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Charge and Optical Stability of Color Centers in Diamond for Quantum Applications

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Abstract

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Certain color centers in wide-bandgap semiconductors, such as the nitrogen-vacancy (NV) and silicon-vacancy (SiV) centers in diamond, possess charge states that combine bright, spin-selective optical transitions with relatively long spin coherence times. Furthermore, these color centers exist inside a solid-state medium which enables integration in various device geometries for a wide range of promising quantum technologies.

Color centers can serve as sub-nm sensors of the electric fields, magnetic fields, strain, temperature, and electron chemical potential. For certain color centers, their electronic structure can be read out through their fluorescence. Within imperfect crystals, these color centers can be indispensable diagnostic tools of the crystal quality. In high-quality crystals they can be used to detect magnetic and electric fields of interest that originate from outside the diamond, or store and process quantum information within quantum spin registers composed of electronic and nuclear spins. Furthermore these color centers are natural single photon emitters, enabling the possibility of on-demand single photon sources for secure quantum communication. Combining these two modalities, quantum processors and single photon emission, enables the creation of delocalized quantum networks.

Two of the biggest limitations in practical implementations of these technologies are

charge and optical frequency instabilities. Charge instability refers to undesirable ionization processes where color centers gain or lose electrons, losing quantum information and entering optically dark states in the process. Even among color centers with stable charge states there can be optical frequency instabilities, a failure of a color center to reliably emit at a fixed frequency. Both of these effects become exacerbated in realistic device environments.

In Chapter 3, we discuss measurements correlating the charge instabilities and optical frequency instabilities to the diamond's exposure to plasma used to fabricate photonic structures. We then demonstrate that photonic structures can be fabricated without exposing the diamond to plasma, while achieving reasonable color center-cavity coupling. In Chapter 4, we discuss measurements of shallow color centers formed via ion implantation and annealing to investigate the remaining sources of optical frequency instabilities. This correlated study of many color centers isolates the contributions to the frequency instabilities caused by the residual damage from ion implantation, the proximity to charge traps on the diamond surface, and the dynamic charge environment created during optical charge re-pumping. The primary contributions to the frequency instabilities are found to be the proximity to the surface, and the charge re-pumping.

In Chapter 5, we discuss the mechanism that causes the chemical treatment of the diamond surface, specifically oxidation and hydrogenation treatments, to modify the charge state of shallow color centers. We demonstrate that correlated scanning probe microscopy and optical spectroscopy are effective techniques for imaging these chemically distinct surfaces with micron-scale resolution, and the effect they have on shallow color center's charge states. We then develop a novel surface treatment utilizing focused laser light which combines optical spatial resolution and dynamic feedback for precise surface functionalization. We use the correlated scanning probe and optical spectroscopy measurements to identify the

physical mechanism underlying this technique, and find that it is laser-assisted oxidation. Finally, in Chapter 6, we discuss the development of a dynamic charge re-pump scheme using above-bandgap excitation that neutralizes rather than charges defects in an effort to minimize optical frequency instabilities. We demonstrate through optical spectroscopy that the neutralization technique works on the two most commonly used optically-active color centers, the nitrogen-vacancy and silicon-vacancy center in diamond.

This thesis does not claim to solve charge and optical frequency instabilities which remains a long-standing and challenging goal within the field. However the tools and techniques we develop are significant advancements in our capabilities to stabilize novel color centers, understand their underlying dynamics, and characterize their performance. We also provide insights into the behavior of color centers in wide-bandgap semiconductors where deviations from thermal equilibrium can be exceptionally long-lived. The exotic charge dynamics in realistic crystal environments complicate even basic observations, but future mastery over these exotic effects may one day lead to brand-new technologies based on color centers in wide-bandgap semiconductors like diamond.

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GLOSSARY

NV: Nitrogen-Vacancy

SiV: Silicon-Vacancy

GeV: Germanium-Vacancy

SnV: Tin-Vacancy

PbV: Lead-Vacancy

IOR: Index of Refraction

PECVD: Plasma-Enhanced Chemical Vapor Deposition

HPHT: High-Pressure High-Temperature

SRIM: Stopping Range of Ions in Matter

FIB: Focused Ion Beam

EPR: Electron Paramagnetic Resonance

DFT: Density Functional Theory

ZFS: Zero Field Splitting

PL: Photoluminescence

PLE: Photoluminescence Excitation Spectroscopy

ZPL: Zero Phonon Line

DWF: Debye-Waller Factor

NIR: Near Infrared

ODMR: Optically Detected Magnetic Resonance

GaP: Gallium Phosphide

ICP-RIE: Inductively Coupled Plasma-Reactive Ion Etch

EBL: Electron Beam Lithography

HSQ: Hydrogen Silsesquioxane

TMAH: Tetramethylammonium hydroxide

CMT: Coupled Mode Theory

SEM: Scanning Electron Microscopy

SIL: Solid Immersion Lens

FDFD: Finite-Difference Frequency-Domain

NA: Numerical Aperture

TO: Topological Optimization

LDOS: Local Density of States

MBE: Molecular Beam Epitaxy

TE: Transverse Electric

PPC: Polypropylene Carbonate

PDMS: Polydimethylsiloxane

DPSS: Diode Pumped Solid State

FWHM: Full Width at Half Maximum

KPFM: Kelvin Probe Force Microscopy

AM-KPFM: Amplitude Modulated-Kelvin Probe Force Microscopy

FM-KPFM: Frequency Modulated-Kelvin Probe Force Microscopy

C-AFM: Conductive Atomic Force Microscopy

PEA: Positive Electron Affinity

NEA: Negative Electron Affinity

CPD: Contact Potential Difference

Pending...

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DEDICATION

To the love of my life Jen, who has been with me before I even began this journey, and
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Chapter 1

INTRODUCTION

1.1 *Background*

The future of technology is quantum. This is partially a consequence of increasing demands for smaller devices with increased capabilities and lower energy footprints across many conventional technologies. This includes flexible, energy-efficient, colored light sources that are continuously improving electronic displays in the TV aisle. This includes sub-micron scale sensors that can detect magnetic and electric fields, pressure, temperature, pH, and more, enabling advancements in electronic devices and medicine. This includes limiting the power consumption of our current optics-based communication network, and the miniaturization of the modern classical computer. It is also due to the promise of a wide range of novel technologies whose core functionality is **only** possible because of quantum phenomena.

For example, bright single photon sources can be used to transmit information between remote locations in a fundamentally secure way. Quantum memories and quantum processors enable the storage and manipulation of quantum information which allows for solutions to certain computational problems which can never be solved on a classical computer. Interfacing flying qubits (e.g. photons) with quantum memories enables the generation of delocalized quantum networks that can combine many small quantum computers into a single powerful quantum computer.

It is not trivial to decide which physical implementation, or combination of implementations, is the best for each of these applications, as each system possesses a unique combination

of advantages and disadvantages. We will not provide a review of the many different promising architectures, but rather focus on the strengths and capabilities of one system: color centers in semiconductors, specifically color centers in diamond.

In particular, this thesis will discuss some of the largest challenges that currently limit the performance of color centers across all applications, their charge and optical frequency instabilities. Increasing charge and optical frequency stability refers to mitigating the unwanted ionization of color centers during a device's operation and minimizing electric noise from charges within and on the surface of diamond that imprint on the color center's optical emission.

1.2 Thesis overview

1.2.1 Theory of color centers

This chapter delves into essential concepts pivotal for understanding the later chapters in this thesis. It describes basic properties of color centers, highlighting their potential for quantum technologies alongside the challenges they present. Various methods of color center formation are examined, including novel discoveries in annealing and the motivation for ion implantation and annealing. The discussion encompasses the formation energy and its utility in predicting the charge state of color centers. Moreover, the physical and electronic structure of NV and SiV centers in diamond is elucidated, which can be used to understand several key metrics of each charge state. A discussion of optical spectroscopy of color centers is included with a focus on the presence of the zero phonon line (ZPL) and phonon sideband, photoionization, and the phenomenon of spectral diffusion. Finally we discuss the basic theory of color center-cavity coupling for forming quantum networks.

1.2.2 GaP-on-diamond photonic interface

We investigate the prospects of a particular architecture for integrated photonics: gallium phosphide (GaP) on diamond. We discuss the impacts of GaP fabrication on the charge and optical frequency instabilities of NV centers within the diamond underneath GaP thin film “photon extractors”. This work motivates us to consider a scalable fabrication technique that avoids any fabrication of the diamond substrate. We demonstrate and characterize diamond fabrication-less cavity integration using 1D photonic crystal cavities (PCC) coupled to SiV⁻ centers.

1.2.3 Surface, implantation, and laser-induced optical instability

This chapter focuses on how charge and optical frequency stability are affected by the diamond surface, implantation and annealing, and the charge re-pump laser. It includes work done to isolate each effect through correlated studies of implanted NV centers across two samples implanted at different angles. By implanting at two different angles, the surface-NV distance is varied while the implantation damage is similar. The results show that the dominant source of spectral diffusion in NV centers within 100 nm of the diamond surface is related to the diamond surface and optical charge re-pumping.

1.2.4 Laser-assisted surface functionalization

This chapter describes a novel technique for functionalizing the diamond surface utilizing an optical laser under ambient conditions. This technique enables precise tuning of the Fermi level near the surface of the diamond. Unlike alternative surface functionalization techniques which are more aggressive and in practice boolean, this laser technique allows spatially localized surface functionalization with continuous optical feedback. In order to determine the mechanism behind the Fermi level tuning, scanning probe techniques are shown

to identify oxidized and hydrogenated diamond surfaces with the spatial resolution needed to image micron-scale features. These scanning probe techniques are used to characterize the surface prepared with the laser functionalization technique and reveal that the mechanism appears to be laser-assisted oxidation. The implantation process is also observed to result in accelerated oxidation of the hydrogenated surface with profound implications for diamond-based electronics.

1.2.5 Charge neutralization via above-bandgap excitation

This chapter discusses development of a technique to neutralize charged defects in the lattice using above-bandgap optical excitation. The effect on NV and SiV centers in bulk-doped samples is explored. Charge neutralization is demonstrated across a temperature range from 10-300 K. This non-thermal neutralized charge distribution remains stable in the dark and the back-conversion of NV^0 to NV^- and SiV^0 to SiV^- is directly related to green optical excitation.

1.2.6 Outlook

We will summarize the major observations of this thesis and discuss exciting new directions of study.

Chapter 2

THEORY OF COLOR CENTERS

2.1 *Introduction to color centers in diamond*

A color center is a point defect in an intrinsically transparent crystal that provides unique coloration in sufficient concentrations. For example, the blue-gray hue of the famous Hope diamond is due to the presence of boron color centers within the diamond [39]. The canary diamonds owe their yellow hue to the presence of substitutional nitrogen color centers [39]. A color center known as the nitrogen-vacancy (NV) center turns diamond a bright pink color [39]. Not every point defect modifies the optical properties of the crystal however, and thus not every defect is a color center. In this thesis, we focus our attention on color centers because they interact strongly with light. More specifically, we focus on a small subset of color centers that possess non-zero electronic spin and spin-selective optical transitions. The color centers in diamond that have received the most excitement for technological applications are shown in Fig. 2.1. The red bonds depict highly reactive dangling bonds that play an important role in the chemical and electronic structure of the defect, while the yellow-shaded region highlights a family of defects, group IV-vacancy complexes, that share very similar chemical/electronic structure.

In many ways color centers are like atoms; color centers trap electrons (or holes) into highly localized, quantized orbitals. In diamond, the dangling bond orbitals and the impurity orbitals are the most significant contributions to these localized orbitals. These correspond to bound states which possess energy levels lying in the normally forbidden bandgap of the semiconductor. Transitions between such localized orbitals as well as transitions to the

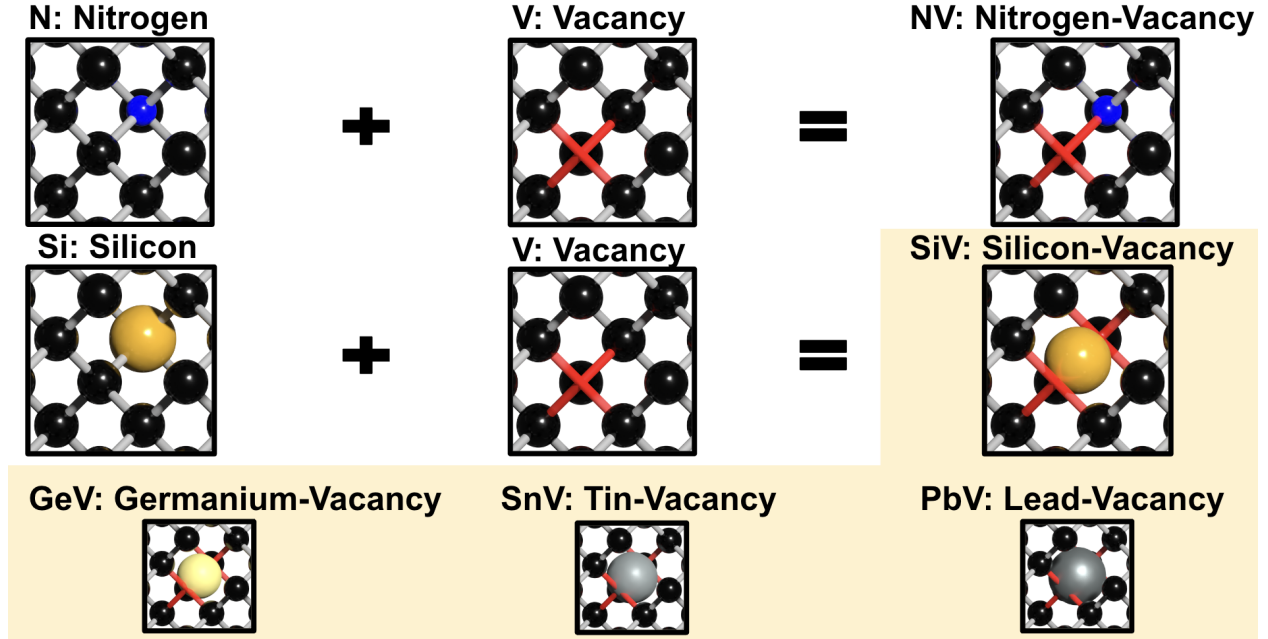


Figure 2.1: Several technologically relevant defects are shown. Nitrogen occupies a substitutional lattice site as a donor. A neutral carbon vacancy is shown containing 4 red dangling sp^3 bonds from the neighboring carbons. An NV center is shown, composed of a substitutional nitrogen immediately adjacent to a vacancy. A substitutional silicon is shown in the diamond lattice. Since it generates no states within the bandgap, it is therefore not a color center. The SiV center is shown, where the silicon adopts an interstitial bond-centered position. The 6 red dangling sp^3 bonds which constitute the majority of the localized orbitals are shown in red. Other group IV-vacancy complexes are shown below, highlighted in yellow.

conduction/valence band are responsible for the coloration imparted on the semiconductor.

Color centers are small. Color centers are likely as small as we can expect any device to be made. Within this tiny package, only a few angstroms or so in diameter, can lie a simple quantum register composed of an electronic spin, and depending on isotopic composition, nuclear spins. Nearby nuclear spins, within a few nanometers of the color center, can also participate in the quantum register [12].

In the presence of a sufficiently strong magnetic field, the Zeeman effect breaks the degeneracy of the spin states, enabling selective, deterministic control over the electronic and

nuclear degrees of freedom. This is often accomplished using microwave and radio frequency pulses precisely tuned in frequency, time, and intensity. Magnetic dipole, and hyperfine interactions between the proximal spins provide a mechanism for quantum entanglement among the register.

Optical access to color centers provides another way to control the color center's spin, read out the quantum state, and even entangle distant color centers. Just as finely-tuned microwaves can precisely drive spin transitions, finely-tuned optical lasers can drive spin-selective transitions to excited electronic orbitals, which can then relax through the emission of optical photons. Optical photons, especially those in the telecom bands, are particularly useful because they can be transported long distances through conventional, room-temperature optical fibers.

Color centers are sensitive. Color centers possess sharp optical, microwave, and radio resonances with small uncertainties in frequency. One can quantify the sharpness of these resonances by their Q factor, where $Q \approx \frac{\nu}{\Delta\nu}$, ν is the frequency of the transition, and $\Delta\nu$ is the linewidth of the transition. The NV center has built a reputation based on its sharp ground state microwave resonances with measured Q's of around 10^5 for DC sensing applications at room temperature [46]. At liquid helium temperatures, its optical Q factor is of the order 10^7 . If one measures changes in these resonance frequencies, with knowledge of the Hamiltonian, it is possible to determine the electric/magnetic fields, strain, and substrate temperature at the location of the color center. The higher the Q, the smaller the frequency shift that can be detected, and thus the higher resolution of the measurement. In the ideal case, this linewidth is limited only by the lifetime of the relevant excited state τ by the Heisenberg uncertainty principle: $\Delta\nu = \frac{1}{2\pi\tau}$. Achieving this physical limit in device-integrated color centers, particularly in the optical regime, is of critical importance for several exciting technologies.

Color centers are identical, once we control for isotope. This is in contrast with their major solid-state competitor, quantum dots. The fabrication of quantum dots, either in solution or epitaxial, leads to slight variations in the size and shape of the quantum dot with dramatic consequences on the optical emission frequency. Differences one observes in color center properties with identical isotopic composition are actually differences in the local crystal environment which perturbs the color centers energy levels.

Color centers can be stable in multiple different charge states depending on the crystal environment. Each charge state will have a completely different optical spectrum, with the possibility that some charge states may even show no optical emission at all. The electronic spin, and its coherence times, will also be unique for each charge state. Some influences of the underlying structure are preserved across charge states, for example, physical symmetries and nuclear spins. Charge states of all defects, not just our desired color centers, play a central role in this thesis. This is due to the strong electric fields produced by all charged defects, and the ionization of the desired defect into an undesirable charge state.

All of the previously mentioned properties are shared between color centers and atoms/molecules in free space. For certain properties, the diamond lattice imitates the vacuum. For example, a perfect diamond lattice consisting of only ^{12}C possesses neither electronic nor nuclear spins, with a magnetic permeability almost equal to 1.

