168-2). [NIL](#page-14-16) can be combined with chemical synthesis to create plasmonic nanostructures with high resolution and control over size and shape. [NIL](#page-14-16) is a replication technique used to fabricate nanostructures by imprinting a pattern onto a substrate using a mold. This technique can be used to fabricate large-area, high-density arrays of plasmonic nanostructures with high resolution. It is a cost-effective method for the large-scale production of plasmonic nanostructures. [NIL](#page-14-16) can produce nanoscale patterns with feature sizes down to sub-10 nm, making it a suitable technique for

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fabricating plasmonic nanostructures such as nanodisks, nanoholes, and nanorods. For instance, [NIL](#page-14-16) have been used to fabricate plasmonic nanostructures for [SERS](#page-14-15) applications. The fabricated structures consisted of gold nanodisks with a diameter of 120 nm and a thickness of 20 nm arranged in a hexagonal pattern. The plasmonic nanostructures exhibited a high enhancement factor for Raman signals, enabling the detection of Rhodamine 6G down to a concentration of  $1 \times 10^{-10}$  M [\[161\]](#page-168-3).

ii) Directed self-assembly: Directed self-assembly involves the use of chemical cues to guide the self-assembly of metallic nanoparticles [\[162\]](#page-168-4). The chemical cues can be functionalized surfaces or block copolymers. Directed self-assembly can be combined with top-down fabrication methods to create plasmonic nanostructures with high resolution and control over size and shape.

In conclusion, plasmonic nanostructures can be fabricated using various techniques, including top-down, bottom-up, and hybrid methods. The choice of fabrication method depends on the desired size, shape, and composition of the plasmonic nanostructures and the application requirements. Each of the discussed fabrication methods has its own advantages and limitations. Therefore, selecting a fabrication method requires careful consideration of the specifc requirements of the intended application.

# <span id="page-67-0"></span>**2.3.4 Design Considerations**

The spontaneous emission rate is not an intrinsic property of an emitter but strongly depends upon the environment in which it is placed. E.M. Purcell was the first scientist who discovered the effect of the spontaneous emission of quantum emitters on the local feld environment [\[163\]](#page-168-5). He showed that the spontaneous emission rate of a quantum emitter could be enhanced compared to the free space [\[36,](#page-155-1) [37\]](#page-155-3). It was realized that the radiative decay rate infuences the modifcation of the lifetime due to photon emission and the non-radiative decay rate due to energy dissipation in the environment. Both rates can be enhanced for atoms or molecules close to metal surfaces. Most semiconductor quantum emitters have a lifetime longer than a few tens of nanoseconds, hindering them from various applications. One way to overcome this issue is by making their spontaneous emission rate, which can be done by manipulating the photo-physics of the quantum emitter through dielectric microstructures or via plasmonic nanostructures [\[103\]](#page-162-2). In both cases, the key factor for achieving a strong modifcation of the spontaneous emission rate with minimal suffering of the non-radiative decay rate lies in the precise fabrication of the optical antennas [\[37,](#page-155-3) [103\]](#page-162-2). In this section [2.3.4,](#page-67-0) the decisive design principles are summarized.

#### **Shape dependence**

To optimize the performance of an optical antenna, several factors must be considered. First, the geometry of the antenna should be adjusted to ensure that the [SPP](#page-14-14) resonance falls within a spectral region where there is minimal dissipation in the metal [\[32,](#page-155-4) [47\]](#page-157-7). Second, elongated objects should be chosen to take advantage of the strong near felds generated at sharp corners. Third, the orientation of the emitter should be adjusted to align its electric dipole moment with that of the antenna. Fourth, it is important to ensure that the higher-order [SPP](#page-14-14) modes of the antenna are separated from the dipolar mode. Finally, the antenna volume should be chosen to ensure that radiation is stronger than absorption [\[36,](#page-155-1) [103\]](#page-162-2).

Modifying the antenna's geometry is an uncomplicated method that changes the polarizability of the antenna and optimizes the feld enhancement and tuning of the spectral response [\[47,](#page-157-7) [147\]](#page-166-10). To illustrate the effect of antenna design on the spontaneous emission rate and antenna efficiency, consider the emission of a dipole close to an elliptical gold nanoparticle. The [SPP](#page-14-14) resonance of the structure is situated in the [NIR](#page-14-7) region, which is a range where the imaginary part of the gold's dielectric function is relatively small. Also, the intensity enhancement *K* is stronger at the nanoparticle apex. In this case, both  $\Gamma_{rad}$ [radiative decay rate] and  $\Gamma_{\text{nrad}}$  [nonradiative decay rate] have a considerable enhancement, however,  $\Gamma_{rad}$  is larger than  $\Gamma_{nrad}$  at the [SPP](#page-14-14) resonance of the long axis. Changing the shape of the optical antenna promotes a huge impact on its performance [\[36,](#page-155-1) [37\]](#page-155-3). In this section, the main emphasis is on the modifcations of the spontaneous emission rate and the antenna efficiency.

There are a few key design ingredients for enhancing the field.

#### **(i) Aspect ratio:**

The aspect ratio (height to base) of an optical antenna is a crucial factor in determining the emission enhancement of the antenna. Generally, an elongated antenna with a high aspect ratio has a stronger near-feld and can produce a more signifcant emission enhancement. This is because the elongated structure of the antenna creates sharp corners and edges, which concentrate the electric field in the near-field region, leading to an enhancement in the [LDOS](#page-13-6) [\[36,](#page-155-1) [37,](#page-155-3) [147\]](#page-166-10). As a result, the optical antenna can improve the coupling efficiency between the emitter and free space, leading to a higher emission enhancement. Therefore, the aspect ratio of an optical antenna is an essential parameter that can be optimized to achieve the desired emission enhancement at the desired spectral range.

One of the issues in achieving maximal antenna efficiency  $(\eta_a)$ , and the Purcell factor [*F*, which is the enhancement of the decay rate of the emitter caused by its coupling to a cavity mode] is that they vary according to the variations in optical antenna parameters. The Purcell factor was frst proposed by Purcell in 1946. The expression for *F* is expressed as follows [\[103,](#page-162-2) [163\]](#page-168-5):

$$
F = \frac{3}{4\pi^2} \frac{Q}{V} \lambda^3
$$
\n(2.11)

Where V is the mode volume and  $\lambda$  is the wavelength. The Purcell effect can be understood in terms of the [LDOS](#page-13-6) of the cavity, which is a measure of the number of modes available for the emitter to couple to [\[36,](#page-155-1) [103\]](#page-162-2).

In the case of gold nanorods, the [LSPR](#page-14-17) peak red-shifts when the nanorod long axis '*a*' increases or the nanorod short axis '*b*' decreases. Thus, via tuning the aspect ratio *b/a*, the [LSPR](#page-14-17) can be tuned to the desired spectral location [\[147\]](#page-166-10). Interestingly, the  $\eta_a$  increases with the volume of the nanorod, i.e., as '*b*' becomes larger. A. Mohammadi et al. in 2008 [\[164\]](#page-168-6) have made the following observations regarding the impact of nanorod shape on Purcell factors and antenna efficiency. A steep decrease in the Purcell factor is observed when the head of the nanorod is fabricated fat. Also, the localized feld enhancement is rapidly lost when the nanorod gets thicker. Thus for rounded nanorods with high aspect ratios, the Purcell factor is smaller compared to the fat nanorods; however, in this case, the *η<sup>a</sup>* remains unchanged [\[37,](#page-155-3) [147\]](#page-166-10). For low aspect ratios, rounded nanorods exhibit a slower decrease in the Purcell enhancement than flat ones, but the red-shift of the resonance peak seems weaker. Apart from that, rounding the nanorod ends is advantageous for achieving prominent Purcell factors near the visible range for the parameters studied. However, for large aspect ratios, fat ends yield better enhancement. If nanorods are replaced with nanospheroids [they have similar geometrical parameters compared to nanorods but have sharper ends than nanorods], as shown in Figure [2.14\(](#page-70-0)a), there are three key observations to make. Firstly, at high aspect ratios, the nanospheroids exhibit smaller enhancements. Secondly, at low aspect ratios, the enhancement decreases more slowly and the [SPP](#page-14-14) resonance is less red-shifted. Thirdly, *η<sup>a</sup>* reaches its plateau at wavelengths close to 650 nm if the aspect ratio is less than 2 [\[36,](#page-155-1) [41\]](#page-156-2). Compared to nanorods, the enhancement is more significant at shorter wavelengths because the smaller aspect ratio of the nanospheroids is partially compensated by a sharper apex of the nanoparticle [\[40\]](#page-156-3).

#### **(ii) Sharpness:**

The most challenging task is to improve the antenna design to enhance *F* without decreasing *η<sup>a</sup>* and losing control of the spectral position of the resonance. One of the most effective ways to overcome this issue is to implement a sharp apex for the nanoparticles as mentioned in Figure [2.14](#page-70-0) (a) or utilize a conical antenna as shown in Figure [2.14\(](#page-70-0)b) [\[36,](#page-155-1) [44\]](#page-156-0). A conical antenna is an ideal candidate for an efficient near-field coupling, thanks to its unique geometry. One end of the cone delivers a sharp end, localizing the feld, thus increasing the spontaneous emission rate and intensity; the other end can be made larger to increase the volume and hence antenna efficiency  $(\eta_a)$ . A significant advantage of the nano-cone over nanorods and nanospheroids is that its [LSPR](#page-14-17) can be adjusted by altering

<span id="page-70-0"></span>

Figure 2.14. (a) The antenna efficiency (dashed curves) and radiative decay enhancement (solid curves) for an emitter coupled to two gold nanospheroids in glass as a function of the aspect ratio for *a* = 80 nm. (b) Effect of the tip termination on nano-cone optical antennas in air. Purcell factor (*F*) (solid curves) and antenna effciency (*ηa*) (dashed curves) for a nano-cone of 140 nm long with a tip diameter of 10 - 20 nm, with a fixed base diameter *b* of 60 nm. The emitter is placed at a distance of 6 or 10 nm from the end of the tip [\[36\]](#page-155-1).

the angle of the nano-cone without experiencing a significant loss in enhancement [\[36\]](#page-155-1).

#### **Material Dependence**

Various instances have been discussed where altering the shape and size of the optical antenna can lead to a modifcation of its properties [\[37,](#page-155-3) [147\]](#page-166-10). This section discusses the effect of the refractive of the background medium on the Purcell factor and the antenna efficiency  $(\eta_a)$ . An optical antenna is often grown on a dielectric substrate or attached to the end of a fiber. Studies have already shown that the presence of the substrate has a negligible effect on the feld enhancement and the [LSPR](#page-14-17) spectral position. If the nano-cone is fabricated on a glass substrate, the [LSPR](#page-14-17) can be shifted up to 50 nm; also, the [LSPR](#page-14-17) peak shows much more substantial radiative broadening, which results in a decrease of the Purcell factor (*F*), and increase in the antenna efficiency ( $\eta_a$ ). Moreover, the shift in the [LSPR](#page-14-17) towards shorter wavelengths improves antenna efficiency  $(\eta_a)$  [\[36\]](#page-155-1).

Figure [2.15\(](#page-71-0)a) shows how the refractive index of the background medium affects the radiative decay rate enhancement ( $\Gamma_{\text{tot}}$ ) and the antenna efficiency ( $\eta_a$ ). Here, an emitter (indicated in the black arrow) is coupled to a gold nanospheroid. The change in the background refractive index *n<sup>b</sup>* , from 1 to 1.5 red-shifts the [LSPR](#page-14-17) up to 200 nm. Also, the resonance gets wider because radiative broadening increases with the refractive index [\[36\]](#page-155-1).

<span id="page-71-0"></span>

**Figure 2.15.** (a) The effect of the background refractive index,  $n_b$ , on the radiative decay enhancement "Γ<sub>tot</sub>" (solid curves) and the antenna efficiency " $η<sub>a</sub>$ " (dashed curves) for an emitter coupled to a gold nanospheroid is shown. (b) The radiative decay enhancement  $T_{\text{tot}}$ " (solid curves) and antenna efficiency " $\eta_a$ " (dashed curves) for an emitter coupled to two aluminum nanospheroids in air [\[36\]](#page-155-1).

### **Near-feld Coupling**

One of the more effective ways to enhance the localized feld is via electromagnetic coupling, which can be implemented by coupling within or between nanostructures arranged with small gaps [\[47,](#page-157-7) [62,](#page-158-1) [70,](#page-159-1) [147\]](#page-166-10). An authorized example of an effective coupling between interfaces is achieved by reducing the thickness of a metallic structure forming nanoshells and/or nanorings [\[64,](#page-158-2) [165\]](#page-168-7). These structures have the ability to produce additional field enhancement by shifting the energy of the oscillator to lower energies owing to the interaction between the inner and outer interfaces [\[64,](#page-158-2) [165,](#page-168-7) [166\]](#page-168-8).

An alternative method was exploiting the coupling between two nanoparticles, like spheres, triangles, etc., separated by small gaps. Figure [2.15\(](#page-71-0)b) shows the manipulation of the total radiative decay rate ( $\Gamma_{\text{tot}}$ ) and the antenna efficiency ( $\eta_a$ ) of a quantum emitter. In this coupling method, a quantum emitter is placed between two nanospheroids separated by a small gap. The fundamental principle here is that an antenna with small gaps can manipulate the photophysical properties, such as fuorescence intensity, lifetime, and quantum yield of quantum emitters, through a phenomenon known as plasmonic coupling. When the gap between the two metal surfaces is smaller than the wavelength of light, the [LSPR](#page-14-17) of the two metal surfaces can couple and generate strong near-feld electromagnetic felds. The enhanced electromagnetic feld in the gap region can interact with nearby quantum emitters, such as molecules, quantum dots, or single atoms, leading to several effects, including increased absorption and emission rates, directional emission, and polarization control. The plasmonic coupling between the antenna and the quantum emitters can be optimized by adjusting the gap size and the geometry of the antenna, such
as the shape and size of the metal structures and the surrounding dielectric environment [\[32,](#page-155-0) [45,](#page-156-0) [147\]](#page-166-0).

Bowtie antenna with sub-10 nm gaps is a typical structure that utilizes the coupling effect combined with the lightning rod effect to manipulate the emission dynamics of quantum emitters [\[39\]](#page-156-1). A bowtie optical antenna is a type of optical antenna that consists of two triangles of metal separated by a small gap at their bases, forming a shape that resembles a bowtie. It is designed to concentrate light into the gap between the triangles, creating strong electric fields and enhancing the interaction of light with nearby molecules or nanoparticles. The bowtie antenna is particularly useful for applications in [SERS,](#page-14-0) where the strongly localized fields in the gap can significantly amplify the Raman scattering signal of molecules adsorbed on the metal surface [\[39\]](#page-156-1).

# <span id="page-72-0"></span>**2.3.5 Modifcation of the Spontaneous Emission Rate**

In this section [2.3.5,](#page-72-0) we briefy discuss reported strategies to control the local density of the optical states.

The modification of the spontaneous emission rate is a well-known phenomenon in cavity quantum electrodynamics (CQED) and is a result of the coupling of a quantum emitter to a cavity mode [\[36,](#page-155-1) [103\]](#page-162-0). In a typical scenario, a quantum emitter such as an atom or a quantum dot is placed inside a high-quality optical cavity, such as a microcavity or a photonic crystal or emitter brought closer to a planar antenna [\[42,](#page-156-2) [87,](#page-160-0) [167\]](#page-168-0). The cavity is designed such that it resonates with the frequency of the emitter, thereby enhancing the coupling between the two. When an excited quantum emitter is coupled to a cavity mode, it can decay to its ground state by either emitting a photon into the cavity mode or by emitting a photon into free space. The probability of the emitter decaying into the cavity mode is proportional to the coupling strength between the emitter and the cavity, while the probability of the emitter decaying into free space is proportional to the spontaneous emission rate of the emitter in the absence of the cavity [\[87\]](#page-160-0).

If a volume, such as a cubic meter of vacuum enclosed by perfectly conductive walls is taken, the number of standing waves that fit within that volume can be counted, and their frequency can be calculated. By determining how many states exist within a frequency range of  $\omega$  to  $\omega + d\omega$ , it can be found that vacuum at visible wavelengths has  $\approx 10^5$ photon states per  $m^3$ , per Hz of spectral bandwidth  $d\omega$ . For example, if an optical cavity is created by containing a mode between two mirrors, it can modify the number of available states. If an optical resonator is placed around the emitter and supports just one photon mode confined to about 1 µm in all directions and has a quality factor  $Q = 10^5$  (0.1 THz bandwidth), the number of available states can be further altered; subsequently enhancing

<span id="page-73-0"></span>

**Figure 2.16.** Schematic representation of different methods for modifying the spontaneous emission rate. (a) Planar antenna confguration. (b) Photonic microcavity. (c) Plasmonic nanoantenna. (d) Metallo-dielectric hybrid antennas.

the [LDOS;](#page-13-0) this extra contribution is defned by the Purcell factor [see equation [2.11\]](#page-69-0) [\[103,](#page-162-0) [163\]](#page-168-1). In a cavity with a high [LDOS,](#page-13-0) the emitter has a higher probability of decaying into the cavity mode, resulting in an enhanced spontaneous emission rate.

In the regime of strong quantum coupling, high Purcell factors are required, and achieving this necessitates high-quality factor (*Q*) cavities with small mode volumes (*V*) [\[103\]](#page-162-0). However, a cavity with high *Q*-factor slows down the photon emission rate; hence the number of photons/second of the single photon sources is reduced. To achieve highquality factors, it is necessary to use optical materials with very low loss, such as dielectrics like glass or semiconductor materials. Whispering gallery modes have been used to realize cavities with very high-quality factors in the range of  $10^6$  to  $10^9$ , with mode volume in the range of tens of microns. In order to acquire a high Purcell factor at lower quality factor *Q*, the optimization of the cavities with the tightest feld confnement is required, which means the mode volume *V* should be maintained smaller in the range of  $V = (\lambda/2n)^3$ [\[87,](#page-160-0) [103\]](#page-162-0). The modification of the spontaneous emission rate has important implications for a wide range of applications, including single-photon sources, quantum information processing, and quantum sensing.

#### **Planar Antenna**

The first experimental demonstration of modifying the spontaneous emission rate of an atom was done by K. Drexhage in the late 1960s, where he examined the fuorescence lifetime of quantum emitters close to flat metallic surfaces [\[168\]](#page-168-2). This configuration is known as a planar antenna configuration. Planar antennas can modify the spontaneous emission rate of a quantum emitter by coupling its radiation to propagating [SPPs](#page-14-1) [\[62,](#page-158-0) [84\]](#page-160-1). The [SPPs](#page-14-1) are generated by the antenna's ability to confine and enhance the electromagnetic feld in its vicinity. When the emitter is placed close to the antenna, its emission can be strongly coupled to the SPPs, resulting in a faster emission rate and an increase in the radiative decay rate of the emitter. This phenomenon is known as Purcell enhancement (given in Equation [2.11\)](#page-69-0), and it is governed by the quality factor (*Q*) of the antenna, which represents its ability to store energy [\[103,](#page-162-0) [163\]](#page-168-1). The higher the *Q* factor of the antenna, the stronger the Purcell enhancement. Planar antennas with subwavelength dimensions, such as bowtie and gap antennas, are particularly effective at achieving high *Q* factors and, thus, large Purcell enhancements. Figure [2.16\(](#page-73-0)a) shows an example of modifying the spontaneous emission rate of a single dye molecule by coupling with a flat silver surface. In Figure [2.16\(](#page-73-0)a), the molecules act as the sub-wavelength antenna, and the interface acts as the planar antenna. The nature of interaction here is a dipole-dipole coupling [\[38\]](#page-156-3).

#### **Microcavities**

Microcavities can modify the spontaneous emission rate of a quantum emitter through the phenomenon "Purcell effect" [see Equation [2.11\]](#page-69-0). This equation is valid only for a well-defned cavity mode [\[163\]](#page-168-1). The Purcell effect arises from the interaction between the emitter and the electromagnetic modes of the microcavity [\[163\]](#page-168-1). When the emitter is placed inside a microcavity, it can couple to the resonant modes of the cavity, leading to an increase in the [LDOS](#page-13-0) of the electromagnetic feld. The [LDOS](#page-13-0) measures the number of available electromagnetic modes at a given energy and determines the emitter's spontaneous emission probability. As a result of the increased [LDOS](#page-13-0) in a microcavity, the spontaneous emission rate of the emitter can be enhanced.

Figure [2.16\(](#page-73-0)b) is a schematic representation of a photonic microcavity accommodating standing optical wave. This enhancement is proportional to the quality factor (*Q*) of the microcavity, which measures the cavity's ability to trap light. A higher *Q*-factor results in a narrower bandwidth of resonant modes, which significantly enhances the spontaneous emission rate. The Purcell effect can also modify the spectral and angular emission properties of the emitter, leading to directional and spectrally narrow emission.

#### **Plasmonic Nanoantenna**

A microcavity-based spontaneous emission enhancement of quantum emitters is one of the most frequently implemented methods. However, microcavities are extremely spectral sensitive and preferred to operate at low temperatures [\[169\]](#page-169-0). This sensitive nature imposes restrictions on the emitter selection, thereby making them impressionable to external conditions like vibrations and temperature drift. Plasmonic nanocavities (plasmonic nanoantennas) are one of the solutions for obtaining large coupling strength while maintaining high photon throughput because they enable very small mode volume (*V*) combined with low-quality factor (*Q*). By reducing the mode volume (*V*), the feld density increases resulting in a large coupling strength hence enhancing the spontaneous emission rate.

A plasmonic nanoantenna modifes the spontaneous emission rate of quantum emitters by coupling the emitter to the [LSPR](#page-14-2) [\[79\]](#page-160-2). When the emitter is placed in close proximity to the nanoantenna, the [LSPR](#page-14-2) of the antenna strongly enhances the local electromagnetic feld, leading to an increase in the radiative decay rate of the emitter through the Purcell effect. The Purcell factor (*F*), which is the ratio of the spontaneous emission rate of the emitter in the presence of the antenna to its rate in free space, is proportional to the square of the electric feld intensity at the location of the emitter [\[103\]](#page-162-0).

Figure [2.16\(](#page-73-0)c) depicts the schematic representation of a plasmonic antenna. In this experiment, a spherical gold nanoparticle is attached to the end of a glass fiber tip positioned against individually oriented molecules with nanometer precision. By engineering the plasmonic nanoantenna's size, shape, and composition, one can control the Purcell factor (*F*) and modify the spontaneous emission rate of the emitter [\[32,](#page-155-0) [36,](#page-155-1) [103\]](#page-162-0). The efficient interaction primarily hinges on the precise configuration of the metallic nanostructure and the alignment and orientation of the molecule with respect to the polarization of the incident light. The most promising plasmonic antenna shape studied is a nano-cone [\[47,](#page-157-0) [147\]](#page-166-0). A detailed discussion on the theoretical studies, fabrication, and characterization of plasmonic nano-cones and how they can be used for manipulating the photo-physics of quantum emitters is discussed later in chapter [4](#page-88-0) and chapter [6](#page-130-0) [\[147\]](#page-166-0).

#### **Metallo-dielectric Hybrid Antennas**

Metallo-dielectric hybrid antennas are designed to enhance the spontaneous emission rate of quantum emitters by manipulating their interaction with light [\[44,](#page-156-4) [45\]](#page-156-0). The antennas consist of a metal nanoparticle and a dielectric material, and they are engineered to have plasmonic resonances that strongly couple with the emitter. The presence of the metal nanoparticle modifes the local density of optical states, leading to an enhancement of the spontaneous emission rate [\[44\]](#page-156-4). The dielectric material serves as a spacer to control the distance between the emitter and the metal nanoparticle, which is essential for achieving the desired coupling strength. There are several examples of such hybrid antennas, including: [\[42,](#page-156-2) [44,](#page-156-4) [81\]](#page-160-3)

- 1. Plasmonic-photonic hybrid antennas: These antennas combine plasmonic and photonic materials and are typically used for sensing applications [\[81\]](#page-160-3).
- 2. Dielectric-loaded plasmonic antennas: These antennas consist of a metallic structure loaded with a high-index dielectric material and are used for applications such as [SERS](#page-14-0) [\[42,](#page-156-2) [44\]](#page-156-4).
- 3. Nanostructured antennas: These antennas are made of metallic or dielectric nanoparticles arranged in a specific pattern to control the interaction between light and matter [\[67\]](#page-159-0).

Figure [2.16\(](#page-73-0)d) is a schematic of a metallo-dielectric hybrid antenna formed by a conical nanoantenna in contact with a planar dielectric antenna, whereby an emitter with a vertically aligned dipole moment is embedded inside the dielectric at a depth below the interface.

The primary benefts of a metallo-dielectric hybrid antenna are as follows: (i) they offer a more signifcant enhancement of spontaneous emission rate, (ii) they have higher quantum efficiency, and (iii) they can maintain the [LSPR](#page-14-2) within the visible or [NIR](#page-14-3) range [\[67,](#page-159-0) [45\]](#page-156-0). The performance of these antennas is based on various physical effects, including maximizing the feld driving the plasmonic nanoantenna, achieving a more uniform feld distribution to obtain a large dipolar polarizability, placing the nanoantenna in a high [LDOS](#page-13-0) location, and inducing a dipole in the nanoantenna for efficient radiation. These principles can also be applied to other types of nanoparticles, such as spheres, ellipsoids, rods, and others. The precise design of the metallo-dielectric hybrid antennas allows for tunability of the coupling strength and directionality, making them promising candidates for applications such as single-photon sources, nanoscale lasers, and quantum information processing [\[32,](#page-155-0) [36\]](#page-155-1).

# **2.4 Conclusions**

In this chapter, we have explored fundamental concepts related to diamond and optical antennas. Diamond, a material with exceptional optical and mechanical properties, has been extensively studied for various applications such as sensing, imaging, and quantum technologies. We have discussed the material and optical properties of diamond and different methods of its synthesis and growth. The physical classification of diamonds based on their impurities has also been explained. Then in section [2.2,](#page-40-0) a detailed discussion on various color centers in diamond, the creation of color centers, and the optical study of [SiV](#page-14-4) centers and their unique optical properties are presented. The [SiV](#page-14-4) color centers,

### 2 Fundamental Concepts of Color Centers in Diamond and Optical Antennas

in particular, have been extensively studied for their optical and spin properties, which are promising candidates for quantum technologies. Finally in section [2.3,](#page-57-0) we explored optical antennas, which are nanoscale resonators, that play a crucial role in enhancing and quenching the fuorescence of color centers in diamond. We have explored different fabrication methods of optical antennas and the design considerations that need to be taken into account for optimal performance. Modification of the spontaneous emission rate through the use of optical antennas has been highlighted as a signifcant advantage for various applications. Overall, this chapter provides a comprehensive understanding of the fundamental concepts related to diamond, color centers, and optical antennas. The unique properties of diamonds and the ability to control the optical emission of color centers through optical antennas have opened up exciting avenues for future research and applications in various felds, including quantum technologies, sensing, and imaging.

In chapter [3,](#page-78-0) we shift our focus to the modeling of gold nano-cones for enhancing quantum emitter performance. The chapter discusses the modeling of a gold nano-cone and the coupling of a single quantum emitter to this structure. These predictions could pave the way for designing efficient and high-performance quantum devices.

# **3**

# <span id="page-78-0"></span>**MODELLING OF GOLD NANO-CONES FOR ENHANCING QUANTUM EMITTER**

#### **3.1 Introduction**

The theoretical aspects regarding the design considerations of nano-cone fabrication and for near-feld coupling of a gold nano-cone with a [SiV](#page-14-4) color center in diamond nanomembranes are discussed in this chapter. Coupling a quantum emitter to a nano resonator requires close proximity between the two systems. The [SiV](#page-14-4) centers are created via silicon ion implantation and annealing on a thin diamond nanomembrane provided the required dimension for near-feld interaction in a controlled manner. We have studied the design considerations of a sharp platinum-based gold nano-cone [\[42,](#page-156-2) [47\]](#page-157-0) on the cantilever of an [AFM](#page-13-1) as an optical antenna, where the sharp tip of the cone enhances the Purcell factor, while the larger base increases the antenna effciency [\[37\]](#page-155-2). The [FDTD](#page-13-2) calculations are performed for the investigation of suitable aspect ratio on the antenna geometry to spectrally match the [LSPR](#page-14-2) of the nano-cone with the [SiV](#page-14-4) center to enhance its total radiative decay rate  $(\Gamma_{\text{tot}})$ . The thickness of a gold layer and its effect on the antenna efficiency and the spontaneous emission rate of the emitter have been investigated. Besides, the emitter-antenna distance dependence on the  $\Gamma_{\text{tot}}$  and antenna efficiency are discussed.