Furthermore, diamond has a wide bandgap of 5.5 eV, so it is transparent to the visible and infrared light emitted by the color centers. This enables the efficient collection of a color center's emitted photons, with some degree of optical engineering needed to overcome diamond's large index of refraction (IOR).

There are significant differences between color centers and isolated atoms that warrant mentioning. First, color centers are sensitive to strain in the lattice. The strain field enters the Hamiltonian and therefore modifies the relevant optical and microwave transitions. If the

strain is inhomogeneous, or the color center takes multiple orientations relative to the strain, then the color center's Hamiltonian will be perturbed and their optical and spin properties will no longer appear identical. Thus strain must be precisely controlled within the diamond lattice. Still, there are times when control over strain can be utilized to improve or tune a color center's properties [60].

Color centers also interact with phonons, quantum excitations of vibrational modes, in the lattice. This results in a wide range of phenomena.

- **Non-radiative emission:** color centers can emit all/some excited state energy in the form of phonons instead of photons
- **Thermal broadening and shifts:** optical transitions that are sharp at low temperature broaden and shift with increasing temperature
- **Spin dephasing:** spin coherence times T_1 , T_2 , T_2^* become ultimately limited by phonon interactions
- **Orbital thermalization:** Within the ground state and excited state manifolds, orbital populations will thermalize. If the thermalization rate is fast compared to the radiative rates, then the intensity of the emission from a given excited state will depend on its thermal occupation.
- **Acoustic interactions:** Orbital degrees of freedom can be manipulated directly using acoustic waves. Spin degrees of freedom can be manipulated in the presence of spin-orbit coupling.

Lastly, charge dynamics involving color centers are much more exotic than those of isolated atoms. This is due to the presence of charged/neutral quasi-particles: electrons, holes

and excitons inside the crystal as well as the presence of other defects. Whereas isolated atoms can only photoionize through the emission of electrons, color centers can photoionize through both electron and hole emission. For some defects, like the NV center, this enables cyclic photoionization where an NV center can emit a stream of electrons and holes under continuous illumination [3]. In addition, other defects may ionize, releasing charge carriers that travel long distances to be captured by a color center under investigation [56]. Excitons can bind to color centers, providing additional optical access for some color centers, for example, SiV^0 [116]. These complex charge phenomena complicate fundamental defect discovery and characterization, but may one day enable brand-new technologies.

In order to realize any kind of color center-based technology, it is critical to understand how these color centers are formed.

2.2 Formation of color centers in diamond

Every diamond contains defects, **even** if the diamond was grown in a perfectly clean environment. Defects that don't require the presence of any foreign contamination are called intrinsic defects. Self-interstitials describe carbon atoms that are present in the lattice, but not at a lattice site. In diamond, the stable form of these carbon atoms are split-interstitials where two carbons effectively share a lattice site [95]. A vacancy describes the absence of a carbon atom at a lattice site.

We can expand the field of defects further by considering extrinsic defects which describe the class of defects incorporating foreign atoms. These foreign atoms can either be incorporated into the lattice as substitutions for the host atoms or by occupying an interstitial position. Beyond these single component defects, there exists the possibility for defects to complex together to form larger defects, just as atoms can react in chemical reactions to form molecules. The two color centers that are the focus of this thesis, the NV and SiV,

are examples of such impurity-vacancy complexes. The large number of single component defects, and their ability to complex with each other results in an almost limitless number of defects. We will discuss several ways that such defects become incorporated into the lattice and complex with each other.

2.2.1 Formation via crystal growth

Some defects will form in the diamond during the growth of the crystal. In this work, we will almost exclusively study single-crystal diamond grown via plasma-enhanced chemical vapor deposition (PECVD). This method involves exposing a seed crystal under low pressure to a plasma, usually composed of hydrogen with a small amount of methane [66]. In the temperature and pressure ranges used, graphite is the stable allotrope, not diamond, so the preference for diamond growth is based on kinetics. Hydrogen in the plasma preferentially etches away sp^2 bonded over sp^3 bonded carbon [66], thus only carbon that incorporates as diamond on the seed crystal survives.

Ideally, for our color centers, nitrogen (silicon) present in the growth chamber is incorporated into the diamond directly as complete NV (SiV) centers. In reality, most of the nitrogen and silicon will be incorporated as substitutional impurities, and some will be incorporated into other defects such as NVH. In fact, in similar substrates the ratio of N:NVH:NV is approximately 300:30:1 [27]. The growth method plays a deciding factor in determining the available species and ratios of defects, for example diamond grown via the high-pressure high-temperature (HPHT) method boasts many defects that one doesn't observe in high-purity PECVD growth. One reason is that it is thermodynamically favorable for many impurities to aggregate in diamond, but the low temperatures used in PECVD, (800-1200°C) [2], don't allow for the diffusion of impurities besides hydrogen. In PECVD growth, complexes are either incorporated into the diamond as a complete unit or created by the diffusion and

binding of vacancies and hydrogen to defects. The importance of hydrogen, which makes up the majority of the growth plasma, and its incorporation into diamond is still being investigated, in part because of the difficulty of directly measuring tiny concentrations of hydrogen.

2.2.2 Formation via annealing

After the growth of a diamond, it is possible to observe additional defect dynamics simply by reheating the diamond to growth condition temperatures under vacuum. In the high-purity samples we use, where single isolated NV centers can be imaged using confocal microscopy, these dynamics can be directly observed. This was precisely the goal of Ref. [15].

Fig. 2.2 shows a confocal scan from this work [15] taken deep within a diamond before and after two different annealing treatments. Each green and pink dot in the pre/post-anneal scans corresponds to a single NV center, with the color differentiating between two sets of NV center orientations. The orientation is measured utilizing the polarization dependence of excitation which is not able to resolve all 4 orientations. The appearances, disappearances, and re-orientations are indicated by blue, grey, and yellow NV centers respectively in the differences panel.

This ability to directly observe NV centers and their orientation offers an unprecedented look into defect annealing dynamics. We will highlight several key observations in this work.

NV center formation NV center formation is observed and significant below 1000°C. The proposed explanation involves a vacancy source, vacancy diffusion, and subsequent capture at substitutional nitrogen sites.

NV center disappearances NV center disappearances are significant at 960°C and 1050°C anneals. A likely explanation involves the dissociation of a hydrogen source such as

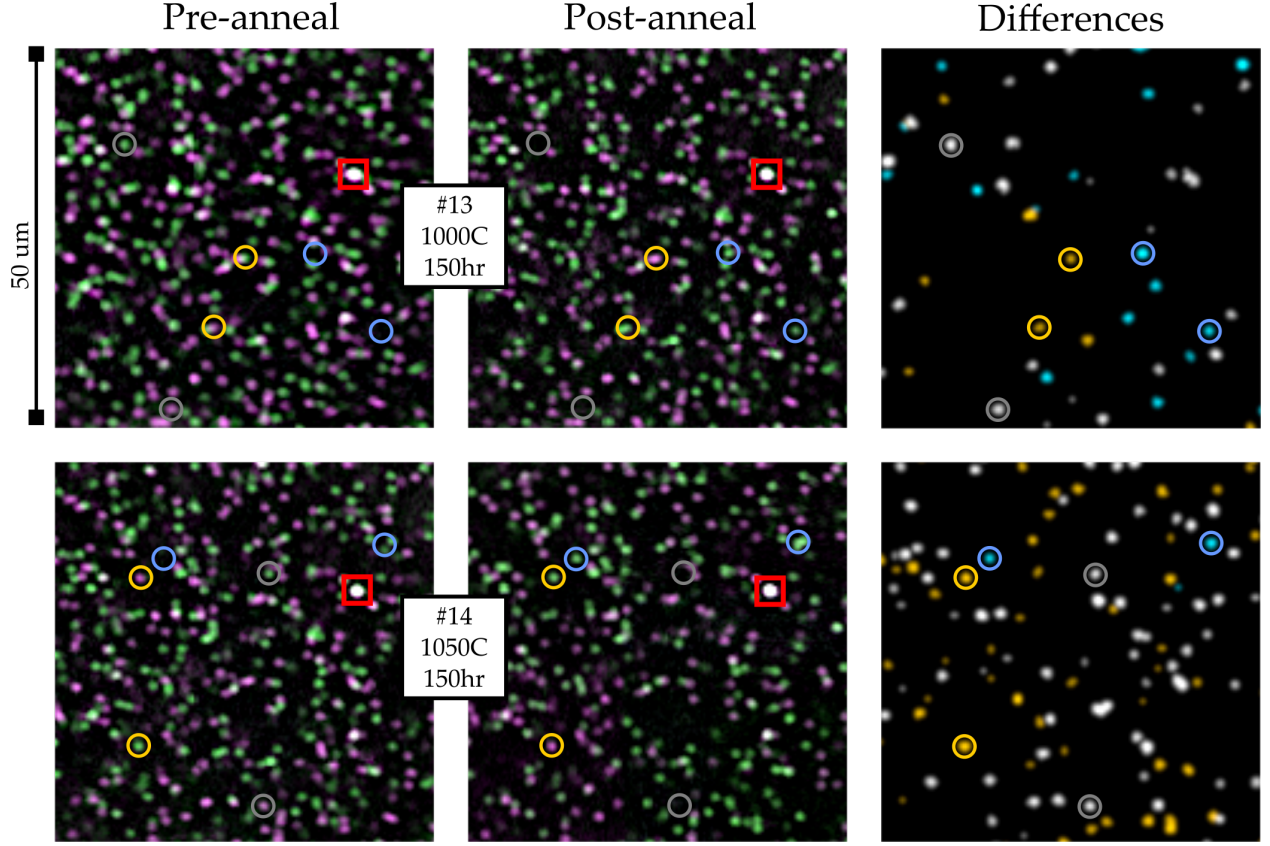


Figure 2.2: Two regions of diamond showing NV^- changes during two different annealing treatments. Green and magenta indicate the two sets of distinguishable NV^- orientations. Two examples each of appearances, disappearances and re-orientations are indicated by blue, grey and yellow circles, respectively. The red square marks a persistent defect used for image alignment. This figure is reproduced from "Srivatsa Chakravarthi, Chris Moore, April Opsvig, **Christian Pederson**, Emma Hunt, Andrew Ivanov, Ian Christen, Scott Dunham, and Kai-Mei C. Fu. Window into NV center kinetics via repeated annealing and spatial tracking of thousands of individual NV centers. Phys. Rev. Mater., 4:023402, Feb 2020" [15]

NVH_3 at 960°C and NVH_2 at 1050°C . The dissociated hydrogen diffuses and is subsequently captured at NV centers converting them to the dark NVH defect.

NV center orientations change NV center orientation changes are significant at 1050°C without the observation of significant disappearances (at least after the H source is depleted). This suggests that the NV partially dissociates at 1050°C , but a long-range

interaction (at least 3rd nearest-neighbor) prevents the vacancy from fully dissociating.

Depletion region A depletion region consisting of only a few well-separated NV centers compared to the high density of NV centers seen in the rest of the bulk appears near one of the surfaces in the diamond. This region continues to grow with annealing. The proposed explanation is the diffusion of hydrogen and the passivation of NV centers into NVH centers. This growing depletion region is seen in Fig. 2.3 as the dark region near the top surface.

In each case above, we have strong evidence that the NV chemical composition was modified, and that these disappearances/formation were not due to charge dynamics. It is known that NV centers possess a dimmer charge state, NV^0 , and even a non-fluorescent charge state NV^+ . These other charge states can be significant near surfaces, where charge states are known to be sensitive to the surface termination of the diamond [41, 32]. However our microscope can detect NV^0 and no NV^0 is observed.

Fig. 2.4(a-b) shows confocal scans taken in the depletion region using two different excitation wavelengths, 450 nm and 532 nm respectively. These confocal scans show exactly the same NV centers, though the spectra show photoluminescence from only NV^0 in Fig. 2.4(a) and primarily NV^- in Fig. 2.4(b) due to the effect excitation has on the charge state. Furthermore, in Fig. 2.4(c), we see an example of NV centers in a separate sample that exist as NV^0 under 532 nm illumination and are still clearly observable. Since the few NV centers that we can observe in the depletion region, all show bright NV^- fluorescence under 532 nm excitation, with no evidence of a varying Fermi level, it is unlikely that variations in charge state are responsible for the disappearances.

This study provides a good case study in the importance of studying charge dynamics, especially in fundamental defect discovery, where such effects complicate observations.

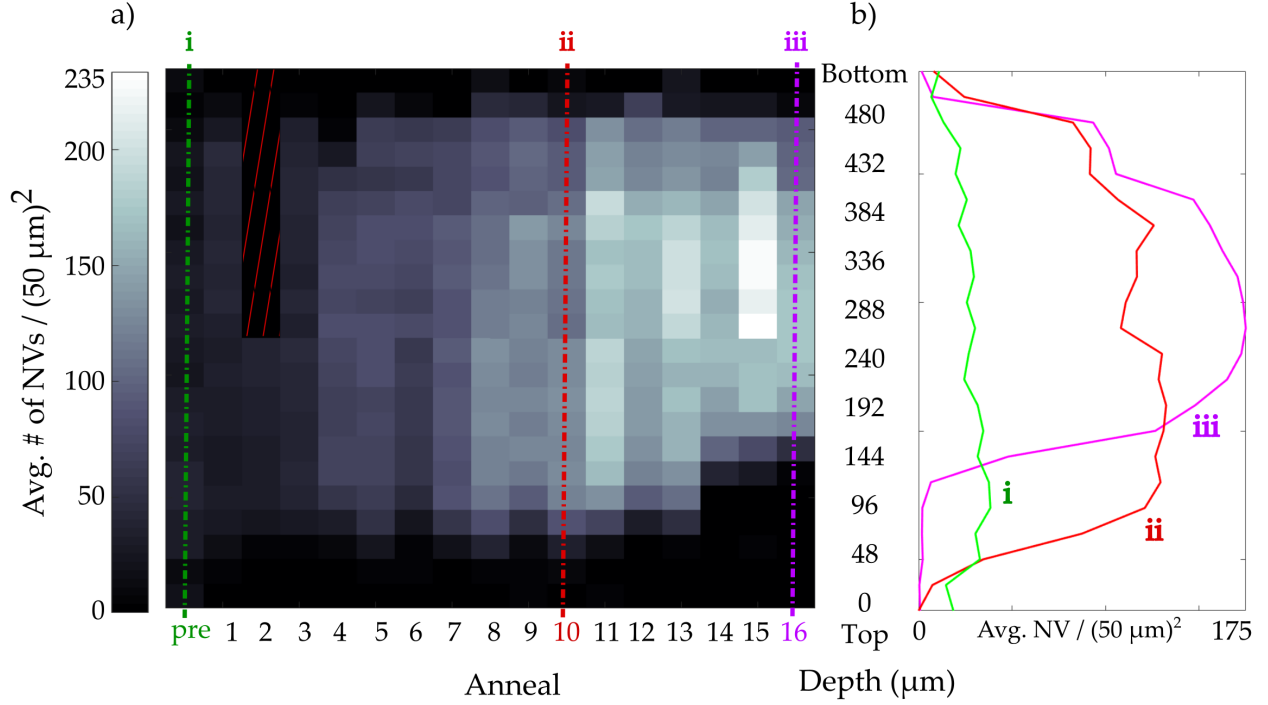


Figure 2.3: (a) Plot of the average number of NV^- centers per $(50 \mu\text{m})^2$ area as a function of sample depth and anneal. In order to access the full depth profile with the limited piezo scan range, the sample is imaged from both the top and bottom surfaces. The two data sets are stitched at $\sim 250 \mu\text{m}$. The red hashed area indicates missing data. (b) Line plots of slices notated in (a). This figure is reproduced from "Srivatsa Chakravarthi, Chris Moore, April Opsvig, **Christian Pederson**, Emma Hunt, Andrew Ivanov, Ian Christen, Scott Dunham, and Kai-Mei C. Fu. Window into NV center kinetics via repeated annealing and spatial tracking of thousands of individual NV centers. Phys. Rev. Mater., 4:023402, Feb 2020" [15]

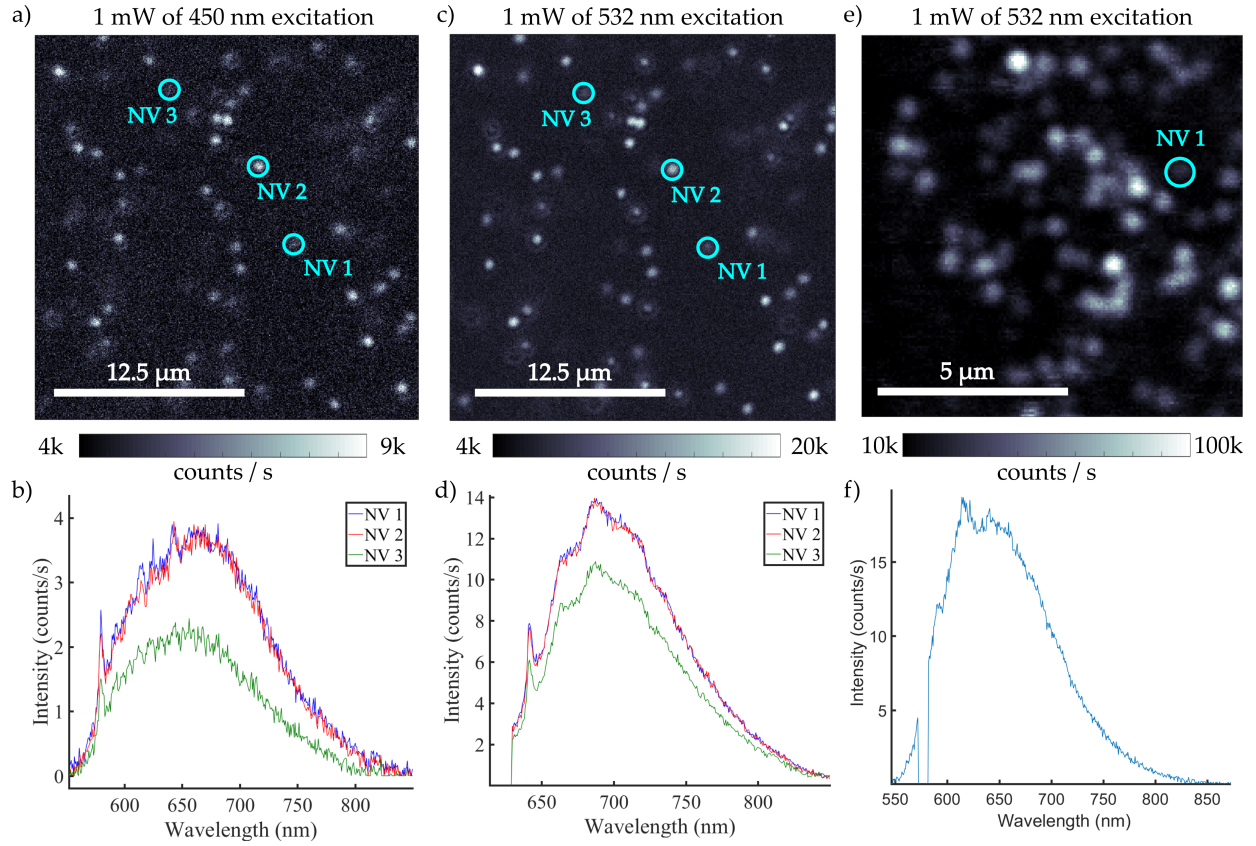


Figure 2.4: (a,b) Confocal scan and spectra of 3 NVs in the depletion region taken with 450 nm excitation. (c,d) Confocal scan and spectra of same 3 NVs in sample B taken with 532 nm excitation. (e,f) Confocal scan and spectra of NV⁰ from a reference sample taken with 532 nm excitation. This figure is reproduced from "Srivatsa Chakravarthi, Chris Moore, April Opsvig, **Christian Pederson**, Emma Hunt, Andrew Ivanov, Ian Christen, Scott Dunham, and Kai-Mei C. Fu. Window into NV center kinetics via repeated annealing and spatial tracking of thousands of individual NV centers. Phys. Rev. Mater., 4:023402, Feb 2020" [15]

It is worth mentioning that the color centers incorporated during growth, or after the annealing treatments, within high-purity, low-strain, isotopically purified crystal environments possess the best-observed qualities, from lifetime-limited optical linewidths, long spin coherence times, and stable charge state. Unfortunately, they form stochastically within the lattice, and represent a small concentration of the incorporated impurities. These limit their applicability in most of the exciting devices we envision.

2.2.3 Formation via irradiation and annealing

Sometimes high concentrations of color centers (usually NV^-) are desired. To achieve higher concentrations of NV centers without adding more nitrogen (a significant source of spin dephasing) into the lattice, it is possible to convert the existing substitutional nitrogen into NV centers. This can be accomplished by irradiating the sample with high-energy particles (e.g. electrons or ions) that create self-interstitial and vacancy pairs within the lattice. At annealing temperatures these intrinsic species become mobile. Interstitial diffusion is thermally activated with an activation energy of 1.6 eV [73] and will diffuse, either recombining with vacancies, complexing with other defects, or annealing out to the surface of the sample. At slightly higher temperatures vacancy diffusion is activated, with an activation energy of 2.3 eV [73], and they too can complex, for example with the native nitrogen to form NV centers, or anneal out of the sample.

We will also discuss single color center applications in quantum sensing, quantum communication and quantum computing where we would like the ability to create color centers at a nearly deterministic location. There is a convenient way to accomplish this for impurity-vacancy complexes. One implants a desired impurity, such as nitrogen for NV formation or silicon for SiV formation into the lattice. We leverage the fact that the implanted ion will not become mobile at the annealing temperature, and thus the location where the ion is

implanted becomes the location of a formed color center. At the annealing temperature, it is the interstitials and vacancies which diffuse and form the color center.

The depth of the ions and the damage they create along the trajectory are estimated using computational methods. This is most commonly achieved using a Monte-Carlo based computational package known as Stopping Range of Ions in Matter (SRIM) [119]. This software has been bench-marked against real ion implantation in diamond with reasonable agreement [72].

There are also some interesting alternatives to directly implanting a species into the crystal. For example, a focused ion beam (FIB) can be utilized to knock atoms from a surface film inside the diamond [40] to form very shallow defects. This can overcome limitations in ion sources, or be used to more carefully control the amount of vacancies produced by the ion implantation.

2.2.4 Formation energy and charge state

In the previous sections, we focused on direct experimental observations of defects in crystals rather than *ab initio* theories. Concentrations of defects, for example the ratio of N:N_{VH}:N_V centers were based on electron paramagnetic resonance (EPR) studies [27] and in high-purity samples, concentrations of N_V centers were directly measured by confocal imaging [15]. One compelling reason to rely on experimental measurements over theoretical predictions, is that we have good evidence that our diamond samples never reach thermal equilibrium during crystal growth or during annealing treatments. One observation in our study of individual N_V centers under repeated anneals [15] is that the number of appearances and disappearances have yet to equilibrate even after several 150 hour-long anneals. Thus defect formation is determined by kinetics, during crystal growth and afterward.

However, there are areas where *ab initio* theories can make reliable predictions regarding

defects. For example, density functional theory (DFT) is quite successful at determining the most stable structure of a defect, or determining if it is favorable for defects to complex together. Another area where DFT routinely finds use is in predicting the charge states of defects. This latter case is of particular interest to us because it is important to know whether our color center will be stable in its desired charge state in the dark.

Even though the chemical species within our diamond do not have time to complex with each other and reach thermal equilibrium, the charge of defects is based on the electrons within the material reaching thermal equilibrium which happens on much faster time scales. At least this is the argument used for traditional semiconductors like silicon where electrons (holes) are present in the conduction (valence) band at room temperature and can thus rapidly be trapped or detrapped at defects. Diamond, being a wide-bandgap semiconductor lacking shallow donors and acceptors, is much more complicated. There is strong evidence that charging of defects within the bulk of even moderate purity diamond is driven almost entirely by photoionization dynamics. For example, there are demonstrations of room temperature data storage persisting for days utilizing charges in diamond [65], indicating that thermal ionization is negligible. This offers exciting possibilities to precisely tailor the charge of defect species within diamond into very non-equilibrium distributions, and is one of the motivations for Chapter 6.

However, thermal equilibrium does appear to hold close to the surface of diamond, where we can see that shallow color centers have charge states determined by the chemical treatment of the surface [41, 32] which dominates over the photoionization dynamics. This is due to surface effects that can pin the Fermi level much closer to the valence band, such that hole concentrations can become appreciable. These near-surface color centers are the most technologically useful for exciting applications, so it is important to understand the theory which is based on the concept of the formation energy.

The formation energy of a defect represents the amount of energy it takes to form a particular defect from its isolated components. Here we will briefly describe how this formation energy is calculated using DFT. We can write the formation energy as [31]:

$$E^f[X^q] = E_{total}[X^q] - E_{total}[bulk] - \sum_i n_i \mu_i + qE_F + E_{corr} \quad (2.1)$$

Here $E^f[X^q]$ is the formation energy of the defect X in the charge state q , $E_{total}[X^q]$ is the energy of a super-cell including the defect X in the charge state q , $E_{total}[bulk]$ represents the energy of the same size super-cell without the defect, n_i and μ_i represent the number and chemical potential of the i th chemical species, E_F is the Fermi level and E_{corr} is a correction term that accounts for the finite size of the super-cell.

It is common to reference the E_F relative to the valence band maximum such that $E_F = 0$ corresponds to the valence band maximum. Thus we can write the following equations for the formation energies of the different charge states of the NV center formed from isolated nitrogen and vacancies within a crystal:

$$E^f[NV^+] = E_{total}[NV^+] - E_{total}[bulk] - \mu_N - \mu_V + (E_F - E_{V.B.M}) + E_{corr,+} \quad (2.2)$$

$$E^f[NV^0] = E_{total}[NV^0] - E_{total}[bulk] - \mu_N - \mu_V + 0(E_F - E_{V.B.M}) + E_{corr,0} \quad (2.3)$$

$$E^f[NV^-] = E_{total}[NV^-] - E_{total}[bulk] - \mu_N - \mu_V - (E_F - E_{V.B.M}) + E_{corr,-} \quad (2.4)$$

$$E^f[NV^{-2}] = E_{total}[NV^{-2}] - E_{total}[bulk] - \mu_N - \mu_V - 2(E_F - E_{V.B.M}) + E_{corr,-2} \quad (2.5)$$

The quantity we are interested in is the equilibrium charge state of our color center as a function of the Fermi level, E_F . Looking at each equation, we can see that the formation

energy is linear in the Fermi level, and the coefficient is equal to the charge state.

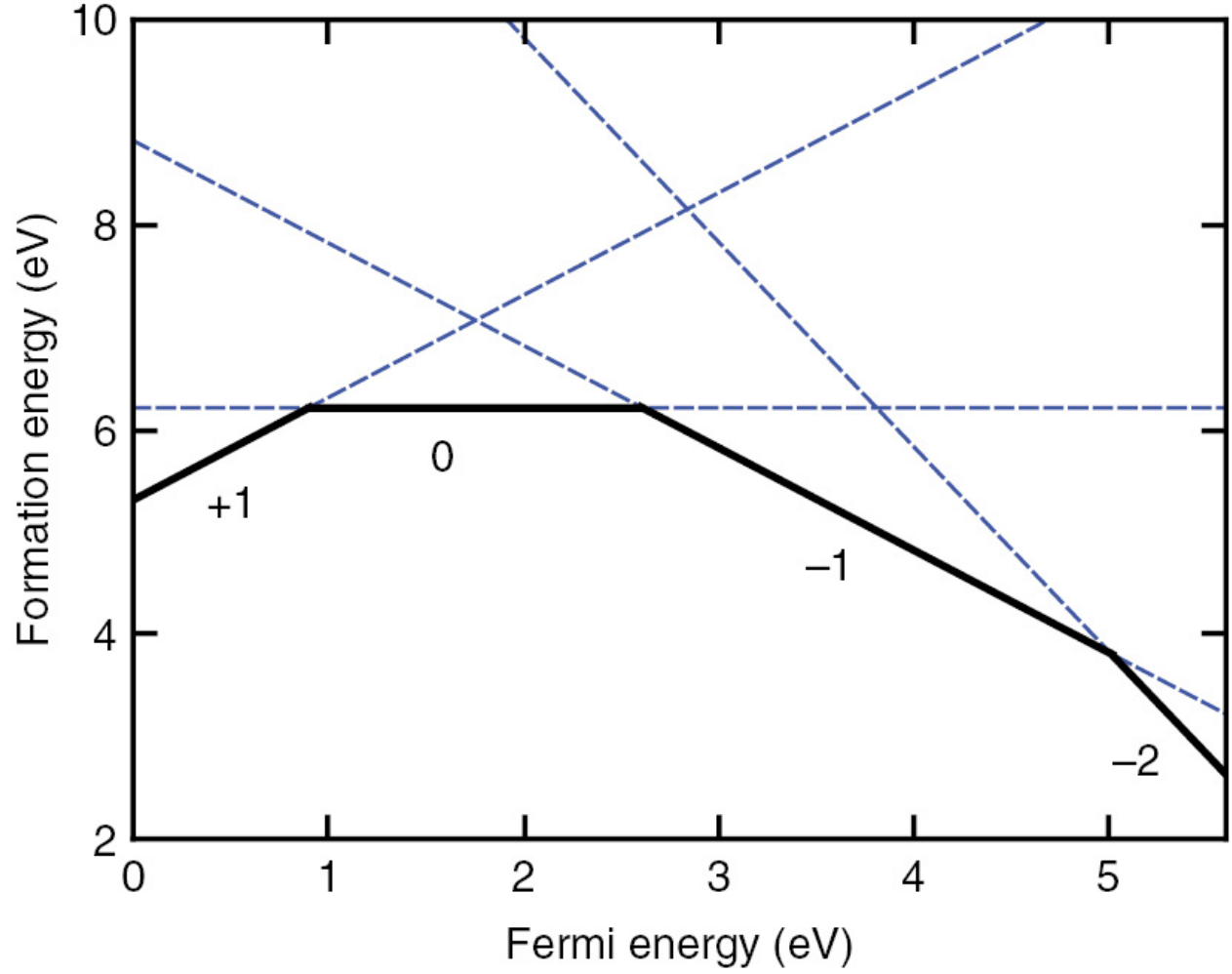


Figure 2.5: Formation energies of the charge states of the NV center in diamond reproduced from Ref. [120]

Formation energy diagrams provide a convenient way to determine the dominant charge state of a particular species, as the charge state with the lowest formation energy will be the dominant charge state. In Fig. 2.5 the formation energies of the NV center in diamond are plotted. The solid black line is illustrating the minimum energy of all charge states with the appropriate charge labeled below. For NV centers, one can see that there exist 4 stable

charge states depending on the Fermi level, within the 5.5 eV bandgap.

What is much more difficult is to actually determine the Fermi level in an arbitrary substrate containing many different species of defects. To find the Fermi level, one must first impose charge conservation over all the defect species within the crystal:

$$0 = \sum_i N_i q_i \quad (2.6)$$

Here N_i is the number of the i th charged species in the crystal and q_i is the charge of that species. Then one finds the Fermi level that minimizes the formation energies.

In certain limiting cases the problem is tractable.

Fermi level dominated by a single defect

If we assume that one defect sufficiently outnumbered every other defect combined in the crystal, then the Fermi level becomes dominated by that defect. In our case of high quality CVD diamond, substitutional nitrogen is the dominant defect. Since the nitrogen outnumbers the other species, charge conservation results in some nitrogen remaining neutral. This limits the possible Fermi levels to the range where N^0 is the charge state. This occurs high in the band gap and corresponds to Fermi levels where NV^- has the lowest formation energy and therefore is the dominant charge state.

Thus the situation is the following: some of the nitrogen is in the form N^0 with a number of N^+ exactly compensating the NV^- centers. The coexistence of N^+ and N^0 only occurs where the two formation energies are equal, at around 3.8 eV [22] above the valence band maximum. This Fermi level corresponds to the singly or doubly negative charge state of many common defects in diamond [22], thus we can say that substitutional nitrogen will act as a donor to most defects within the lattice.

If the situation is reversed, and we convert the majority of substitutional nitrogen to NV centers, then the Fermi level gets pinned at the NV^0/NV^- level, and we will have some amount of NV^0 . Thus for applications where NV^- is desired, one needs a sufficient quantity of donors to supply the extra electrons. This is an inherent limitation of sensing applications based on NV centers, where in the best case half of the nitrogen is substitutional and half of the nitrogen is incorporated into NV centers. Substitutional nitrogen is paramagnetic and can limit the NV coherence.

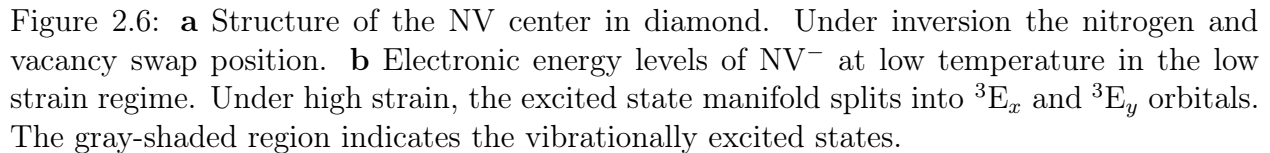
2.3 Electronic structure of NV and SiV centers

2.3.1 NV

Here we show the physical structure and electronic energy levels of the NV^- center. A symmetry that is desirable for color centers is centrosymmetry, as it results in decreased sensitivity to electric noise as we will see in Sec. 2.4.3. Under the inversion operation about the center of the NV center, the position of nitrogen and vacancy swap, and therefore the NV center lacks inversion symmetry.

The electronic ground state of the NV^- center is an orbital-singlet, spin-triplet state denoted 3A_2 . The $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$ states are split by 2.87 GHz in the absence of a magnetic field. This zero field splitting (ZFS) corresponds to microwave frequencies easily achievable with today's microwave sources. Furthermore, the NV center's unique zero field splitting means that we can selectively drive spin transitions of NV centers, without driving the spin bath in our sample which contains many spin- $\frac{1}{2}$ systems.

The optically accessible excited state of the NV^- center is an orbital-doublet, spin-triplet state denoted 3E located 1.95 eV above the ground 3A_2 state, corresponding to optical emission at 637 nm. The NV^- center is believed to be a highly efficient quantum emitter, with an internal quantum efficiency exceeding 0.86 [77], meaning that after excitation, the NV^-



In addition to the spin triplet states there are two singlet states, 1A_1 and 1E . The relevance of the singlet states, is that they provide a non-radiative decay channel for the NV center to relax to the ground state without emitting a photon in the visible band. The branching ratio is higher for the $m_s = \pm 1$ excited states, therefore an NV center in the $m_s = 0$ state is brighter. This small change in brightness provides a way to read out the spin-state at room

temperature.

The gray shaded regions of the figure correspond to vibrationally excited states of the defect that we will discuss in more detail in Sec. 2.4.1, when we discuss the optical absorption and emission of these defects.

Last, we will mention that the NV center possesses other charge states, NV^0 and NV^+ , but we will not address their structure in detail. The NV^+ is optically inactive and thus useless for our purposes. The fine structure of NV^0 in EPR and photoluminescence excitation spectroscopy (PLE) has never been demonstrated and is only discussed in this thesis because its optical spectrum appears whenever we excite NV^- centers off resonantly. It has an optical splitting of 2.16 eV or 575 nm. It is sometimes claimed that the NV^- center is perfectly photostable, in that it can be excited with high powers over long durations of time without bleaching. A better description is that the NV^- center rapidly ionizes into NV^0 , but NV^0 rapidly ionizes to NV^- . This cyclic photoionization [3] under off-resonant excitation process is interesting but unfortunate from a technological standpoint. In Chapter 6, we will demonstrate a color center that seems to be excited without photoionizing.