The structure of this chapter is as follows: section [3.2](#page-79-0) presents the [FDTD](#page-13-2) simulations for the modeling of gold nano-cones based on two distinct scenarios. Section [3.2.1](#page-79-1) explains the process of modeling a gold nano-cone to enhance the  $\Gamma_{\text{tot}}$ . Lastly, in section [3.2.2,](#page-80-0) the controlled coupling of a gold nano-cone with a single [SiV](#page-14-4) center in a [PCD](#page-14-5) membrane for Purcell enhancement is discussed. The section concludes by addressing the changes in Purcell enhancement when the emitter has been introduced into a metal-dielectric interface rather than in free space. Moreover, we have discussed in some detail the design

This chapter is based on the Conference Proceedings publication "Exploring ultrafast single-photon emission of silicon-vacancy color centers in diamond nano-membranes coupled with gold nano-cones" by H. Kambalathmana, A. M. Flatae, S. Lagomarsino, H. Galal, F. Tantussi, G. C. Messina, E. Wörner, C. Wild, N. Gelli, S. Sciortino, L. Giuntini, F. De Angelis, M. Agio, Proc. SPIE 11091, Quantum Nanophotonic Materials, Devices, and Systems 2019, 1109108 (3 September 2019); doi: 10.1117/12.2528749. I contributed to the implementation of the experimental setup, recorded the data, analyzed the data, prepared fgures for the manuscript, and contributed to the preparation of the manuscript.

considerations of gold nano-cones followed by [FDTD](#page-13-2) calculations on different aspect ratios of the nano-cone.

# <span id="page-79-0"></span>**3.2 Theoretical Predictions**

The manipulation of the [LDOS](#page-13-0) of a single quantum emitter by changing the surrounding environment is always an outstanding possibility to control the emission dynamics for different applications [\[62\]](#page-158-0). To achieve this, early studies have investigated different aspects of coupling a single quantum emitter with dielectric interfaces, microcavities, and plasmonic structures [refer section [2.3.5\]](#page-72-0). Exploiting surface plasmon resonances from sharp metal tips as an optical nano-antenna could seem a quite straightforward method for achieving Purcell enhancement. However, the fact that the antenna efficiency decreases as the emitter approaches the plasmonic structure makes it difficult to experimentally implement. Accordingly, fnding an appropriate design of nano-antenna is necessary for strong Purcell enhancement. Comparing different optical antenna structures such as planar antenna, nano-rods, and bowtie antenna, it turns out that plasmonic structures with sharp tips support [LSPRs](#page-14-2) that lead to stronger feld confnement [\[37,](#page-155-2) [47,](#page-157-0) [45,](#page-156-0) [75\]](#page-159-1). These plasmonic nanostructures can concentrate the electromagnetic feld in tiny mode volumes and the [LSPR](#page-14-2) can be easily tuned by changing the aspect ratio of the nanostructure [\[75\]](#page-159-1). Finally, the broad resonances of these plasmonic devices can be matched with the emission spectrum of quantum emitters such as quantum dots, color centers in diamonds, and fuorescent molecules at room temperature. This section discusses the modeling of plasmonic gold nano-cones for fnding the desired nano-cone geometry [section [3.2.1\]](#page-79-1) and the quantitative analysis of the spontaneous emission rate enhancement of quantum emitters as a result of the near-field coupling of plasmonic gold nano-cones [section [3.2.2\]](#page-80-0).

# <span id="page-79-1"></span>**3.2.1 Modeling of a Gold Nano-cone**

Recently, the fabrication of sharp platinum-based gold nano-cones with a tip radius of curvature down to 5-10 nm using electronic beam-induced deposition [\(EBID\)](#page-13-3) followed by gold sputter deposition were reported by A. M. Flatae et.al [\[47\]](#page-157-0). These nanostructures provide three orders of magnitude enhancement for the  $\Gamma_{\text{tot}}$  with 80% of antenna efficiency according to theoretical studies. The nano-cones can be fabricated on the probe of an [AFM](#page-13-1) and can be approached to the quantum emitter with nanometer precision. However, defning the geometry of gold nano-cones that can match the [LSPR](#page-14-2) with the emission of the quantum emitters [in this simulation [SiV](#page-14-4) color center is considered as the quantum emitter] is a requisite.

The [FDTD](#page-13-2) [\[99\]](#page-162-1) simulation has been performed to obtain the [LSPR-](#page-14-2)related optical properties of the platinum-based gold coated [AFM](#page-13-1) probe. Consider a single quantum emitter

<span id="page-80-1"></span>

**Figure 3.1.** Schematic representation of a hybrid quantum system. A [SiV](#page-14-4) color center in a diamond nanomembrane is coupled with a gold nano-cone. The inset describes the cone structure: A platinum-based cone is fabricated on top of a 50 nm thick silicon nitride  $(Si<sub>3</sub>N<sub>4</sub>)$  cantilever followed by 30 nm gold coating to create the gold nano-cone structure

<span id="page-80-0"></span>close to a metal-dielectric interface, where a gold nano-cone structure acts as a simple metallic nano-antenna and a diamond nanomembrane as a dielectric substrate, as shown in Figure [3.1.](#page-80-1) A 50 nm thick diamond nanomembrane is implanted with [SiV](#page-14-4) color centers having [ZPL](#page-15-0) emission at 738 nm. The simulation can find a suitable aspect ratio of the nano-cone to spectrally match the emission spectrum of the [SiV](#page-14-4) center [in the [FDTD](#page-13-2) simulation, the emitter is considered as an electric dipole source]. An electric dipole source oriented along the symmetry axis of the gold nano-cone placed at a distance of a few nanometers from the tip [geometrical parameters are similar to previously fabricated structure] [\[47\]](#page-157-0). The tip radius of curvature is chosen as 10 nm for the gold cone and 6 nm for the platinum cone. The inset shows the platinum-based nano-cone with a fixed base of 80 nm and a height of 80 nm fabricated on top of a 50 nm thick  $Si<sub>3</sub>N<sub>4</sub>$  substrate (cantilever) followed by 30 nm gold coating [\[170,](#page-169-1) [171,](#page-169-2) [172\]](#page-169-3). The thickness *'t'* of the gold layer (yellow) on the platinum-carbon-based nano-cone (gray) is changing from 15, 20, 25, and 30 nm for tuning the desired [LSPR](#page-14-2) of the gold nano-cone. Symmetric boundary conditions were used on X and Y boundaries for all the simulations. To accurately simulate the near-feld effects on the tip, the mesh size was set to 1 nm in the vicinity of the metallic nano-antenna system and 1 nm elsewhere. Non-uniform [FDTD](#page-13-2) mesh method was implemented to save the simulation time. A feld monitor and a transmission box were added to investigate the antenna efficiency and  $\Gamma_{\text{tot}}$  of the system. The refractive index values for gold,  $Si<sub>3</sub>N<sub>4</sub>$ , and platinum were taken from Ref[\[170\]](#page-169-1), Ref[\[171\]](#page-169-2), and Ref[\[172\]](#page-169-3) respectively.

#### **3.2.2 Single Quantum Emitter Coupled to a Gold Nano-Cone**

#### **Finite Difference Time Domain (FDTD) Solver Introduction**

The calculation principle of [FDTD](#page-13-2) relies on solving Maxwell's curl equations in nonmagnetic materials [\[173,](#page-169-4) [174,](#page-169-5) [175\]](#page-169-6).

$$
\frac{\partial \vec{D}}{\partial t} = \nabla \times \vec{H}
$$

where,  $\vec{D}(\omega) = \epsilon_0 \epsilon_r(\omega) \vec{E}(\omega)$ .

$$
\frac{\partial \vec{H}}{\partial t} = -\frac{1}{\mu_0} \nabla \times \vec{E}
$$

where H, E, and D represent the magnetic, electric, and displacement felds respectively, while,  $\epsilon_r(\omega)$  indicates the complex relative dielectric constant ( $\epsilon_r(\omega) = n^2$ , where n is the refractive index). In three dimensions, Maxwell's equations consist of six electromagnetic field components:  $E_x$ ,  $E_y$ ,  $E_z$  and  $H_x$ ,  $H_y$ ,  $H_z$ . If we assume that the structure is infinite in the z dimension and that the fields are independent of z, specifically,

$$
\epsilon_r(\omega, x, y, z) = \epsilon_r(\omega, x, y)
$$

$$
\frac{\partial \vec{E}}{\partial z} = \frac{\partial \vec{H}}{\partial z} = 0
$$

In this case, Maxwell's equations split into two independent sets of equations composed of three vector quantities each of which can be solved in the x-y plane only, which are the TE (transverse electric), and TM (transverse magnetic) equations. Both of these equations can be solved using the  $E_x$ ,  $E_y$ ,  $E_z$  components corresponding to TE and  $H_x$ ,  $H_y$ ,  $H_z$ corresponding to TM respectively. The [FDTD](#page-13-2) method resolves the governing equations on a discretized spatial and temporal grid, with each feld component calculated at a slightly offset location within the Yee cell. By default, data obtained from the [FDTD](#page-13-2) solver undergoes automatic interpolation to the origin of each grid point, alleviating the need for the end user to address this matter in their analysis.

Incorporating dispersive materials with tabulated refractive index (n,k) data dependent on wavelength is facilitated through the use of multi-coefficient material models, automatically generating a material model based on the provided tabulated data. Alternatively, specific models such as Plasma (Drude), Debye, or Lorentz may be employed. The [FDTD](#page-13-2) solver accommodates various boundary conditions, including a perfectly matched layer [\(PML\)](#page-14-6), periodic, and Bloch. A variety of sources are supported by the [FDTD](#page-13-2) solver, including point dipoles, beams, plane waves, a total-field scattered-field (TFSF) source, a guided-mode source for integrated optical components, and an imported source for interfacing with external photonic design software. Moreover, [FDTD](#page-13-2) uses a rectangular,

<span id="page-82-0"></span>

**Figure 3.2.** (a) Metallic nano-antenna coupled to a single emitter in free space. The emitter has dipole moment orientation along the symmetry axis of the gold nano-cone placed at a distance  $p = 10$  nm (b) Emitter embedded 4 nm inside 50 nm thick dielectric diamond membrane. (c) Emitter inside the dielectric membrane (diamond membrane) coupled to a gold nano-cone. The nano-cone-emitter distance *p* varies from 0 - 10 nm. The emitter is embedded at a depth of *q* varies from 0 - 4 nm on the substrate with a refractive index of 2.4. The  $\Gamma_{\text{tot}}$  in this case is normalized with respect to the radiative decay rate of the emitter inside the dielectric membrane  $\Gamma_{\rm (rad,diel)}$ .

Cartesian style mesh, where the fundamental simulation quantities [material properties and geometrical information, electric and magnetic felds] are calculated at each mesh point.

#### **Modeling of Single Quantum Emitter Coupled to a Gold Nano-Cone**

The design considerations for the fabrication of gold nano-cones by the [FDTD](#page-13-2) Lumerical simulation method are investigated in this section. To set the ground, consider a single quantum emitter inside a 50 nm thick dielectric diamond membrane with an electric dipole moment oriented along the symmetry axis, as shown in Figure [3.2\(](#page-82-0)b). The respective  $\Gamma_{\text{tot}}$ ,  $\Gamma_{\text{rad}}$ , and  $\Gamma_{\text{nrad}}$  when the emitter is embedded in a dielectric medium is indicated as  $\Gamma_{\rm (tot,diel)}$ ,  $\Gamma_{\rm (rad,diel)}$ , and  $\Gamma_{\rm (nrad,diel)}$  respectively. If the quantum emitter inside the dielectric substrate is close to a metal interface, the  $\Gamma_{\text{tot}}$  of the emitter changes in accordance with the coupling strength [\[42\]](#page-156-2). To maximize this coupling and, ultimately the overall radiative decay rate ( $\Gamma_{rad}$ ), it is beneficial to decrease the metal-emitter distance [\[37,](#page-155-2) [42,](#page-156-2) [170\]](#page-169-1). However, very small distances result in an enhanced non-radiative decay rate ( $\Gamma_{\text{nrad}}$ ) owing to the dissipation of metal. There are many possible dimensions (base and height or aspect ratio) of gold nano-cones, which can yield plasmon resonance in the [NIR.](#page-14-3) Since the dissipation of gold is smaller in the [NIR](#page-14-3) region, enhancements of the spontaneous emission rate by more than three orders of magnitudes are feasible [\[46,](#page-156-5) [68,](#page-159-2) [74,](#page-159-3) [176\]](#page-169-7). Here, the emission of [SiV](#page-14-4) color centers in diamond in the [NIR](#page-14-3) region is of specific interest.

The current investigation broadens those concepts by monitoring the  $\Gamma_{\text{tot}}$  and antenna efficiency for two cases, where the electric dipole source is coupled to a gold nano-cone in free space [see Figure [3.2\(](#page-82-0)a)] as well as in the (dielectric medium) diamond membrane [see Figure [3.2\(](#page-82-0)c)]. Figure [3.3\(](#page-83-0)a), and Figure 3.3(b) displays the change in  $\Gamma_{\text{tot}}$  with respect

<span id="page-83-0"></span>

**Figure 3.3.** An electric dipole source is coupled to gold nano-cone in free space [see Figure [3.2\(](#page-82-0)a)]. (a)  $\Gamma_{tot}$  is normalized to  $\Gamma_{(rad,0)}$ , where  $\Gamma_{tot}$  is the total radiative decay rate of electric dipole source under near-field coupling with gold nano-cone in free space. (b) The antenna efficiency as a function of wavelength for different gold thicknesses. Parameters: aspect ratio  $\approx 1$  (height (*h*) = 80 nm, base (*b*) = 80 nm). Gold thickness changing from 15 - 30 nm. The [LSPR](#page-14-2) tuning is clearly observed as the dielectric effect of the platinum on the gold cone varies (Figure [3.2\(](#page-82-0)a)). For *t* = 30 nm at 738 nm wavelength, the spectral matching of the plasmonic cone and the [SiV](#page-14-4) emitter is achieved with Purcell enhancement about 900 [see Figure [3.3\(](#page-83-0)a))] with 70% antenna efficiency [see Figure [3.3\(](#page-83-0)b)].

to the radiative emission rate in free space  $[\Gamma_{(rad,0)}]$  and antenna efficiency depending on the aspect ratio of a platinum-based gold nano-cone [based on Figure [3.2\(](#page-82-0)a)]. The modifed emission rates due to the interaction of gold nano-cone with a single emitter in free space without the presence of dielectric interfaces are represented as  $\Gamma_{\text{tot}}$ ,  $\Gamma_{\text{rad}}$ , and Γnrad respectively. The [LSPR](#page-14-2) in the [NIR](#page-14-3) region can be obtained by choosing a suitable gold layer thickness, *'t'*. Since the platinum-carbon composite material has a large refractive index, screening the core with a thicker gold layer results in a blue-shift of the [LSPR](#page-14-2) [\[47\]](#page-157-0). Consequently, increasing the gold layer thickness, whereby the aspect ratio, reduces the interaction between the dielectric core, which results in further enhancement of  $\Gamma_{\text{tot}}$  [\[47\]](#page-157-0), as shown in Figure [3.3\(](#page-83-0)a). Besides, the antenna efficiency is also enhanced from  $60\%$  to 80% as the dielectric effect reduces [shown in Figure [3.3\(](#page-83-0)b)].

The simulation on a gold nano-cone with aspect ratio  $\approx 1$  ( $h = 80$  nm,  $b = 80$  nm,  $t = 30$ nm) is considered for further calculations on the  $\Gamma_{\text{tot}}$  enhancement and antenna efficiency, where it shows the [LSPR](#page-14-2) around the emission wavelength range of [SiV](#page-14-4) emitter [In this case, the aspect ratio of  $\approx 1$  along with the gold thicknesses tuned the [LSPR](#page-14-2) in the [NIR](#page-14-3) region]. Considering the coupling between the emitter and the metallic nano-antenna in free space, the dipole moment of the emitter is oriented along the optical axis of the gold nano-cone at a distance of  $p = 10$  nm from the tip [see Figure [3.2\(](#page-82-0)a)]. The  $\Gamma_{\text{tot}}$  and antenna efficiency of the emitter in free space interacting with a gold nano-cone have been normalized to  $\Gamma_{(tot)}$ 

<span id="page-84-0"></span>

**Figure 3.4.** (a) A gold nano-cone is coupled to a single emitter in free space without the presence of dielectric interfaces [see Figure [3.2\(](#page-82-0)a)], where  $p=10$  nm.  $\Gamma_{\rm tot}$  is normalized to  $\Gamma_{\rm (rad,0)}$  and antenna efficiency as a function of the emission wavelength. (b) A gold nano-cone is coupled to a single emitter in the dielectric membrane.  $\Gamma_{\text{tot}}$  is normalized to  $\Gamma_{\text{(rad,diel)}}$  and antenna efficiency as a function of the emission wavelength. The emitter is embedded in the dielectric substrate, *q* = 4 nm [see Figure [3.2\(](#page-82-0)c)]. Introducing the dielectric interface close to the emitter enhances  $\Gamma_{\text{tot}}$  up to four orders of magnitude. (c) The change in Γ<sub>tot</sub> as the distance *p* varies from 0 to 25 nm. There is an optimum distance *p* for a fixed distance  $q = 2$  nm, to achieve an enhancement in  $\Gamma_{\text{tot}}$  [see Figure  $3.3(c)$  $3.3(c)$ ].

in free space [denoted as  $\Gamma_{(rad,0)}$ , since  $\eta_0 = 1$ ,  $\Gamma_{(rad,0)} = \Gamma_{(tot,0)}$ ] as a function of the distance *p*, is shown in Figure [3.4\(](#page-84-0)a). Indeed, the decay rate corresponding to a single emitter shows that the modification of  $\Gamma_{\text{tot}}$  begins to be significant only for distances smaller than 10 nm, while beyond 10 nm, the near-feld interaction is weak. Conversely, the spontaneous emission of an electric dipole embedded in a diamond membrane is reduced by a factor of  $\approx$  100 with respect to  $\Gamma_{\rm (rad,0)}$ . However, a small intrinsic quantum yield reduces the effect of the diamond membrane on the decay rate and what we expect to fnd is a relatively weak modifcation of the total emission rate, if we consider the typical quantum yields attributed to the [SiV](#page-14-4) [\[6,](#page-152-0) [7,](#page-152-1) [8,](#page-152-2) [177\]](#page-169-8). In the following,  $\Gamma_{\rm (rad,diel)}$  is the spontaneous emission rate of a dipole in the dielectric membrane, while  $\Gamma_{(\mathrm{rad},0)}$  is the spontaneous emission rate of a dipole in free space.

Consider an emitter [shown in the red dotted circle in Figure [3.2\(](#page-82-0)b)] embedded  $q = 4$  nm from the surface of the dielectric membrane with a dipole moment oriented along the optical axis of the nano-cone. Now, combine the emitter is embedded inside a dielectric membrane with the gold nano-cone as shown in Figure [3.2\(](#page-82-0)c). A gold nano-cone of aspect ratio  $\approx$  1 is placed in contact with the membrane containing a quantum emitter at *q* = 4 nm beneath the surface. The depth *q* of the emitter inside the dielectric diamond membrane can be varied, but the calculations of  $\Gamma_{\text{tot}}$  and antenna efficiency are optimized for  $q = 2$ nm. Figure [3.4\(](#page-84-0)a) displays the spectral dependencies of  $\Gamma_{\text{tot}}$  and the antenna efficiency for an emitter in free space coupled to a gold nano-cone, while Figure [3.4\(](#page-84-0)b) is the case when the emitter is embedded inside the diamond membrane coupled to a gold nano-cone. In Figure [3.4\(](#page-84-0)b),  $\Gamma_{\text{tot}}$  is normalized to  $\Gamma_{\text{(rad,diel)}}$  and antenna efficiency as a function of the emission wavelength. We found that  $\Gamma_{tot}$  is enhanced to about four orders of magnitude at 738 nm wavelength when a metal-dielectric interface is introduced around the emitter, compared to the same emitter antenna system in free space  $(n = 1)$ . i.e. without the presence of a diamond membrane  $(n = 2.4)$ . This effect is due to the modifications in the [LDOS](#page-13-0) with respect to the emitter's environment (here n represents the refractive index of the environment). Hence, Figure [3.4\(](#page-84-0)b) reveals that a metal-dielectric antenna system gives a higher antenna efficiency and Purcell enhancement than a metallic nano-antenna alone (in free space) [\[45\]](#page-156-0) (for distances *p* of the order of 25 nm, the coupling strength decreases almost to zero). The enhancement in the radiative decay rate has been calculated as the ratio of the power radiated by the electric dipole in the presence of a diamond membrane near the nano-cone to the power radiated by the electric dipole in a diamond membrane. Similarly, the antenna efficiency is calculated as the ratio of the power radiated to the far-feld when the electric dipole is in the presence of a diamond membrane near the nano-cone to the power radiated by the electric dipole kept inside a diamond membrane.

Figure [3.4\(](#page-84-0)c) displays the Purcell enhancement as a function of the distance *p*. By changing the distance *p* between the dielectric membrane and gold nano-cone [as shown in Figure [3.2\(](#page-82-0)c)] changes the [LDOS,](#page-13-0) which results in a shift of the [LSPR](#page-14-2) resonance peaks, hence the modified  $\Gamma_{\text{tot}}$ . It is clear from Figure [3.4\(](#page-84-0)c) that the near-field coupling is stronger when the emitter is closer to the tip of the nano-cone. This is attributed mainly due to the close proximity, and the spectral matching between the systems. As shown in Figure [3.4\(](#page-84-0)a) and Figure [3.4\(](#page-84-0)b) one can understand the change in the Purcell factor and antenna efficiency. It is evident that even though the simulation is done for the same aspect ratio, the Purcell factor is enhanced up to  $\approx$  35000 when the emitter is in the metal-dielectric interface at 738 nm compared to an enhancement of  $\approx 100$  at the same wavelength without the presence of the membrane. Hence, the Purcell enhancement of a single quantum emitter in a metallic nano-antenna alone [Figure [3.2\(](#page-82-0)a)] is comparable at a distance of 10 nm, whereas, with the metal-dielectric antenna [Figure [3.2\(](#page-82-0)c)], the enhancement is higher but, strongly dependent on the emitter dielectric distance *p*. Therefore, if one could establish a

well-coupled emitter-antenna system, it would be possible to see at least three orders of magnitude enhancement in  $\Gamma_{\text{tot}}$ . Thus the underlined factor in this work that can limit the expected enhancement will be the coupling parameters and the precise fabrication of the optical antenna.

## **3.3 Conclusions**

A theoretical study on the Purcell enhancement of a [SiV](#page-14-4) center coupled to a gold nano-cone was discussed in this chapter. We proposed the design of nano-antennas by combining the gold nano-cone with a diamond membrane, obtaining enhancement in both Purcell factor and antenna efficiency compared to the case without the presence of a dielectric. Moreover, satisfactory antenna designs with realistic parameters such as antenna geometry and distance to the emitter were discussed. To accelerate the emission of an emitter using a metal-dielectric antenna, the [LSPR](#page-14-2) of nano-cones close to the emission wavelength range of [SiV](#page-14-4) were tuned using [FDTD](#page-13-2) simulations. Also, we designed a hybrid quantum system, where the total decay rate of quantum emitters showed enhancement up to four orders of magnitude by placing the emitter close to a metal-dielectric interface [\[99\]](#page-162-1). The fabrication and execution of the controlled coupling of a gold nano-cone in the close proximity of a single emitter is a promising yet challenging task for ultrafast single-photon emission. In the next chapter [4,](#page-88-0) the preliminary experimental results are described, and indicates the feasibility of our approach and provides new insight into the optical properties of [SiV](#page-14-4) color centers in thin diamond membranes.

In chapter [4,](#page-88-0) the focus shifts towards the experimental methods and results obtained from the fabrication and spectroscopy of gold nano-cones. The chapter begins by outlining the fabrication and spectroscopy techniques employed in the study, followed by a detailed discussion of the simulation and theory behind the results obtained. The chapter concludes with a description of how the [LSPR](#page-14-2) of the gold nano-cones can be tuned to enhance their properties.

# **4**

# <span id="page-88-0"></span>**FABRICATION AND OPTICAL CHARACTERIZATION OF A PLASMONIC NANO-CON[E](#page-0-0)**

Optical antennas are nanostructures that introduce unprecedented possibilities for lightmatter interaction at the nanoscale. An appropriately tailored plasmonic antenna can enhance the  $\Gamma_{\text{tot}}$  and modify the angular radiation pattern of a single quantum emitter through controlled near-feld coupling. Despite their ability to surpass the fundamental diffraction limit and confne the electromagnetic feld to a tiny mode volume, fabricating three-dimensional (3D) sharp scanning nanoscale plasmonic structures with the desired aspect ratio is yet an ambitious goal. In this chapter, we discuss the fabrication technique of gold nano-cones fabricated by gold evaporation on commercial [AFM](#page-13-1) probes followed by [FIB](#page-13-4) milling technique. The method is versatile and allows the fabrication of nano-cones with desired dimensions of around 100 nm along with an aspect ratio of  $\approx$  1. We have studied their optical properties and show how the variation in the refractive index of the dielectric substrate affects the [LSPR](#page-14-2) of the nano-cones, the decay rate enhancement, and the quantum yield of an emitter relevant for fuorescence/Raman scanning experiments. Theoretical studies using [FDTD](#page-13-2) calculations have guided the fabrication process and are consistent with experimental results. These nanostructures can now be used to manipulate quantum emitters to investigate for instance their photo-physics and single-photon emission properties, as well as for spectroscopic and sensing applications.

#### **4.1 Introduction**

For the last decades, research in nano-optics has been growing at exponential speed. The implementation of strongly enhanced, tightly confned electromagnetic radiation is of great interest for a wide range of applications, including manipulating the photo-physics of quantum emitters [\[35,](#page-155-3) [86,](#page-160-4) [65\]](#page-158-1), sensing [\[178\]](#page-169-9), information processing [\[179,](#page-170-0) [180\]](#page-170-1), scanning

This chapter is based on the publication "Plasmonic Nanocone Scanning Antenna: Fabrication and Optical Properties" by H. Kambalathmana, A.M. Flatae, C. Biagini, F. Tantussi, F. De Angelis and, M. Agio, Advanced Photonics Research (2023), p. 2300058; doi: 10.1002/adpr.202300058. I contributed to the implementation of the experimental setup, recorded the data, analyzed the data, prepared fgures for the manuscript, and contributed to the preparation of the manuscript.

near-feld microscopy [\[181\]](#page-170-2), etc. The ideal candidates employed for these applications are often plasmonic nanostructures acting as optical antennas [\[31,](#page-155-4) [36\]](#page-155-1). Here, the [LSPR](#page-14-2) of the nanostructures can be tuned by modifying the aspect ratio and it can achieve further field enhancement by introducing sharp features to the nanostructures. Hence, the electromagnetic radiation from a distant source is concentrated near the sharp edges of the antenna through the lightning rod effect, beating the fundamental diffraction limit. The primary proof of this concept was done by E.H. Synge et al. in 1928 [\[182\]](#page-170-3), which was later demonstrated in the optical spectral range by D. Pohl et al. [\[183\]](#page-170-4) in 1984, and fnally translated from the context of near-feld optics to optical antennas later in 2005 [\[184\]](#page-170-5). Optical antennas are also able to enhance the spontaneous emission rate of quantum emitters via efficient near-field coupling, but one must find a balance between the Purcell enhancement [\[163\]](#page-168-1) and the antenna efficiency [\[36\]](#page-155-1). Previous studies have shown that nano-cones deliver strong confinement of electromagnetic fields compared to nanorods and nanospheroids [\[77\]](#page-159-4); introducing a sharp tip on one end promotes feld enhancement, and increasing the other end (the base of the cone) helps to increase the volume, thus the antenna efficiency [\[37\]](#page-155-2).