2.3.2 *SiV*

Here we show the structure and electronic energy levels of the SiV^- center. Unlike the NV center, the SiV center does possess inversion symmetry as the silicon atom sits in the bond-centered interstitial position. We will work in the hole picture, such that the SiV^- ground state can be thought of as a single hole ($S=\frac{1}{2}$) in an orbital-doublet. This orbital-doublet denoted 2E_g split by approximately 50 GHz [42] due to the spin-orbit coupling. Both the orbital degeneracy and the spin- $\frac{1}{2}$ contribute to poorer spin coherence times than the NV center. The mechanism for short coherence times involves phonon interactions in the crystal. These phonons are not able to directly flip the spin of the SiV^- , thus long T_1 (2.4 ms

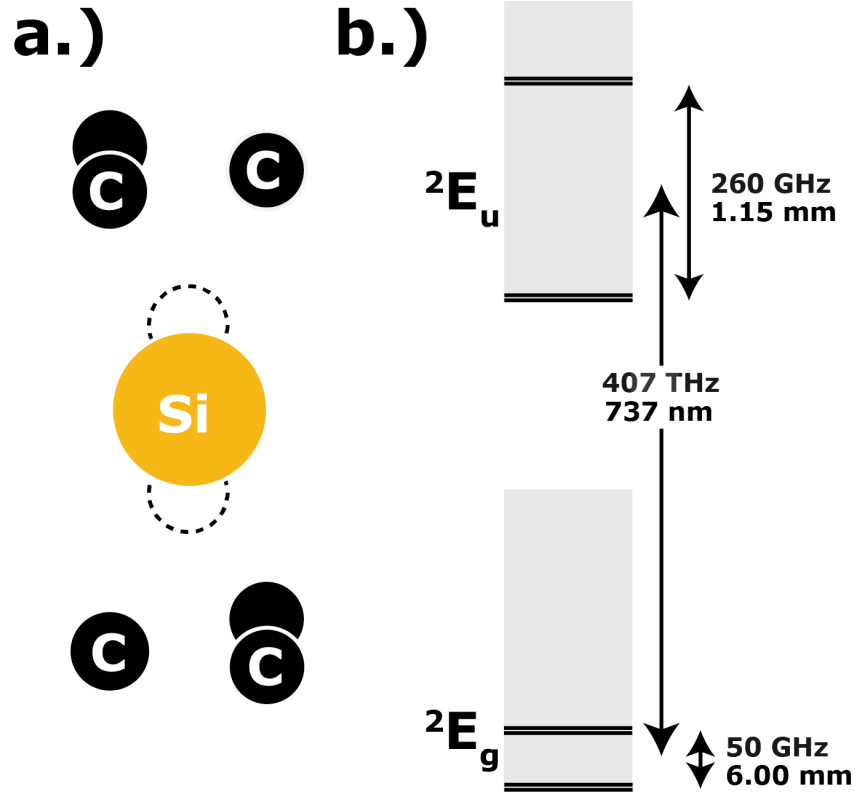


Figure 2.7: **a** Structure of the SiV center in diamond. The center is symmetric under inversion because of the silicon's location. **b** Electronic energy levels of SiV^- . The gray shaded region indicates the vibrationally excited states.

at 4 K [83]) have been observed for SiV^- . However, if phonons excite the hole from the lower ground state orbital into the excited ground state orbital, then phase information between the spin states is lost. At low temperatures, the 50 GHz phonons resonant with this orbital transition have a sufficiently large density of states and are sufficiently populated that T_2 and T_2^* are limited to 35 ns [83]. Furthermore, due to its spin, a strong magnetic field needs to be applied to resolve the spin sub-levels, and it will be resonant or nearly resonant with other $S = \frac{1}{2}$ systems in the crystal.

The direct optical transition of the SiV^- occurs at 737 nm, or 1.68 eV. The SiV^- is believed to not possess the quantum efficiency of the NV center, with a quantum efficiency less than

0.1 [67]. However, charge dynamics can complicate such quantum efficiency estimations. Recent measurements show that SiV^- photoionizes under red excitation and requires hole capture to back convert [109], providing an alternative explanation for low emission rates. The excited state of SiV^- is also an orbital-doublet, 2E_u and is split by 260 GHz. The larger splitting is due to the hole's increased proximity to the nucleus.

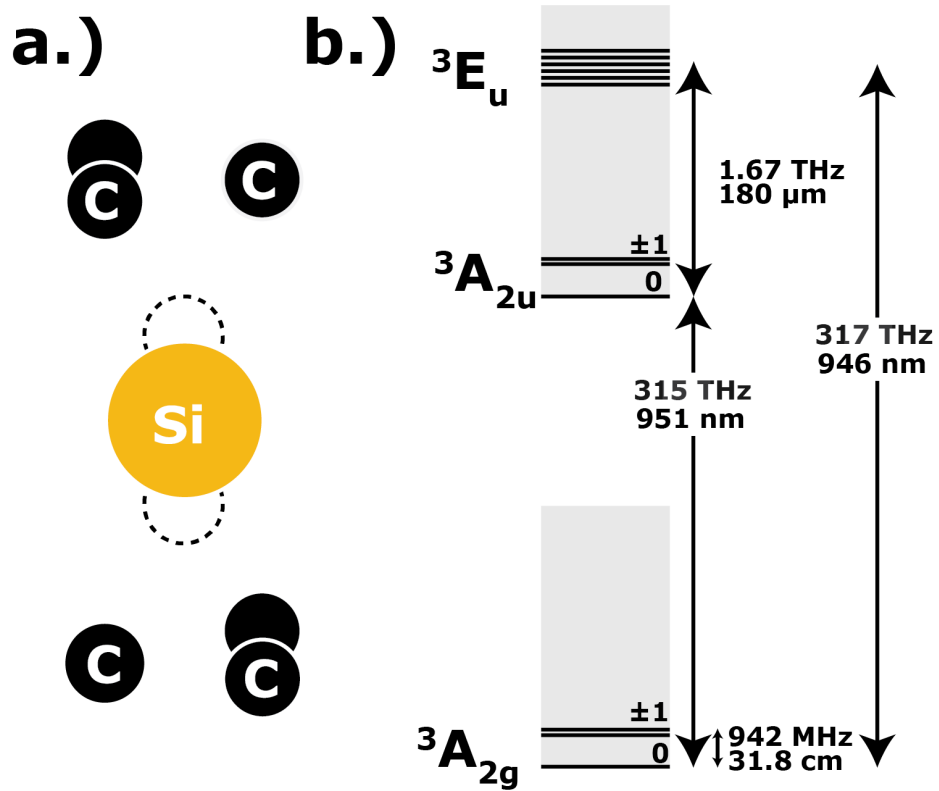


Figure 2.8: **a** Structure of the SiV center in diamond. **b** Electronic energy levels of SiV^0 . The splittings of most of the excited state levels are not known, and neither are the presence and significance of any singlet states.

Unlike neutral NV^0 , the neutral SiV^0 remains an interesting physical system that may have potential for quantum applications. The study of the SiV^0 center will end up being a central topic in Chapter 6. It possesses the same physical structure as SiV^- , and therefore is centrosymmetric. Furthermore, its ground state is analogous to the NV^- ground state, an

orbital singlet, spin-triplet denoted $^3A_{2g}$ [38]. The ZFS is slightly smaller than the NV^- at around 1 GHz. The excited state of SiV^0 exhibits many phenomena that are not present in the other charge states we discuss, for example, there is a bright optical emission at 946 nm that becomes frozen out at low temperature. Furthermore, SiV^0 exhibits broad optical linewidths even at low temperatures, even in crystals with small amounts of strain, with no current explanation.

2.4 Color center spectroscopy

The color centers that we are interested in possess sharp optical transitions (at low temperature) that arise from transitions between orbitals lying within the band gap. The spectrum of light we achieve from color centers is distinct from the spectrum we observe from isolated atoms due to interactions with the host lattice.

2.4.1 Zero phonon line and the phonon sideband

Atoms in free space can only radiate energy through the emission of optical photons, typically through single photon emission. This means that the emitted photons have energies determined only by the splitting of the energy levels. In contrast, color centers can radiate phonons thus the energy of the photons is not precisely fixed, only the total energy of the photons and phonons together.

This results in two features, called the zero phonon line (ZPL) and phonon sideband. The ZPL occurs when the entire emission occurs through a single photon, and this appears as a sharp spectral line. The phonon sideband is a broad feature that corresponds to an optical photon emitted in conjunction with 1 or more phonons.

The phonon sideband occurs not just in emission, but also results in a broad absorption band. This is the reason why NV^- centers can be excited efficiently off resonance from

the ZPL via green excitation, even though its emission is distinctly red. In fact, 532 nm excitation occurs near the peak of the absorption band of NV^- .

The percentage of emitted light that falls in the ZPL is termed the Debye-Waller (DWF) factor. For an NV^- center, the DWF is only 0.03 [120], whereas for the SiV^- , the DWF is 0.7 [42]. A high DWF is desired for efficient emission into the ZPL, but often its importance is overstated.

In many sensing experiments, it doesn't matter if light is in the ZPL or the phonon side-band, and therefore only the total quantum efficiency matters. Thus the NV^- center is a much brighter quantum sensor than the SiV^- center despite its small DWF. Even in quantum communication and quantum computation, it is the combination of the quantum efficiency and the DWF that determines the efficiency of emission into the ZPL. This means NV^- and SiV^- are comparable for these applications.

Nevertheless we will briefly summarize the basic theory of emission, and why these two color center's possess such different DWFs, using the Franck-Condon principle. We consider the wave function of some emitter with the electronic and nuclear degrees of freedom decoupled, due to the Borne-Oppenheimer approximation. The generalized coordinates of the nuclei are treated as fixed parameters, $\mathbf{Q}$, in order to solve the purely electronic wave function. We will call the generalized coordinates of the nuclei that minimize the total energy of the electronic ground state, $\mathbf{Q}_{\text{ground}}$. In the excited state the procedure can be repeated: the excited electron wave function is solved and the coordinates of the nuclei that minimize the total energy are denoted $\mathbf{Q}_{\text{excited}}$. In a fully quantum theory, the generalized nuclear coordinates $\mathbf{Q}$ are then promoted to operators $\hat{\mathbf{Q}}$ and the nuclear contribution to the Hamiltonian takes the form of a quantum harmonic oscillator.

If $\mathbf{Q}_{\text{ground}} \neq \mathbf{Q}_{\text{excited}}$, then the ground and electronic excited states have vibrational ground states that are displaced from each other. The ZPL corresponds to emission with

no change in the nuclear vibrational state, which is related to the overlap of the two ground vibrational ground states. The larger the magnitude of $\mathbf{Q}_{\text{ground}} - \mathbf{Q}_{\text{excited}}$, the less overlap of the vibrational ground states.

Thus, defects that undergo large nuclear displacements between ground and excited states will have small DWF, like the NV center. Defects where the nuclei remain roughly fixed will have large DWF.

2.4.2 Thermal line shifts and broadening

Color centers have optical lines whose position and linewidth are sensitive to the temperature of the crystal. Overall shifts of the optical emission are due to two different effects: thermal expansion and electron–phonon interactions [48]. These shifts should be taken into consideration when photonic cavities are designed, but are not of critical importance to this work.

More significant is the linewidth broadening which causes sharp spectral lines to broaden. In the ideal case, the sharpness of the linewidth, $\Delta\nu$, is limited by the lifetime, τ , of the excited state:.

$$\Delta\nu = \frac{1}{2\pi\tau} \quad (2.7)$$

The thermal broadening is due to a reduction in the lifetime of the particular excited state. This could either be due to rapid thermalization amongst the known excited states, or due to increased non-radiative emission, which can be studied via temperature-dependent studies [48]. For the NV and SiV, spectra taken at low temperature have significantly sharper features compared to room temperature spectra. For device applications, we can neglect thermal broadening by working at some sufficiently low temperatures where phonon interactions are frozen out, a problem solved by modern cryogenics.

Examples of SiV^- emission at 10 K and 300 K are shown below:

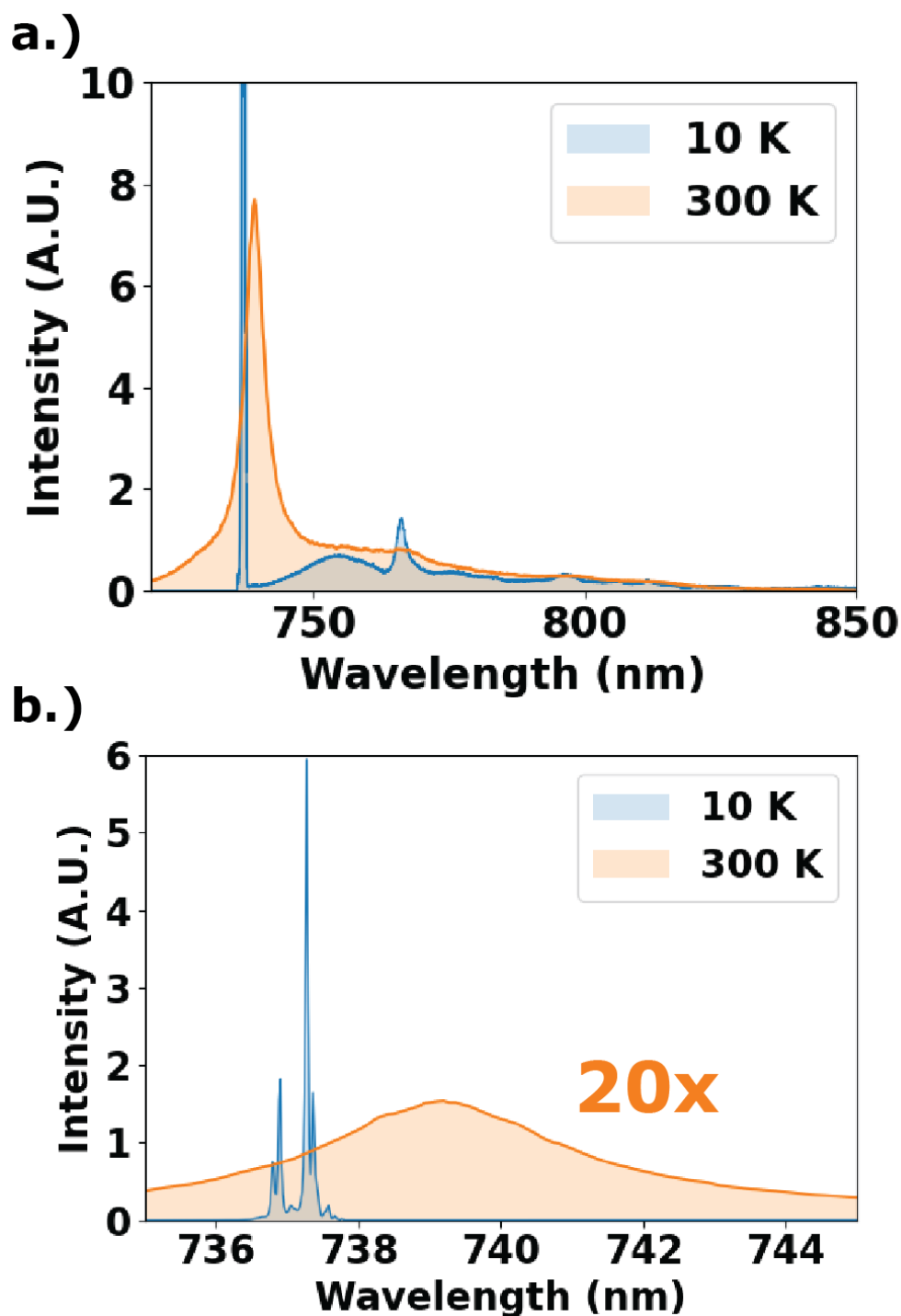


Figure 2.9: **a.** SiV^- spectra taken at 10 K (blue) and 300 K (orange). The spectra are normalized to the same total intensity, so the narrow ZPL at 10 K is truncated. **b.** A zoom in on the SiV^- ZPL at 10 K and 300 K. The spectra at 300 K is scaled up by a factor of 20 for visibility. The 10 K spectra reveals the 4 ZPL transitions of the SiV^- which are significantly broadened and red shifted at 300 K.

2.4.3 Spectral diffusion

Spectral diffusion is the phenomena wherein the central frequency of a spectral line (usually the ZPL) shifts stochastically in time. Spectral diffusion can be measured using photoluminescence excitation spectroscopy (PLE), where a laser is scanned across an emitter's ZPL while collecting light emitted in the phonon sideband. If the spectral diffusion is fast compared to the scan speed of the laser, spectral diffusion occurs as a line broadening. If the spectral diffusion is slow compared to the scan speed of the laser, the spectral diffusion can be directly observed. Some examples of spectral diffusion can be seen in Fig. 2.10 from a shallow, implanted SiV^- center. Spectral diffusion is the discrete jumps in frequency that occurs between scans.

One important nuance of PLE, is that for the case of NV^- and SiV^- centers, a secondary light source is eventually needed to recharge the defect. Above each scan is an indicator of whether charge re-pump light was used before that scan, and of what color. A white rectangle (for example scans 15-24 in Fig. 2.10(a)) indicates no charge re-pump. This corresponds to the least amount of spectral diffusion. Green rectangles, for example the entirety of Fig. 2.10(b), show the spectral diffusion caused with green excitation before every scan. Blue rectangles indicate illumination by a blue LED, for example the entirety of Fig. 2.10(c).

Spectral diffusion is widely attributed to stochastic Stark shifts of the defect's optical emission due to the ionization of nearby charge traps. Optical illumination, which causes photoionization, exacerbates spectral diffusion. It is instructive to treat the electric field as a perturbation and Taylor expand in the strength of the electric field [21]. (In our notation $\vec{E}$ is the electric field the color center experiences, which is not the same as an applied field.):

$$\Delta\nu = -\frac{1}{h}\Delta\mu|\vec{E}| - \frac{1}{2h}\Delta\alpha|\vec{E}|^2 - \frac{1}{6h}\Delta\beta|\vec{E}|^3 - \frac{1}{24h}\Delta\gamma|\vec{E}|^4 + \mathcal{O}(|\vec{E}|^5) \quad (2.8)$$

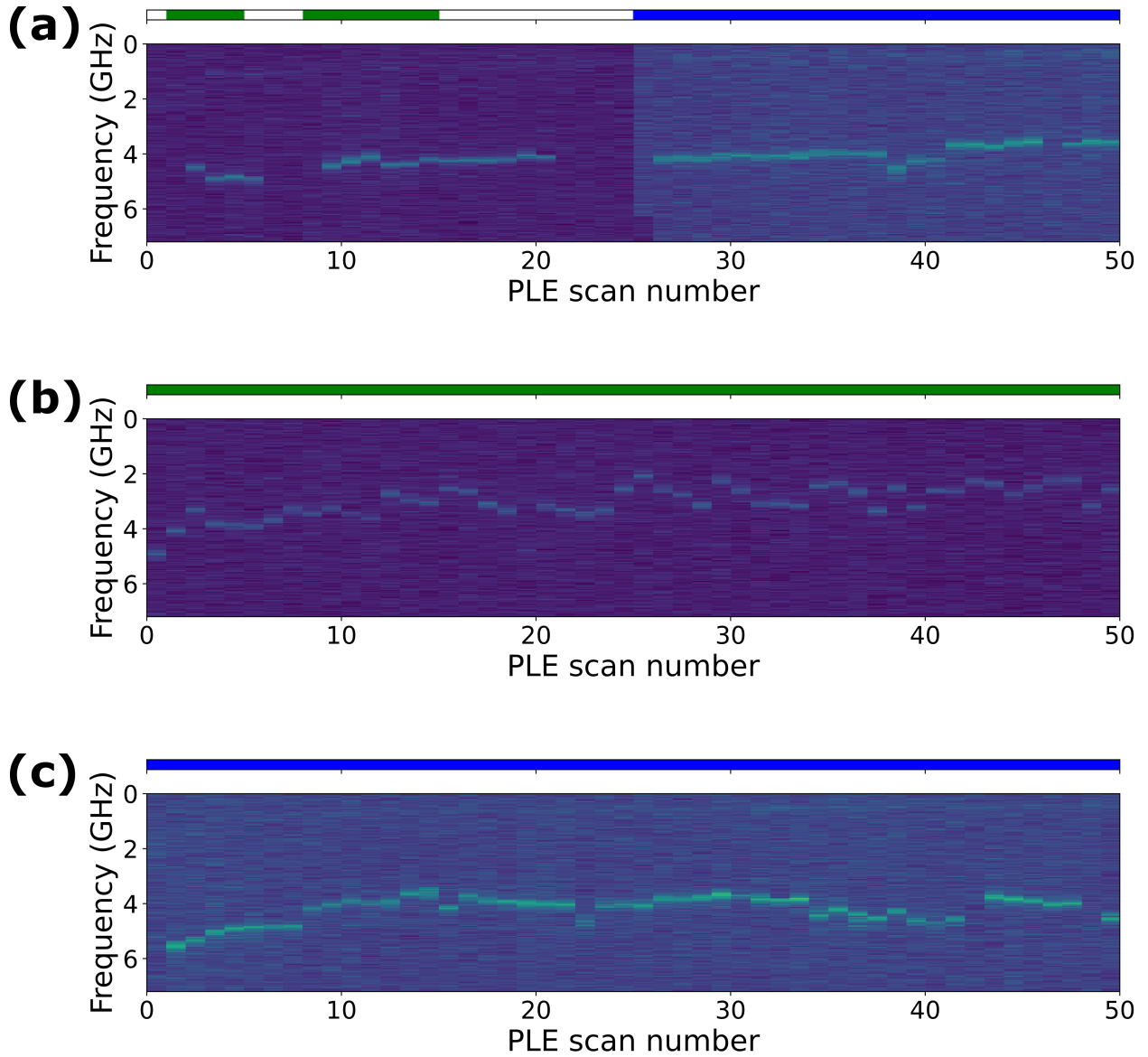


Figure 2.10: Three SiV⁻ centers, formed via implantation and annealing exhibiting spectral diffusion. Green bars indicate scans including charge re-pumping via a focused green laser, white bars indicates regions without charge re-pumping, and blue bars indicates charge re-pumping with a blue LED. (a) SiV⁻ with and without green and blue charge re-pumping schemes. The least amount of spectral diffusion occurs under no charge re-pumping, scans 15-18, but the SiV⁻ eventually photoionizes (b) SiV⁻ PLE with continuous green recharge pump. (c) SiV⁻ PLE with continuous blue recharge pump.

Here differences in quantities (e.g. $\Delta\mu$) correspond to differences in dipole moment, polarizability, etc. between the respective ground and excited states related to that transition. We will focus primarily on the first two terms related to difference in dipole moments, and the difference in polarizability.

For centrosymmetric defects, such as the group IV-vacancy complexes (e.g. SiV), there can be no dipole moment in any eigenstate and thus the linear Stark effect vanishes. The NV center, which lacks inversion symmetry, has a non-zero Stark effect on the order of $\Delta\mu = 6 \text{ GHz}/(\text{MV}/\text{m})$ [99], which is quite large.

2.4.4 Ionization

Photoionization is the process wherein an emitter gains or loses electrons due to energy gained from optical excitation. For atoms in free space, atoms can only photoionize via the emission of electrons, but things are more complicated inside a semiconductor. In general there are 2 direct photoionization processes.

- **Electron emission:** A defect emits an electron into the conduction band and the defect's charge increases by 1.
- **Hole emission:** A defect emits a hole into the valence band and the defect's charge decreases by 1.

In addition to direct photoionization (direct meaning happening at our defect), there is also the possibility that a defect nearby photoionizes and emits charge carriers that are captured by our emitter. This has been studied intentionally [56], but may result in some of the bleaching events observed in PLE.

We will discuss the photoionization cycling of the NV center under 532 nm excitation as it is well understood [3].

- 1. Excitation of NV^- from ground state to excited state
- 2. Photoionization of an NV^- electron in the excited state into the conduction band, leaving NV^0
- 3. Excitation of NV^0 from ground state to excited state
- 4. Photoionization of a hole from the NV^0 excited state into the valence band, leaving NV^-

This cycling means that the NV^0 spectra is always present under green excitation. Under resonant excitation, only NV^- spectra is observed, however it will inevitably photoionize into NV^0 . Once in NV^0 , the NV is stuck, as 637 nm is not able to efficiently excite or photoionize NV^0 . This cyclic photoionization is fairly special to NV, as it requires mid-gap states that can couple to both the conduction and valence band.

Green excitation is particularly problematic as it can also photoionize substitutional nitrogen with a binding energy of 1.7 eV [22] (532 nm corresponds to 2.33 eV). Currently the only strategy for selectively photoionizing NV^0 back into NV^- involves the resonant photoionization of NV^0 at 575 nm. This is still able to photoionize substitutional nitrogen, but resonant excitation can be done at much lower powers.

The SiV is no longer believed to participate in the same photoionization dynamics as NV centers. Its energy levels are much closer to the valence band [34], and thus only couple to the valence band, not the conduction band, under typical optical excitation. Thus typical optical excitation has been shown to cause SiV^0 to photoionize into SiV^- which subsequently photoionizes into SiV^{-2} [115]. The reverse process requires the capture of holes.

One exciting prospect for SiV^0 is that it has near infrared (NIR) emission at 946 nm with efficient optical excitation at 830 nm due to bound exciton transitions [116]. This

is energetically below all of the other defects we consider, which implies that SiV^0 may be a charge state that can be excited continuously without photoionization. This will be investigated in Chapter 6.

2.5 *Selected applications*

2.5.1 *Quantum communication*

Quantum communication schemes rely on quantum emitters that deterministically emit single photons at a fixed frequency and polarization such that photons emitted at different locations or at different times remain indistinguishable from each other. This is difficult to achieve in color centers for many reasons.

One obvious reason is because color centers aren't perfect emitters. Sometimes they don't emit photons at all (low quantum efficiency), or they emit them over a broad range of frequencies (phonon sideband) leaking energy and information in the form of phonons. Furthermore they emit photons in all directions. However, a single solution resolves all these issues, a phenomena known as Purcell enhancement. In principle a quantum emitter coupled to an optical cavity mode can be engineered to have nearly deterministic emission into the cavity mode.

We discuss the physics of Purcell enhancement below, however it is worth mentioning that Purcell enhancement does not solve every issue with regards to using color centers as indistinguishable photon sources. Purcell enhancement only solves the challenges with deterministic photon emission and collection, but does not mitigate the challenges of an inhomogeneous spread of frequencies among multiple color centers, or the dynamic spectral diffusion. Furthermore, ionization of the color center is another major limitation, as it temporarily limits photon emission until the color center can be re-pumped into the desired charge state. These currently remain significant unsolved issues.

Purcell enhancement and cooperativity

A detailed derivation of Purcell enhancement and cooperativity can be found in Ref. [17]. Here we will merely summarize the major ideas and equations. Inside an infinite dielectric medium, the emission rate due to a dipole transition is given by the Wigner-Weisskopf theory,

$$\gamma_{eg} \equiv \frac{\omega_e^3 n |\mu|^2}{3\pi\epsilon_0 \hbar c^2}, \quad (2.9)$$

where ω_e is the frequency of the transition, n is the refractive index of the dielectric, $|\mu|$ is the amplitude of the dipole moment of the relative transition, ϵ_0 is the permittivity of free space, $\hbar$ is Planck's reduced constant, and c is the speed of light.

In addition to this dipole emission, color centers can also have non-radiative (or partially non-radiative in the case of the phonon sideband) relaxation from the excited to ground state. The combination of the radiative and non-radiative rates determines the lifetime of the excited state of the color center.

If the color center is within the optical mode of a cavity, it will have a coupling rate to that cavity mode given by

$$g = \frac{|\mu|}{n} \sqrt{\frac{\omega}{2\epsilon_0 \hbar V}} \left(\frac{\mathbf{E} \cdot \boldsymbol{\mu}}{|\mathbf{E}_{\max}| |\mu|} \right) \quad (2.10)$$

where $\mathbf{E}/|\mathbf{E}_{\max}|$ is the vector electric field profile of the cavity mode normalized to a maximum of unity and V is the cavity mode volume.

This equation illustrates some of the important quantities that can be optimized to increase the coupling. The emitter will have the strongest coupling if it is placed where the optical mode's field is strongest, the dipole moment is aligned to the mode's polarization, and the mode volume is minimized.

This coupling rate can significantly enhance the total radiative emission rate of the color

center. We can compare the cavity-modified radiative emission to the intrinsic radiative emission rate (e.g. Eq. 2.9) with a quantity called the Purcell enhancement. The Purcell enhancement is given by

$$F \equiv \frac{\gamma_{eg,\perp}}{\gamma_{eg}} + \frac{4g^2}{\kappa\gamma_{eg}} \frac{(\kappa/2)^2}{(\kappa/2)^2 + \delta^2}. \quad (2.11)$$

Here $\gamma_{eg,\perp}$ is the radiative emission from the dipole transition that doesn't couple to the cavity, κ is the loss rate of the cavity, and δ is the detuning between the cavity and the emission. This illustrates some of the other important quantities that should be optimized to increase the Purcell enhancement. The cavity's loss rate should be minimized, or in other words, the cavity quality factor should be maximized, and the emission and cavity should be on resonance.

The Purcell enhancement is a useful metric for quantifying the radiative enhancement, but fails to include the non-radiative emission which is important for accurately characterizing how deterministic the emitter-cavity coupling is. This is better described by the cooperativity, given by $C = 4g^2/\kappa(\gamma + \gamma_d)$. Here γ is the combination of radiative and non-radiative emission, and γ_d describes the contribution to the loss via pure dephasing of the emission linewidth, i.e. the broadening due to elevated temperature or spectral diffusion. When $C \gg 1$, the emission into the cavity can be considered nearly-deterministic.

2.5.2 Quantum networks

Remote heralded entanglement

One of the major benefits of the color center architecture is the possibility of forming quantum networks that span over a large geographic area. The theoretical details of forming and performing quantum algorithms on this quantum network are discussed in Ref. [8] in a

paradigm known as “Brokered Graph State Quantum Computing”.

We will not describe the whole technique, just focus on one aspect, the formation of the quantum network, and more specifically the requirements on our color centers. The formation of a delocalized quantum network is possible because of a technique called “remote heralded entanglement”. The technique involves entangling the electronic spins of two remote color centers through the interference of the color center’s optical emission at an intermediate location. Since the technique uses interference of optical photons, it can be done over a long distance through optical fiber, hence the ability to make delocalized quantum networks.

The technique requires color centers with at least three levels, two ground sub-levels and an optically excited state with optically resolved coupling to one qubit state, as shown in Fig. 2.11(a). The ground sub-levels form the logical qubits. Photonic cavities and waveguides are designed and fabricated to collect photons emitted by each color center and guide them to a 50:50 beam splitter, the outputs of which are terminated by two single photon detectors, as shown in Fig. 2.11(b).

As in Fig. 2.11(b), we will call the two optical input modes of the beam splitter A and B with creation operators $\hat{a}^\dagger$ and $\hat{b}^\dagger$ respectively. The two optical output modes denoted C and D have creation operators $\hat{c}^\dagger$ and $\hat{d}^\dagger$ respectively.

The technique begins by preparing each color center in an equal superposition state of the two logical qubit states. The total wave function can be written

$$|\psi\rangle = \frac{1}{2}(|0\rangle + |1\rangle) \otimes (|0\rangle + |1\rangle) \quad (2.12)$$

Then the two color centers are simultaneously resonantly excited. After subsequent emission into the respective optical mode, the wave function can be written.

$$|\psi\rangle = \frac{1}{2}(\hat{a}^\dagger|0\rangle + |1\rangle) \otimes (\hat{b}^\dagger|0\rangle + |1\rangle) \quad (2.13)$$

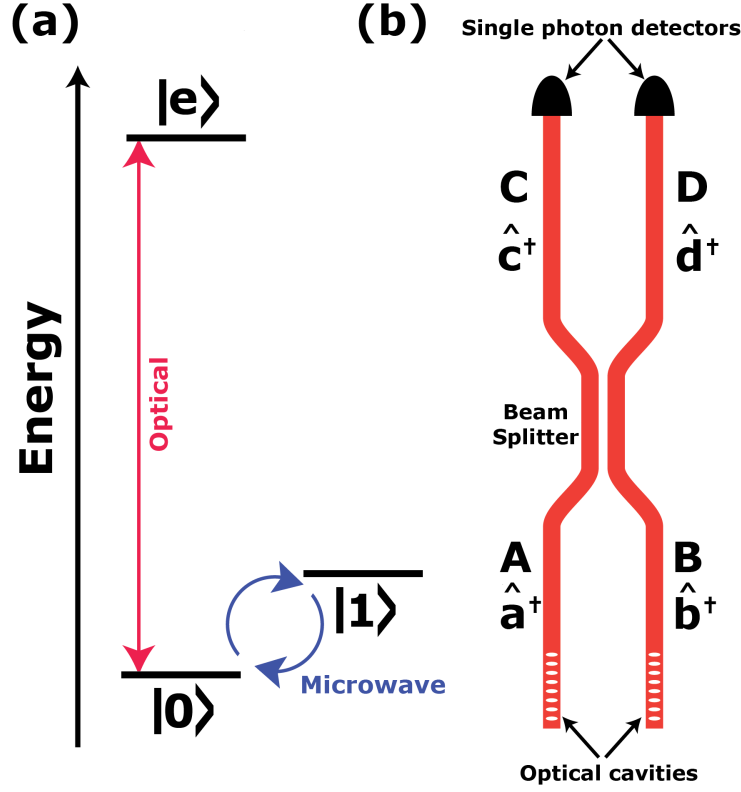


Figure 2.11: **a.** Electronic structure required for remote heralded entanglement. The ground state splitting is typically on the order of GHz, while the splitting between the ground and excited state is typically on the order of 100's of THz. **b.** Simplified diagram of photonic layout for remote heralded entanglement. Color centers are coupled to the optical cavities, depicted here as 1D photonic crystal cavities. These cavities are coupled to waveguides which lead to a 50:50 beamsplitter and then single photon detectors.

The beam splitter transforms the creation operators as follows.

$$|\psi\rangle = \frac{1}{2} \left(\left(\frac{1}{\sqrt{2}} (i\hat{c}^\dagger + \hat{d}^\dagger) |0\rangle + |1\rangle \right) \otimes \left(\frac{1}{\sqrt{2}} (\hat{c}^\dagger + i\hat{d}^\dagger) |0\rangle + |1\rangle \right) \right) \quad (2.14)$$

This can be expanded out into

$$|\psi\rangle = \frac{1}{2}(\frac{i}{2}(\hat{c}^{\dagger 2} + \hat{d}^{\dagger 2}))|00\rangle + \hat{c}^{\dagger} \frac{1}{\sqrt{2}}(i|01\rangle + |10\rangle) + \hat{d}^{\dagger} \frac{1}{\sqrt{2}}(|01\rangle + i|10\rangle) + |11\rangle \quad (2.15)$$

The relevant terms of the wave function are those proportional to $\hat{c}^{\dagger}$ and $\hat{d}^{\dagger}$. These correspond to a single photon detection in mode C and a single photon detection in mode D. The subsequent wave function collapse leaves the spins of the color centers in a maximally entangled state. Unfortunately this technique fails 50% of the time, as 25% of the time there will be two photons emitted in mode C or mode D, and the other 25% no photon is emitted at all.

First and foremost, the whole experiment relies on efficient collection of the photons emitted by the color centers. Thus cavity integration with high cooperativities is the first necessity. Second, the experiment relies on our color centers remaining in the correct charge state throughout the measurement, so charge stability is another necessity. Third, in order for the quantum interference to result in an entangled state, the photons emitted by the two color centers must be indistinguishable (this was implicit in the beam splitter transformation). This means indistinguishable in frequency, time, and polarization. The polarization dependence is ultimately set by the cavity, so it is primarily a matter of photonic design. Indistinguishability in time means using color centers with similar excited state lifetimes, and thus similar cooperativities. This is a minor challenge compared to indistinguishability in frequency, which is completely destroyed by spectral diffusion.

Chapter 3

GAP-ON-DIAMOND PHOTONIC INTERFACE

3.1 *Introduction to GaP-on-diamond platform*

As discussed in Sec. 2.5.2, remote heralded entanglement provides a path towards realizing large quantum networks assuming we can engineer color centers to efficiently emit photons into well-defined optical modes which are indistinguishable in frequency and polarization. This necessitates coupling color centers to photonic cavities where the coupling to a particular mode can be greatly enhanced.