Ultra-sharp nanoantennas fabricated on scanning near-feld probes have shown controlled manipulation of the photo-physics of quantum emitters. The most commonly used scanning probes nanostructures are uncoated or metalized [AFM](#page-13-1) probes. B. Hecht et al. [\[58\]](#page-158-2) have shown photoluminescence enhancement over the non-radiative losses of a single quantum dot coupled with a bowtie antenna. Here the antenna fabricated at the apex of a pyramidal [AFM](#page-13-1) probe by [FIB](#page-13-4) milling enabled effcient light-matter interaction of the hybrid system. Similarly, the infuence of different scanning probes on the excitation intensity, excited state lifetime, and the angular emission of single molecules are also reported [\[59\]](#page-158-3). N. F. Hulst et al. have demonstrated the possibility of nanometer resolution optical microscopy by exploiting resonant optical nanoantenna positioned at the end of a metal-coated glass fiber near-field probe [\[60\]](#page-158-4). F. De Angelis et al. introduced conical structures based on the principle of nano-focusing for [SERS](#page-14-0) [\[185\]](#page-170-6). A highly reproducible near-feld optical imaging with a sub-20-nm resolution based on template-stripped gold pyramids was established by L. Novotny et al. [\[82\]](#page-160-5) in 2012.

However, the bottom line for an efficient near-field coupling was the nanofabrication of sharp plasmonic nanostructures. In the last decade, scientists have developed several fabrication techniques to create sharp plasmonic structures for various applications in information processing [\[58,](#page-158-2) [59\]](#page-158-3), sensing [\[186\]](#page-170-7), spectroscopy [\[82\]](#page-160-5), microscopy [\[60\]](#page-158-4), etc. The underlying physics of these nanostructures relies on the light-matter interaction at a single emitter level. Based on the fabrication technique used, the control of the ideal/critical dimension of the nanostructures varies accordingly. Thus, achieving suitable structures without sophisticated or expensive fabrication methods is still under investigation. Nanofabrication techniques, in general, can be categorized mainly into two: the "top-down" approach and the "bottom-up" approach [\[187\]](#page-170-8). As the name suggests, the top-down approach creates nanostructures by deconstructing bulk materials via lithographic tools or by dry etching. Such methods allow the devising of rigorously controlled complex 2.5-dimensional (2.5D) geometries with high precision. However, the challenge of creating high-quality three-dimensional (3D) structures is still challenging. On the other hand, the bottom-up approach creates nanostructures from the self-organization of basic atomic/molecular levels amidst great control over the fabrication of 2D and 3D molecular structures. However, the technique needs compatible surfaces and selectively adding atoms to create the desired nanostructures is not trivial. The widely experimented fabrication techniques to create 3D nano-cones comprise etching processes like wet chemical etching or dry reactive ion etching [\(RIE\)](#page-14-7) and various lithography processes such as [FIB](#page-13-4) lithography and [EBL,](#page-13-5) natural lithography, nanoimprint lithography [\(NIL\)](#page-14-8), and colloidal lithography. Among these largely practiced top-down approaches are [FIB](#page-13-4) etching and [EBL,](#page-13-5) while colloidal lithography and reactive ion etching processes are the broadly used bottom-up approaches[\[188,](#page-170-9) [189\]](#page-171-0).

A versatile, simple, and relatively fast fabrication approach of plasmonic gold nano-cones by combining gold evaporation followed by [FIB](#page-13-4) milling on a commercially available [AFM](#page-13-1) cantilever [\[147\]](#page-166-0) was carried out. These nanostructures fabricated on the tip apex of sharp [AFM](#page-13-1) probes can be exploited for a plethora of near-feld optical phenomena. For instance, plasmonic nanostructures fabricated on the tip of [AFM](#page-13-1) probes can be exploited for controlled near-feld coupling. The coupling strength can be manipulated by precisely controlling the distance between the emitter and the plasmonic structure [\[47\]](#page-157-0). Particularly if the emitter is embedded in a relatively thin medium, as in the case of color centers in thin diamond membranes, [AFM](#page-13-1) probe-based plasmonic nanostructures allow an effcient near-field coupling scheme. Employing a dark-field spectroscopy setup, we optically characterized the nano-cones and ensured the [LSPR](#page-14-2) was in the [NIR](#page-14-3) at the desired wavelength range for future experiments. Besides, the modification of the [LSPR](#page-14-2) with various dielectric substrates is also reported.

The theoretical studies have already verifed that nano-cones of dimensions around 100 nm with an aspect ratio of  $\approx$  1 can enhance the spontaneous emission rate of quantum emitters without compromising the quantum efficiency [\[42,](#page-156-2) [44\]](#page-156-4). Also, we addressed the role of the substrate and of the intrinsic quantum yield in determining the decay rates of a quantum emitter coupled to a nano-cone. Starting from quantitative expressions that offer more insight into the process, we presented [FDTD](#page-13-2) simulations under different conditions to guide future experimental work on fuorescence enhancement.

In this chapter, the section [4.2.1](#page-91-0) describes the fabrication process of nano-cones on [AFM](#page-13-1)

probes, followed by the optical characterization of these nanostructures. The simulation and theoretical studies of the nano-cone structures to understand how a dielectric environment's change in refractive index correlates with the [LSPR](#page-14-2) is discussed. Finally, the theoretical fndings are verifed with the experimental results and conclude with ideas for future studies.

## **4.2 Experimental Methods**

This section provides an overview of the fabrication and optical characterization of the plasmonic gold nano-cones utilized for manipulating the photo-physics of [SiV](#page-14-4) color centers. The section [4.2.1](#page-91-0) elaborates on some of the remarkable nanofabrication techniques developed in the last decade. The section [4.2.2](#page-96-0) discusses the optical characterization techniques and the spectroscopy of nano-cones.

#### <span id="page-91-0"></span>**4.2.1 Fabrication**

We summarize a few of the fabrication techniques in chronological order, which have marked their success in the history of plasmonic nanostructure fabrication, especially the fabrication of nano-cones. Ching Mei Hsu et al. [\[190\]](#page-171-1) have developed a technique to fabricate closely packed sharp silicon nanotips by combining Langmuir–Blodgett assembly and [RIE.](#page-14-7) Monodispersed  $SiO<sub>2</sub>$  nanoparticles assembled into a closely packed monolayer on a silicon wafer via the Langmuir–Blodgett mechanism. Utilizing the [RIE](#page-14-7) process, they tuned the nanoparticle's diameter and spacing. Even though this approach has unprecedented control over the dimension of the nano-particle, the fabrication of nanocones at the desired location using this method is wholly arduous. M Fleischer et al.[\[191\]](#page-171-2) created nano-cones by merging thin-flm deposition, [EBL,](#page-13-5) and [FIB](#page-13-4) techniques. A thin flm of titanium is deposited by electron beam evaporation followed by thermal evaporation of the gold layer. Then the etch mask is patterned onto the gold flm by [EBL.](#page-13-5) Finally, using a [FIB](#page-13-4) milling system, the unprotected metal, and the etching mask are dry-etched to create nanostructures. The conical shapes are created because of the ion bombardment of gold, where the cone axis was pointing along the direction of ion incidence. However, the ultimate shape, cone angle, and size of the nano-cone depend entirely on lots of fabrication parameters such as lateral erosion, sputtering yield, etching conditions, etc. Wei Wu et al. [\[192\]](#page-171-3) used the [NIL](#page-14-8) technique to fabricate nano-cones. Initially, a master mold of silicon nano-cones created by the Bosch etching process was pressed into a polymer layer to make a daughter mold. Then polymer cones were imprinted from the daughter mold, followed by gold coating to create 3D nano-cone arrays. [NIL](#page-14-8) is cost-effective and deterministic; however, the quality of the imprinting structure is highly dependent on proper [NIL](#page-14-8) resist. Moreover, the mechanical stiffness of the polymer is one of the prerequisites for nano-cone fabrication; the softer the mold, the higher the chances of getting deformed nanostructures.

The vital drawback of this fabrication method is the formation of nano-cones with multiple tips. The lack of circular tips eventually prevents them from potential applications such as near-feld coupling with quantum emitters. Juha M. Kontio et al. [\[152\]](#page-167-0) introduced a nano-cone fabrication technique by combining UV-nanoimprint lithography [\(UV-NIL\)](#page-15-1) and electron beam evaporation on flat surfaces. First, cylindrical holes are patterned onto a thick resist layer using [UV-NIL](#page-15-1) and [RIE,](#page-14-7) followed by a metal layer deposition onto the holes by e-beam evaporation until the holes are filled completely. Finally, a lift-off process using ultrasonic agitation was performed to create an array of scalable metallic nano-cones on the substrate. The metal evaporation makes the top of the hole shrink, leaving a conical shape for the nanostructure. The technique is relatively simple, low cost, and versatile, but controlling the radius of curvature of the nano-cone is challenging. Moreover, the structure's sharpness and final height solely depend on the evaporation material. Mana Toma et al. [\[193\]](#page-171-4) employed a combination of colloidal lithography and oxygen plasma to fabricate nano-cone arrays. This process is also known as nanosphere lithography [\(NSL\)](#page-14-9). The 2D periodic nanostructures are created by single-step simultaneous distinctive oxygen plasma etching of polystyrene bead monolayers on Tefon flms. Similarly, Dong Zhang et al. [\[194\]](#page-171-5) have also used a similar technique, where [NSL](#page-14-9) is combined with [RIE](#page-14-7) to fabricate ordered arrays of nano-cones. The major drawback of this fabrication technique was poorly sharpened tips of gold nano-cones over simultaneous etching, which hinders their applications from near-feld coupling with quantum emitters. Moreover, obtaining good quality gold nano-cones with the desired size, lattice periods, and sharp tips depends on various parameters such as the nanosphere size, the etching power, and the etching time. Björn Hoffmann et al. [\[78\]](#page-160-6) reported the fabrication of nano-cones using [FIB](#page-13-4) milling of sputtered nano-crystalline gold layers. This process enables precision control; however, it is a multistep [FIB](#page-13-4) etching process where the removal speed of each processing stage and patterning resolution need different ion beam properties to create desired nano-cone structures. Thus, this top-down process is also not suitable for large-scale fabrication of nano-cones, as it is time-consuming and limited in the total obtainable structured area. Previously the crystallization of excimer laser and the formation of surface texturing have already been reported. However, the formation of a well-defned array of nano-cones at the desired location with controlled dimensions has not yet been shown.

Recently a controlled fabrication of sharp plasmonic gold nano-cones on a 100 nm thick Si3N<sup>4</sup> transparent substrate via [EBID](#page-13-3) followed by gold deposition technique was reported by Assegid. M. Flatae et al. [\[47\]](#page-157-0). This technique enables the fabrication control over the size, shape, and radius of curvature of the nano-cone. Sara Magdi et al. [\[195\]](#page-171-6) have demonstrated the fabrication of an array of random silicon nano-cones via a lithographyfree one-step process by KrF excimer laser. In this case, the silicon nano-cones are not formed by etching; instead, the silicon mass has been re-distributed to form nano-cones. It is a relatively fast process that does not require sophisticated fabrication environments.

<span id="page-93-0"></span>

**Figure 4.1.** Schematic representation of the [FIB](#page-13-4) milling of deposited gold from the [AFM](#page-13-1) probe to create a plasmonic gold nano-cone at the tip apex.

However, according to the change in the maximum laser energy used, arrays of nano-cones with random sizes were formed.

Unlike conventional fabrication methods, our process enables the fabrication of highquality, sharp [tip radius of curvature  $\approx 20$  nm] metallic gold nano-cones on a commercially available [AFM](#page-13-1) probe (qp-fast, NanoAndMore GmbH) apt for several applications such as single-molecule fuorescence microscopy, tip-enhanced Raman spectroscopy [\(TERS\)](#page-15-2), etc [\[147\]](#page-166-0). The antennas were fabricated at the apex of the conical-shaped quartz  $(SiO<sub>2</sub>)$ [AFM](#page-13-1) probe using gold deposition followed by [FIB](#page-13-4) milling, as shown in Figure [4.1,](#page-93-0) and Figure [4.2\(](#page-94-0)a). Initially, 30 nm of gold was deposited on the [AFM](#page-13-1) probe via sputtering technique, using a Kenosistec KS500 Confocal system at a power of 18 W, which resulted in a deposition rate of 0.47 A◦/*s*. Since the metal flm is conductive, the precise focusing of the ion beam at a distinct position for the ideal nano-cone fabrication is possible. FEI Helios Nanolab 650 Dual Beam system (combined with a scanning electron microscope [\(SEM\)](#page-14-10)) and [FIB](#page-13-4) was used for both sample inspection and [FIB](#page-13-4) milling. The milling was performed by bombardment using high-energy gallium ions at 30 kV and 1.1 pA, removing the deposited gold in a controlled way to define the nanostructure shape and dimension. The ion beam waist is around 40 - 60 nm. The [AFM](#page-13-1) tip was placed in a rotating stage and the longitudinal axis was at an angle of 90◦ with the beam axis. After one of the sides was exposed, the stage was rotated to expose the other one [see schematic representation in Figure [4.1\]](#page-93-0). The deposited gold was removed in a controlled way to defne the desired

<span id="page-94-0"></span>

**Figure 4.2.** (a) Schematic representation of the [FIB](#page-13-4) milling of deposited gold from the [AFM](#page-13-1) probe to create plasmonic gold nano-cone at the tip apex. (The sketch is not to scale). (b) The [SEM](#page-14-10) image of the fabricated gold nano-cone on the [AFM](#page-13-1) probe. (c) The [SEM](#page-14-10) images of plasmonic nano-cones fabricated using [FIB](#page-13-4) milling on commercial [AFM](#page-13-1) probes. Each [AFM](#page-13-1) chip contains three cantilevers, and the fabricated nano-cones have different aspect ratios. The values of the base (*b*), and height (*h*) of the nanostructures are also indicated in nanometer.

nanostructure shape and dimension (base, height, and radius of curvature) [\[147\]](#page-166-0).

The probe characterization to optimize the desired geometry of the tip (base, height, and radius of curvature) before and after [FIB](#page-13-4) milling was possible using the integrated [SEM.](#page-14-10) Moreover, in order to improve the nano-cone quality by enlarging the grain sizes and increasing the surface smoothness [\[196\]](#page-171-7), we tested two different annealing processes: 2 hours at 100◦*C* and 1 hour at 200◦*C*, on a hot plate in a nitrogen atmosphere. The nanostructures didn't show any change in shape or roughness, while the metal on the rest of the tip appeared to be ruined after the annealing. We believe these different effects were due to the discontinuity in the thermally conductive metal film, which prevents heat from reaching the nanostructure. Hence, in the final samples, we refrained from performing annealing. All the fabrication steps were performed at the clean room facility in the Istituto Italiano di Tecnologia (IIT) in Genova.

<span id="page-95-0"></span>

**Figure 4.3.** (a-h) SEM images of front and back sides (sides 1 and 2) of the selected nano-cones (probe 1, probe 2, probe 3, and probe 4 are indicated as the nano-cones fabricated on [AFM](#page-13-1) probes). The dimensions of the nano-cones are indicated in red letters in the [SEM](#page-14-10) images. (a-b) **probe 1 front**: *h* = 120 nm, *b* = 100 nm; **probe 1 back**: *h* = 125 nm, *b* = 100 nm. (c-d) **probe 2 front**: *h* = 110 nm, *b* = 90 nm; **probe 2 back**: *h* = 115 nm, *b* = 100 nm. (e-f) **probe 3 front**: *h* = 90 nm, *b* = 80 nm; **probe 3 back**: *h* = 95 nm, *b* = 85 nm. (g-h) **probe 4 front**: *h* = 90 nm, *b* = 90 nm; **probe 4 back**: *h* = 105 nm,  $b = 85$  nm.

A schematic representation of the fabrication process is depicted in Figure [4.2\(](#page-94-0)a). Figure [4.2\(](#page-94-0)b) and Figure [4.2\(](#page-94-0)c) show the [SEM](#page-14-10) images of the [FIB](#page-13-4) nano-cone structures [\[147\]](#page-166-0). Figure [4.2\(](#page-94-0)c) shows selected [SEM](#page-14-10) images of the fabricated structures, where the main geometrical parameters (base and height) have been measured. Since the [AFM](#page-13-1) tip is placed in a rotating stage, the exposed front and back sides of the probes are monitored. Figure [4.3\(](#page-95-0)ah) shows the front and back sides (sides 1 and 2) of selected nano-cones. The fabricated nano-cones have different bases, heights, curvature radius, and gold thickness. Hence the [LSPR](#page-14-2) varies according to the overall shape of the nanostructure on each [AFM](#page-13-1) chip. According to our previous theoretical studies [\[37,](#page-155-2) [44\]](#page-156-4) the ideal aspect ratio required for strong modifcation in the spontaneous emission using the nano-cone should be nearly 1, where the base and height of the nano-cones are around 100 nm. We successfully fabricated nano-cones with base diameters in the range of 70 - 120 nm and heights in the range of 60 - 150 nm, respectively. The aspect ratio of the nanostructures was between 1 - 1.5 and the radius of curvature was down to 20 nm [\[147\]](#page-166-0).

Different from I. Maouli, et al., [\[72\]](#page-159-5) we were able to produce controlled structures with signifcantly smaller dimensions and with a stronger electromagnetic decoupling between

the nano-cone and the gold coated [AFM](#page-13-1) probe, also verifed by the feld plots [see Figure [4.6\]](#page-105-0). T. L. Vasconcelos et al., [\[197\]](#page-171-8) followed a different approach, where they milled a gap in the [AFM](#page-13-1) probe and then evaporated a metal from the front side. Overall, the structures have dimensions comparable to our approach, but the rugosity of the deposited metal flm is substantial and part of the metal evaporation could fll the gap between the apex and the [AFM](#page-13-1) probe.

#### <span id="page-96-0"></span>**4.2.2 Spectroscopy of Nano-cones**

We investigate the optical properties of gold nano-cones fabricated on a commercially available quartz [AFM](#page-13-1) probe (qp-fast, NanoAndMore GmbH) [refer Ref [\[147\]](#page-166-0) for more details]. A detailed description of our fabrication process is given in the previous section [4.2.1.](#page-91-0)

For tailoring the accurate nano-cone geometry to enhance the near-feld coupling with a quantum emitter, we performed [FDTD](#page-13-2) calculations [see section [3.2.2](#page-80-0) for understanding the theoretical aspects of [FDTD](#page-13-2) calculations]. We primarily addressed the longitudinal plasmon resonance of the nano-cone to match the emission of a quantum emitter. For this purpose, we optically characterized the nano-cones with an inverted microscope in darkfeld microscopy confguration [\[47\]](#page-157-0). This enabled us to flter the weak scattering signal of the nanostructures effectively. The mode of illumination to excite both longitudinal and transversal modes is demonstrated in Figure [4.4\(](#page-97-0)a). A linearly polarized collimated supercontinuum laser (SuperK COMPACT, NKT Photonics) illuminates the nanostructures using a high numerical-aperture (NA) microscope objective (ZEISS Epiplan-NEOFLUAR 100X/0.75NA-BD DIC). The central part of the excitation laser is blocked by a central beam blocker (CBB), creating a hollow ring beam. The polarization orientation of the ring beam is adjusted via a half-wave plate (HWP). To manipulate the polarization of the hollow ring beam, part of the beam is blocked using a beam blocker (BB). Thus, the partially blocked ring beam can generate both S- and P-polarization once it gets focused on the dielectric (namely, we obtain S-polarization along the substrate transverse axis and P-polarization along the nano-cone longitudinal axis). Apart from that, to excite the plasmon modes of the nano-cone, it is signifcant to generate P-polarization along the longitudinal axis. In general, the spot size is around  $1.3 \mu m$ , but the use of a confocal pinhole defines the detection volume and makes the lateral- and axial- resolution of detection around 529 nm and 1.4 µm, respectively. We scan through the focal plane to increase the signal-to-noise ratio of the nanoparticles at the tip of the [AFM](#page-13-1) probe [\[147\]](#page-166-0).

The partially blocked hollow ring beam enters the objective lens via a refecting mirror (M). The mirror sends the beam towards the beam-splitter (BS). The BS sends the broken ring beam to excite the nano-cones through the high-NA objective and blocks the

<span id="page-97-0"></span>

**Figure 4.4.** (a) Schematics of the experimental setup for dark-feld microscopy of nanostructures. A beam blocker is used to create a longitudinal polarization in the focal spot of the microscope objective. (b) Schematic representation of a hybrid quantum system. Plasmonic gold nano-cone fabricated on [AFM](#page-13-1) cantilever is brought closer to a quantum emitter embedded in the dielectric. (c) A wide-feld image of plasmonic gold nano-cone closer to a [PCD](#page-14-5) membrane.

refected laser part which is coming towards the collection beam path. The collection optics are maintained so that only the scattered light from the nanoparticles will enter the objective for spectroscopic measurements. As shown in Figure [4.4\(](#page-97-0)a), the illumination supercontinuum laser beam (red line) along the collection path is blocked by BB, thus only the desired scattering signal (signal coming from the nano-cone) is fltered later by the confocal system (confocal system consists of two plano-convex lenses (L) and a pinhole (P) at the focus). Then the collected signal gets refected from a refecting mirror (RM) and sent to an [EM-CCD](#page-13-6) camera (Princeton Instruments, ProEM-HS: 512 BX3, back-illuminated [EM-CCD,](#page-13-6) more than 90% quantum efficiency in the [NIR](#page-14-3) region) for dark-field imaging by a fippable mirror (FM). FM can be switched to access the spectrometer (Andor, Newton DU970P-BVF) to measure the [LSPR](#page-14-2) or towards the [EM-CCD](#page-13-6) camera for dark-feld imaging.

Additionally, an atomic force microscope scan head (Nanowizard4, JPK Instruments AG) is placed on top of the microscope, allowing the [AFM](#page-13-1) probe to be positioned at the center of the optical axis. The nano-cones fabricated on the tip apex of the [AFM](#page-13-1) cantilevers are mounted on the [AFM](#page-13-1) for controlled positioning of the nano-cone in the vicinity of a dielectric substrate [see Figure [4.4\(](#page-97-0)b)]. Figure [4.4\(](#page-97-0)c) depicts the wide-feld image of an [AFM](#page-13-1) cantilever closer to a [PCD](#page-14-5) membrane with the plasmonic gold nano-cone (a bright spot at the center of the cantilever represents the gold nano-cone). [PCD](#page-14-5) membrane is a good platform as photo-stable quantum emitters, for example, [SiV](#page-14-4) color centers, can be easily implanted in the frst few nanometer layers for near-feld plasmon coupling [\[28,](#page-155-5) [44\]](#page-156-4).

The [AFM](#page-13-1) head facilitates three directional degrees of freedom to control the probe. Besides, the sample is mounted on an XY piezo stage, and thus in total, we have five directional degrees of freedom. In this fashion, our setup can move both the emitter and the nanocone with nanometer precision. Considering we have used a coherent broadband white light source to illuminate the sample, the scattering signal (*Is*) encompasses contributions from the white light illumination  $(I_w)$ . Therefore, to get the scattered signal  $(I_s)$ , we must normalize the measured signal (*Im*) with the white light (*Iw*). We should also consider the background signals incorporated into our measured signal (*Is*), such as weak scattering from the substrate (in this case, it would be the scattering from the cantilever) and dark counts of the detector. Since the background signal from the cantilever and the dark counts from the detector are fairly negligible, we can eliminate it [\[147\]](#page-166-0).

The [LSPR](#page-14-2) of the nanoparticles depend on their dielectric environment. Hence, the change in the refractive index of the nearby medium changes its resonance position and the [LDOS](#page-13-0) at the emitter's position. The [LSPR](#page-14-2) shift with a dielectric substrate is verifed experimentally as follows: initially, we looked at the [LSPR](#page-14-2) of one nano-cone (with an aspect ratio of about 1) in the air as a reference point without the presence of any dielectric. Then we investigated the shift in [LSPR](#page-14-2) under two cases: the same nano-cone was brought closer to a dielectric, and the [LSPR](#page-14-2) shift was monitored in terms of the change in distance between the nano-antenna and the dielectric. (i) firstly, the scattering measurements are done for the nano-cone closer to a commercial glass coverslip, (ii) secondly, the measurements were repeated with a thin [PCD](#page-14-5) membrane [\[28\]](#page-155-5).

#### **4.3 Results & Discussions**

For tailoring the accurate cone geometry and to enhance the near-field coupling with a quantum emitter, we performed [FDTD](#page-13-2) calculations. In this section, we have shown the theoretical fndings on the spectral dependencies of the decay rate, and the quantum efficiency (QE) on the refractive index of the dielectric substrate  $(n_d)$ . The decay rate can also be written as the sum of the radiative decay rate, the intrinsic non-radiative decay rate, and the additional non-radiative decay rate due to absorption in the antenna system.

#### **4.3.1 Simulation and Theory**

The spontaneous emission is not an intrinsic property of the quantum emitter and it is also dependent on the electromagnetic environment. Hence, it is important to consider the modifcation in spontaneous emission by the interaction of plasmonic gold nanostructures in the presence of a dielectric substrate [\[36,](#page-155-1) [147\]](#page-166-0). We have calculated this quantity by [FDTD](#page-13-2) [Lumerical FDTD Solutions, the mesh size is 0.1 nm near the dipole-nano-cone gap and 1 nm elsewhere] simulations of a classical dipole placed in proximity of a plasmonic gold nano-cone, in which the  $n_d$  varies.

To calculate the quantum efficiency and the modification of the decay rate of color centers embedded in a dielectric membrane near a nano-cone, we start from the intrinsic quantum yield  $\eta_0$  and the decay rates in free space;  $\Gamma_{\rm (tot,0)}$ (total decay rate),  $\Gamma_{\rm (rad,0)}$  (radiative decay rate) and  $\Gamma_{(\text{nrad},0)}$  (nonradiative decay rate) respectively. The decay rates are changed to  $\Gamma_{\rm tot}$  and  $\Gamma_{\rm rad}$  and  $\Gamma_{\rm nrad}$  respectively by the nano-cone plus membrane and to  $\Gamma_{\rm (tot,diel)}$ ,  $\Gamma_{\rm (rad,diel)}$ , and  $\Gamma_{\rm (nrad,diel)}$ , by the dielectric membrane alone, if  $\eta_0$  = 1. Thus, the new quantum yield becomes  $\eta = \frac{\Gamma_{\rm rad}}{\Gamma_{\rm tot}}$  $\frac{\Gamma_{\rm rad}}{\Gamma_{\rm tot}}$  and  $\eta_{\rm diel} = \frac{\Gamma_{\rm (rad,diel)}}{\Gamma_{\rm (tot,diel)}}$  $\frac{\Gamma_{\text{(rad,diel)}}}{\Gamma_{\text{(tot,diel)}}}$ , respectively.

If  $\eta_0$  < 1, we need to take into account that the Purcell effect modifies only the radiative decay rate and that the intrinsic non-radiative rate, which can be expressed as follows:

$$
\Gamma_{(\text{nrad},0)} = \Gamma_{(\text{tot},0)} - \Gamma_{(\text{rad},0)}
$$
  
=  $(1 - \eta_0)\Gamma_{(\text{tot},0)}$   
=  $\frac{(1 - \eta_0)\Gamma_{(\text{rad},0)}}{\eta_0}$ , remains unchanged.

Now the quantum yield is written as,

$$
\eta = \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{tot}} + \frac{(1 - \eta_0)\Gamma_{(\text{rad},0)}}{\eta_0}}
$$
(4.1)

and,

$$
\eta_{\text{diel}} = \frac{\Gamma_{\text{(rad,diel)}}}{\Gamma_{\text{(tot,diel)}} + \frac{(1 - \eta_0)\Gamma_{\text{(rad,0)}}}{\eta_0}}
$$
(4.2)

In a dielectric environment without material absorption,  $\Gamma_{(rad,diel)} = \Gamma_{(tot,diel)} = \Gamma_{diel}$ , hence;

$$
\eta_{\text{diel}} = \frac{\Gamma_{\text{diel}}}{\Gamma_{\text{diel}} + \frac{(1 - \eta_0)\Gamma_{(\text{rad},0)}}{\eta_0}}
$$

$$
= \frac{\eta_0}{\eta_0 + \frac{(1 - \eta_0)\Gamma_{(\text{rad},0)}}{\Gamma_{\text{diel}}}}
$$

The FDTD simulations output for the decay rates are normalized with respect to an emitter in free space, i.e., with respect to  $\Gamma_{(\rm rad,0)}$ . However, we are interested in the modification with respect to the radiative decay rate in bulk, which is  $n_{diel}$  Γ<sub>(rad,0)</sub>, where  $n_{diel}$  is the refractive index of the dielectric. Therefore, we multiply the radiative decay rate  $\Gamma_{(rad,0)}$ by, e.g., n<sub>diel</sub> = 2.4 for diamond, and simply drop the term  $\Gamma_{(\rm rad,0)}$  in the equations. The quantum yields are therefore:

$$
\eta = \frac{\eta_a \eta_0}{\eta_0 + \frac{(1 - \eta_0)n_{\text{diel}}}{\Gamma_{\text{tot}}}}
$$
(4.3)

and

$$
\eta_{\text{diel}} = \frac{\eta_0}{\eta_0 + \frac{(1 - \eta_0)n_{\text{diel}}}{\Gamma_{\text{diel}}}}
$$
(4.4)

where we introduced the term  $\eta_a$  as  $\eta_a = \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{tot}}}$  $\frac{1_{\text{rad}}}{\Gamma_{\text{tot}}}$  to account for the absorption losses in the nano-cone. Here, the intrinsic quantum yield  $\eta_0$  refers to the emitter in the bulk dielectric.

In conclusion, if the [SiV](#page-14-4) center is embedded in a dielectric membrane and it is approached by a nano-cone, the modifcation of the quantum yield is described as follows:

$$
\frac{\eta}{\eta_{\text{diel}}} = \frac{\eta_a[\eta_0 + \frac{(1-\eta_0)n_{\text{diel}}}{\Gamma_{\text{diel}}}]}{\eta_0 + \frac{(1-\eta_0)n_{\text{diel}}}{\Gamma_{\text{tot}}}}
$$
(4.5)

In the calculations, we assumed  $\eta_0 \approx 10\%$  for a [SiV](#page-14-4) center in diamond [\[177\]](#page-169-8). The calculation of the modifcation of the total decay rate follows a similar approach. We are interested in the modifcation of the decay rate with respect to the decay rate in the membrane alone, which is the quantity that we can experimentally measure. Hence,

<span id="page-100-0"></span>
$$
\frac{\Gamma_{\text{tot}}'}{\Gamma_{(\text{tot,diel})}'} = \frac{\Gamma_{\text{tot}} + [1 - \eta_0] \Gamma_{(\text{tot,0})}}{\Gamma_{\text{diel}} + (1 - \eta_0) \Gamma_{(\text{tot,0})}}
$$
(4.6)

Here,  $\Gamma'_{\text{tot}}$  indicates the modified total radiative decay rate that we experimentally measure, which is the sum of  $\Gamma_{\rm rad}$ ,  $\Gamma_{\rm nrad}$  and  $\Gamma_{\rm nrad}^0$  (intrinsic non radiative) respectively.  $\Gamma'_{\rm q}$  $'_{\text{(tot,diel)}}$  is the total raditaive decay rate from the membrane alone, and it is calculated as the sum of  $\Gamma_{\rm (rad,diel)}$ , and  $\Gamma_{\rm (nrad,diel)}$ . Both  $\Gamma_{\rm tot}'$  and  $\Gamma_{\rm tot}'$  $_{(\mathrm{tot,diel})}'$  are the cases, when  $\eta\neq 1$ , whereas  $\Gamma_{\rm tot}$  and  $\Gamma_{\text{(tot,diel)}}$  is considered for cases when  $\eta$  = 1. The apex in the quantities at the right-hand side of the equation denotes the total decay rates including the intrinsic non-radiative channel. Considering that  $\Gamma_{(rad,0)} = \eta_0 \Gamma_{(tot,0)}$ , Equation [\(4.6\)](#page-100-0) can be written as:

$$
\frac{\Gamma'_{\text{tot}}}{\Gamma'_{\text{(tot,diel)}}} = \frac{\eta_0 \frac{\Gamma_{\text{tot}}}{\Gamma_{\text{(rad,0)}}} + (1 - \eta_0)}{\eta_0 \frac{\Gamma_{\text{diel}}}{\Gamma_{\text{(rad,0)}}} + (1 - \eta_0)}
$$
(4.7)

Since the [FDTD](#page-13-2) software outputs the decay rates normalized with respect to free space, but we are interested in the decays normalized with respect to the dielectric medium, we

<span id="page-101-0"></span>

**Figure 4.5.** (a) Schematics of the simulated structure showing metal-dielectric antenna system. The electric dipole is embedded *Q* = 5 nm beneath the dielectric substrate and the minimum distance between the nano-cone and the dielectric is  $P = 1$  nm; it can be varied. The thickness of the gold layer is *t* = 30 nm. The sketch is not to scale. Here in the [FDTD](#page-13-2) calculations, the mesh in the gap is 0.1 nm and 1 nm elsewhere. (b) The shift in the normalized decay rate  $(\Gamma'_{\text{tot}})$  correlates with the change in  $n_d$ , where  $P = 1$  nm and  $Q = 5$  nm. Here  $n_d$  varies from  $n = 1$  (air: dashed blue curve), 1.5 (glass slide: dotted red curve), and 2.4 (diamond membrane (130 nm): solid black curve), respectively. The shift in *QE* (" $\eta$ ") in correlation with  $n_d$  is represented by  $\eta_{(n=1)}$ ,  $\eta_{(n=1.5)}$ , and  $η_{(n=2.4)}$ , indicated by the blue curve (plus symbol), red curve (line symbol), and black curve (square symbol). (c) Modification of  $\Gamma'_{tot}$  (solid curves with solid symbols) and  $\eta'$  (solid curves with hollow symbols) of an electric dipole embedded in glass (*n* = 1.5, red curve) and diamond (*n*  $= 2.4$ , black curve) concerning distance *P*, where the intrinsic QE ( $\eta_0$ ) is 100%. (d) Modification in Γ ′ tot (solid curves with flled symbols) and "*η* ′ " (solid curves with hollow symbols) of an electric dipole embedded in glass (*n* = 1.5, red curve) and diamond (*n* = 2.4, black curve) for distance *P*, where the intrinsic  $QE(\eta_0)$  is 10%.

obtain:

$$
\frac{\Gamma'_{\text{tot}}}{\Gamma'_{\text{(tot,diel)}}} = \frac{\eta_0 \frac{\Gamma_{\text{tot}}}{n_{\text{diel}}} + (1 - \eta_0)}{\eta_0 \frac{\Gamma_{\text{diel}}}{n_{\text{diel}}} + (1 - \eta_0)}
$$
(4.8)

The normalized decay rate,  $\Gamma_{\text{tot}}$  is calculated as the ratio of the power radiated by the classical dipole in the presence of the nano-cone, hence considering possible metal losses to the power radiated by the dipole in free space by considering the possible metal losses. The *QE* is represented by the symbol ("*η*"), and it is defned as the ratio between the power radiated to the total power transferred from the emitter to the antenna. The intrinsic *QE*  $(\eta_0)$  is defined as the ratio of the radiative decay rate to the total decay rate in free space. In the ideal case, we assume that  $\eta_0$  is 100% to calculate both  $\eta$  and  $\Gamma_{\text{tot}}$ . In reality,  $\eta_0$  of for example [SiV](#page-14-4) color centers in thin [PCD](#page-14-5) [\[28\]](#page-155-5) membranes is presumably not more than 10%. Thus, in the case of an emitter-antenna interaction, both *QE* and the total radiative decay rate must take  $\eta_0$  into account. The expressions are given as follows, where the meaning of the primed quantities  $\Gamma'_{tot}$  and  $\eta'$  is explained in the next paragraph:

<span id="page-102-0"></span>
$$
\Gamma_{\text{tot}}' = \frac{\eta_0 \frac{\Gamma_{\text{tot}}}{n_d} + 1 - \eta_0}{\eta_0 \frac{\Gamma_{\text{diel}}}{n_d} + 1 - \eta_0} \tag{4.9}
$$

<span id="page-102-1"></span>
$$
\eta' = \frac{\frac{\Gamma_{\text{rad}}}{\Gamma_{\text{tot}}} * \eta_0}{\frac{n_{\text{d}}}{\Gamma_{\text{tot}}} * [1 - \eta_0] + \eta_0} \tag{4.10}
$$

where  $\Gamma_{rad}$  is the normalized radiative decay rate in the coupled system i.e. without the additional non-radiative decay rate due to absorption by the antenna.

We remark that  $\Gamma'_{tot}$ , for the case of an emitter-antenna system [see Figure [4.5\(](#page-101-0)a)], is normalized with respect to the normalized decay rate  $(\Gamma_{diel})$  in the dielectric substrate, to consider the actual experimental conditions [see Equation [4.9\]](#page-102-0). Likewise, *η*' represents the quantum effciency normalized with respect to that in the dielectric substrate [see Equation [4.10\]](#page-102-1). Here the modifcation factor also includes the fact that the spontaneous emission rate in a bulk medium is equal to the value in free space multiplied by the refractive index, indicated here as  $n_d$  (because all the calculated values are normalized with respect to free space by the [FDTD](#page-13-2) software). Notice that for  $\eta_0$  equal to 1 the two equations reduce to  $\Gamma_{\rm tot}$  $\frac{1_{\text{tot}}}{\Gamma_{\text{diel}}}$  and to  $\eta$ , respectively.

Previously we have delineated the design considerations and reasons for choosing nanoantennas with plasmon resonance in the [NIR](#page-14-3) [\[44\]](#page-156-4). Any plasmonic nanostructure can manipulate the photonic environment of a quantum emitter, thanks to their [LSPR,](#page-14-2) leading to a confined electric field in a tiny mode volume. However, to have an efficient near-field coupling between the antenna and the quantum emitter, we should optimize the design parameters of the antenna so that we can achieve spectral matching between the antenna and the emitter emission. The results enhanced the total radiative decay rate of a quantum emitter with a more significant antenna efficiency of 80%. However, the interaction of the nano-cone plasmonic antenna with a dielectric substrate can lead to the [LSPR](#page-14-2) shift of the nano-cones due to the change in the dielectric environment near the tip. Indeed, the main factor responsible for this is the radiation coupling due to the dielectric substrate. We have investigated the [LSPR](#page-14-2) shift in correlation with the change in the dielectric environment of

gold nano-cones by [FDTD](#page-13-2) calculations (previously, we have performed simulations on the optimal aspect ratio for the nano-cones, which is not shown in this paper [\[44\]](#page-156-4)).

To set the ground, we have simulated the near-feld interaction of a nano-cone of aspect ratio  $\approx$  1 with the presence of dielectric substrates, such as a (semi-infinite) glass coverslip  $(n = 1.5)$  and 130 nm thick [PCD](#page-14-5) membrane  $(n = 2.4)$ , respectively (where *n* is the refractive index of the dielectric substrate). The substrates will not give rise to relevant wave-guiding or Fabry-Perot effects at wavelengths around 700 nm. The nano-cone dimension used for the [FDTD](#page-13-2) simulation is based on a real fabricated structure (Probe 1, i.e., base, *b* = 85 nm, height, *h* = 103 nm, radius of curvature, *r* = 25 nm). The simulated structure is a gold nano-cone created on a quartz [AFM](#page-13-1) probe situated on a quartz substrate of a few microns thickness along with a gold layer thickness of *t* = 30 nm. The schematics depicted in Figure [4.5\(](#page-101-0)a) is a single quantum emitter embedded  $Q = 5$  nm beneath a dielectric substrate placed closer to a plasmonic nano-cone structure [Figure [4.5\(](#page-101-0)a)]. The electric dipole source-oriented along the symmetry axis of the gold nano-cone placed at a variable distance *P* from the nano-cone tip, which efficaciously excites the longitudinal plasmon mode of the nano-cone [\[147\]](#page-166-0).

Figure [4.5\(](#page-101-0)b) represents the spectral dependencies of  $\Gamma'_{\text{tot}}$  and  $\eta'$  of an emitter embedded  $(Q = 5$  nm) in a dielectric substrate coupled with the plasmonic gold nano-cone, where *η*<sup>0</sup> is assumed to be 100%. The dielectric-antenna distance *P* is kept as 1 nm for all the calculations in Figure [4.5\(](#page-101-0)b), but similar fndings occur for larger distances, provided that near-feld coupling with the substrate occurs. It is evident that a small change in the refractive index of the photonic environment shifts the [LSPR](#page-14-2) resonance by around 50 - 80 nm due to the modifcation of the local environment caused by the boundary conditions at the interface. Apart from that, the decay rate and the quantum efficiency of the quantum emitter also become evidently dependent on the substrate [see Figure [4.5\(](#page-101-0)b)] [\[45\]](#page-156-0). Here,  $\Gamma_{(n=1.5)}$ , and  $\Gamma_{(n=2.4)}$  corresponds to the spectral dependencies of  $\Gamma'_{tot}$ , whereas *η*(n=1.5) , and *η*(n=2.4) corresponds to the shift in *QE* with respect to glass coverslip, and diamond membrane respectively. The [LSPR](#page-14-2) linewidth gets broader with higher refractive index due to the radiative broadening [\[36\]](#page-155-1), as observed in Figure [4.5\(](#page-101-0)b), the blue curve corresponding to  $\Gamma_{(n=2.4)}$ . Moreover, the overall enhancement gets larger, despite the linewidth broadening. This contradictory trend can be explained by the fact that  $\Gamma'_{\text{tot}}$  is normalized with respect to the decay rate in the substrate. We have found that the latter environment can significantly change the [LDOS](#page-13-0) [\[147\]](#page-166-0).

For example, an ideal emitter in a [PCD](#page-14-5) membrane exhibits a radiative decay rate that is more than an order of magnitude smaller than in free space, depending on the dipole position and orientation. On the other hand, a dipole in a semi-infnite glass substrate exhibits a moderate change in the spontaneous emission rate, hence the smaller enhancement with respect to air. Thus, the very same nanostructure can lead to significantly different enhancements depending on the substrate parameters. Another interesting effect of a dielectric substrate is the increase in the quantum yield, which results from the radiative broadening of the [LSPR](#page-14-2) [\[37\]](#page-155-2) and to a weaker excitation of non-radiative modes [\[45\]](#page-156-0). The emitter's total radiative decay rate,  $\Gamma'_{\text{tot}}$  enhanced by one order of magnitude and the *QE*, *η* ′ enhanced up to 70% as the dielectric substrate's refractive index increased for the similar emitter-antenna separation ( $P = 1$  nm). As the distance  $P$  increases,  $\Gamma'_{\text{tot}}$  rapidly decreases; hence it is desirable to optimize *P* for controlled, efficient near-field coupling [as demonstrated in Figure [4.5\(](#page-101-0)c)]. However, the change in  $\eta'$  is less than 10% even if the distance *P* is 25 nm. At minimal distances, it is known that the non-radiative channels of the plasmonic antenna result in significant fluorescence quenching. Hence, it is ultimately essential to devise a structure that could provide larger enhancement in  $\Gamma'_{\text{tot}}$  while keeping a higher value for  $η'$ , as shown here. Interestingly, for the same distance a nano-cone near a [PCD](#page-14-5) membrane provides a considerably larger enhancement, although it should be kept in mind that the absolute rate might not be higher than in the case of a nano-cone in free space, given the different values of  $\Gamma_{diel}$  in the denominator. Nonetheless, a stronger relative change of the rates may be advantageous for investigating the photo-physics of the emitter under a wider parameter space [\[147\]](#page-166-0).

In Figure [4.5\(](#page-101-0)d) we present  $\Gamma'_{\text{tot}}$  (solid curves with filled symbols) and  $\eta'$  (solid curves with hollow symbols) for different values of *n*, (*n* = 1.5 and *n* = 2.4) in correlation with the change in distance *P* in nanometer for  $\eta_0 = 10\%$ . There is an evident change with respect to the previous situation. In the case of  $\Gamma_{(n=2.4)}$ , it decreased compared to  $\Gamma_{(n=1.5)}$ , due to the smaller value of  $\Gamma_{\text{diel}}$  in the [PCD](#page-14-5) membrane. The modification of  $\eta'$  with a change in  $n_{\text{d}}$ reduces when  $\Gamma_{\rm tot}$  is larger than about  $\frac{1}{\eta_0}$  as it can be inferred from Equaion [4.10.](#page-102-1) However, for *n* = 2.4, this occurs only for distances smaller than 5 nm. Furthermore, the variation of  $\eta'$  with distance encodes the relationship between  $\Gamma_{\text{tot}}$  and  $\eta_0$ . One can thus gain more insight into the modification of  $\eta_0$  in complex environments, such as polycrystalline versus nanocrystalline host matrices or bulk versus surface boundaries, for the same emitter [\[147\]](#page-166-0).

#### **Field Patterns**

The electric field radiation pattern of a plasmonic nanostructure under the influence of a quantum emitter can exhibit complex and intricate behavior [\[103\]](#page-162-0). Plasmonic nanostructures, such as nanoparticles or nanoantennas, are known for their ability to concentrate and enhance local electromagnetic felds, which can be exploited in various applications, including quantum optics and sensing. The radiation pattern in the context of enhancement of local felds is as follows: a plasmonic nanostructure can signifcantly enhance the local electric field strength in their vicinity. When a quantum emitter, such as a molecule, quantum dot, or color center, is placed within or in close proximity to the nanostructure,

<span id="page-105-0"></span>

Figure 4.6. Normalized electric field patterns (logarithmic scale) of the nano-cone structure excited by a dipole source placed at 5 nm depth in a diamond membrane. The plots are shown as a function of "P"; the distance between the nano-cone tip and the diamond membrane. The chosen wavelength corresponds to the maximum Purcell enhancement near the [SiV](#page-14-4) zero-phonon line (738 nm).

the local electric feld around the emitter becomes greatly intensifed [\[103\]](#page-162-0). This enhanced feld strength can lead to increased excitation rates and modifed emission properties of the quantum emitter [\[102,](#page-162-2) [103\]](#page-162-0).

We used a feld monitor in the [FDTD](#page-13-2) lumerical calculations and calculated the electric feld patterns excited by a dipole source placed 5 nm inside the diamond membrane while systematically varying the separation distance between the nano-cone and the diamond membrane. The results for the wavelength corresponding to the maximum Purcell enhancement in the spectral region near the zero-phonon line of the [SiV](#page-14-4) is presented in Figure [4.6,](#page-105-0) where the distance ranges from 5 to 50 nm [\[147\]](#page-166-0). Examination of the feld profles reveals that the truncated cone beneath the structure plays a minor role in determining the optical properties of the nano-cones, in line with our design objectives. Conversely, the distinctive geometry of the nano-cone prominently infuences the observed feld enhancement. The patterns calculated for other wavelengths (not shown) did not exhibit significant deviations from those in Figure [4.6](#page-105-0) [\[147\]](#page-166-0).

#### **4.3.2 Tuning Localized Surface Plasmon Resonance of Gold Nano-cones**

Usually, the nano-antennas are grown on a substrate, but here they are fabricated on a quartz [AFM](#page-13-1) probe via gold evaporation followed by [FIB](#page-13-4) milling, which creates a gold nano-cone structure at the tip apex [\[147\]](#page-166-0). Previous studies have shown that the changes in the substrate on which the nanostructures are grown can shift the [LSPR](#page-14-2) [\[47,](#page-157-0) [147\]](#page-166-0). A. Mohammadi et al. show that the nano-cone grown on a glass substrate can shift its [LSPR](#page-14-2) by more than 50 nm [\[37\]](#page-155-2). Nevertheless, the [LSPR](#page-14-2) shows extensive radiative broadening, enhancing the antenna effciency with a trade-off of reduction in the Purcell factor and the feld enhancement [\[37\]](#page-155-2). Thus, it's essential to know how much the [LSPR](#page-14-2) shift is

<span id="page-106-0"></span>

**Figure 4.7.** (a) [LSPR](#page-14-2) spectra of gold nano-cones in the air for different dimensions. The dotted green curve represents the supercontinuum laser spectrum. (b) [LSPR](#page-14-2) shift of a gold nano-cone (dimension  $b = 92$  nm,  $h = 107$  nm) when approaching a glass cover slide. The red curve shows the [LSPR](#page-14-2) in air without the presence of the dielectric. The LSPR shift is  $\approx$  50 nm when the nano-cone and glass coverslip are in contact. (c) [LSPR](#page-14-2) shift of a gold nano-cone (*b* = 92 nm, *h* = 107 nm ) when approaching a [PCD](#page-14-5) membrane. The [LSPR](#page-14-2) shift is  $\approx$  100 nm when the nano-cone and membrane are in contact .

attributed to an ideal nano-cone aspect ratio when changing the substrate or its nearfeld environment from air to dielectric [\[45\]](#page-156-0). The nanostructures are engineered to have resonances in the [NIR](#page-14-3) as the absorption in gold is smaller in this spectral region, also resulting in a smaller relative intrinsic linewidth in the [LSPR.](#page-14-2) In addition, the emission of some of the photostable quantum emitters, e.g., silicon, nickel, and chromium-related color centers in diamonds are in the [NIR](#page-14-3) region. Furthermore, it is of interest for biomedical applications as the tissue has a transparent window in the [NIR](#page-14-3) [\[83,](#page-160-7) [198\]](#page-172-0). To attain [LSPR](#page-14-2) at the desired spectral wavelength, the nano-cones are fabricated with an aspect ratio of  $\approx 1$ . 1.5 (height in the range of 60 - 150 nm and base in the range of 70 - 120 nm) along with a gold layer thickness of  $\approx 30$  nm on a commercial [AFM](#page-13-1) probe [\[147\]](#page-166-0).

Employing a home-built dark-feld microscopy setup, we have characterized the gold nano-cone and its [LSPR](#page-14-2) [see Figure [4.4\(](#page-97-0)a)]. Figure [4.7\(](#page-106-0)a) shows the [LSPR](#page-14-2) of individual nano-cones for various aspect ratios. The nano-cone samples are named as follows: Probe 1 (*b* = 85 nm, *h* = 103 nm), Probe 2 (*b* = 111 nm, *h* = 150 nm), and Probe 3 (*b* = 92 nm, *h* = 107 nm). The dotted green curve represents the spectrum of the supercontinuum laser taken on a clean glass coverslip, where the laser shows oscillation and a peak at 806 nm related to the Raman line of the laser. Usually, the [LSPR](#page-14-2) shifts towards the red with an increase in aspect ratio, however in here, the dimension of the plasmonic gold nano-cones, including the height, base, thickness of the gold layer deposited, and the separation of the nano-cone from the truncated cone, is not similar. Thus, the [LSPR](#page-14-2) red-shift in correlation with the increase in aspect ratio is not clearly visible in Figure [4.7\(](#page-106-0)a). However, the fabricated structures show [LSPR](#page-14-2) in the [NIR](#page-14-3) region as desired. The difference in the [LSPR](#page-14-2) linewidth is attributed to the variations in shape, size, radius of curvature, and sample quality related to surface smoothness [refer Figure [4.2\(](#page-94-0)c) and Figure [4.3\]](#page-95-0). Compared to the [LSPR](#page-14-2) spectral linewidths of several plasmonic nano-antennas, these gold nano-cone shows a narrow line-width of 30 - 60 nm in the air [\[199,](#page-172-1) [200\]](#page-172-2). The highest Q-factor we obtained was around 22, other geometries report a Q-factor as high as 30 [\[147\]](#page-166-0).

The linewidth of the [LSPR](#page-14-2) spectra get broadened when the plasmonic structure is in close proximity to a dielectric substrate [\[47,](#page-157-0) [147\]](#page-166-0). This is due to the collective electron oscillation contributed by both radiative and dissipative mechanisms [\[63\]](#page-158-5). Comparing the [LSPR](#page-14-2) linewidths of Probe 3 ( $b = 92$  nm,  $h = 107$  nm), it is noticeable that the linewidth upsurges from 60 nm to 80 nm as the plasmonic antenna is brought closer to dielectric [see Figure  $4.7(a)$  $4.7(a)$ , Figure  $4.7(c)$ ]. As the aspect ratio increases, the linewidth of the [LSPR](#page-14-2) spectra becomes smaller, while for larger sizes, radiation damping is more signifcant, which in turn determines the linewidth [see Figure [4.7\(](#page-106-0)a)] [\[47,](#page-157-0) [63\]](#page-158-5). Figure 4.7(b), and Figure 4.7(c)) demonstrate the [LSPR](#page-14-2) shift corresponding to the nano-cone with  $b = 92$  nm and  $h = 107$ nm corresponding to two scenarios: nano-cone near glass coverslip and [PCD](#page-14-5) membrane. Figure [4.7\(](#page-106-0)b) represents the [LSPR](#page-14-2) shift as the nano-cone brings closer to a glass coverslip [the inset in Figure [4.7\(](#page-106-0)b) is a schematic representation] The red curve indicates the [LSPR](#page-14-2) in the air without the presence of a dielectric substrate. The peak around 805 nm is due to the laser scattering [see the laser spectrum Figure [4.7\(](#page-106-0)a), green curve]. Figure [4.7\(](#page-106-0)a) shows more prominent noise compared to Figure [4.7\(](#page-106-0)b) and Figure [4.7\(](#page-106-0)c) owing to the choice of different integration times during the experimental sessions. The integration time used for Figure [4.7\(](#page-106-0)a) was 30 seconds, while for Figure [4.7\(](#page-106-0)b) and Figure [4.7\(](#page-106-0)c) was 60 seconds, respectively [\[147\]](#page-166-0).

Initially, the nano-cone approached the glass coverslip using the [AFM](#page-13-1) piezo stage. A set point force [few nanonewtons (nN)] was chosen so that the probe will be at proximity, around  $8 \pm 1$  nm from the substrate. We defined zero when the probe and the surface were in contact, at this point, even further approach will not change the spectral features. Our starting point was  $X = 8$  nm from the substrate. From  $X$ , the nano-cone was brought
at different distances from the glass coverslip by moving the [AFM](#page-13-0) cantilever using a piezo stage in nm precision. The [LSPR](#page-14-0) was monitored during various positions, as depicted in Figure [4.7\(](#page-106-0)b). When the distance between the nano-cone and the glass coverslip reduced from 8 nm to 0 nm, the [LSPR](#page-14-0) red-shifted from 725 nm to 775 nm. Furthermore, as shown in Figure [4.7\(](#page-106-0)c), the [LSPR](#page-14-0) becomes significantly broader and shifted more towards a higher [NIR](#page-14-1) region when the index of refraction of the substrate increased to *n* = 2.4, [PCD](#page-14-2) membrane. Once the nano-cone encountered the membrane, the [LSPR](#page-14-0) shifted to  $\approx 820$ nm, as shown in Figure [4.7\(](#page-106-0)c). When the distance between the nano-cone and the glass coverslip reduced from *X*+9 nm to *X*+3 nm, the [LSPR](#page-14-0) red-shifted from 725 nm to 775 nm. Also, the [LSPR](#page-14-0) becomes significantly broader and shifted more towards higher [NIR](#page-14-1) region as  $n_d$  increased to  $n = 2.4$  [see Figure [4.7\(](#page-106-0)c), the inset in the Figure 4.7(b) is a schematic representation]. Once the nano-cone encounters the [PCD](#page-14-2) membrane [represented as contact point *X* in Figure [4.7\(](#page-106-0)c)], the [LSPR](#page-14-0) shifted to  $\approx 820$  nm, as shown in Figure 4.7(c). When the distance between the two systems reduced to a few nanometers, the [LSPR](#page-14-0) shift was prominent towards [NIR.](#page-14-1) The ripples shown in the [LSPR](#page-14-0) spectra corresponding to Figure [4.7\(](#page-106-0)c) were due to the oscillation of the supercontinuum laser itself.