There are two main strategies for incorporating color centers into photonic structures. The first strategy is a monolithic approach where the diamond itself is patterned into the structure. This has a number of advantages: diamond already has a large index of refraction (2.41) at visible wavelengths, so suspended diamond structures can support long lived optical modes [69, 10]. The other primary advantage is that the color centers exist within diamond, so ion implantation and annealing can form color centers at the maximum of a cavity mode's field, which is one factor in the cooperativity defined in Sec. 2.5.1. For these reasons, monolithic diamond photonic devices are at the forefront of ongoing research and have been used to realize small quantum networks [10].

However, there are trade-offs to consider. First, these all-diamond devices rely on techniques non-amenable to commercial wafer-scale fabrication. Angled reactive ion etching is used to achieve the desired cavity cross-section, requiring a Faraday cage [92]. This scalability issue is a minor concern compared to the fact that fabrication and proximity to surfaces are major sources of charge and optical instability as we will discuss later in this chapter.

It is this degradation of color centers properties due to diamond etching that motivates a different strategy. Instead of patterning the diamond itself, a thin membrane of a second semiconductor is chosen as the active photonics layer. This membrane is patterned into the desired photonic device without etching the diamond. As long as the color center is sufficiently close to the surface of the diamond, within the top 20 nm or so, then the color center can still efficiently couple to the evanescent tail of the cavity mode. This effectively decouples the challenges associated with fabricating photonic structures from the challenges associated with achieving shallow color centers with stable charge-states and optical emission.

This second semiconductor must satisfy two important properties. First, the semiconductor must have a bandgap large enough that it doesn't absorb the color center's light. The semiconductor must also have an index of refraction much larger than diamond's for good optical confinement. These are difficult to satisfy simultaneously, and gallium-phosphide (GaP) is one of the few semiconductors that accomplishes both. It possesses a bandgap of 2.23 eV and an index of refraction of 3.34 at 600 nm[11].

In addition to meeting our two basic requirements, GaP possesses some remarkable properties that may enable a wide-range of auxiliary devices within our GaP-on-diamond architecture. For starters GaP is a non-linear material with a relatively large $\chi^{(2)}$ [19]. Non-linearity enables on-chip frequency conversion, for example from the visible wavelengths that our color centers emit into the telecom wavelengths [55] that propagate with minimal losses in standard optical fiber. Furthermore, GaP-on-diamond is a promising platform for acousto-optics due to the large contrast in their acoustic indices of refraction [106, 105]. Acousto-optic modulation, which can shift optical frequencies over a bandwidth of a few GHz, is useful because it can be used to achieve indistinguishable photons from color center's that are inhomogeneously broadened within this bandwidth.

Developing and characterizing this GaP-on-diamond approach, will be the focus of this

chapter. Prior work has successfully demonstrated efficient coupling of NV centers to GaP disk resonators [37], and even the Stark tuning of NV centers coupled to similar devices [89]. Unfortunately, these devices were fabricated before the damaging effects of plasma exposure on charge and optical stability were fully understood. These early devices required etching vertically into the diamond substrate to achieve both high quality factors and small mode volumes. The NV centers coupled to these devices had optical linewidths orders of magnitude broader than the lifetime limit. This was in spite of the fact that the diamond surface above the NV centers was protected by the GaP membrane, and the devices didn't require the undercutting that would be required of an all-diamond device.

We will discuss in Sec. 3.2 the fabrication and characterization of later GaP-on-diamond devices, so-called “photon extractors”, which ultimately highlighted the need to eliminate diamond's plasma exposure from fabrication all-together. These “photon extractors” were designed to enhance photon collection from shallow color centers through efficient upward scattering of the light, not an enhanced local density of states. Thus these devices did not require any etching into the diamond, though the diamond was still exposed to the plasma used to etch the GaP. Various optical techniques characterizing the NV centers reveal the extent of the damage to shallow color centers.

Finally we will discuss in Sec. 3.3 the fabrication and characterization of GaP-on-diamond devices that simultaneously achieve small mode volumes and high quality factors without ever exposing the diamond to plasma. This is done by patterning the GaP on a sacrificial substrate, and subsequently stamp-transferring them onto diamond. We demonstrate successful coupling between SiV centers and the cavity-mode, while highlighting the need for better diamond surfaces.

3.2 Photon extractors

In this section, we will discuss the impact of devices we call “photon extractors” on the charge and optical stability of near-surface NV^- centers. These devices were conceived to provide the enhancements observed in solid-immersion lenses (SILs) to much shallower emitters (100 nm as opposed to $\approx \mu\text{ms}$) without etching diamond.

We will start by briefly summarizing the design and fabrication process. Then we will discuss the optical measurements of NV centers coupled to devices and their charge and optical stability. We will also provide a discussion of the modelling of the $g^{(2)}$ measurement which provides additional evidence of charge instability.

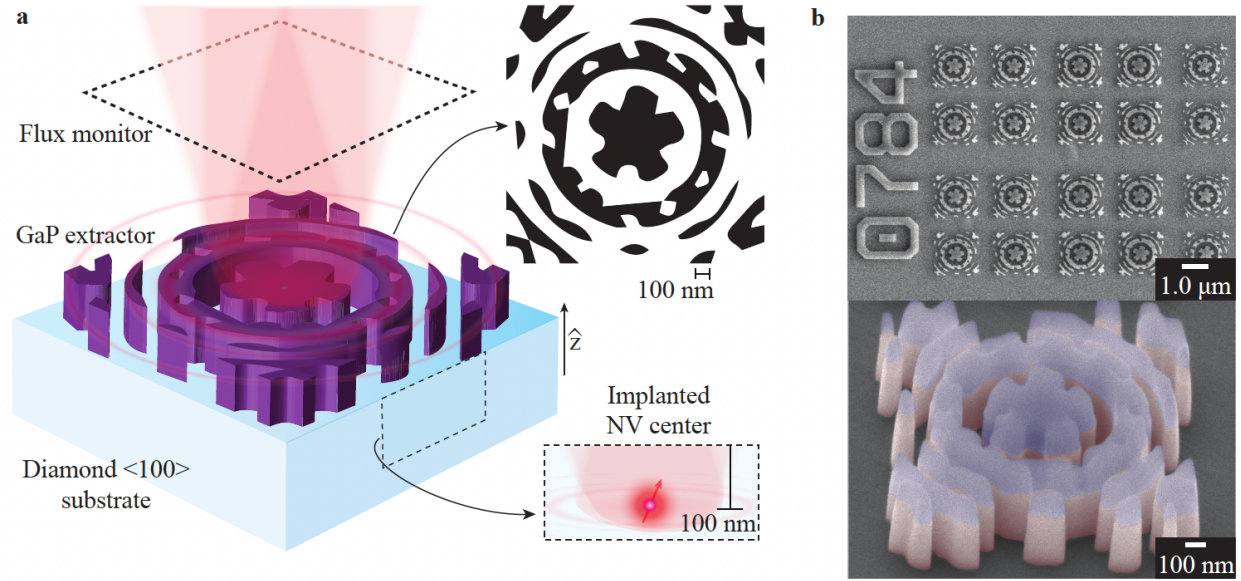


Figure 3.1: **a.** Schematic of the photon extractor designed via topology optimization (TO). **b.** Top: SEM image of an array of fabricated inverse design extractor structures. Bottom: colorized SEM of a single device indicating the different layers; HSQ resist (blue), GaP (pink) and diamond (grey). This figure was reproduced from "Srivatsa Chakravarthi, Pengning Chao, **Christian Pederson**, Sean Molesky, Andrew Ivanov, Karine Hestroffer, Fariba Hatami, Alejandro W. Rodriguez, and Kai-Mei C. Fu. Inverse-designed photon extractors for optically addressable defect qubits. *Optica*, 7(12):1805, December 2020"

3.2.1 *Design of inverse-designed photon extractors*¹

The photon extractors are designed for robust enhancement of ZPL photon collection from near-surface NV centers, and modeled via a 3D finite-difference frequency-domain (FDFD) solver, with the frequency set at the negatively-charged NV⁻ ZPL of 637 nm. Topology optimization (TO) [63] was used to design the device within a design region situated directly on top of the diamond substrate with dimensions $1.5\ \mu\text{m} \times 1.5\ \mu\text{m} \times 0.25\ \mu\text{m}$. A harmonic dipole source representing the NV center is situated 100 nm below the diamond-GaP interface.

Finally, with regards to the device footprint and material choice, we note that for the target emitter depth of 100 nm for the fabricated design, the device footprint of $(1.5\ \mu\text{m})^2$ covers a large effective NA (relative to the dipole), and TO attempts with larger device footprints show diminishing increase in device performance. As GaP is a strong dielectric with a high susceptibility, there are limited gains to switching to a higher susceptibility material (Fig. SI.4, Supplement 1 [14]), and the low loss of GaP among high susceptibility materials in this frequency range make it particularly attractive for integrated photonics applications [89].

3.2.2 *GaP photon extractors coupled to implanted NVs*²

We fabricate photon extractors (Fig. 3.1(b)) on two samples, one for ensemble-averaged measurements (Sample A) and the other for single-emitter characterization (Sample B). Sample A is a high pressure high temperature synthesised diamond (Element Six, N < 200 ppm,

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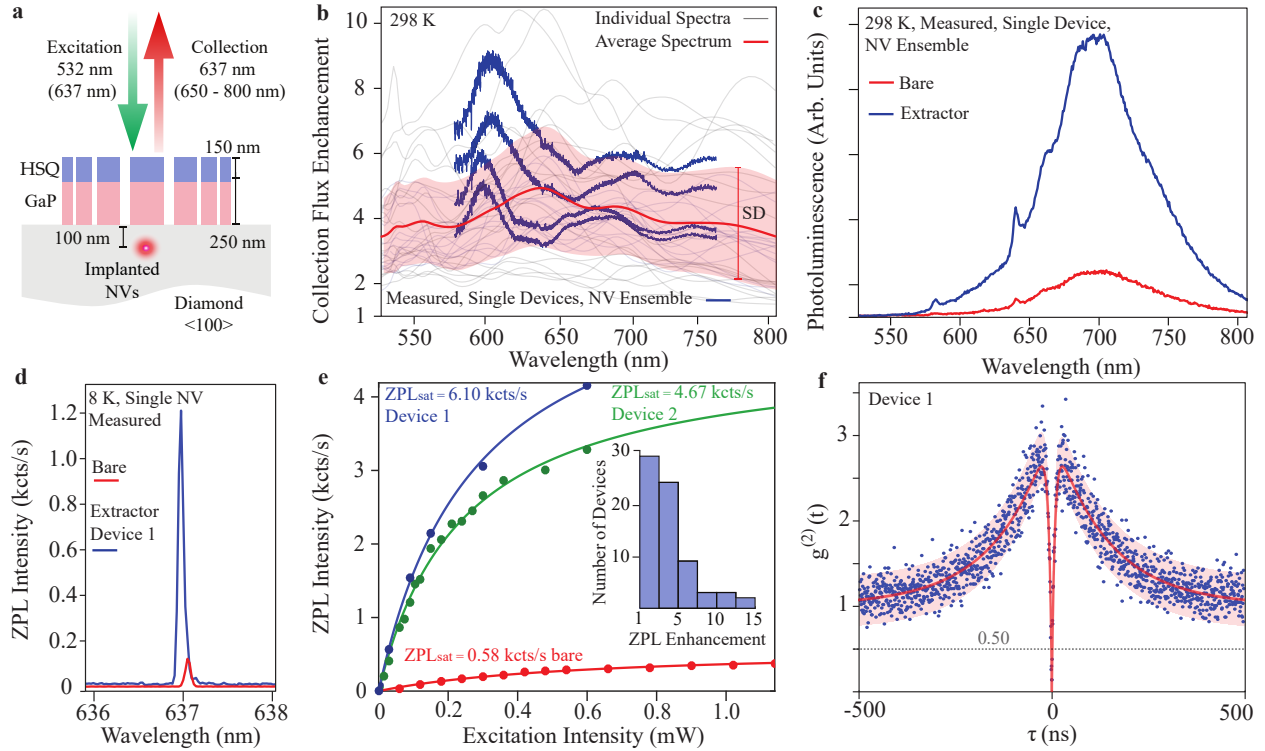


Figure 3.2: **a.** Illustration of measurement configuration with implanted NV centers coupled to extractor devices. **b.** Comparison of simulated (grey) and measured (blue) broadband enhancement for devices coupled to NV ensemble (Sample A). The red line indicates the average simulated spectrum and the red envelope is one standard deviation around the average. Variation in individual spectra for both simulation and measurement stems from randomness of NV positions relative to any given device. **c.** The broadband PL emission by NV ensemble from an extractor device (blue) vs. the bare-diamond interface (red). **d.** Single NV ZPL emission on sample B from an extractor device (blue) vs. the bare-diamond interface (red). **e.** Saturation count rates from devices coupled to single NV centers. Inset: Histogram of measured devices and the observed ZPL enhancement (Sample B). **f.** $g^2(\tau)$ measurement of device coupled to single NV (Sample B) under 532 nm 300 μ W excitation. This figure was reproduced from "Srivatsa Chakravarthi, Pengning Chao, **Christian Pederson**, Sean Molesky, Andrew Ivanov, Karine Hestoffer, Fariba Hatami, Alejandro W. Rodriguez, and Kai-Mei C. Fu. Inverse-designed photon extractors for optically addressable defect qubits. *Optica*, 7(12):1805, December 2020"

B < 0.1 ppm) implanted with ^{14}N accelerated to 20 keV and vacuum annealed at 800 $^{\circ}\text{C}$. Here, annealing forms NVs primarily by vacancy recombination with native nitrogen. The

resulting NV distribution is dictated by the vacancy diffusion profile [87], yielding a dense layer (≈ 100 NVs per 800 nm excitation spot diameter) of NV centers $\lesssim 100$ nm below the diamond surface. Sample B is a chemical vapor deposition diamond (Element Six, electronic grade, N < 5 ppb, B < 1 ppb) implanted with ^{15}N accelerated to 85 keV and vacuum annealed at 1200°C (see Methods). During annealing, NV centers are formed primarily by vacancy recombination with the implanted nitrogen, yielding a thin layer (≈ 3 NVs per excitation spot) of single NV centers $100 \text{ nm} \pm 20 \text{ nm}$ from the surface.

After NV⁻ formation, a 250 nm thick gallium phosphide (GaP) membrane is transferred to each sample via a wet lift-off process [110, 37, 89]. Electron beam lithography and subsequent plasma RIE etching of the GaP layer forms the $1.5 \mu\text{m} \times 1.5 \mu\text{m}$ photon extractors. The small footprint was chosen for compatibility with on-chip electrodes enabling optical frequency tuning [1, 89]. Over 100 000 devices are fabricated in multiple arrays on the $2 \text{ mm} \times 2 \text{ mm}$ diamond substrate. An array of fabricated devices and a false color SEM image highlighting the material stack is shown in Fig. 3.1(b). On average, each feature is measured to be within 10% of the design, with near vertical ($\theta = 88^\circ$) GaP sidewalls. See Sec. SI.5, Supplement 1 of [14] for more details on fabrication.

3.2.3 Enhanced photon extraction³

To study NV PL enhancement from the fabricated devices, we use spatially-resolved photoluminescence spectroscopy (Sec. SI.6, Supplement 1 [14]) under off-resonant 532 nm excitation (Fig. 3.2(a)). First, sample A is utilized for broadband characterization of ensemble-averaged enhancement over the entire NV spectrum. In this measurement, the 532 nm laser with a spot diameter of ≈ 800 nm is focused on the center of the device, optimized for max-

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imum PL collection. Due to both the lateral extent of the excitation spot and the depth distribution of the NV ensemble, the NV⁻ device coupling is highly inhomogeneous. The room temperature spectra from devices are normalized to the PL from the nearby bare-diamond, which spatially varies in intensity by $\approx 14\%$ (Fig. SI.7b, Supplement 1 [14]). We observe an average six-fold enhancement that is relatively flat over 575 to 750 nm and matches reasonably well to the theoretical 4-fold enhancement (Fig. 3.2(b-c)) calculated by averaging over the NV spatial and dipole distributions (for details on the simulation see Sec. SI.2, Supplemental 1 [14]).

Having demonstrated broadband NV PL enhancement, we move on to single-NV coupled devices on sample B and characterize the enhancement of the NV zero-phonon line (ZPL) emission. Identification of single-NV coupled devices is performed by comparing the low temperature (8 K) NV⁻ ZPL spectra under 532 nm excitation of devices to nearby bare-diamond NV centers (Fig. 3.2(d)). Enhanced ZPL collection rates (Fig. 3.2(e)) were exhibited in 74 of 480 tested devices. The distribution of observed enhancement can be seen in Fig. 3.2(e)(inset). Enhancement as high as 14-fold can be observed, which is based on the NV saturation intensity to eliminate the effect of excitation polarization. The saturation intensity of bare-diamond NV centers varies by $\approx 8\%$ (Fig. SI.7d, Supplement 1 [14]). The placement of NVs with respect to the device optical mode is random; coupled device yield can thus be significantly improved by targeted implantation or pattern alignment to registered defect centers [59] during fabrication.

We verify that the observed enhanced PL emission corresponds to single-emitters using an autocorrelation measurement on the NV⁻ ZPL at 637 nm. Fig. 3.2(f) shows the normalized coincidences under continuous off-resonant excitation for a device-coupled NV. The dip in coincidences at 0 time delay is $0.12 < 0.5$ and verifies single-photon emission. Autocorrelation measurements on the eight brightest devices confirm single-NV coupling in six of the devices.

In addition to the dip at zero time delay, significant bunching is observed in all devices on the 100 ns timescale. In modeling the autocorrelation curve (red line, Fig. 3.2(f)), we find it is necessary to include both the NV^- singlet state and the NV^0 charge state to reproduce the magnitude and timescale of the bunching for a series of power-dependent measurements. Consideration of charge state dynamics is a critical for NV device performance as discussed further below. Consistent with theoretical expectations, a significant excited state lifetime reduction (due to an increased LDOS, Fig. 3.1(c), dashed lines) is not necessary to obtain good agreement between the experimental data and model.