#### **4.4 Conclusions**

To conclude, we explained the fabrication technique and optical characterization of sharp plasmonic gold nano-cones fabricated through gold sputtering on commercial [AFM](#page-13-0) probes followed by the [FIB](#page-13-1) milling technique. The method enables the fabrication of plasmonic nanostructures of dimensions around 100 nm and an aspect ratio of about one, for quantum nano-optics applications without sophisticated fabrication procedures. Moreover, the method endorsed the fabrication with great precision over height, radius of curvature, and sidewalls. By changing the dimension of the structure, the aspect ratio of nano-cones was tuned, thereby, the [LSPR](#page-14-0) into the [NIR](#page-14-1) regime. The optical properties of the nano-cones were studied by using an inverted dark-feld spectroscopy system combined with [AFM.](#page-13-0) Since the gap between the nano-cone and the truncated [AFM](#page-13-0) tip varied for different nanostructures, the extent of the [LSPR](#page-14-0) shift was different. However, the [LSPR](#page-14-0) linewidth was relatively narrow (around 30 - 50 nm) and spanned the required [NIR](#page-14-1) spectral region, enabling them to implement near-feld coupling with [NIR](#page-14-1) quantum emitters. We also demonstrated the dielectric effect on the [LSPR](#page-14-0) of the nano-cones as the [LDOS](#page-13-2) with the nano-cone changed upon substrate variations. Nano-cone with an aspect ratio of  $\approx 1$ showed 100 nm red-shift as the refractive index of the dielectric changed from  $n = 1$ to  $n = 2.4$ . Also, the study revealed that the experimental results were in correlation with the [FDTD](#page-13-3) simulations of the spontaneous emission rate and quantum yield. The analysis unveiled the relationship between the modification of the decay rate for an emitter in the dielectric substrate with and without nano-cone, considering the intrinsic quantum yield. The [FDTD](#page-13-3) calculations provided spectral features in good agreement with

the experimental findings. However, the fabrication technique lacked extremely sharp features (down to < 10 nm radius of curvature) and reproducible nano-cone dimension. As the thickness of the evaporated gold layer increased, the radius of curvature of the nano-cones tended to increase even though the initial [AFM](#page-13-0) probe had relatively sharp (about 10 nm) tips. By optimizing the [FIB](#page-13-1) milling parameters, the aspect ratio of the antenna as well as the surface plasmon coupling from the truncated gold part to the nano-cones can be amended in the future. Alternatively, the nano-cones can be fabricated on a commercial [AFM](#page-13-0) probe by adapting the [EBID](#page-13-4) fabrication technique [\[47,](#page-157-0) [187\]](#page-170-0), which allows even better control over the nanostructure; however, the method is time-consuming. The goal of this work was to show the potential of scanning plasmonic gold nano-cones with [NIR](#page-14-1) resonances in a plethora of nano-optics applications, for example, to modify the spontaneous emission rate and the quantum yield of quantum emitters in order to study their photo-physics in different dielectric environments.

The next chapter [5](#page-110-0) focuses on the fabrication and characterization of [PCD](#page-14-2) membranes. Specifcally, the chapter discusses the methods used for fabricating [PCD](#page-14-2) membranes, as well as the experimental results and discussions on the grain-size studies and optical studies of both [PCD](#page-14-2) membranes and polycrystalline bulk diamond. Additionally, the chapter delves into the determination of Si distribution in both un-implanted and implanted [PCD](#page-14-2) membranes through time-of-fight secondary ion mass spectrometry [\(TOF-SIMS\)](#page-15-0) analysis.

## **5**

## <span id="page-110-0"></span>**SILICON VACANCY COLOR CENTERS IN POLYCRYSTALLINE DIAMOND MEMBRANE[S](#page-0-0)**

In this chapter, the investigation of the optical properties of [PCD](#page-14-2) membranes containing [SiV](#page-14-3) color centers is discussed. Initially, the correlation between the Raman signal, the [SiV](#page-14-3) emission, and the background luminescence in the crystalline grains and in the grain boundaries are analyzed, and the conditions for the addressability of single [SiV](#page-14-3) centers are identifed. The scanning transmission electron microscopy [\(STEM\)](#page-15-1) analysis reveals the microscopic structure of the membranes and the evolution of the diamond crystals along the growth direction, as well as the [TOF-SIMS](#page-15-0) reports the distribution of Si in the membrane. The results of the [TEM](#page-15-2) and [TOF-SIMS](#page-15-0) studies are consistent with the outcome of the optical measurements and provide useful insight into the preparation of polycrystalline samples for quantum nano-optics.

#### **5.1 Introduction**

The negatively-charged [SiV](#page-14-3) color center in diamond [\[4,](#page-152-0) [7,](#page-152-1) [16,](#page-153-0) [98,](#page-161-0) [140,](#page-166-0) [134\]](#page-165-0) is a unique quantum emitter due to its strong [ZPL](#page-15-3) emission, photon indistinguishability, high repetition rate, the possibility to operate at room temperature and higher temperatures, and its controlled creation. However, the poor out-coupling efficiency of [SiV](#page-14-3) centers due to the high refractive index of the diamond and the position of the color centers in the host may hinder the efficient optical interaction needed for emerging quantum science applications. Nano-photonic structures, such as solid-immersion lenses [\[201\]](#page-172-0), nanopillars [\[202,](#page-172-1) [203\]](#page-172-2), and photonic-crystal cavities [\[76,](#page-159-0) [204,](#page-172-3) [205\]](#page-172-4) have shown remarkable improvements in the coupling efficiency and/or the emission rate, but they require advanced nanofabrication tools. Alternatively, color centers in thin diamond membranes would more easily allow to manipulate their radiation pattern for bright directional emission [\[55,](#page-157-1) [56\]](#page-157-2), and the realization of ultrafast single-photon emission [\[44\]](#page-156-0). While [SCD](#page-14-4) membranes require sophisticated

This chapter is based on the publication "Optical Characterisation of Silicon Vacancy (SiV) Color Centers in Polycrystalline Diamond Membranes" by H. Kambalathmana, A.M. Flatae, L. Hunold, F. Sledz, J. Müller, M. Hepp, P. Schmuki, M.S. Killian, S. Lagomarsino, N. Gelli, S. Sciortino, L. Giuntini, E. Wörner, C. Wild, B. Butz, M. Agio, Carbon 174 (2021) 295-304. I contributed to the implementation of the experimental setup, recorded the data, analyzed the data, prepared fgures for the manuscript, and contributed to the preparation of the manuscript.

technological approaches and so far have not achieved thicknesses below 100 nm [\[23,](#page-154-0) [24\]](#page-154-1), fabricating thin [PCD](#page-14-2) membranes represents a viable approach. Over the past 20 years, a broad variety of diamond synthesis techniques have been developed. Among them, [MPCVD](#page-14-5) has emerged as the preferred fabrication method for high-quality thin diamond membranes, with control over the size and geometry [\[206,](#page-172-5) [106\]](#page-162-0).

At first, the optical properties of [SiV](#page-14-3) centers in [PCD](#page-14-2) membranes of thicknesses from 3 µm down to 55 nm fabricated using [MPCVD](#page-14-5) on a silicon wafer [\[44\]](#page-156-0) has been investigated. However, isolating single emitters was limited by the dimensions of the single grains and by the fuorescence background originating from the grain boundaries [\(GBs](#page-13-5)s). On the other hand, the deposition of thicker [PCD](#page-14-2) membranes would create larger grains, thereby allowing the emitter to be located within the grain centers [\(GCs](#page-13-6)s) with a higher signal-to-noise (S/N) ratio suitable for addressing single color centers. It is therefore critical to understand the relationship between the morphology of micrometer-thick [PCD](#page-14-2) membranes and the optical properties of [SiV](#page-14-3) centers.

#### **5.2 Fabrication of Polycrystalline Diamond Membranes**

The basic idea of all fabrication processes of [PCD](#page-14-2) membranes is via the deposition of the diamond from the gaseous phase [\[207\]](#page-172-6). Initially, the process gas consisting of a hydrogen and hydrocarbon mixture will be activated for the generation of atomic hydrogen. The stabilized formation of synthetic diamonds, along with the suppression of graphitic phase formation during growth, is enabled by atomic hydrogen [\[208\]](#page-172-7). The activation of the gas can be done either thermally (e.g., the hot flament chemical vapour deposition [\[209\]](#page-173-0) or by a plasma [\[206,](#page-172-5) [210\]](#page-173-1)(e.g., [MPCVD\)](#page-14-5). Depending on the deposition method used, the quality of the diamond, the growth rate, and the deposition area will vary. The crystal quality and texture of the diamond film are tangled with a few key parameters, such as the material of the substrate used, the substrate temperature, the ratio of the process gas mixture, etc [\[112\]](#page-163-0).

Diamond membranes grown by the [MPCVD](#page-14-5) technique fall into either the [PCD](#page-14-2) or [SCD](#page-14-4) category. Unlike the [SCD,](#page-14-4) the [PCD](#page-14-2) is grown on a non-diamond substrate. Owing to the growth process the grain structure of [PCD](#page-14-2) has a non-uniform composition compared to other polycrystalline structures. In contrast to a pure diamond with  $SP<sup>3</sup>$  bonded carbon on every lattice point, a [PCD](#page-14-2) forms [GBs](#page-13-5) between crystallites with different orientations. Primarily, a high density of nucleation sites is formed on the substrate, however, the grains with preferential facets and orientation grow to form the desired crystal structure. Besides, the properties and applications of [PCD](#page-14-2) flms strictly rely on the [GBs](#page-13-5) size and the presence of unwanted carbon phases (such as  $SP<sup>2</sup>$  carbon phase, unwanted carbon phases, etc.) at the [GBs](#page-13-5) [considered as impurity content]. Generally, in an [MPCVD](#page-14-5)

<span id="page-112-0"></span>

**Figure 5.1.** [PCD](#page-14-2) membranes. (a) The image represents a batch of 5 um-thick PCD membranes grown on an 8-inches Si wafer. (b) Microscope image of a laser segregated single [PCD](#page-14-2) membrane with a diameter of 2 mm.

method, decreasing the CH<sub>4</sub> content in the mixture of  $CH<sub>4</sub>/H<sub>2</sub>$  gas leads to [PCD](#page-14-2) films with micrometer size grains, while, increasing the  $CH_4$  content leads to diamond films with nanocrystalline grains [\[211\]](#page-173-2). Accordingly, the morphology of the crystal is modifed from faceted microcrystals to ball-shaped nanocrystals. Moreover, the ratio of the  $CH_4/H_2$ gas mixture defines the quality of [CVD](#page-13-7) diamond film via balancing the SP $^{3}/\mathrm{SP}^{2}$  content in the crystal [\[107,](#page-162-1) [212\]](#page-173-3). Modification in the morphology and texture of the [PCD](#page-14-2) films along with increment in the growth rate and suppression of [GBs](#page-13-5) can be obtained by ppm level incorporation of nitrogen. Despite this, adding oxygen enables deposition under low temperatures, but it is not beneficial for [PCD](#page-14-2) film growth. Furthermore, choosing an appropriate substrate for crystal growth is imperative. The [CVD](#page-13-7) growth process on the non-diamond substrate initially forms a carbide interfacial layer [which protects from stress at the interface] and later on diamond grows. The growth process generally takes place at elevated temperatures, but, upon cooling, the compressive stress resulting from the thermal expansion coefficient mismatch between the substrate and the diamond can induce structural damage to the film [\[112\]](#page-163-0). Therefore, matching the thermal expansion coefficient of the substrate and the diamond [diamond has the lowest thermal expansion coefficient of any material] determines whether it is possible to grow an adherent [CVD](#page-13-7) film on the substrate of interest or not.

We have grown 5 µm-thick diamond films by [MPCVD](#page-14-5) using a 6-kW ellipsoidal plasma reactor as described in Ref [\[141\]](#page-166-1). Prior to deposition, the silicon substrate was seeded with diamond nanoparticles for high nucleation densities. It was then coated using a  $CH_4/H_2$ gas mixture, at a substrate temperature of 800◦C, at 150 mbar gas pressure, and 300 sccm total gas flow rate. The concentration of  $CH_4$  was 1%. These parameters facilitated the growth of high-quality diamond films. After deposition, the diamond film was polished using conventional diamond polishing techniques to a surface roughness below 5 nm (rms). Then, circular grooves and windows were etched into the diamond flm using deep [RIE,](#page-14-6) resulting in self-standing [PCD](#page-14-2) membranes of about 5 µm thickness with an

unsupported area of 2 mm in diameter stabilized by a silicon frame [see Figure [5.1\(](#page-112-0)b)].

#### **5.3 Experimental Results and Discussion**

A bulk [PCD](#page-14-2) sample was chosen to validate the experimental approach. The detailed description of creating the [SiV](#page-14-3) color centers on the [PCD](#page-14-2) membranes is described in section [2.2.3.](#page-52-0) Here, a bulk [PCD](#page-14-2) sample and four different [PCD](#page-14-2) membrane samples (from the same batch) were studied in order to identify the properties of the [PCD](#page-14-2) membranes and the modifcations introduced by ion implantation and annealing. Table [2](#page-114-0) describes the investigated samples. Sample "POLY" is a bulk [PCD](#page-14-2) sample implanted with 9 MeV Si ions at various fuences followed by thermal annealing. The sample ["PCD1](#page-14-2)" refers to a virgin sample, where no implantation or annealing is performed. The ["PCD2](#page-14-2)" sample refers to an annealed sample, the ["PCD3](#page-14-2)" sample represents an implanted and annealed sample [400 keV energy with a Si-ion fluence of  $10^{-12}$  cm $^{-2}$ , corresponding to a [SiV](#page-14-3) depth distribution of 200 - 350 nm], and fnally the ["PCD4](#page-14-2)" is an implanted and annealed sample [9 MeV energy with a Si-ion fluence of  $10^{-8}$  cm<sup>-2</sup>, due to the presence of two aluminum foils only 20% of the ions are implanted with a tail corresponding to a [SiV](#page-14-3) depth distribution of 0 - 250 nm]. Before the optical characterization, the [PCD](#page-14-2) samples were rinsed in a mixture of acetone and isopropanol (1:1) for 20 minutes. The diamond surface was also cleaned in a UV-ozone cleaner for 15 minutes to remove the surface contamination. Besides, we also performed surface treatments, such as oxygen plasma cleaning to understand the incorporation of contamination thereby the crystal quality.

#### **5.3.1 Optical Setup**

The optical properties of [PCD](#page-14-2) membranes were explored using a home-built scanning confocal microscope [\(SCM\)](#page-14-7) [see Figure [5.2\(](#page-115-0)a)]. For the Raman and photoluminescence [\(PL\)](#page-14-8) measurements, the sample was excited by a 656.15 nm laser diode (Pico Quant, LDH D-C-660 driven by PDL800-D), unless otherwise stated, using a high numerical-aperture [\(NA\)](#page-14-9) objective (Olympus, MPlan Apo N 100x/0.95 [NA\)](#page-14-9). The same objective was used for both excitation and collection. The Raman and [PL](#page-14-8) signals were carefully fltered by suppressing unwanted contributions (e.g., scattering, laser emission) using a confocal system. The sample was imaged using an [EM-CCD](#page-13-8) camera (Princeton Instruments, ProEM-HS:512BX3). The spectrum was monitored using a spectrometer (Andor, Shamrock SR-500i-D2-SIL) equipped with an [EM-CCD](#page-13-8) detector (Andor, Newton DU970P-BVF).

Alternatively, the Raman and PL signals were detected by two avalanche photodiodes [\(APDs](#page-13-9)) (Micro Photon Devices, MPD-100-CTC) connected to time-correlated single-photon counting electronics [\(TCSPC\)](#page-15-4) (Pico Quant, PicoHarp 300). To generate confocal maps, the sample was scanned in the xy-direction using a piezo stage (Physik Instrumente,

<span id="page-114-0"></span>

Sample	Terminology	Dimension	Properties
Polycrystalline bulk diamond	POLY	$5 \text{ mm} \times 5 \text{ mm}$	Implanted with 9 MeV Si ions at fluences of 3.7 $\times$ 10 <sup>11</sup> cm <sup>-2</sup> , 2.3 $\times$ 10 <sup>12</sup> cm <sup>-2</sup> , 1.1 $\times$ 10 <sup>13</sup> cm <sup>-2</sup> and $5.6 \times 10^{13}$ cm <sup>2</sup> . at $2.1 \,\mathrm{\upmu m}$ depth. Thermally an- nealed at 1000°C for 1 hr
Un-implanted, un-annealed PCD membrane	PCD1	dia- $5 \mu$ m-thick mond membrane with 2 mm-thick silicon ring	Polished, virgin sample
Un-implanted, thermal annealed PCD membrane	PCD <sub>2</sub>	$5 \mu m$ -thick dia- mond membrane with 2 mm-thick silicon ring	Thermally an- nealed at 1150°C for 1 hr after polishing
Implanted, ther- mal annealed PCD membrane	PCD3	$5 \mu$ m-thick dia- mond membrane with 2 mm-thick silicon ring	Implanted with Si ions a fluence of $10^8$ cm <sup>-2</sup> followed by an annealing cy- cle of 1150°C for 1 hr
Implanted, ther- annealed mally PCD membrane	PCD4	$5 \mu$ m-thick dia- mond membrane with 2 mm-thick silicon ring	Shallow implanta- tion with 9 MeV energy with a Si- ion fluence of $10^8$ $\rm cm^{-2}$

**Table 2.** Description of polycrystalline bulk diamond and polycrystalline diamond membranes

P-542.2CL) following the scheme shown in Figure [5.2\(](#page-115-0)b). To investigate the grain size evolution in the [PCD](#page-14-2) membranes, mapping along the z-axis was performed using a piezo objective scanner (Physik Instrumente, P-725 PIFOC) as shown in Figure [5.2\(](#page-115-0)c).

The [SCM](#page-14-7) mapping had an axial resolution of  $1.4 \mu$ m and a lateral resolution of  $0.4 \mu$ m, which allowed scanning the [PCD](#page-14-2) membrane at different depths and analyzing the grain size. The theoretical calculations for the axial and lateral resolution were made by assuming the [SiV](#page-14-3) color centers in the air. However, the presence of diamond (refractive index of 2.4) could lead to optical aberrations and reduction of the axial resolution. To distinguish between the Raman and the [PL](#page-14-8) signals, each [APD](#page-13-9) was preceded by two different bandpass flters that generate two confocal maps. Filter 1 was centered at 720 nm with 10 nm

<span id="page-115-0"></span>

**Figure 5.2.** Optical setup and confocal scanning. (a) Scheme of the experimental setup for imaging, Raman, and [PL](#page-14-8) analysis. The laser beam has been expanded using a telescopic system. A dichroic mirror (DM1) directs the laser toward an objective to excite the sample. The same objective collects the emission from the [PCD](#page-14-2) membrane. DM1 transmits the Raman and [PL](#page-14-8) signals from the sample and refects the excitation laser. The signal is then fltered by a confocal system with 2 lenses (*L*<sup>1</sup> and *L*2), and a pinhole (*P*1) (pinhole size 150 µm) and by a long-pass flter. A fipping mirror (*F*1) in the optical path sends the light towards the [EM-CCD](#page-13-8) camera for fuorescence imaging. The signal can also be sent towards the spectrometer using a fipping mirror (*F*2). A 50/50 non-polarizing beam splitter (BS) sends the emitted photons to two [APDs](#page-13-9) (SPAD 1 and SPAD 2) after focusing with the lenses ( $L_3$  and  $L_4$ ) for mapping. Two band-pass filters corresponding to the diamond Raman line (Filter 1) and the [SiV](#page-14-3) [ZPL](#page-15-3) (Filter 2) are placed in front of the [APDs](#page-13-9). The signal from the [APDs](#page-13-9) is recorded using a [TCSPC](#page-15-4) device. (b) XY mapping by scanning the sample over the objective. (c) Z mapping by moving the objective.

bandwidth [corresponding to the diamond Raman peak at 1332 cm $^{-1}$  (719 nm) [\[108\]](#page-163-1)] and Filter 2 was centered at 740 nm with 13 nm bandwidth [corresponding to the [ZPL](#page-15-3) of the [SiV](#page-14-3) center at 738 nm] [\[213\]](#page-173-4).

Since the [APDs](#page-13-9) does not allow us to distinguish the Raman and the [SiV](#page-14-3) fuorescence signals from the background, we performed spectral line scanning at certain regions on the sample surface to acquire the full spectral information. To identify the contributions of different spectral components to the overall emission, the signal at each point along the lines was analyzed at a 0.5 nm spectral resolution [150 lines/mm grating, 357 nm bandpass]. The intensity at Filters 1 and 2 meant the cps recorded by the [APDs](#page-13-9), which was then traced by the spectral data via integrating the acquired signal over the wavelength range corresponding to the flters used in the mapping. Before performing this step, the

background was identifed by introducing a baseline corresponding to the counts averaged at the edges of the Filter 2 spectral window. Since the strongly inhomogeneous background prevents a proper fit of the [SiV](#page-14-3) peak in some samples, this robust method allowed an alternative estimation of the background. Finally, the background and the [SiV](#page-14-3) signals were separately integrated, where the contribution below the baseline corresponded to the background fuorescence, and the one above the baseline indicated the [SiV](#page-14-3) luminescence.

#### **5.3.2 Surface Treatments of Polycrystalline Diamond Membranes**

The presence of impurity defects and surface contaminations are evident in the [PL](#page-14-8) spectra, and it reveals that the current cleaning procedures were not effective in eliminating them. Moreover, these  $SP^2$  carbon impurities and surface imperfections are correlated with the crystal quality of [PCD](#page-14-2) membrane and the S/N ratio of the activated [SiV](#page-14-3) color centers. Hence, we exploited surface treatments based on oxygen plasma cleaning on [PCD1](#page-14-2) and [PCD3](#page-14-2) membranes using [RF](#page-14-10) oxygen plasma (Plasma prep 2 Gala instruments) technique. The samples were exposed to oxygen plasma for 30 minutes with 30% of the maximum power (200 W). The color centers implanted at the few tens of nanometers were etched away during the plasma cleaning. After the oxygen plasma cleaning, the [PCD](#page-14-2) membranes were characterized using the home-built confocal microscopy setup.

Figure [5.3\(](#page-117-0)a), and Figure [5.3\(](#page-117-0)c) indicates the Filter 2 [SCM-](#page-14-7)[PL](#page-14-8) map [\(SiV](#page-14-3) signal) corresponding to [PCD1](#page-14-2) and [PCD3](#page-14-2) respectively. The [PL](#page-14-8) spectra obtained from [PCD1](#page-14-2) and [PCD3](#page-14-2) after the plasma cleaning had suppressed the background and improved the S/N ratio [see Figure [5.3\(](#page-117-0)b), and Figure [5.3\(](#page-117-0)d)]. The background due to the presence of amorphous carbon phases was removed by plasma cleaning on both [GBs](#page-13-5) and [GCs](#page-13-6). The Raman lines at 1150 cm<sup>-1</sup> and the accompanying peak at 1447.31 cm<sup>-1</sup> related to the trans-polyacetylene lying in grain boundaries were also eliminated after the plasma cleaning as observed in the [PL](#page-14-8) spectra of [PCD1](#page-14-2) and [PCD3](#page-14-2) [\[PL](#page-14-8) spectra taken after plasma cleaning, where the blue curve related to [GB](#page-13-5) and green curve related to [GC](#page-13-6) respectively].

To distinguish the surface characteristics before and after the oxygen plasma treatment, [AFM](#page-13-0) surface topography mapping was performed on both [PCD](#page-14-2) samples, shown in Figure [5.4.](#page-118-0) Figure [5.4\(](#page-118-0)a), and Figure [5.4\(](#page-118-0)b) represent the [AFM](#page-13-0) topography mapping of [PCD1](#page-14-2) before and after oxygen plasma cleaning. Similarly, the [AFM](#page-13-0) topography mapping corresponding to [PCD3](#page-14-2) before and after oxygen plasma cleaning is shown in Figure [5.4\(](#page-118-0)c), and in Figure [5.4\(](#page-118-0)d) respectively. The [AFM](#page-13-0) mapping after oxygen plasma shows that the surface roughness had reduced but at the cost of etching a few nanometers of the diamond layer. The preliminary analysis showed that by careful surface treatment protocols, the crystal quality and the S/N ratio of the quantum emitter can be optimized. The lifetime studies of [SiV](#page-14-3) centers done before and after the oxygen plasma process verifed that the

<span id="page-117-0"></span>5 Silicon Vacancy Color Centers in Polycrystalline Diamond Membranes



**Figure 5.3.** The optical characterization of [PCD](#page-14-2) membranes after oxygen plasma treatment. (a) The [SCM-](#page-14-7)[PL](#page-14-8) map of [PCD1](#page-14-2) from flter 2 after the oxygen plasma cleaning. (b) The [PL](#page-14-8) spectra of [PCD1](#page-14-2) before and after oxygen plasma cleaning on the [GBs](#page-13-5) (luminescence with higher count rates) and [GCs](#page-13-6) (luminescence with lower count rates). (c) The [SCM](#page-14-7)[-PL](#page-14-8) map of [PCD3](#page-14-2) after oxygen plasma cleaning shows the [GB](#page-13-5) and [GC.](#page-13-6) (d) The comparison of the room temperature [PL](#page-14-8) spectra taken from the [GBs](#page-13-5) and [GCs](#page-13-6) before and after oxygen plasma cleaning on [PCD3](#page-14-2).

background signal originated from the amorphous phases of carbon and the non-radiative decay rate enhancement was not correlated. This indicated that the quality of the crystal was satisfactory.

#### **5.3.3 Grain-size Studies on Polycrystalline Diamond Membranes**

The grain size-dependent physical and chemical properties of thick [PCD](#page-14-2) flms have already been studied [\[114\]](#page-163-2). This section reports a comprehensive study of the optical properties of few-microns-thick [PCD](#page-14-2) membranes via [SCM](#page-14-7) maps generated from different depths. The diffraction-limited excitation laser that performs the [SCM](#page-14-7) mapping on the [PCD](#page-14-2) membrane starts from the top surface and it eventually approaches the surface close to the substrate [see Figure [5.2\(](#page-115-0)c)] using the piezo movement. Initially, the piezo performs a scan in the z-direction, which gives the information about the focal points corresponding to two surfaces of the [PCD](#page-14-2) membrane in terms of count rates. When the confocal volume probes most of the diamond sample (surface close to the substrate), the count rate increases. Then, the home-built confocal setup selects different planes for the depth-related scanning.

<span id="page-118-0"></span>

**Figure 5.4.** Roughness characterization of  $\approx$  5 µm thick [CVD](#page-13-7) diamond membranes via [AFM](#page-13-0) topography mapping before and after oxygen plasma treatment. The [AFM](#page-13-0) mapping reveals that the surface roughness becomes better after plasma treatment on the [PCD](#page-14-2) membranes. The x-axis corresponds to the scan range in the micrometer and the y-axis indicates the height measured in the nanometer respectively. (a) The [AFM](#page-13-0) topography mapping of [PCD1](#page-14-2) before oxygen plasma cleaning. (b) The [AFM](#page-13-0) topography mapping of [PCD1](#page-14-2) after oxygen plasma cleaning. (c) The [AFM](#page-13-0) topography mapping of [PCD3](#page-14-2) before oxygen plasma cleaning. (d) The [AFM](#page-13-0) topography mapping of [PCD3](#page-14-2) after oxygen plasma cleaning.

The [SCM](#page-14-7) maps from Filter 1 and Filter 2, shown in Figure [5.5\(](#page-119-0)a), and Figure [5.5\(](#page-119-0)b), are generated from the top surface of [PCD3](#page-14-2), whereas Figure [5.5\(](#page-119-0)c), and Figure [5.5\(](#page-119-0)d) display the corresponding [SCM](#page-14-7) maps obtained from the surface close to the substrate. The grain size decreases from about  $3 - 5 \mu m$  near the top surface to less than 1  $\mu m$  (diffraction limited) near the substrate. Moreover, the [SCM](#page-14-7) maps generated from both flters show higher counts near the substrate. From the larger overlap of the confocal volume with the [PCD](#page-14-2) membrane near the substrate, we can infer that Si contamination incorporated near the nucleation layer during the [PCD](#page-14-2) growth creates additional [SiV](#page-14-3) centers. To verify the grain size distribution estimated via the [SCM](#page-14-7) maps at various depths, we performed [STEM](#page-15-1) measurements on the [PCD1](#page-14-2) membrane (the [PCD](#page-14-2) membranes belong to the same batch). The [TEM](#page-15-2) lamella is prepared by conventional [FIB](#page-13-1) (FEI Helios Nanolab 600) lift-out. Additionally, to a platinum (Pt) protective layer on top, a thin protective gold (Au) layer of only a few nanometers is applied at the bottom of the [PCD](#page-14-2) membrane to ensure that the original bottom surface is preserved during milling. In the bright-feld [STEM](#page-15-1) image

<span id="page-119-0"></span>

**Figure 5.5.** Optical characterization of the grain size in [PCD](#page-14-2) membranes [\(PCD3](#page-14-2)). (a) and (b) [SCM](#page-14-7) maps from Filter 1 and Filter 2, respectively, acquired on the top surface of the membrane. (c) and (d) [SCM](#page-14-7) maps from Filter 1 and Filter 2, respectively, acquired near the substrate/nucleation layer. The scale bar in the [SCM](#page-14-7) maps is  $5 \mu m$  and the step size is  $0.2 \mu m$ .

shown in Figure [5.6\(](#page-120-0)a), the dislocations created during the diamond growth, and the nucleation layer are clearly visible. Moreover, Figure [5.6\(](#page-120-0)b) points out that above the nucleation layer, the crystal size grows rapidly, such that one can fnd diamond grains of nearly single crystalline quality having lateral dimensions of about 2 µm. The crystals are clearly visible due to the resulting Bragg contrast. The image shown in Figure [5.6\(](#page-120-0)b) obtained from one section of the [PCD1](#page-14-2) membrane confrms the growth of larger crystals immediately after the formation of an initial nucleation layer.

The grain selection for the growth of larger grains takes place already after about 200 nm. Moreover, stacking faults and dislocations are rarely visible in Figure [5.6.](#page-120-0) The small discrepancy between the grain size inferred from the [SCM](#page-14-7) maps and the [STEM](#page-15-1) analysis must be attributed to the resolution of the confocal volume, which smears the grain boundaries and effectively increases the grain dimensions.

<span id="page-120-0"></span>

**Figure 5.6.** [STEM](#page-15-1) characterization of the grain size in [PCD](#page-14-2) membranes [\(PCD1](#page-14-2)). (a) Bright-feld [STEM](#page-15-1) image showing crystal growth, dislocations, and the nucleation layer. (b) Bright-feld [STEM](#page-15-1) image showing crystal growth, where the grain size is larger at the top surface ( $\approx$  2 µm grain size). The [STEM](#page-15-1) image at the bottom of the diamond layer shows that grain selection takes place rapidly.

#### **5.3.4 Optical Studies of Silicon Vacancy Centers in Polycrystalline Bulk Diamond**

First of all, we have examined the optical properties of [SiV](#page-14-3) centers on a bulk polycrystalline diamond sample [named here as sample "POLY"] [\[214\]](#page-173-5). The [SCM](#page-14-7) has been performed on the lower implantation zone. Figure [5.7\(](#page-121-0)a) and Figure [5.7\(](#page-121-0)b) show the [PL](#page-14-8) map associated with flter 1 and flter 2. The higher count rate is observed from the [GBs](#page-13-5) due to the accumulation of activated [SiV](#page-14-3) centers, whereas in the [GCs](#page-13-6), the count rate is found to be less. The line spectral scanning [shown in Figure [5.7\(](#page-121-0)c)], depicted as a black line in Figure [5.7\(](#page-121-0)a) and Figure [5.7\(](#page-121-0)b), reveals that the background around the [ZPL](#page-15-3) emission of [SiV](#page-14-3) centers, as well as the [PL](#page-14-8) intensities from flter 1 and flter 2, increase along with the [GB,](#page-13-5) while they drop as one move to the [GC.](#page-13-6) The [PL](#page-14-8) spectra corresponding to the [GC](#page-13-6) and the [GB](#page-13-5) [the positions are marked as small red circles on the [SCM](#page-14-7) maps in Figure [5.7\(](#page-121-0)a) and Figure [5.7\(](#page-121-0)b)] are shown in Figure 5.7(d). It is confirmed that the  $S/N$  ratio is higher in the [GCs](#page-13-6) compared to the [GBs](#page-13-5) since the [PL](#page-14-8) background is higher in the [GB](#page-13-5) due to poor crystal quality. Additionally, the intensity from filter 1 also varies from grain to grain, where the

<span id="page-121-0"></span>

**Figure 5.7.** Optical properties of the poly sample. (a) [SCM](#page-14-7) map (1 µm step size) corresponding to the signal from flter 1 (Raman signal). The dark regions correspond to the [GCs](#page-13-6) (In the [GC\)](#page-13-6) and the bright ones to the [GBs](#page-13-5) (In the [GB\)](#page-13-5). (b) [SCM](#page-14-7) map (1 µm step size) corresponding to the signal from flter 2 [\(SiV](#page-14-3) [PL](#page-14-8) signal). (c) Manual spectral scanning (1 µm step size), performed along the black line indicated in Figure [5.7\(](#page-121-0)a) and Figure [5.7\(](#page-121-0)b), showing the background around the [ZPL](#page-15-3) emission of [SiV](#page-14-3) centers (yellow curve), the background-subtracted [PL](#page-14-8) of [SiV](#page-14-3) centers (red curve) and the background-subtracted Raman (blue curve). (d) [PL](#page-14-8) spectra in the [GCs](#page-13-6) centers (red curve) and in the [GBs](#page-13-5) (black curve) taken at the corresponding red points marked in Figure [5.7\(](#page-121-0)a) and Figure [5.7\(](#page-121-0)b). The band-pass flters for the Raman and [SiV](#page-14-3) signals are represented as Filter 1 and Filter 2.

size of one grain ranges from tens to hundreds of microns, as observed in Figure [5.7\(](#page-121-0)c). These interesting features that appeared on the [PL](#page-14-8) spectra are mainly due to the random crystal orientations of the grains in [PCD](#page-14-2) samples [\[112\]](#page-163-0). The close correlation between the higher [PL](#page-14-8) intensity of the [SiV](#page-14-3) signal (filter 2) at the [GB](#page-13-5) indicates that the concentration of activated [SiV](#page-14-3) centers is relatively prominent [\[204\]](#page-172-3).

#### **5.3.5 Optical Studies of Silicon Vacancy Centers in Polycrystalline Diamond Membranes**

This section presents the optical characterization of [PCD](#page-14-2) membranes, which are essential for the controlled fabrication of [SiV](#page-14-3) color centers. The optical properties of [PCD](#page-14-2)

membranes are characterized using confocal microscopy and spectroscopy. A detailed description of the different [PCD](#page-14-2) membranes used for this optical study is mentioned in Table [2.](#page-114-0)

#### **Virgin polycrystalline diamond membranes [\(PCD1](#page-14-2))**

Figure [5.8\(](#page-123-0)a) and Figure [5.8\(](#page-123-0)b) depict the [SCM](#page-14-7) maps at Filter 1 and Filter 2 acquired near the upper surface of the [PCD1](#page-14-2) membrane, respectively. The grain size is about 3 − 5 µm; nonetheless, the [GBs](#page-13-5) are still clearly visible in the [SCM](#page-14-7) map of [PCD1](#page-14-2). The sample is not implanted, which means spectral features corresponding to the emission of [SiV](#page-14-3) color centers are not expected unless there are diffused Si ions created during the growth process. The line spectral scanning shown in Figure [5.8\(](#page-123-0)c), performed across the black line in Figure [5.8\(](#page-123-0)a), and Figure [5.8\(](#page-123-0)b), indicates that background-subtracted [PL](#page-14-8) signal from Filter 2 (red curve) remains nearly constant, whereas the background [PL](#page-14-8) signal from Filter 2 (black curve) and the [PL](#page-14-8) signal from Filter 1 vary. They are maximal over the [GB](#page-13-5) and drop near the [GC.](#page-13-6) We thus consider the [PL](#page-14-8) spectra at the [GB](#page-13-5) (black curve) and at the [GC](#page-13-6) (red curve) in Figure [5.8\(](#page-123-0)d). [PCD1](#page-14-2) exhibits a broad spectral feature at around 740 nm, which could be the signature of the [SiV](#page-14-3) center, the GR1 center [\[215\]](#page-173-6), or a combination of the two. Since this sample is not thermally treated nor ion-implanted, this contribution to the PL signal must be attributed to diffused Si ions introduced via the non-optimal growth conditions and to interstitial defects. In fact, the feature appears more prominent and broader at the [GB.](#page-13-5) Lifetime measurements (not shown) confrm that the features near 740 nm can be associated with the [SiV](#page-14-3) center since the [SiV](#page-14-3) and the GR1 centers have clearly different excited-state lifetimes [\[119,](#page-164-0) [133\]](#page-165-1). Additionally, the lower wavelength range presents three extra peaks associated with Raman scattering. The peak located at 710 nm corresponds to a Raman shift of 1150 cm<sup>-1</sup> and the peak at 719 nm is related to a Raman shift of 1332  $\rm cm^{-1}.$  The latter is the fingerprint of diamond [\[109,](#page-163-3) [111,](#page-163-4) [216\]](#page-173-7) and it is clearly visible in both [GC](#page-13-6) and [GB.](#page-13-5) Moreover, the peak related to the  $1150\ \mathrm{cm}^{-1}$  shift is accompanied by a peak at 725 nm corresponding to a Raman shift of 1447.31 cm $^{-1}$ . The origin of both 1150 cm $^{-1}$  and 1447.31 cm $^{-1}$  lines has been under debate for a long time [\[217\]](#page-173-8). A. C. Ferrari et al. suggested that the peak at 1150 cm<sup>-1</sup> and the accompanying peak at 1447.31 cm<sup>-1</sup> are associated with trans-polyacetylene lying in [GBs](#page-13-5) and not with amorphous/nanocrystalline diamond [\[110\]](#page-163-5). It is clear from Figure [5.8\(](#page-123-0)d) that in the [GC](#page-13-6) the band at 1447.31 cm $^{-1}$  (725 nm) is barely visible and that the PL background is also lower, indicating that this region is mostly free from impurity carbon phases (SP<sup>2</sup> carbon phases). On the other hand, in the [GB,](#page-13-5) the signature Raman line at 1332 cm $^{-1}$  (719 nm) has emerged with a 1447.31 cm $^{-1}$  (725 nm) line. Moreover, a Raman shift of 1560.53 cm $^{-1}$ (731 nm), which is the G mode of graphite [\[144\]](#page-166-2), is more present in the [GBs](#page-13-5) due to the existence of SP<sup>2</sup> carbon. Hence, the SP<sup>3</sup> phase of carbon content appears higher in the [GC](#page-13-6) than in the [GB](#page-13-5) [\[28\]](#page-155-0).

<span id="page-123-0"></span>

**Figure 5.8.** Optical characterization of a virgin [PCD](#page-14-2) membrane [\(PCD1](#page-14-2)). (a) [SCM](#page-14-7) map of the signal from Filter 1. The dark regions correspond to the [GCs](#page-13-6) and the bright ones to the [GBs](#page-13-5). (b) [SCM](#page-14-7) map of the signal from Filter 2. The scale bar in the [SCM](#page-14-7) maps is  $2 \mu m$  and the step size is 0.1  $\mu$ m. (c) Manual spectral scanning (0.1 µm step size) performed along the black line indicated in Figure [5.8\(](#page-123-0)a), and Figure [5.8\(](#page-123-0)b), showing the background around the [ZPL](#page-15-3) emission of [SiV](#page-14-3) centers (black curve), the background-subtracted [PL](#page-14-8) from Filter 2 (red curve), and the signal from Filter 1 (blue curve). (d) [PL](#page-14-8) spectra in the [GC](#page-13-6) (red curve) and in the [GB](#page-13-5) (black curve) taken at the corresponding red points marked in Figure [5.8\(](#page-123-0)a), and Figure [5.8\(](#page-123-0)b). The band-pass of Filter 1 and Filter 2 is indicated.

#### **Un-implanted, thermally annealed polycrystalline diamond membranes [\(PCD2](#page-14-2))**

The [SCM](#page-14-7) maps from Filter 1 [Figure [5.9\(](#page-124-0)a)) and Filter 2 (Figure [5.9\(](#page-124-0)b)] display the [GCs](#page-13-6) and the [GBs](#page-13-5) near the upper surface of the [PCD2](#page-14-2) membrane. Figure [5.9\(](#page-124-0)c) shows a line spectral scanning performed along the black lines marked in Figure [5.9\(](#page-124-0)a) and Figure [5.9\(](#page-124-0)b) to monitor the variations of the [PL](#page-14-8) background signal in the spectral window of Filter 2 (black curve), the [PL](#page-14-8) intensity from Filter 1 (blue curve), and the background-subtracted [PL](#page-14-8) intensity from Filter 2 (red curve). A significant remark is that both PL background and signal from Filter 2 are larger than the [PL](#page-14-8) at Filter 1. On the one hand, thermal activation suppresses the spectral peaks associated with trans-polyacetylene, although a small signature remains in the [GB,](#page-13-5) as shown by the [PL](#page-14-8) spectra in Figure [5.9\(](#page-124-0)d) [acquisition

<span id="page-124-0"></span>

**Figure 5.9.** Optical characterization of un-implanted and annealed [PCD](#page-14-2) membranes [\(PCD2](#page-14-2)). (a) [SCM](#page-14-7) map of the signal from Filter 1. The dark regions correspond to the [GCs](#page-13-6) and the bright ones to the [GBs](#page-13-5). (b) [SCM](#page-14-7) map of the signal from Filter 2. The scale bar in the SCM maps is  $2 \mu m$  and the step size is 0.1 µm. (c) The spectral scanning (0.1 µm step size) performed at different positions along the black line indicated in Figure [5.9\(](#page-124-0)a) and Figure [5.9\(](#page-124-0)b), showing the background around the [ZPL](#page-15-3) emission of [SiV](#page-14-3) centers (black curve), the background-subtracted [PL](#page-14-8) from Filter 2 (red curve) and the signal from Filter 1 (blue curve). (d) [PL](#page-14-8) spectra in the [GC](#page-13-6) (red curve) and in the [GB](#page-13-5) (black curve) taken at the corresponding red points marked in Figure [5.9\(](#page-124-0)a) and Figure [5.9\(](#page-124-0)b). The band-pass of Filter 1 and Filter 2 is indicated.

points corresponding to [GC](#page-13-6) and [GB](#page-13-5) marked in Figure [5.9\(](#page-124-0)a), and Figure [5.9\(](#page-124-0)b)]. Moreover, the presence of the G band is particularly strong at the [GB.](#page-13-5) The strong spectral feature at 738 nm suggests the formation of [SiV](#page-14-3) centers via diffused Si ions in the sample, both at the [GC](#page-13-6) and at the [GB.](#page-13-5) Repeated measurements performed on the [GBs](#page-13-5) and [GCs](#page-13-6) reproduced the results shown in Figure [5.9\(](#page-124-0)c), and Figure [5.9\(](#page-124-0)d).

#### **Implanted and annealed polycrystalline diamond membranes [\(PCD3](#page-14-2))**

Finally, we study the optical properties of implanted [PCD](#page-14-2) membranes [\(PCD3](#page-14-2)). Figure [5.10\(](#page-125-0)a) is the [SCM](#page-14-7) map near the upper surface of [PCD3](#page-14-2) corresponding to the intensity from Filter 1. The [SCM](#page-14-7) map from Filter 2 is shown in Figure [5.10\(](#page-125-0)b). The fact that the [SCM](#page-14-7) map does not exhibit a substantially larger signal than the one in Figure [5.9\(](#page-124-0)b) indicates

<span id="page-125-0"></span>

**Figure 5.10.** Optical characterization of implanted and annealed [PCD](#page-14-2) membranes [\(PCD3](#page-14-2)). (a) [SCM](#page-14-7) map of the signal from Filter 1. The dark regions correspond to the [GCs](#page-13-6) and the bright ones to the [GBs](#page-13-5). (b) [SCM](#page-14-7) map of the signal from Filter 2. The scale bar in the [SCM](#page-14-7) maps is 2 µm and the step size is  $0.1 \mu$ m. (c) Manual spectral scanning  $(0.1 \mu$ m step size) performed along the black line indicated in Figure [5.10\(](#page-125-0)a), and Figure [5.10\(](#page-125-0)b), showing the background around the [ZPL](#page-15-3) emission of [SiV](#page-14-3) centers (black curve), the background-subtracted [PL](#page-14-8) from Filter 2 (red curve), and the signal from Filter 1 (blue curve). (d) [PL](#page-14-8) spectra in the [GC](#page-13-6) (red curve) and in the [GB](#page-13-5) (black curve) taken at the corresponding red points marked in Figure [5.10\(](#page-125-0)a), and Figure [5.10\(](#page-125-0)b). The band-pass of Filter 1 and Filter 2 is indicated.

that overall the [SiV](#page-14-3) centers created by ion implantation are not overwhelming the PL signal. In the spectral line scan of Figure [5.10\(](#page-125-0)c), both background and [PL](#page-14-8) signals from Filter 2 (black and red curves, respectively) increase at the [GB](#page-13-5) and drop at the [GC,](#page-13-6) as observed for the previous two situations. Moreover, the integrated counts at Filter 1 (blue curve) are less compared to those at Filter 2, because of the [SiV](#page-14-3) center activation. Different iterations of the spectral line scan on the [PCD3](#page-14-2) samples showed similar results verifying the fndings. The [PL](#page-14-8) spectrum of [SiV](#page-14-3) centers at the [GB](#page-13-5) and at the [GC](#page-13-6) (marked as red circles in Figure [5.10\(](#page-125-0)a) and Figure [5.10\(](#page-125-0)b) is presented in Figure [5.10\(](#page-125-0)d). The [PL](#page-14-8) background is enhanced due to the presence of impurities formed during diamond deposition followed by ion-implantation and thermal annealing although, compared to [GCs](#page-13-6), it is larger at the [GBs](#page-13-5). Moreover, the background appears more pronounced than in [PCD2](#page-14-2), probably due to

ion implantation. Compared to the [PCD1](#page-14-2), the post-annealing process performed on [PCD3](#page-14-2) has quenched the spectral peaks represented by trans-polyacetylene (at 710 nm and 725 nm) lying in [GBs](#page-13-5) and [GC.](#page-13-6) Because of the higher  $SP<sup>2</sup>$  phase impurities accumulated at the [GB,](#page-13-5) the G band at 731 nm correlated with the disordered graphitic carbon is noticeable in the spectra at the [GBs](#page-13-5), while it is completely suppressed in the [GC](#page-13-6) [\[28\]](#page-155-0).

In order to further understand the origin of the increased background and optimize the PL signal of the [SiV](#page-14-3) color centers, we investigate the [PCD1](#page-14-2) and [PCD3](#page-14-2) membranes using 532 nm and 690 nm laser excitation (not shown). The [NV](#page-14-11) related background is evident in the spectra of both samples when excited by the 532 nm laser. These features are strongly suppressed when the samples are excited by the 690 nm laser, as [NV](#page-14-11) centers have signifcantly less absorption in this spectral range. However, the [PCD3](#page-14-2) membrane exhibits a higher background as compared to [PCD1](#page-14-2), as shown by Figure [5.8](#page-123-0) and Figure [5.10.](#page-125-0) This can be ascribed to the creation of [NV](#page-14-11) centers and other defects, since ion implantation creates vacancies and thermal annealing favors the formation of color centers [not only [SiV,](#page-14-3) but also [NV,](#page-14-11) if nitrogen is present in the diamond sample]. This suggests that effectively reducing the nitrogen concentration during [MPCVD](#page-14-5) growth can improve the S/N ratio required for the detection of single [SiV](#page-14-3) color centers in [PCD](#page-14-2) membranes.

#### **5.3.6 Determination of Si Distribution in Un-implanted and Implanted Polycrystalline Diamond membranes**

To determine the Si distribution through [PCD](#page-14-2) membranes we perform [TOF-SIMS](#page-15-0) depth profling on both un-implanted [\(PCD1](#page-14-2)) and implanted [\(PCD4](#page-14-2)) samples [\[28\]](#page-155-0). The technique is suitable for the investigation of low concentrated species with a high depth resolution [\[218\]](#page-174-0). Depth profles are recorded on a [TOF-SIMS](#page-15-0) (Ion. ToF, Münster, Germany) using a 25 keV Bi+ ion beam bunched down to < 0.8 ns in negative polarity. Two sputter regimes are used: high rate for investigation of the entire membrane [Cs 2kV, 150 x 150 µm crater size with  $30 \times 30$  µm measurement spot in the center of the crater] and low rate for a comparison of implantation depth [Cs 2kV, 250 x 250 µm crater size with 50 x 50 µm measurement spot in the center of the crater]. At the top surface, PDMS containing contaminations are observed for all samples (not shown), probably originating from sample handling and transport. In negative [TOF-SIMS](#page-15-0) spectra, the characteristic signals for diamond  $\mathrm{C}_{\mathrm{x}}^{-}$ ;  $C_9^ _9^-$ , and  $C_{10}^-$  are chosen for display as their intensities are comparable to other signals of interest. The composition of the [PCD](#page-14-2) membranes is observed to be homogeneous over the entire thickness [see Figure [5.11\(](#page-127-0)a), normalized to  $C_{10}^-$  to account for fluctuations of the ion beam], except for both interfaces. Within the un-implanted sample [\(PCD1](#page-14-2)), no Si-containing signals are detected, which indicates no significant contamination with Si in the [PCD](#page-14-2) membrane prior to implantation. The bottom interface of the sample is examined to investigate the diffusion of Si from the removed substrate, caused by the

<span id="page-127-0"></span>

**Figure 5.11.** [TOF-SIMS](#page-15-0) analysis of un-implanted [\(PCD1](#page-14-2)) and implanted [\(PCD4](#page-14-2)) [PCD](#page-14-2) membranes, depth profles in negative polarity. (a) Entire [PCD1](#page-14-2) depth profle, where the marked area shows the maximum diffusion depth of the substrate, (b) magnification of the bottom interface of [PCD1](#page-14-2), and (c) overlay of the top interfaces of [PCD1](#page-14-2) (unim) and [PCD4](#page-14-2) (im).

growth process of diamond, depicted in Figure [5.11\(](#page-127-0)b). The profle is cut off at the signal level of spectral noise and not normalized [at interfaces, normalization induces artifacts]. The appearance of SiO<sub>2</sub> after the decay of  $C_x^-$  signals indicates a non-complete removal of the substrate. The overlap area of these signals can be explained by either surface roughening induced during the sputter depth profling process, diffusion of substrate into the diamond, or a combination of both effects. Thus, a maximum diffusion depth of less than 100 nm is determined for Si migrating into the [PCD1](#page-14-2) membrane during the growth process [shaded area in Figure [5.11\(](#page-127-0)b)]. In combination with the surface roughening induced by the substrate removal, as observed in Figure [5.6\(](#page-120-0)b), this indicates that no significant amount of Si is incorporated from the silicon substrate [\[28\]](#page-155-0). The presence of Si at the top surface is compared for both implanted (fluence  $10^8$  cm<sup>-1</sup>) and un-implanted [PCD](#page-14-2) membranes [\(PCD1](#page-14-2) and [PCD4](#page-14-2)). In Figure [5.11\(](#page-127-0)c) the profiles are normalized to the  $C_{10}^-$  signals for quantitative comparison. The  $C_9^ _9^-$  signals overlap perfectly, indicating that the profles are comparable. At the surface (≈ 20 nm), the Si<sup>−</sup> signal is caused by the presence of PDMS contamination. In the depth profile, the Si<sup>−</sup> signal is clearly enhanced on the implanted sample [\(PCD4](#page-14-2)) for  $\approx 200$  - 250 nm sputter depth, which is consistent with the implantation conditions (tail with penetration up to 250 nm estimated by SRIM simulations [\[219\]](#page-174-1).

These fndings indicate that by careful etching of the top and bottom interfaces, it is possible to eliminate any remaining Si contamination in [PCD](#page-14-2) membranes so that the creation of [SiV](#page-14-3) centers can be obtained in a controlled manner by Si-ion implantation.

#### **5.4 Conclusions**

We investigated the properties of [PCD](#page-14-2) membranes containing [SiV](#page-14-3) centers to identify procedures, which eventually allowed addressing single emitters. Firstly, the dimension of the diamond grains was crucial for the interrogation of single [SiV](#page-14-3) centers away from the background-rich [GBs](#page-13-5). To this end, we probed the evolution of the grain size by confocal scanning and [STEM](#page-15-1) analysis, showing that near the top surface, the dimensions of the diamond crystalline grains were sufficiently large to address [SiV](#page-14-3) centers by confocal microscopy, without undesired excitation at the [GBs](#page-13-5) (according to the achievable resolution set by diffraction). Next, we correlated the Raman signal with the [SiV](#page-14-3) emission and the luminescence background for different types of [PCD](#page-14-2) membranes (unprocessed, annealed, implanted, and annealed). Because the signal at Filter 1 contained several Raman peaks, a spectral analysis was necessary to identify the Raman signal from the diamond. While annealing reduced the background, it activated unwanted [SiV](#page-14-3) centers originating from the Si contamination. The implantation process led to an increase in the background due to the creation of vacancies that combine with Si and nitrogen impurities in the subsequent annealing step. Finally, we performed a [TOF-SIMS](#page-15-0) analysis of un-implanted and implanted [PCD](#page-14-2) membranes that clarified the depth profile of the Si implantation and contamination. In practice, the latter is closely confned to the interfaces and thus it can be removed by controlled etching. Our study solidifed that [PCD](#page-14-2) membranes with a thickness of a few microns can be suitable for quantum optical applications, provided that the nano-crystalline regions are removed, for instance by back thinning, or if the spatial resolution in the optical excitation is substantially increased, by near-feld or antenna-enhanced microscopy [\[73\]](#page-159-1).

In the next chapter, chapter [6,](#page-130-0) the experimental methods used to study the [SiV-](#page-14-3)nano-cone hybrid quantum system are presented. The chapter begins with a section on sample preparation and optical characterization, followed by a description of the coupling scheme and optical setup used in the experiment. Finally, the [SiV-](#page-14-3)nano-cone hybrid quantum system is introduced and its properties are discussed.

# **6**

### <span id="page-130-0"></span>**COUPLING SILICON VACANCY COLOR CENTERS TO NANO-CONE ANTENNA**

Hybrid quantum systems fascinate the scientifc community owing to their novel possibility of probing light-matter interaction at the nanoscale. [SiV](#page-14-3) color centers in diamond are versatile semiconductor quantum emitters, thanks to their sharp [ZPL](#page-15-3) emission, short lifetime, indistinguishability, and the possibility to operate at room temperature. However, the poor out-coupling efficiency, thereby the effective count rate, is limited by the non-radiative decay channels, and the total internal refection at the diamond surface hinders the opportunity of [SiV](#page-14-3) centers in a wide range of applications. This chapter discusses how the photo-physics of quantum emitters can be manipulated using optical antennas. Theoretical studies have verifed that precise coupling of gold nano-cones with a single [SiV](#page-14-3) color center can enhance the Purcell factor by more than four orders of magnitude with an antenna efficiency of 80% [refer chapter [3](#page-78-0) for details]. We fabricated nano-cones with dimensions around 100 nm along with an aspect ratio of  $\approx$  1 by gold sputtering on commercial [AFM](#page-13-0) probes followed by a [FIB](#page-13-1) milling technique. Here we present experimental fndings on the controlled coupling of an ensemble of [SiV](#page-14-3) centers with a plasmonic gold nano-cone, showing the total radiative decay rate  $(\Gamma_{\text{tot}}')$  of the [SiV](#page-14-3) color center enhanced by a Purcell factor of  $F \approx 57$ . Our studies show the potential of a hybrid-quantum system based on integrated photonics and quantum technologies.