3.2.4 Charge state and spectral stability⁴

Single defect qubit devices have requirements beyond photon collection efficiency including charge state stability and spectral homogeneity and stability. These properties should be preserved during device integration. Our autocorrelation model suggests that rapid charge-state conversion occurs between the neutral (NV^0) and negatively-charged (NV^-) states. For both sensing and quantum information applications, the NV^- charge state is required, hence we need to minimize ionization into the NV^0 charge state. Every NV center, whether or not it is coupled to a device, has emission at both NV^0 and NV^- ZPL transitions, with the ratio of the ZPL intensities (Fig. 3.3 a) determined by the local Fermi-level [32, 51] and excitation intensity [94]. We also observe a broadening in the inhomogeneous NV^- ZPL distribution and an overall blue shift of 30 ± 15 GHz (Fig. 3.3(b)) for device-coupled NVs vs nearby bare-diamond NVs. These effects can be attributed to local variation in the strain environment [6, 52]. Identical photon emission from different coupled defects are essential for photon-mediated defect qubit entanglement schemes [9, 45]. The observed static

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inhomogeneity can be bridged by Stark tuning [1, 89] or quantum frequency conversion techniques [98, 28]. Characterization of the local strain environment for individual device-coupled NV centers and the prospect of additional inhomogeneous broadening due to strain induced by the GaP-diamond interface at low temperatures (8 K) is provided in Sec. SI.9, Supplement 1 [14].

High resolution photoluminescence excitation (PLE) spectroscopy gives us further insight into the optical coherence (Fig. 3.3(c)) and temporal spectral stability of individual defects (Fig. 3.3(d)). In PLE measurements, a narrow-band tunable laser is scanned across the NV^- ZPL while collecting the NV^- phonon-sideband PL (650 nm to 800 nm). From the PLE spectra we obtain the average optical linewidth as well as the scan-to-scan variation in the ZPL frequency, indicating spectral diffusion. During PLE we can sometimes observe a loss of the NV^- PL signal due to ionization to the NV^0 state. When PL is lost, we apply a short 532 nm re-pump pulse (0.1 s) between scans to reinitialize into the NV^- charge state (as indicated by the green markers in Fig. 3.3(d)). Hence, the interval between re-pump pulses is another indicator of the NV^- charge state stability.

For a deep, single NV center incorporated during growth, NV^- is the preferred charge state at low excitation power ($\text{NV}^-/\text{NV}^0 = 3.4$ at 60 μW of 532 nm excitation). An average linewidth of 44 MHz is observed (Fig. 3.3(d.i)). Minimal spectral diffusion is observed between re-pump pulses, with the NV^- ZPL frequency exhibiting a standard deviation of 48 MHz. It is a challenge to demonstrate this level of optical stability with device-coupled implanted near-surface NVs. Prior to device fabrication, the implanted single NV centers exhibit an average optical linewidth of < 100 MHz (Fig. 3.3(c), green). Between re-pump pulses, the standard deviation of the NV^- ZPL frequency is ~ 100 MHz, indicating low spectral diffusion. (Fig. 3.3(d.ii)). The NV^- charge state remains stable, no ionization is observed for multiple scans over ten minutes of measurement time. This data compares

favourably with the grown-in NVs.

Post-fabrication, for both device and bare-diamond implanted NV centers, the preferred charge state at low excitation power is NV^0 . In addition to the low NV^-/NV^0 ratio (Fig. 3.3 a dashed lines), we observe broadening of the average single NV^- linewidth (Fig. 3.3(c), blue), rapid ionization and large spectral diffusion. We suspect that although our design avoids etching into the diamond, the GaP photonics plasma etch ($\text{Ar}/\text{Cl}_2/\text{N}_2$) modifies the surface termination [107, 101] of the diamond and introduces new surface charge traps. Encouraged by prior studies [32, 112], we performed a post-fabrication oxygen anneal of the sample at 400°C (for details see Sec. SI.10, Supplement 1 [14]). From Fig. 3.3(a) (solid lines), we see that the surface treatment more than doubles the NV^-/NV^0 ratio. For the bare-diamond NV centers, we recover the pre-fabrication average NV^- linewidth (Fig. 3.3(c), red), but the centers retain the larger spectral diffusion (Fig. 3.3(d.iii)). For device-coupled NV centers (Fig. 3.3(d.iV)), we measure an average device-coupled NV linewidth of 844 MHz (1.5 GHz pre- O_2 annealing). This linewidth is ≈ 8 times larger than bare-diamond NVs. Further studies are needed to determine if this fast spectral diffusion can be attributed to the GaP-diamond interface or laser-induced due to modification of the excitation intensity profile. One promising avenue for further reduction in fabrication-induced NV instability is to fabricate the GaP device prior and transfer it via a stamping process [24]. Our inverse-design optimization framework can accommodate additional constraints such as interconnected support structures required by the stamp-transfer fabrication technique.

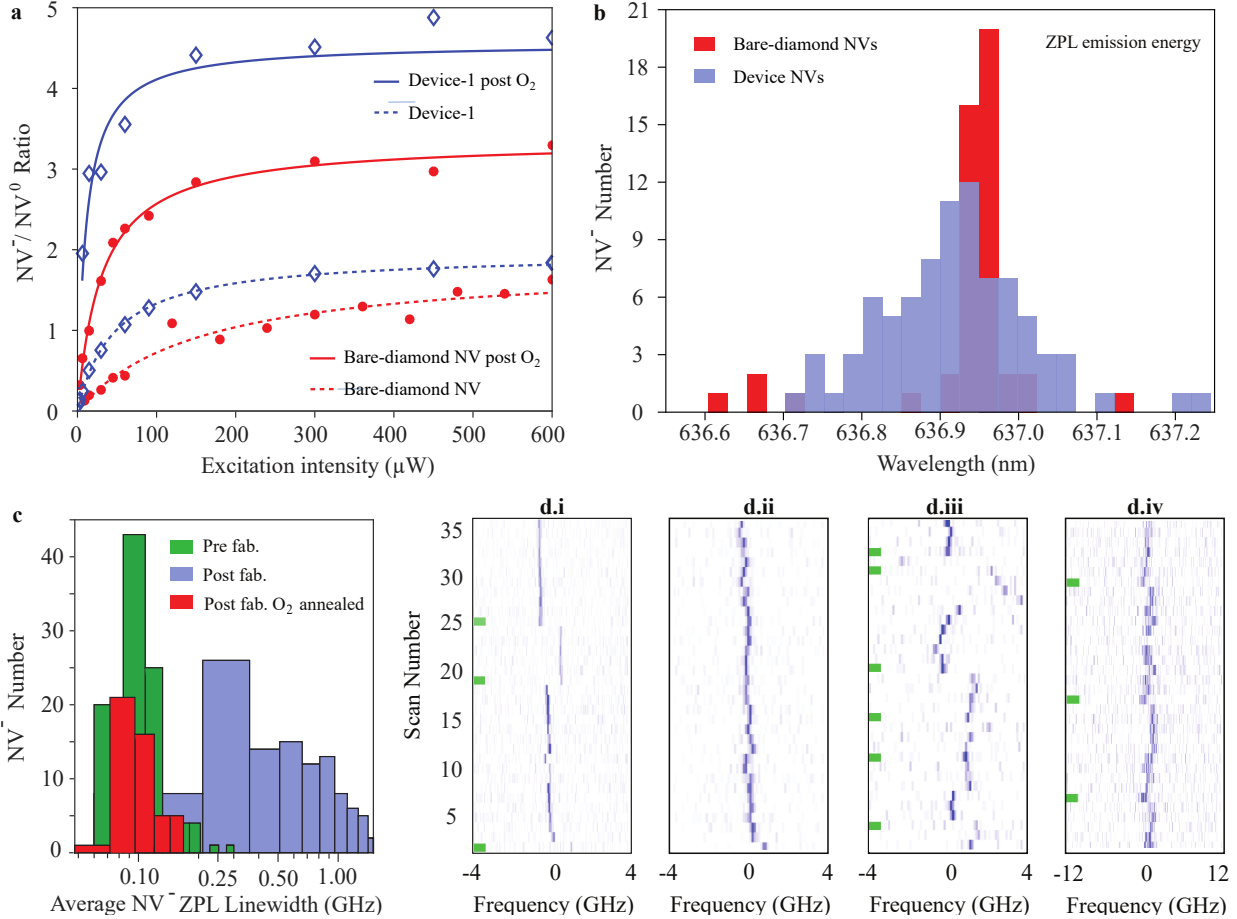


Figure 3.3: (Sample B, $T=8\text{ K}$) **a.** The ratio of ZPL intensities of NV^- (637 nm) and NV^0 (575 nm) charge states for device-coupled and bare-diamond implanted NVs as a function of the 532 nm excitation intensity. **b.** The distribution of ZPL wavelength for device-coupled and bare-diamond NVs. **c.** The distribution of observed average PLE linewidth for bare-diamond NVs. **d.** PLE characterization of NVs; (d.i) Grown-in deep NV avg. linewidth = 44 MHz, (d.ii) Implanted NV pre-fabrication avg. linewidth = 66 MHz, (d.iii) Bare-diamond NV post-fabrication after oxygen annealing avg. linewidth = 59 MHz, (d.iv) Device-coupled NV after oxygen annealing avg. linewidth = 844 MHz. The green markers indicate 532 nm re-pump pulses that re-initialize the NV into the NV^- charge state. This figure was reproduced from "Srivatsa Chakravarthi, Pengning Chao, **Christian Pederson**, Sean Molesky, Andrew Ivanov, Karine Hestroffer, Fariba Hatami, Alejandro W. Rodriguez, and Kai-Mei C. Fu. Inverse-designed photon extractors for optically addressable defect qubits. *Optica*, 7(12):1805, December 2020"

3.2.5 Model for $g^{(2)}(t)$ measurements⁵

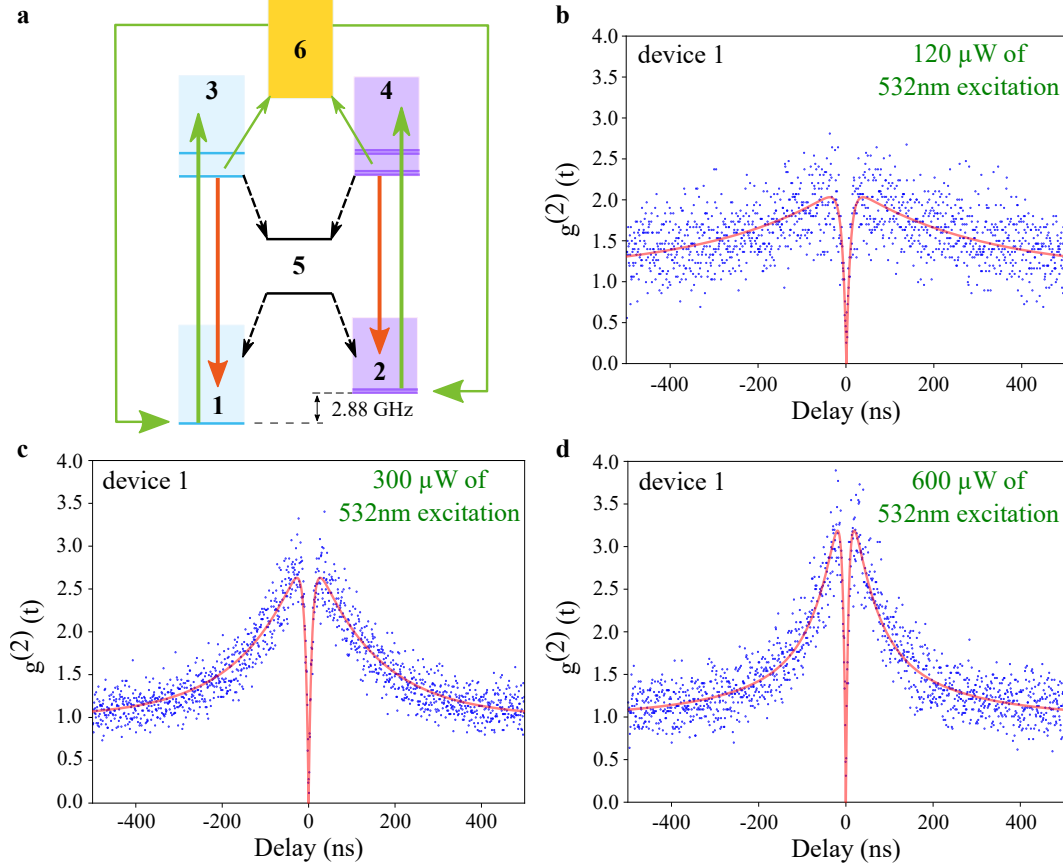


Figure 3.4: **a.** Energy levels and transitions of the NV⁻ and NV⁰ charge states utilized for modelling the $g^{(2)}(\tau)$ data. **b.** $g^{(2)}(\tau)$ for 120 μ W non-resonant excitation. **c.** $g^{(2)}(\tau)$ for 300 μ W off-resonant excitation. **d.** $g^{(2)}(\tau)$ for 600 μ W non-resonant excitation. Note the increase in bunching peaks with increase in excitation intensity. This figure was reproduced from "Srivatsa Chakravarthi, Pengning Chao, **Christian Pederson**, Sean Molesky, Andrew Ivanov, Karine Hestroffer, Fariba Hatami, Alejandro W. Rodriguez, and Kai-Mei C. Fu. Inverse-designed photon extractors for optically addressable defect qubits. *Optica*, 7(12):1805, December 2020"

The normalized autocorrelation measurements on the NV⁻ ZPL photons emitted shown

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in Fig. 3.4(b-d) provide definitive evidence that we are observing enhancement from a single quantum emitter, yet also reveal significant photon bunching. Power-dependent photon bunching is a well-documented effect in NV centers, however the number of coincidences we observed at delays around 20 ns for the 300 μW and 600 μW data is larger than typically observed in literature. We observe similar bunching in implanted, non-device coupled NV centers in the same sample, but under higher excitation intensity. This similarity suggests that the devices enhance the excitation field at the defect, but are not responsible for the presence of the bunching. Photon bunching is detrimental for many applications since it arises from non-cycling transitions shelving the NV center into inaccessible, or dark, states.

The connection between the photon statistics and the NV center's state is given by the following equation,

$$g^{(2)}(\tau) = \frac{p(e, \tau | g, 0)}{p(e, \infty)}, \quad (3.1)$$

where $p(e, \tau | g, 0)$ is the probability of finding the NV center in the excited state at time delay τ given that it was in the ground state at 0 time delay, and $p(e, \infty)$ is the steady state population in the excited state under continuous excitation.

We model the NV center as a 6 level system in order to account for the NV^- ground states, excited states, singlet states, and NV^0 states as shown in Fig. 3.4(a). In our labelling scheme, manifolds 1 and 3 corresponds to the $m_s = 0$ ground and excited states respectively. Manifolds 2 and 4 correspond to the $m_s = \pm 1$ ground and excited states. Manifold 5 contains the singlet states, and manifold 6 consists of the NV^0 states. The probability of being in level i is p_i and the rate from level i to j is given by k_{ij} , and P is the optical excitation power. Coherences between the different energy levels are assumed to decay on time scales faster than the excitation/relaxation rates due to the non-resonant pumping, which simplifies the model to following set of 6 rate equations.

$$\begin{bmatrix} \dot{p}_1 \\ \dot{p}_2 \\ \dot{p}_3 \\ \dot{p}_4 \\ \dot{p}_5 \\ \dot{p}_6 \end{bmatrix} = \begin{bmatrix} -k_{13}(P) & 0 & k_{31} & 0 & k_{51} & k_{61}(P^2) \\ 0 & -k_{13}(P) & 0 & k_{31} & k_{52} & 2k_{61}(P^2) \\ k_{13}(P) & 0 & -(k_{31} + k_{36}(P) + k_{35}) & 0 & 0 & 0 \\ 0 & k_{13}(P) & 0 & -(k_{31} + k_{36}(P) + k_{45}) & 0 & 0 \\ 0 & 0 & k_{35} & k_{45} & -(k_{51} + k_{52}) & 0 \\ 0 & 0 & k_{36}(P) & k_{36}(P) & 0 & -3k_{61}(P^2) \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ p_3 \\ p_4 \\ p_5 \\ p_6 \end{bmatrix} \quad (3.2)$$

One subtlety is that each level of our model corresponds with a manifold of NV states. This has implications in our treatment of off-resonant excitation into the excited state, the multiplicity of the $m_s = \pm 1$ level, and the NV^0 internal dynamics. We address the issue of off-resonant excitation by taking the excitation rate to depend linearly on power, while the photon emission rate is power independent. We account for the multiplicity of the $m_s = \pm 1$ states by properly normalizing the branching ratios. For example, the recombination from the NV^0 manifold into $m_s = \pm 1$ is taken to be twice the recombination into $m_s = 0$. Lastly, we ignore the internal dynamics of NV^0 , and treat recombination as a two-photon process that in the weak excitation limit should scale as the power squared.

The initial condition is determined by the spin polarization, $p_1/(p_1 + p_2)$, and is determined by forcing our solution to be self consistent. In other words $p_1(0)/(p_1(0) + p_2(0)) = p_1(\infty)/(p_1(\infty) + p_2(\infty))$. We find that the equilibrium spin polarization approaches a maximum value of 0.8 at low power and decreases with power.

Older models of NV dynamics ignore ionization and recombination, and focus on the role of the NV^- singlet state and spin non-conserving transitions [58]. We are unable to reproduce the power dependent bunching we observe with the rates from these models. Our model is more similar to recent literature models which account for both the long-lived NV^- singlet state, as well as the NV^0 charge state, but we ignore internal dynamics within the singlet and neutral states [61, 4] as we are able to obtain satisfactory agreement simultane-

Rate (μs^{-1})	Model 1 NV 1 [61]	Model 1 NV 2 [61]	Model 2 [58]	Model 3 [4]	This Model
k_{13} (1 mW)	10	10	NA	59	82
k_{31}	77	66	77	75	89
k_{35}	0	7.9	0	11	17
k_{45}	30	53	30	80	17
k_{51}	5	1.7	3.3	2.6	1.7
k_{52}	0	1	0	2.3	0.50
k_{36} (1 mW)	852	852	0	2.2	24
k_{61} (1 mW)	45	45	0	47	11

Table 3.1: Rates for modelling NV dynamics

ously fitting the three power-dependent $g^{(2)}$ curves with the simplified model (Fig. 3.4). We begin the optimization with rates taken directly from these models and optimize over each parameter. This is necessary, since the rates can vary significantly between different NV centers (Table 3.1). We find the final optimized rates are in reasonable agreement with reported values, with the only disagreement being in lower shelving rates into the singlet state, and lower deshelling rates out of the singlet states. Nevertheless, it is clear that ionization and recombination are important factors in the emission properties of an NV center, and should be considered in a variety of applications.