#### **6.1 Introduction**

Generally, quantum networks are implemented via high-operational bandwidth quantum nodes through spin-photon interfaces where the atomic transitions are coupled to the resonant mode of an optical antenna, resulting in spontaneous emission rate enhancement, thereby boosting the efficiency of a quantum node. However, significant Purcell enhancement happens only if a quantum emitter interacts with an optical antenna of the desired dimension [\[36,](#page-155-1) [37,](#page-155-2) [42,](#page-156-1) [45\]](#page-156-2). Semiconductor quantum emitters such as single molecules, quantum dots, and color centers in diamonds are suitable for on-chip integrated quantum information processing.

In comparison with quantum dots at ambient conditions, color centers in diamonds are distinctly promising for scalable operations, thanks to their small inhomogeneous broadening and long coherence time in the range of  $\approx$  50 µs [\[48,](#page-157-3) [49\]](#page-157-4). Out of over 500 color centers in diamonds studied, [SiV](#page-14-3) color centers are in high demand by virtue of robust [ZPL](#page-15-3) emission with low phonon coupling, narrow inhomogeneous distribution, short lifetime, and room temperature stability [\[2,](#page-152-2) [3,](#page-152-3) [5\]](#page-152-4). Apart from that, the creation of [SiV](#page-14-3) centers is comparatively easily feasible by ion implantation and/or by doping during the [CVD](#page-13-7) growth of diamonds [see section [2.2.2\]](#page-46-0) [\[28,](#page-155-0) [115,](#page-163-6) [135,](#page-165-2) [132\]](#page-165-3). Nonetheless, the poor out-coupling efficiency due to the high refractive index of bulk diamonds and the long dephasing time is crucial.

The lifetime time of the quantum emitter can be shortened by manipulating the emitter's [LDOS](#page-13-2) by changing the emitter's photonic environment via dielectric microstructures or by plasmonic nanostructures [\[28,](#page-155-0) [57\]](#page-158-0). In section [2.3.5,](#page-72-0) different methods for modifying the spontaneous emission rate of a quantum emitter are discussed in detail. Plasmonic nanostructures and nanoparticles support [LSPR](#page-14-0) via coupling electromagnetic radiation into collective oscillation at their resonance frequency. At the same time, they can localize the electromagnetic felds massively through [LSPR](#page-14-0) into a tiny mode volume, thereby increasing the excitation rate of the quantum emitter, which comes in close proximity to the plasmonic nanostructure [\[31,](#page-155-3) [62,](#page-158-1) [103\]](#page-162-2). Our recent studies have shown that creating [SiV](#page-14-3) color centers in thin [PCD](#page-14-2) membrane offers an excellent platform where the quantum emitters are created in a controlled manner in nanoscale dimension, which in turn enables extraordinary near-feld coupling with plasmonic nanostructures [\[28,](#page-155-0) [44,](#page-156-0) [147\]](#page-166-3). A relevant outcome would be a hybrid quantum system that emits lifetime-limited photons at room temperature by accelerating spontaneous emission over non-radiative transitions and dephasing processes.

Some of the examples where the Purcell enhancement of quantum emitters were observed through the near-feld coupling of quantum emitters with plasmonic structures are the following.

Here we experimentally demonstrate the spontaneous emission enhancement of an en-semble of [SiV](#page-14-3) color centers in an  $\approx$  130 nm-thick [PCD](#page-14-2) membrane via near-field plasmonic coupling. To unravel this novel observation for the hybrid quantum system, we performed the near-feld coupling in nanometer precision by utilizing [AFM](#page-13-0) integrated confocal microscopy. To enhance the spontaneous emission decay rate of the quantum emitter, [SiV](#page-14-3) centers in thin [PCD](#page-14-2) membranes [\[28\]](#page-155-0) are coupled to gold nano-cones fabricated on commercial [AFM](#page-13-0) probes [\[147\]](#page-166-3). Since the [LSPR](#page-14-0) shift is linearly proportional to the refractive index modifcation of the embedding medium, the optical response of the nano-cone [\(LSPR\)](#page-14-0) is optimized via tuning the aspect ratio of the nanostructure, verifying the spectral

match between the emitter and nano-cone [see section [4.3.2\]](#page-105-0) [\[37,](#page-155-2) [47,](#page-157-0) [147\]](#page-166-3).

#### **6.2 Experimental Methods**

This section gives an overview of the experimental methods, including the fabrication, characterization, and near-feld coupling of the hybrid quantum system, in detail. The section [6.2.1](#page-132-0) focuses on a brief description of the fabrication and characterization of plasmonic gold nano-cones. A more detailed study on the nano-cones is in section [4.2.1](#page-91-0) and in section [4.2.2.](#page-96-0) The optical setup and experimental method for the near-feld coupling are explained in section [6.2.2.](#page-135-0) Finally, in section [6.3,](#page-139-0) the results and discussions are explained.

#### <span id="page-132-0"></span>**6.2.1 Fabrication and Optical Characterization**

#### **Theoretical Considerations**

We have created high-quality plasmonic gold nano-cones at the apex of conical quartz (SiO2) [AFM](#page-13-0) probes through a process involving gold sputtering and subsequent [FIB](#page-13-1) milling, as depicted in the [SEM](#page-14-12) image presented in Figure [6.2\(](#page-135-1)a) [\[147\]](#page-166-3). Employing [FDTD](#page-13-3) Lumerical simulations, we have explored the design considerations associated with the production of gold nano-cones on [AFM](#page-13-0) probes. Here we study the effect on the total radiative decay rate  $(\Gamma_{\text{tot}})$  of the quantum emitter when coupled to a plasmonic gold nano-cone. Initially, we examined a scenario where a gold nano-cone on [AFM](#page-13-0) cantilever coupled to an electric dipole (single quantum emitter) in free space, with the emitter positioned at a fixed distance of  $P = 1$  nm from the nano-cone [Figure [6.1\(](#page-133-0)a)]. The spectral dependencies of  $\Gamma_{\text{(tot,0)}}$  for such an emitter-nano-cone system in free space are presented in Figure [6.1\(](#page-133-0)c), revealing a clear infuence of the refractive index change in the cantilever material on the  $\Gamma_{(tot,0)}$  of the emitter, while the emitter-nano-cone separation remains constant at 1 nm.

However, when a metal-dielectric interface is introduced in the vicinity of the emitter, as compared to the same emitter-antenna system in free space [as illustrated in Figure [6.1\(](#page-133-0)b)], we observed a remarkable enhancement of  $\Gamma'_{\text{tot}}$  by approximately four orders of magnitude, particularly at the [ZPL](#page-15-3) emission of the [SiV](#page-14-3) color center [\[ZPL](#page-15-3) of [SiV](#page-14-3) is at a wavelength of 738 nm]. We remark that  $\Gamma'_{tot}$  indicates the near-field coupling of an emitter antenna system in the presence of a dielectric interface, and this quantity is normalized with respect to the normalized decay rate  $(\Gamma_{diel})$  in the dielectric substrate, to consider the actual experimental conditions [see section [4.3.1](#page-99-0) for more details]. The  $\Gamma'_{\text{tot}}$ plotted in Figure [6.1\(](#page-133-0)d) is normalized with respect to the radiative decay rate inside the dielectric membrane  $(\Gamma_{diel})$ . The enhancement in the radiative decay rate is calculated as the ratio of the power radiated by the electric dipole when positioned in the presence of a

<span id="page-133-0"></span>

**Figure 6.1.** (a) A metallic nano-antenna is interacting with a single emitter in a free space. The emitter possesses a dipole moment aligned along the symmetry axis of the gold nano-cone, which is positioned at a distance  $P = 1$  nm. (b) The emitter is located within a dielectric substrate (diamond membrane) and is coupled to a gold nano-cone. The nano-cone-to-emitter separation is  $P = 1$  nm. The emitter is embedded at a depth of  $Q = 2$  nm on a substrate with a refractive index of 2.4. The value of  $\Gamma'_{\text{tot}}$  is normalized with respect to the radiative decay rate within the dielectric membrane, denoted as  $\Gamma_{\rm diel}$ . (c) The  $\Gamma_{\rm (tot,0)}$  is normalized with respect to  $\Gamma_{\rm (rad,0)}$ , as a function of wavelength while varying the refractive indices of the cantilever. Key parameters include the aspect ratio of ≈ 1, with dimensions such as height *h* = 80 nm and base *b* = 80 nm. The emitter is situated at a distance of  $P = 1$  nm in free space and coupled to the gold nano-cone [refer to Figure [6.1\(](#page-133-0)a)]. (d) The  $\Gamma'_{tot}$  is normalized with respect to  $\Gamma_{diel}$  and antenna efficiency, plotted as a function of the emission wavelength. The emitter is situated  $Q = 2$  nm inside the dielectric substrate, with the gap between the diamond membrane and the gold nano-cone set at  $P = 1$  nm [refer to Figure [6.1\(](#page-133-0)b)].

diamond membrane near the nano-cone to the power radiated by the electric dipole within a diamond membrane. Similarly, antenna effciency is around 70%, which is computed as the ratio of the power radiated to the far-feld when the electric dipole is located in the presence of a diamond membrane near the nano-cone, to the power radiated by the electric dipole within a diamond membrane. In this case, the single [SiV](#page-14-3) quantum emitter is embedded within a dielectric membrane at  $Q = 2$  nm, and the distance  $P$  is kept at 1 nm. The depth *Q* at which the emitter is positioned within the dielectric diamond membrane can be adjusted, to improve  $\Gamma'_{\text{tot}}$  and antenna efficiency. Here, the calculations are optimized for a value of  $Q = 2$  nm. Therefore, establishing a well-coupled emitter-

antenna system could potentially yield an enhancement in  $\Gamma'_{\text{tot}}$  of at least three orders of magnitude. The pivotal factor that may limit the expected enhancement within this study is the precise control of coupling parameters and the accurate fabrication of the optical antenna.

#### **Optical Studies**

Fabricated nanostructures have dimensions of  $\approx 100$  nm, with an aspect ratio of  $\approx 1$ [refer section [4.2.1](#page-91-0) for the detailed fabrication process]. The nano-cones exhibit relatively sharp tips with a radius of curvature close to 25 nm. The fabrication process enabled precise control over the nano-cone's size, shape, and tip radius, which is essential for an outstanding light-matter interaction of a hybrid-quantum system. The gold nano-cone exhibited [LSPR](#page-14-0) around 660 nm along with a line-width of 60 nm without being in close proximity with a dielectric substrate. Our previous studies verifed that a nano-cone with an aspect ratio of  $\approx$  1 showed 100 nm red-shift in the [LSPR](#page-14-0) as the dielectric environment changes from air to diamond [described in section [4.3.2\]](#page-105-0). Figure [6.2\(](#page-135-1)a) shows the [SEM](#page-14-12) image of the nano-cone utilized for the near-feld coupling. We tuned the [LSPR](#page-14-0) into the [NIR](#page-14-1) by optimizing the aspect ratio, which in turn promoted the spectral matching of the nano-cone [LSPR](#page-14-0) with the emission wavelength of the [SiV](#page-14-3) color center. As shown in Figure [6.2\(](#page-135-1)b), the [LSPR](#page-14-0) of the nano-cone is around 800 nm when it is placed in close proximity with a dielectric medium [diamond *n* = 2.4]. Hence the spectral matching in this case between the two quantum systems was not optimal; thus, achieving a four orders of magnitude spontaneous emission rate enhancement was challenging. Figure [6.2\(](#page-135-1)c) shows the excited state lifetime comparison of [SiV](#page-14-3) color centers in bulk [SCD,](#page-14-4) 130 nm [PCD](#page-14-2) and 3 µm [PCD](#page-14-2) membrane respectively. The excited state lifetime has been measured in the range of 0.4 - 1 ns in a [PCD](#page-14-2) membranes. The lifetime curve corresponding to [SCD](#page-14-4) and 3 µm [PCD](#page-14-2) membrane in Figure [6.2\(](#page-135-1)c) are ftted using single exponential fts, whereas the lifetime curve corresponding to 130 nm [PCD](#page-14-2) membrane in Figure [6.2\(](#page-135-1)c) is ftted using double exponential fits, where the long lifetime representing the [SiV](#page-14-3) color centers emission channel and the short lifetime corresponding to the unwanted background components emission pathway.

Performing the near-feld coupling of nano-cones with [SiV](#page-14-3) centers in the [NIR](#page-14-1) region is fascinating because the absorption of gold in the [NIR](#page-14-1) is negligible. Also, the emission of many photo-stable quantum emitters is in this region [\[7,](#page-152-1) [54\]](#page-157-5). The dielectric host for the quantum emitters is based on [PCD](#page-14-2) membranes fabricated by [MPCVD](#page-14-5) growth method [see section [2.1.2\]](#page-32-0). Initially, we grew a  $5 \mu m$ -thick diamond film by [MPCVD](#page-14-5) using a 6-kW ellipsoidal plasma reactor on a silicon substrate. The concentration ratio of the precursor gas was optimized to get a high-quality diamond membrane. As the thickness of the [PCD](#page-14-2) membrane increased, the grain size at the top surface was expected to be more extensive compared to the one at the interfacial layer on the substrate. Moreover, in contrast with

<span id="page-135-1"></span>

**Figure 6.2.** (a) [SEM](#page-14-12) image of a gold nano-cone fabricated on commercial [AFM](#page-13-0) probe (b) Spectral matching of [SiV](#page-14-3) color center (emission at  $\approx$  738 nm) with gold nano-cone (broad [LSPR](#page-14-0) with central maxima at  $\approx$  775 nm). The incident laser is at  $\approx$  690 nm, detuned from resonance to avoid excitation enhancement. (c) Comparison of the excited-state lifetime of [SiV](#page-14-3) color center created on [PCD](#page-14-2) membrane (blue curve) with 3 µm [PCD](#page-14-2) membrane (red curve) and bulk [SCD](#page-14-4) (black curve).

the size of the [GC](#page-13-6) ( $\approx$  2 µm) at the top surface of the [PCD](#page-14-2) membrane, the confocal volume of the laser was smaller. Hence, one can address [SiV](#page-14-3) emitters within the [GC](#page-13-6) which is not limited by the confocal volume, that could improve the desired fuorescence signal while the background signal from [GC](#page-13-6) was negligible. Since the substrate used to grow a [PCD](#page-14-2) membrane was silicon, the probability of incorporating silicon impurities into the diamond membrane during the diamond growth process was high. Hence the back etching of the diamond membrane is a must to remove silicon impurities. Employing the [RIE](#page-14-6) method, the diamond membrane was back etched. Finally, we obtain polished, self-standing [PCD](#page-14-2) membranes with an unsupported area of 2 mm diameter and a thickness of  $\approx$  130 nm stabilized by a silicon frame [\[28\]](#page-155-0).

<span id="page-135-0"></span>The SiV color centers were created via  $Si^{3+}$  ion implantation [ion fluence of the order  $10^9$ cm−<sup>2</sup> ] followed by thermal annealing on the [PCD](#page-14-2) membrane[\[132\]](#page-165-3) [explained in section [2.2.2\]](#page-46-0). The membrane was shallow implanted by controlling the implantation depth by degrading the Si ion energy down to a few tens of keV using aluminum foils as stoppers. This enabled to locate the [SiV](#page-14-3) color centers close to the diamond surface ( $\approx$  5 - 10 nm beneath the surface) possibly within the [GCs](#page-13-6) for the near-feld coupling with the gold nano-cone. The [SiV](#page-14-3) color center emits at a central wavelength of 738 nm and exhibits a lifetime of 0.8 - 0.9 ns at room temperature. The section [2.2.4](#page-54-0) contains a thorough exploration of the factors contributing to the discrepancies in the excited state lifetime of a [SiV](#page-14-3) color center created on a [PCD](#page-14-2) membrane in comparison to 3  $\mu$ m PCD and bulk [SCD.](#page-14-4)

#### **6.2.2 Coupling Scheme and Optical Setup**

The near-feld coupling between the [SiV](#page-14-3) color center and the gold nano-cone was implemented through [AFM.](#page-13-0) The detector side of the quartz [AFM](#page-13-0) cantilever was metallic coated, resulting in the [AFM](#page-13-0) cantilever being partially transparent. The gold nano-cones were fabricated at the tip apex of the quartz [AFM](#page-13-0) probe [\[147\]](#page-166-3) and brought closer to the top surface of the [PCD](#page-14-2) membranes in a controlled manner via a closed loop 6-axes piezo stage (Nanowizard®4, JPK Instruments AG). This enabled the tip positioning down to 1 nm distance from the top surface of [PCD](#page-14-2) membrane, along with long-term position stability.

The optical characterization of the [SiV](#page-14-3) color centers was performed using a commercial inverted microscope (Axio Observer Inverted Microscope) in spectral and temporal resolved confocal microscopy manner connected with an [APD](#page-13-9) (Micro Photon Devices, MPD-100-CTC) as shown in Figure [6.3\(](#page-137-0)a). The quantum emitters were excited by a linearly polarized 690 nm tunable pulsed laser (Toptica AG, FemtoFiber Pro TVIS Special, spectral range 480 - 700 nm, <300 fs pulse duration, repetition rate 80 MHz) at a power of  $\approx 1.4$ mW using a high [NA](#page-14-9) objective lens (ZEISS Epiplan-NEOFLUAR 100X/0.75NA-BD DIC). The same objective lens collected the fuorescence emission and directed it toward the detectors after fltering the unwanted background signals. Utilizing a fippable mirror (FM), the signal was sent either to the spectrometer (Andor, Shamrock SR-500i- D2-SIL) for photo-luminescence spectroscopy or towards the [APD](#page-13-9) for excitation lifetime analysis. The [APDs](#page-13-9) was connected to a [\(TCSPC](#page-15-4) (Pico Quant, PicoHarp 300) which repeatedly measured the delay time between the arrival times of the photons and generated a histogram with picosecond time bin ( $\approx$  4 ps). The overall timing precision of a [TCSPC](#page-15-4) system depends upon the instrument response function [\(IRF\)](#page-13-10); this experimental setup had an [IRF](#page-13-10) of less than 100 ps.

#### **Polarization selection mechanism**

To generate the polarization selection at the desired focal plane of the optical system, the central part of the excitation beam was blocked by a central beam blocker, which creates a hollow ring beam. Later, part of the hollow ring beam was blocked using a stopper to manipulate the polarization. A longitudinally polarized excitation (P-polarization) at the location of the desired focal plane is a prerequisite for creating an electric field component along the nano-cone axis, leading to an efficient near-field coupling.

The [SiV](#page-14-3) color centers were created on [PCD](#page-14-2) membranes instead of [SCD,](#page-14-4) hence the dipole moment orientation of the quantum emitters [\(SiV\)](#page-14-3) could be completely random. So, the Purcell enhancement happens only with the emitters that have dipole moment orientation along the longitudinal mode of the gold nano-cone, as shown in Figure [6.3\(](#page-137-0)b). Figure [6.3\(](#page-137-0)b) depicts the polarization selection scheme for efficient near-field coupling between [SiV](#page-14-3)

<span id="page-137-0"></span>

**Figure 6.3.** (a) Schematics of the experimental setup for the near-feld coupling scheme. (b) Polarisation selection for the near-feld coupling of the hybrid quantum system. The plasmonic nano-cone fabricated on the [AFM](#page-13-0) probe is brought closer to the [SiV](#page-14-3) color centers in [PCD](#page-14-2) membranes.  $E_{\text{dipole}}$ (solid yellow arrow)and *E*long (broken red arrow) have the same dipole moment orientation.

color centers in [PCD](#page-14-2) membranes with plasmonic gold nano-cone fabricated on an [AFM](#page-13-0) probe. The focal plane of the excitation laser, the top surface of the [PCD](#page-14-2) membrane, and the gold nano-cone are made into one single focal plane. The partially blocked incident ring beam (*E<sup>i</sup>* ) [which is pointing out of the screen, shown as a red dot circle] focused on the top surface of the [PCD](#page-14-2) membrane at an angle, hence created two electric feld components; one along the transverse axis and another one along the longitudinal axis (*E*long) (shown as broken red arrows). Assuming the quantum emitter has an electric field component along the longitudinal mode of the gold nano-cone  $(E_{\text{dipole}})$  (solid yellow arrow) from one of the many possible orientations of the dipole moment, the modifcation in the spontaneous emission decay rate of the quantum emitter arises only at maximum coupling strength between the hybrid-quantum system [\[42\]](#page-156-1). The polarization of the excitation laser, the dipole moment orientation of the [SiV](#page-14-3) color center, and the distance between the hybrid quantum system determine the coupling strength.

The optical characterization of the gold nano-cone was performed in an inverted dark-feld microscopy setup with a P-polarized supercontinuum laser in a different experimental setup [description is given in section [4.2.2\]](#page-96-0). The scattered signal from the gold nano-cone was collected and normalized for the non-coherent supercontinuum laser across the broad wavelength range accurately determining the [LSPR](#page-14-0) of the nano-cone. The excitation laser used for the near-coupling was detuned from the [LSPR](#page-14-0) of the nano-cone to eliminate the

<span id="page-138-0"></span>

**Figure 6.4.** (a) Schematic representation of defning the contact point "*X* µm". The contact point "*X*" is the distance between the top surface of the [PCD](#page-14-2) membrane and the tip of the nano-cone when they are separated by the set point force distance. The distance "*P*" corresponds to "*X*+µm" when moving the cantilever towards the [PCD](#page-14-2) membrane. Similarly, the distance "*P*" corresponds to "*X*-µm" when retracting the cantilever from the contact point "*X*". (b) A wide-feld microscopy image of the [AFM](#page-13-0) cantilever close to the [PCD](#page-14-2) membrane. When the nano-cone at the tip apex of [AFM](#page-13-0) is in close proximity with the surface of the membrane, one can see a bright spot at the center of the [AFM](#page-13-0) cantilever.

possibility of excitation enhancement [see Figure [6.2\(](#page-135-1)b)].

#### **The near-feld coupling procedure**

The gold nano-cone was positioned closer to the top surface of the [PCD](#page-14-2) membrane by using the contact mode of the [AFM.](#page-13-0) The critical parameters, such as the set point force, the Q-factor, and the probe sensitivity, were obtained by calibrating the [AFM](#page-13-0) probe. The [AFM](#page-13-0) motor stage moves the probe closer to the [PCD](#page-14-2) surface, and it stops when the predetermined set point force is reached; this position is defned as the contact point "*X*". The contact point "*X*" is typically a few hundred micrometers away from the top surface of the [PCD](#page-14-2) membrane. The "*X*" is considered the distance between the top surface of the [PCD](#page-14-2) membrane and the tip of the nano-cone when they are separated by the set point force distance. Figure [6.4\(](#page-138-0)a) is a schematic representation of defning the contact point "*X* µm". As depicted in the Figure [6.4\(](#page-138-0)a), the distance "*P*" can be written as "*X*+µm" or "*X*-µm"; where moving the cantilever towards the [PCD](#page-14-2) membrane is indicated as "*X*+µm" and retracting the cantilever from the contact point "*X*" can be calculated as "*X*-µm" respectively. The approach or retraction of the cantilever was controlled in nanometer precision by utilizing the piezo stage. By looking at the wide-feld microscopy image as seen in Figure [6.4\(](#page-138-0)b), one can confrm that the nano-cone has reached close proximity with the surface of the membrane. When the [AFM](#page-13-0) probe reaches in close proximity to the surface of the membrane, the nano-cone appears as a bright spot at the center of the cantilever. The fuorescence lifetime data was acquired in each step. Initially, the fuorescence lifetime of the ensemble of [SiV](#page-14-3) emitters was taken. Then, the fuorescence lifetime was taken

<span id="page-139-1"></span>

**Figure 6.5.** (a) Spectral matching of a [SiV](#page-14-3) color centers with a gold nano-cone. The incident laser (blue curve) is detuned from the resonance to avoid excitation enhancement. (b) Measured excited-state decay curves for different coupling strengths in the spectral range shown in (a). The lifetime without near-feld coupling was 1.09 ns (black curve) and after the near-feld coupling, the lifetime was 0.4 ns (red curve) and the blue curve indicates the IRF. The extracted lifetime exhibits a shortening of the spontaneous emission rate by a Purcell factor of  $\approx$  57 (red curve).

for the same [SiV](#page-14-3) color centers but with the presence of the [AFM](#page-13-0) cantilever containing the nano-cone. The fuorescence lifetime at each approaching step was taken until the efficient near-field coupling has approached. As depicted in the Figure  $6.5(b)$ , the lifetime of the [SiV](#page-14-3) emitters decreases from 1.09 ns to 0.4 ns, which corresponds to the scenario without near-feld coupling and with near-feld coupling, respectively. The corresponding photo-physics is discussed in the next section.

#### <span id="page-139-0"></span>**6.3 The Silicon Vacancy-Nano-cone Hybrid Quantum System**

To investigate the alteration in the spontaneous emission rate, a pulsed laser with a duration of 70 ps excited the [SiV](#page-14-3) color centers, and the emitted photons were recorded and plotted as a function of the delay time after the laser pulse. The fuorescence curves were then ftted using two decay times, with the long lifetime representing the [SiV](#page-14-3) color centers emission channel and the short lifetime corresponding to the unwanted background components emission pathway. To adjust the coupling strength, the distance between the [SiV](#page-14-3) color centers and nano-cone, the polarization of the excitation laser, and the dipole moment orientation of the [SiV](#page-14-3) color centers were controlled and optimized. When the [LSPR](#page-14-0) of a gold nano-cone was spectrally matched with the [ZPL](#page-15-3) emission of the [SiV](#page-14-3) color centers oriented in the longitudinal mode, the emission was signifcantly enhanced, while the emission far from the plasmon resonance was suppressed. Figure [6.5\(](#page-139-1)a) shows the spectral matching between the [SiV](#page-14-3) color center (red curve) and the plasmonic gold nanocone. For the near-feld coupling, the emitter fuorescence was fltered using a band-pass filter [shown as a shaded area in Figure  $6.5(a)$ ]. As depicted in the figure, the [LSPR](#page-14-0) of the gold nano-cone red-shifts as the surrounding medium changes from the air (black curve) to a diamond membrane (green curve). The excitation laser wavelength (blue dotted curve) was kept far from the plasmon resonance to avoid excitation enhancement.

By positioning an ensemble of [SiV](#page-14-3) color centers near a gold nano-cone in a controlled manner, the spontaneous emission rates of [SiV](#page-14-3) color centers were boosted by a Purcell factor of  $F \approx 57$ , as illustrated in Figure [6.5\(](#page-139-1)b). The discrepancy between the theoretical fndings and the experimental results is due to 3 primary reasons: 1) poor crystal quality of the [PCD](#page-14-2) membranes, 2) the random orientations of the dipoles in [PCD](#page-14-2) membranes causing difficulty to an effective near-field coupling with the nano-cone, 3) background signals generated due to the scattering from the gold-sputtered truncated [AFM](#page-13-0) probe. These signals can introduce noise and interfere with the measurements, potentially masking or distorting the signals related to the near-feld coupling of [SiV](#page-14-3) color centers with the plasmonic gold nano-cones. The impact of these background signals might not have been accurately incorporated into the theoretical predictions, leading to a mismatch between theory and experiment. The [SiV](#page-14-3) color centers without coupling (black curve) show lifetimes of 1.09 ns. When the [SiV](#page-14-3) color centers were brought near a gold nano-cone, the emission rates became higher and the lifetime shortened to 0.4 ns [see the red curve]. The measured lifetime was not deconvoluted from the [IRF,](#page-13-10) since the components of [IRF](#page-13-10) (calculated as 90ps) are close to the fast decay component.

The measurement of fuorescence lifetime (*τ*) serves as a valuable indicator of the overall decay rate, where  $\tau = 1/\Gamma'_{\text{tot}}$ . To discern between radiative  $[\Gamma_{(\text{rad},0)}]$  and nonradiative [Γ(nrad,0) ] decay rates, it is essential to determine the quantum effciency *η*, where *η* is defined as  $\eta = \Gamma_{(rad,0)}/[\Gamma_{(rad,0)} + \Gamma_{(nrad,0)}]$  both in the presence and absence of the nanostructure, because with the presence of nanostructure the  $\eta$  changes. Here,  $\Gamma_{\text{(rad,0)}}$ corresponds to the radiative decay rate in free space without near-field coupling, and  $\Gamma_{(tot)}$ indicates the total radiative decay rate under efficient near-field coupling [\(SiV](#page-14-3) in [PCD](#page-14-2)) membrane coupled to gold nano-cone). The quantum efficiency (η) exhibits remarkable sensitivity to the surrounding environment. Hence, it's worth mentioning that due to the poor crystalline quality of a [PCD](#page-14-2) membrane,  $\eta = \Gamma_{(rad,0)}/[\Gamma_{(rad,0)} + \Gamma_{(nrad,0)}] = 0.03$  for [SiV](#page-14-3) color centers, in this case [\[57\]](#page-158-0). Without the near-feld coupling, the total decay rate of the quantum emitter can be written as the sum of radiative and non-radiative decay rates, i.e.  $\Gamma_{\text{(tot,0)}} = \Gamma_{\text{(rad,0)}} + \Gamma_{\text{(nrad,0)}}$ . After the near-field coupling only the radiative decay rate modifies, because the non-radiative part is intrinsic. Hence, the modified decay rate will be:  $\Gamma'_{\text{tot}} = F * \Gamma_{(\text{rad},0)} + \Gamma_{(\text{nrad},0)}$ , where, F is the Purcell factor. By comparing

lifetime measurements before and after near-feld coupling, we can derive the following relationship:

<span id="page-141-0"></span>
$$
\frac{\Gamma'_{\text{tot}}}{\Gamma_{\text{(tot,0)}}} = \frac{F * \Gamma_{\text{(rad,0)}} + \Gamma_{\text{(nrad,0)}}}{\Gamma_{\text{(rad,0)}} + \Gamma_{\text{(nrad,0)}}}
$$
(6.1)

Substituting  $\Gamma_{(\text{nrad},0)}$  with  $\Gamma_{(\text{nrad},0)} = \frac{\Gamma_{(\text{rad},0)}(1-\eta)}{\eta}$ *η*<sup>(1,4,7</sup>), and using Equation [6.1,](#page-141-0) we incorporate the intrinsic quantum yield of [SiV](#page-14-3) centers to calculate the Purcell factor, yielding:

$$
\frac{\Gamma'_{\text{tot}}}{\Gamma_{\text{(tot,0)}}} = \frac{F + (1 - \eta)/\eta}{1 + (1 - \eta)/\eta}
$$
(6.2)

which simplifies to:

$$
\frac{\Gamma'_{\text{tot}}}{\Gamma_{\text{(tot,0)}}} = \eta(F-1) + 1\tag{6.3}
$$

Finally, the Purcell factor can be expressed as:

<span id="page-141-1"></span>
$$
F = 1 + \frac{1}{\eta} \left( \frac{\Gamma_{\text{tot}}'}{\Gamma_{\text{(tot,0)}}} - 1 \right)
$$
 (6.4)

Prior to coupling, the [SiV](#page-14-3) color center demonstrates a lifetime of  $\tau$  = 1.09 ns, where,  $\tau = 1/\Gamma_{\text{(tot,0)}}$ . So,  $\Gamma_{\text{(tot,0)}}$  corresponds to 917.43 MHz. Similarly, upon proximity to a gold nano-cone in the near-feld, the emission rates are signifcantly altered, and the measurement of the [SiV](#page-14-3) color center count rate is conducted using an [APD.](#page-13-9) In this case the [SiV](#page-14-3) color center demonstrated a lifetime of  $τ = 0.4$  ns, where,  $τ = 1/Γ'_{tot}$ . So, Γ'\_{tot} corresponds to 2500 MHz. The total decay rates for both coupled  $[\Gamma'_{tot}]$  and uncoupled  $[\Gamma_{\text{(tot,0)}}]$  cases can be calculated, as shown in Figure [6.4\(](#page-138-0)b). So, for the uncoupled case we get  $\Gamma_{\text{(tot,0)}} = 0.03 \times 917.43 \text{ MHz} = 27.51 \text{ MHz}$ . While for the coupled case we get  $\Gamma_{\text{tot}}' = 0.03$  $\times$  2500 MHz = 75 MHz.

Since we know the modifcation of the total decay rate from lifetime measurements and that we can estimate the quantum yield by other means, we can obtain the Purcell factor according to Equation [6.4,](#page-141-1)  $\frac{\Gamma'_{\rm tot}}{\Gamma_{\rm (tot,0)}}=$  2.7; hence, we get the Purcell factor,  $F\approx$  57. For all the calculations, the parameters were optimized on the orientation and position of the [SiV](#page-14-3) color center with respect to the nano-cone. Given that the excitation laser is detuned from the spectral region of [SiV](#page-14-3) color center emission and surface plasmonpolariton resonance, the excitation enhancement  $K_{\text{exc}}$  is approximately unity. Additionally, a high numerical aperture (NA) oil-immersion microscope objective results in an extensive collection efficiency ( $\mathrm{K}_{\delta}$ ), rendering  $\mathrm{K}_{\delta}$  also close to unity.

In general, the interaction of quantum emitters with plasmonic nanostructures signifcantly alters their photo-dynamics, providing a route to overcome some of the inherent limitations of these emitters [\[42,](#page-156-1) [80,](#page-160-0) [167,](#page-168-0) [220\]](#page-174-2). There are various quantum emitters that can be manipulated by strong near-feld light-matter interactions. For instance, colloidal

quantum dots (QDs) are known for their photoluminescence versatility, but they suffer from issues like fuorescence intermittency, non-radiative Auger recombination, and surface traps [\[46,](#page-156-3) [86,](#page-160-1) [87\]](#page-160-2). These are often addressed by growing wide-band-gap shells, which unfortunately isolate the excitonic wave function, reducing its interaction with external environments and limiting their applicability in high-speed opto-electronics due to long emission lifetimes. By leveraging plasmon coupling, as demonstrated in bare core CdTe quantum dots, it is possible to control photo-physics without relying on chemical modifcations. The coupling with plasmonic nanostructures quenches more than 99% of surface defect-state emissions and signifcantly enhances the excitonic and biexcitonic emission rates through Purcell enhancement [\[46\]](#page-156-3). Similarly, the plasmonic coupling has been shown to enhance multi-excitonic emission in semiconductor QDs, which are attractive for optoelectronics but are often quenched by non-radiative decay channels like Auger recombination. Through precise positioning of quantum dots near gold nanocone antennas, the radiative decay rates of mono-excitons and biexcitons have been enhanced by 109 and 100-fold, respectively, offering new possibilities for quantum efficiency improvements [\[35,](#page-155-4) [58,](#page-158-2) [87,](#page-160-2) [88\]](#page-161-1). In 2D materials, quantum emitters in hexagonal boron nitride (hBN) exhibit enhanced emission rates and reduced lifetimes when coupled to high-quality plasmonic nanocavities, providing a scalable approach for integrating these emitters into nanophotonic systems with potential applications in on-chip quantum technologies [\[221,](#page-174-3) [222,](#page-174-4) [223\]](#page-174-5). For [SiVs](#page-14-3) in diamond, coupling to sub-diffraction-limited plasmonic cavities has demonstrated dramatic photodynamic enhancements [\[44,](#page-156-0) [54,](#page-157-5) [224\]](#page-174-6). A 135-fold spontaneous emission rate increase and an < 8ps instrument response limited excited-state lifetime have been achieved, which could facilitate the development of ultrafast, bright quantum emitters [\[76,](#page-159-0) [225\]](#page-174-7). Likewise, [NV](#page-14-11) centers in nanodiamonds coupled to low-loss silver nanocavities have shown up to a 70-fold reduction in fuorescence lifetimes and a 90-fold increase in photon counts, highlighting the promise of plasmonic nanostructures for generating ultra bright single-photon sources [\[226\]](#page-174-8).

Across various platforms, the coupling of quantum emitters to plasmonic structures has proven to be a powerful method to enhance emission rates, reduce lifetimes, and improve quantum efficiency, positioning it as a transformative approach for next-generation quantum photonic devices and opto-electronics.

#### **6.4 Conclusions**

To summarize, we successfully manipulated the emission photo-physics of an ensemble of [SiV](#page-14-3) color centers in a thin [PCD](#page-14-2) membrane by relying solely on plasmonic coupling. Additionally, we observed a moderate enhancement in the total radiative transitions  $(\Gamma'_{\text{tot}})$ of [SiV](#page-14-3) color centers under maximum coupling strength. Since the quantum effciency (*η*) of the system was only 0.03, the Purcell factor achieved was  $F \approx 57$ . This boost in

#### 6 Coupling Silicon Vacancy Color Centers to Nano-cone Antenna

transitions was primarily due to a faster photon emission rate compared to competing non-radiative rates. Since the nanoscale hybrid system can be integrated into microand nano-structures, such as microresonators and planar antennas, to achieve higher collection efficiency and directionality, this technique can also be used to control the emission spectra of a quantum emitter by selectively favoring transitions to a specifc vibrational ground state. Besides fuorescence enhancement, effective radiative decay rates have potential applications in solid-state spectroscopy as more extensive radiative decay rate enhancement is directly linked to a larger extinction cross-section, which can impact the feld of coherent plasmonics.

The fnal chapter [7](#page-144-0) of this dissertation presents the concluding remarks and future prospects of the research undertaken in the previous chapters. This chapter begins with a summary of the work done and the key fndings of the study. The chapter highlights the signifcance of the fabrication of plasmonic nanostructures for near-feld coupling and the photo-physics investigation of [SiV](#page-14-3) color centers in [PCD](#page-14-2) membranes. Additionally, the chapter discusses the successful creation of the [SiV-](#page-14-3)nano-cone hybrid quantum system. Furthermore, the author presents their outlook toward achieving a lifetime-limited hybrid-quantum system in the future.
# **7**

# **CONCLUSIONS AND OUTLOOK**

<span id="page-144-0"></span>The incentive of the work performed in this thesis is the nano-optical study of [SiV](#page-14-0) color centers in [PCD](#page-14-1) membranes and their plasmon-assisted ultrafast photo-dynamics. A hybrid quantum system offers versatility and the potential to overcome some of the limitations inherent in individual quantum platforms. Understanding the infuence of plasmonic nanostructures on the photo-physics of quantum emitters is of universal importance in various quantum platforms. In recent years, the feld of quantum physics, particularly the study of light-matter interaction, made remarkable developments in quantum communication for secure data transmission and long-distance quantum networking; the emergence of quantum sensors with applications in precision measurements and imaging; quantum simulation techniques for understanding complex quantum systems; innovations in quantum optics and photon control; the discovery and exploration of quantum materials for potential quantum computing applications; and the ongoing development of quantum algorithms for optimization, machine learning, and cryptography. The work performed in the framework of this thesis paves the way to the aforementioned optical studies on plasmon-assisted photo-physics manipulation of [SiV](#page-14-0) color centers in [PCD](#page-14-1) membranes for achieving enhanced photon emission. Such comparative studies to investigate the infuence of plasmonic nanoantennas on the photodynamics of quantum emitters can answer the existing questions related to quantum optics and material behavior, contributing to fundamental research. Furthermore, this work aims to bridge the gap between plasmonic nanostructures, as well as to understand the signifcance of integrating plasmonic nanostructures into quantum technologies.

Three important milestones were achieved in this thesis. Firstly, we introduced an innovative approach to achieve optimal near-feld coupling between color centers in diamond and plasmonic nanostructures while enhancing the antenna efficiency [\[147\]](#page-166-0). Furthermore, our fndings indicate that the polycrystalline nature of the diamond membranes does not impede their suitability for quantum optics applications, provided that the [SiV](#page-14-0) color centers are generated within the [GC](#page-13-0) of back-etched, high-crystalline-quality [PCD](#page-14-1) membranes [\[28,](#page-155-0) [57\]](#page-158-0). The second milestone encompasses the employment of [FDTD](#page-13-1) theoretical modeling, fabrication, and optical characterization of a plasmonic gold nano-cone on a commercial scanning probe microscope [\(AFM\)](#page-13-2) facilitating nanometer-precise, controlled

near-feld coupling. The [FDTD](#page-13-1) calculations demonstrated that gold nano-cones possessing an aspect ratio of  $\approx$  1 and dimension 100 nm can yield a Purcell enhancement exceeding four orders of magnitude with an impressive antenna efficiency of 80% [\[44,](#page-156-0) [147\]](#page-166-0). The ultimate achievement encompasses the realization of a hybrid quantum system through the precise manipulation of near-feld interactions between [SiV](#page-14-0) color centers within [PCD](#page-14-1) membranes. Although the quantum efficiency  $(\eta)$  of the system reached a modest 3%, the attained Purcell factor stood at  $F \approx 57$ , representing a substantial enhancement under optimal near-feld coupling conditions.

In chapter [3,](#page-78-0) the theoretical modeling regarding the nano-cone fabrication design considerations for near-feld coupling of a gold nano-cone with single quantum emitters in thin diamond membranes was focused. Chapter [4](#page-88-0) delved into the details of the fabrication process of gold nano-cones on commercial [AFM](#page-13-2) probes, achieved through gold evaporation followed by [FIB](#page-13-3) milling, and provided insights into their optical characterization. Chapter [5,](#page-110-0) was dedicated to the examination of the optical properties of [SiV](#page-14-0) color centers in [PCD](#page-14-1) membranes. Finally, in chapter [6,](#page-130-0) the study shifted its attention to the impact of near-feld coupling within a hybrid-quantum system. In the following section, a summary of the outcome of this thesis is given, together with conclusions and an outlook on prospective projects to extend the scope of work presented in this thesis in the future.

#### **7.1 Fabrication of Plasmonic Nanostructures for Near-feld Coupling**

Plasmonic antennas, designed for nanoscale light-matter interaction, offer unique opportunities. An appropriately tailored plasmonic antenna can enhance the radiative decay rates and alter the radiation patterns of single quantum emitters by precise near-feld coupling. While they surpass diffraction limits and confne felds to small volumes, crafting desired 3D nanoscale plasmonic structures remains challenging. The utility of theoretical simulations in comprehending the fabrication of plasmonic nanostructures is of paramount significance. In chapter [3,](#page-78-0) the [FDTD](#page-13-1) Lumerical simulations explored an in-depth delving into the intricate interplay of electromagnetic fields, material properties, and geometric confgurations, facilitating the design and optimization of plasmonic structures for efficient near-field light-matter interactions.

The [FDTD](#page-13-1) simulation was employed to determine the desired aspect ratio and dimensions of a platinum-based gold-coated [AFM](#page-13-2) probe to be used in the fabrication process. Through the adjustment of the nano-cone's aspect ratio, the simulation enabled the localization of the [LSPR](#page-14-2) of these nano-cones within the [NIR](#page-14-3) wavelength region. The primary focus of the simulation revolved around assessing the total radiative decay rate and antenna efficiency. This assessment encompassed two key scenarios: coupling an electric dipole source to a gold nano-cone in free space and within the diamond membrane. The manipulation of the

gold layer thickness (*t*) was instrumental in fne-tuning the [LSPR](#page-14-2) to the [NIR](#page-14-3) region. Given the substantial refractive index of the platinum-carbon composite material, increasing the thickness of the gold layer resulted in a blue-shift of the [LSPR.](#page-14-2) Consequently, the augmentation of the gold layer thickness, concurrently affecting the aspect ratio, led to a reduction in the interaction with the dielectric core, thereby further enhancing the total radiative decay rate. In addition, the antenna efficiency exhibited an increase from 60% to 80%, attributed to the diminishing dielectric effect. To expedite the emission of a single quantum emitter employing a metal-dielectric antenna, adjustments were made to the [LSPR](#page-14-2) of the nano-cones, aligning them closely with the emission wavelength range of [SiV](#page-14-0) using [FDTD](#page-13-1) simulations. Further elaboration on these fndings will be presented in Section [7.3](#page-148-0) of the conclusions.

As the next step, in chapter [4,](#page-88-0) we discussed the fabrication techniques and optical characterizations of plasmonic nano-cones. These structures were produced with desired dimensions,  $\approx 100$  nm in size and an aspect ratio of  $\approx 1$ , on commercial [AFM](#page-13-2) probes through a process involving gold evaporation followed by [FIB](#page-13-3) milling. The fabricated nano-cones exhibited variations in base diameter (70 - 120 nm) and height (60 - 150 nm), featuring a radius of curvature as small as 20 nm and an aspect ratio ranging from 1 to 1.5. Albeit the fabrication process is non-reproducible, were able to produce controlled structures with significantly smaller dimensions and with a stronger electromagnetic decoupling between the nanocone and the gold-coated [AFM](#page-13-2) probe. The radiation coupling due to the dielectric environment around the nanoparticles alters the [LSPR.](#page-14-2) Experimental verifcation of [LSPR](#page-14-2) shifts when altering the substrate's refractive index (*n*) from 1 to 2.4 was carried out using inverted dark-feld spectroscopy combined with [AFM](#page-13-2) [\[47\]](#page-157-0). This investigation indicated a 100 nm red-shift for nano-cones with an aspect ratio of  $\approx 1$ . Furthermore, we demonstrated that the experimental results were consistent with [FDTD](#page-13-1) simulations concerning the spontaneous emission rate and quantum yield. Our analysis unveiled the correlation between the modifcation of the decay rate for an emitter in a dielectric substrate with and without a nano-cone while considering the intrinsic quantum yield. The [FDTD](#page-13-1) calculations provided spectral features in good agreement with the experimental fndings. However, in the fabrication point of few, increasing the thickness of the evaporated gold layer resulted in the tendency for the radius of curvature of the nano-cones to increase. To improve the quality of nano-cone structures, optimization of [FIB](#page-13-3) milling parameters could potentially amend the aspect ratio of the antenna and surface plasmon coupling in the future. An alternative fabrication approach involving [EBID](#page-13-4) [\[47,](#page-157-0) [187\]](#page-170-0) on commercial [AFM](#page-13-2) probes could offer even greater control over the nanostructure, albeit at the cost of increased time consumption. The ultimate aim of this work is to showcase the potential of scanning plasmonic gold nano-cones with [NIR](#page-14-3) resonances in numerous nano-optics applications.

#### 7 Conclusions and Outlook

### **7.2 Investigation of Silicon Vacancy Color Centers in Polycrystalline Diamond Membranes**

Diamond membranes with reduced thickness facilitate efficient near-field coupling of quantum emitters with plasmonic nanostructures, enhancing light-matter interactions by allowing close proximity between the emitters and nanostructures. Furthermore, they typically exhibit fewer defects and impurities, resulting in longer coherence times for quantum states, a valuable characteristic for quantum optics experiments. In chapter [5,](#page-110-0) we explored the impact of creating [SiV](#page-14-0) color centers in [PCD](#page-14-1) membranes. The method involved ion implantation to generate [SiV](#page-14-0) color centers within [PCD](#page-14-1) membranes, ensuring the emission of photons with minimal absorption or distortion. This makes them particularly well-suited for quantum optics investigations.

The initial phase involved the growth and characterization of [PCD](#page-14-1) membranes. We grew 5 µm-thick diamond flms by [MPCVD](#page-14-4) on a silica substrate. Owing to the growth process, the grain structure of [PCD](#page-14-1) membranes had a non-uniform composition compared to other polycrystalline structures. Since the  $SP<sup>2</sup>$  carbon impurities and surface imperfections are linked to the crystal quality of [PCD](#page-14-1) membranes and the S/N ratio of activated [SiV](#page-14-0) color centers, we employed oxygen plasma cleaning for both untreated and implanted [PCD](#page-14-1) membranes. The implemented surface treatments have validated the crystal quality by demonstrating that the background signal stemming from carbon amorphous phases is not correlated with the increase in non-radiative decay rate.

Next, a comprehensive Raman spectroscopy analysis was conducted to investigate the crystal quality of [PCD](#page-14-1) membranes and its interplay with optical properties. The study revealed several key fndings. Firstly, the dimensions of the diamond grains proved critical for the effective assessment of individual [SiV](#page-14-0) centers while avoiding interference from [GB.](#page-13-5) This was achieved by examining grain size evolution through techniques such as scanning confocal microscopy and [STEM.](#page-15-0) These analyses indicated that the top surface featured sufficiently large diamond crystalline grains for precise confocal microscopy studies of [SiV](#page-14-0) centers, without undesired [GB](#page-13-5) excitation dictated by diffraction-limited resolution. Furthermore, correlations were established between the Raman signal, [SiV](#page-14-0) emission, and luminescence background across various [PCD](#page-14-1) membrane types [unprocessed, annealed, implanted, and annealed]. The annealing procedure was found to diminish the background but simultaneously activated undesired SiV centers resulting from Si contamination. Conversely, the implantation process increased the background due to the generation of vacancies that later combined with Si and nitrogen impurities during subsequent annealing. Finally, [TOF-SIMS](#page-15-1) analysis of both un-implanted and implanted [PCD](#page-14-1) membranes elucidated the depth profile of Si implantation and contamination. Importantly, the contamination was primarily confned to the interfaces and could

be effectively removed through controlled back etching processes of [PCD](#page-14-1) membranes. This comprehensive investigation suggests that [PCD](#page-14-1) membranes with a thickness of a few microns hold promise for quantum optical applications, provided that the nano-crystalline regions are eliminated, potentially through back-thinning techniques.

## <span id="page-148-0"></span>**7.3 Hybrid Quantum System Based on Silicon Vacancy Color Center and Plasmonic Nano-Cone Antenna**

Hybrid quantum systems captivate the scientifc community due to their exciting potential for investigating light-matter interactions at the nanoscale. [SiV](#page-14-0) color centers in diamond represent versatile semiconductor quantum emitters, offering advantages like precise emission lines, short lifetimes, indistinguishability, and the ability to operate at room tem-perature. Nevertheless, these [SiV](#page-14-0) centers suffer from poor out-coupling efficiency, limiting their effective count rate due to non-radiative decay channels. Moreover, total internal refection at the diamond surface constrains their utility across a wide range of applications. Theoretical calculations suggested that coupling [SiV](#page-14-0) centers with gold nano-cones dramatically increases their spontaneous emission rates by several orders of magnitude. However, our results indicated a signifcant reduction in the spontaneous emission rate of [SiV](#page-14-0) centers within thin diamond membranes. This implies the possibility of achieving an enhancement in the spontaneous emission rate of [SiV](#page-14-0) centers exceeding a factor of 1000 or more, which could be detected by fast [APDs](#page-13-6). Nevertheless, the primary obstacle to enhancing the rate of spontaneous emission lies in the fabrication of nanostructures and their effective near-feld coupling with quantum emitters. To overcome challenges related to nano-cone aspect ratios and enabling close proximity with [PCD](#page-14-1) membrane, this thesis explored an alternative approach, as mentioned in the chapter [4:](#page-88-0) fabricating gold nano-cones on the tip of a scanning probe [AFM](#page-13-2) cantilever, resulting efficient near-field coupling with quantum emitters in [PCD](#page-14-1) membrane.

Drawing from the discoveries presented in earlier chapters, chapter [3,](#page-78-0) chapter [5,](#page-110-0) chapter [4,](#page-88-0) and chapter [6,](#page-130-0) the chapter [7](#page-144-0) delves into the exploration of manipulating the photo-physics of quantum emitters using optical antennas. The experimental results from our controlled coupling of [SiV](#page-14-0) ensembles with scanning probe-based nano-cone antennas are quite intriguing. Notably, we observed a moderate increase in the total radiative transitions of [SiV](#page-14-0) color centers when subjected to maximum coupling strength. Despite the quantum efficiency (*η*) of the system being only 0.03, the achieved Purcell factor (*F*) stood at  $\approx$ 57. In chapter [6,](#page-130-0) the [FDTD](#page-13-1) calculations based on the real nano-cone structure showed four orders of magnitude enhancement in the  $\gamma_{\text{tot}}$  along with 70% upon introducing a metal-dielectric interface close to the emitter. This discrepancy between the theoretical and the experimental data prompts two primary conclusions: frstly, the suboptimal crystal quality of [PCD](#page-14-1) membranes, and secondly, inadequate coupling strength. The

enhancement observed in the experiment is due to the transitions primarily arising from a faster photon emission rate when compared to competing non-radiative processes. Given the ability to integrate this nanoscale hybrid system into micro- and nano-structures, such as microresonators and planar antennas, higher collection efficiency and directional control can be achieved. This technique also offers the potential to infuence the emission spectra of a quantum emitter by selectively favoring transitions to specific vibrational ground states.

#### **7.4 Outlook: Towards Hybrid-Quantum System**

In summary, the combination of nano-cones with [SiV](#page-14-0) centers in thin diamond membranes provides a prospective avenue to explore substantial enhancements in the spontaneous emission rate within a previously uncharted realm. The advantageous traits of [SiV](#page-14-0) centers, including their high photostability and narrower linewidth, enabled them to fully exploit the potent enhancements offered by nanoantenna plasmon resonances. Additionally, the polarization selected emission of [SiV](#page-14-0) centers harnessed to maximize coupling strength. While the [SiV](#page-14-0) centers have relatively low quantum efficiency, coupling with a nanostructure can amplify their efficiency. However, the diamond membrane reduces the spontaneous emission rate, hence large enhancement of the decay rate can still be measured by fast [APDs](#page-13-6).

Furthermore, leveraging a groundbreaking femtosecond laser system operating at a 1 GHz repetition rate will allow exploration of count rates in the GHz range. In principle, the [SiV](#page-14-0) center could achieve count rates approaching the GHz regime if the excited-state lifetime can be reduced to shorter than 200 ps [at 1 GHz repetition rate, a full fuorescence decay occurs only for lifetimes as short as 200 ps without longer decay components]. As [APDs](#page-13-6) aren't suitable for measuring such high count rates, the detection efficiency needs controlled reduction to accurately quantify the [SiV](#page-14-0) center output. For instance, one could reduce the collection efficiency or introduce controlled optical losses in the setup. Notably, the quantum efficiency of the hybrid system may likely be around 50 - 70%, thereby restricting the count rate to 500 – 700 MHz at a 1 GHz excitation rate. Achieving a radiative decay rate enhancement of more than three orders of magnitude implies that a nanoantenna[-SiV](#page-14-0) hybrid system exhibits an excited-state lifetime of about 1 ps, provided the membrane thickness is increased or a dielectric layer is deposited on one side to reduce the refractive index contrast, akin to the 1 ns excited-state lifetime of a bare [SiV](#page-14-0) center in bulk. Consequently, the linewidth of the [ZPL](#page-15-2) would predominantly rely on the radiative decay rate, rendering the emitted photons almost lifetime-limited and practically treating the [SiV](#page-14-0) as a two-level system. Such conditions for a solid-state system have thus far been achieved exclusively at cryogenic temperatures [\[227\]](#page-174-0), which complements current room-temperature cavity QED investigations [\[167,](#page-168-0) [87,](#page-160-0) [228\]](#page-174-1). In this context, an

endeavor will be made to measure faster decay times using swift [APDs](#page-13-6), although new detection methodologies must be devised to comprehensively characterize the ultrafast single-photon emission.

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# **LIST OF PUBLICATIONS**

- 1. [Single-Photon Emission from Silicon-Vacancy Color Centers in Polycrystalline Dia](https://pubs.aip.org/aip/apl/article/124/9/094001/3267501/Single-photon-emission-from-silicon-vacancy-color)[mond Membranes.](https://pubs.aip.org/aip/apl/article/124/9/094001/3267501/Single-photon-emission-from-silicon-vacancy-color) A. M. Flatae, F. Sledz, **H. Kambalathmana**, et. al., Appl. Phys. Lett. 124, 094001 **(2024)**.
- 2. [Plasmonic Nanocone Scanning Antenna: Fabrication and Optical Properties.](https://onlinelibrary.wiley.com/doi/10.1002/adpr.202300058) **H. Kambalathmana**, A. M. Flatae, C. Biagini, et. al., Adv. Photonics Res.; 2699-9293, 2300058 **(2023)**.
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