3.2.6 *Photon extractor summary*

Although the photon extractors were effective for their designed purpose of increasing collection efficiency, they illustrated just how sensitive shallow color centers are to plasma exposure. We were able to observe the induced charge instabilities in three different measurements. First we saw in Fig. 3.3(a) that the preferred charge state of the NV centers was NV^0 at low powers, and even under high power excitation, the ratio of NV^- to NV^0 never reached the value observed in bulk diamond. Second, the PLE data, Fig. 3.3(d), showed increased ionization events after fabrication. Third the $g^{(2)}$ measurements, Fig. 3.4, showed power-dependent photon bunching suggesting rapid ionization.

These measurements demonstrate that plasma exposure, even a plasma that doesn't etch the diamond strongly modifies the surface. These measurements are further corroborated by the effect of the oxygen anneal, which mitigates some but not all of the negative effects of the plasma. The conclusions we draw from these photon extractors motivates much of the work in this thesis. Not only is a new fabrication process that avoids exposing diamond to plasma is needed, but also a deeper understanding of the origins of spectral diffusion and developments in surface treatments which strongly modify color center's charge stability.

3.3 *Photonic crystal cavities*

The main challenges we observed with the GaP-on-diamond platform itself was the degradation of the charge and optical stability of shallow color centers due to plasma exposure. Luckily, an advantage of the hybrid platform is that plasma etching need not be performed on the diamond, unlike monolithic devices where the diamond itself must be etched. Here we will demonstrate a proof-of-principle device design that allows for fabrication and tuning of devices separately from the treatment of the diamond surface. The GaP membrane is etched on a sacrificial substrate and pre-characterized. The devices are then transferred to

the diamond via a stamp process which is a mature technology.

Another important improvement to the previous GaP-on-diamond infrastructure is the move away from NV centers to SiV centers. As discussed in Sec. 2.4.3, spectral diffusion is caused by stochastic Stark shifts. Different color centers have different sensitivities to spectral diffusion, and the SiV center which possesses inversion symmetry has no linear Stark effect [21]. This effect is significant enough that the entire community has effectively switched to group IV-vacancy complexes for any application demanding stable optical emission.

We will start by summarizing the device design and fabrication, demonstrate the successful coupling of color centers to the cavity, and estimate the Purcell factor and cooperativity of the device. We will discover that the major limitation in the cooperativity remains optical instability of the SiV, but will discuss why these results are so promising for the GaP-on-diamond platform.

3.3.1 Device design⁶

The device consists of a 1-D array of elliptical holes etched into the GaP (Fig. 3.5(a)). The designed GaP layer thickness is constrained to 222 nm. A unit cell of the cavity consists of a single elliptical hole with major-axis h_y and minor-axis h_x , GaP width w and a lattice constant a_{cav} . The of the cavity can be divided into the taper and mirror sections as shown in Fig. 3.5(b). Within the mirror region, the hole periodicity, a_{mir} , is chosen to maximize the TE quasi-band gap around the target frequency of the SiV zero-phonon transition at 737 nm. Within the taper region, the hole periodicity is adiabatically reduced from a_{mir} so as to create a defect mode for the target frequency. The presence of the high index diamond substrate underneath the GaP introduces design challenges towards achieving high

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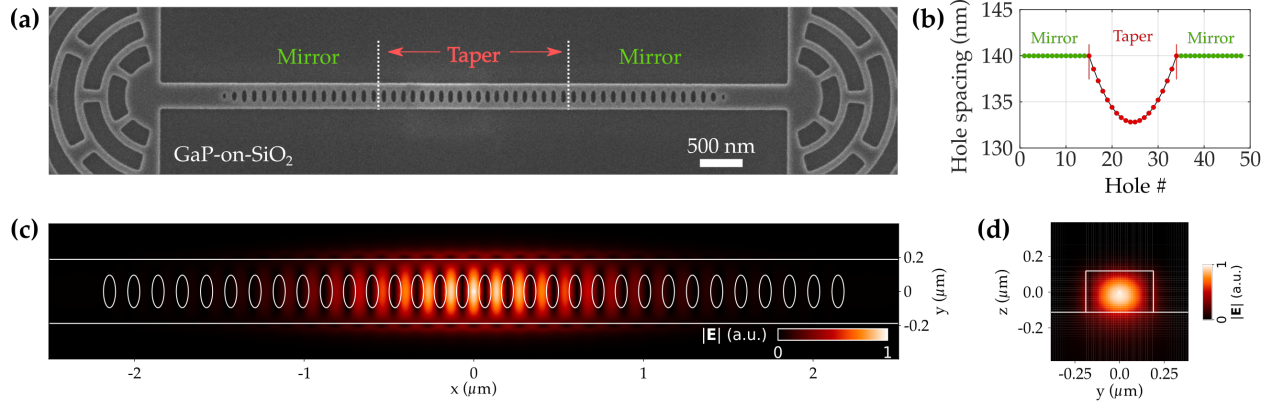


Figure 3.5: (a) SEM image of a GaP 1-D cavity. (b) The variation of the hole spacing across the cavity, distinguishing the mirror and taper regions. (c, d) Simulated E-field intensity of the primary cavity mode across the xy-plane ((c), $z=0$ centered on GaP layer) and yz-plane ((d), $x=0$ centered on cavity maxima) within the GaP-on-diamond structure. This figure was reproduced from "Srivatsa Chakravarthi, Nicholas S. Yama, Alex Abulnaga, Ding Huang, **Christian Pederson**, Karine Hestroffer, Fariba Hatami, Nathalie P. de Leon, and Kai-Mei C. Fu. Hybrid integration of gap photonic crystal cavities with silicon-vacancy centers in diamond by stamp-transfer. *Nano Letters*, 23(9):3708–3715, May 2023." [17]

Q because the substrate expands the light-line such that photons can couple to the continuum of modes in the diamond and thus leak out of the cavity. Full details of the cavity design and optimization can be found in Ref. [78, 44].

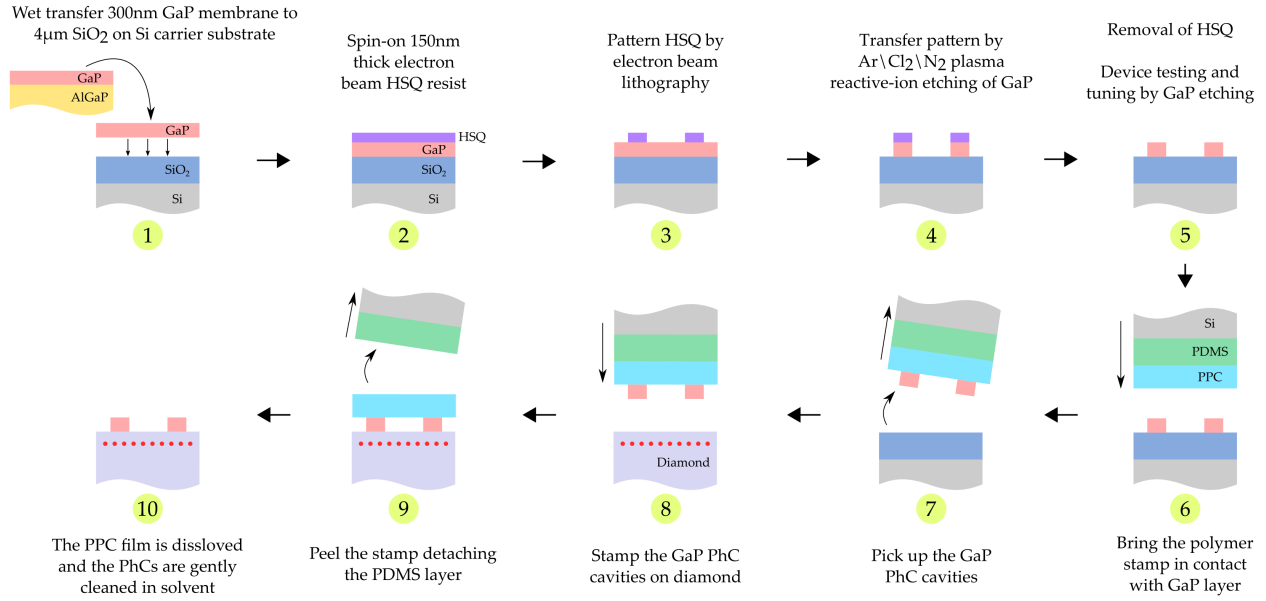


Figure 3.6: An illustration of the stamp transfer process. We begin with GaP cavities fabricated on a silicon oxide carrier chip and finish with cavities integrated with implanted SiV centers in a host diamond chip. Microscope images from various stages of fabrication are provided in SI.2. [17]. This figure was reproduced from "Srivatsa Chakravarthi, Nicholas S. Yama, Alex Abulnaga, Ding Huang, **Christian Pederson**, Karine Hestroffer, Fariba Hatami, Nathalie P. de Leon, and Kai-Mei C. Fu. Hybrid integration of gap photonic crystal cavities with silicon-vacancy centers in diamond by stamp-transfer. Nano Letters, 23(9):3708–3715, May 2023." [17]

3.3.2 Device fabrication⁷

The cavity structure is fabricated using a 300 nm GaP membrane (Fig. 3.6:1-5) that is released from a GaP substrate by etching an intermediate $\text{Al}_{0.8}\text{Ga}_{0.2}\text{P}$ sacrificial layer with dilute HF. The GaP membrane is then transferred to a silicon-oxide on Si substrate using a wet-transfer process [110, 89, 14]. Electron-beam lithography is performed using hydrogen silsesquioxane (HSQ) resist to pattern the cavity devices. Subsequent inductively coupled plasma reactive-ion-etching (RIE) of the GaP layer forms the photonic devices.

A chemical vapor deposition diamond (Element Six, electronic grade, $\text{N} < 5$ ppb, $\text{B} < 1$ ppb) is implanted with Si accelerated to 26 keV ($5 \times 10^{11} \text{ cm}^{-2}$ dose, 7° angle) and vacuum annealed at 1200°C for 2 hrs. During annealing, SiV centers are formed by vacancy diffusion and recombination with the implanted silicon, yielding a layer of SiV centers 20 nm from the surface (~ 50 SiV centers per ~ 800 nm diameter excitation spot).

To transfer the cavities to the diamond, a stamping procedure [78, 43] is utilized, as shown in (Fig. 3.6:6-10). The process is carried out in a flip-chip wafer-bonder which controls both pressure and temperature. The process uses a PDMS stamp fabricated into a mesa structure and an intermediate polypropylene carbonate (PPC) film. The PDMS/PPC stack is brought in contact with the devices and heated to 60°C to promote adhesion. Next, the PDMS/PPC/cavity stack is lifted-off the carrier substrate. The diamond substrate is cleaned in a piranha 3:1 bath prior to stamping. The PDMS/PPC/cavity stack is aligned and pressed down on the diamond substrate. The stamp and diamond are heated to 130°C , which softens the PPC layer to release the PPC film from the PDMS stamp. Finally, we dissolve the PPC in trichloroethylene and soak the diamond in acetone followed by IPA.

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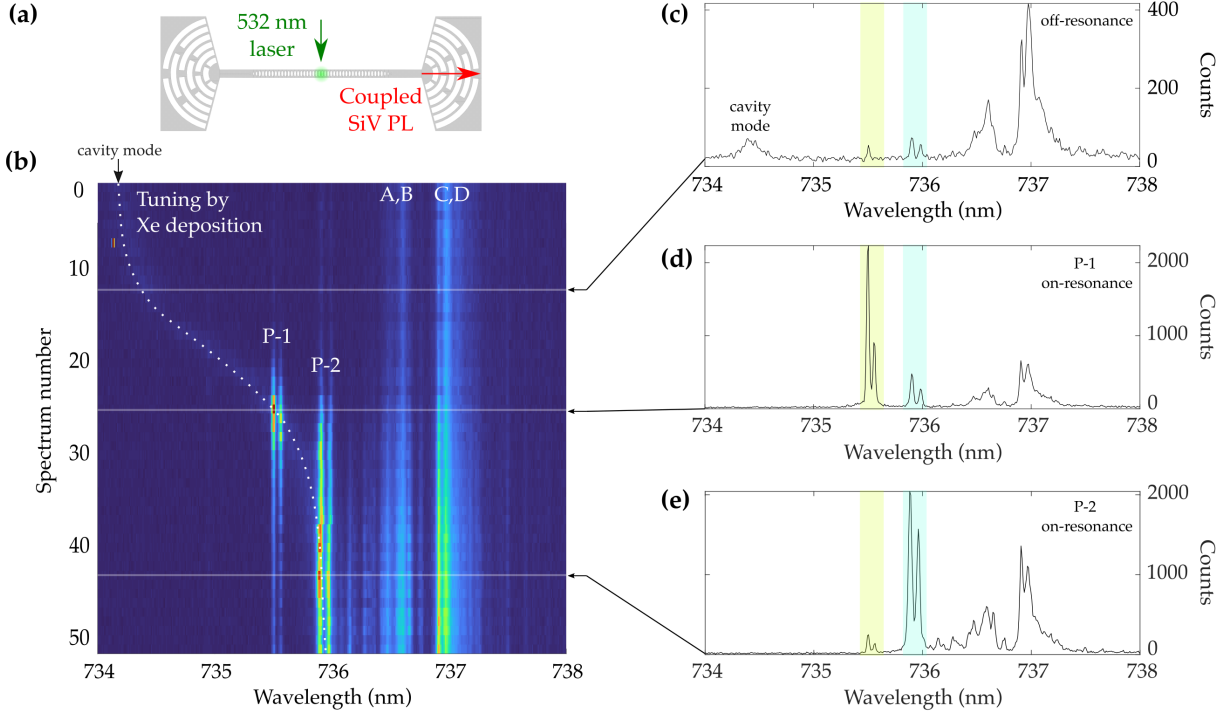


Figure 3.7: *(LT 10 K cavity tuning)* (a) Illustration of the measurement geometry with the 532 nm excitation at the cavity and grating coupled SiV PL collection. (b) A sequence of spectra (60 s exposures) showing the cavity mode red-shifting from xenon gas deposition with a maximum tuning range of ≈ 1.9 nm. The cavity is tuned through two SiV ZPL pairs (P-1, P-2). (c) Spectra of the cavity off-resonance. (d, e) Spectra of the cavity on-resonance with P-1 (d) and P-2 (e). The green and blue boxes indicate the filtering windows utilized for on-resonance lifetime measurements. This figure was reproduced from "Srivatsa Chakravarthi, Nicholas S. Yama, Alex Abulnaga, Ding Huang, **Christian Pederson**, Karine Hestroffer, Fariba Hatami, Nathalie P. de Leon, and Kai-Mei C. Fu. Hybrid integration of gap photonic crystal cavities with silicon-vacancy centers in diamond by stamp-transfer. *Nano Letters*, 23(9):3708–3715, May 2023." [17]

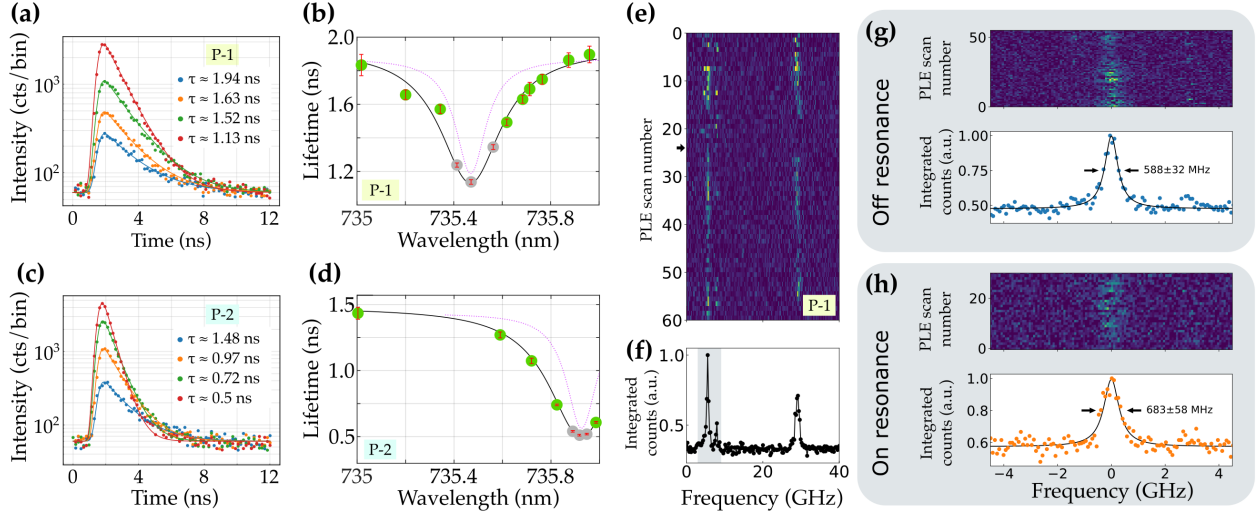


Figure 3.8: (*LT 10 K measurements*) Time-resolved PL and extracted excited-state lifetime of SiV pairs (a, b) P-1 and (c, d) P-2 as a function of cavity detuning. We observe an enhancement of the decay rate by a factor of 1.7 ± 0.1 and 3.0 ± 0.1 for P-1 and P-2 respectively. A Lorentzian fit (blue) to the lifetime data results in a linewidth that is broader than the cavity linewidth (dashed gray). (e) PLE scans on ZPL P-1 when the cavity is significantly red detuned. Each scan is taken over 2s at 10s intervals. After each scan, a 532nm pulse was occasionally used to reset the SiV charge state if ionization occurred; one such instance is indicated by the black arrow at scan 24. (f) Integrating all scans in (e) shows two bright lines separated by around 25 GHz approximately corresponding to the spacing observed in spectra. The highlighted line near 5 GHz is further examined by tuning the cavity from (g) off resonance to (h) on resonance while continuously performing PLE scans. The linewidth is observed to broaden by 95 ± 66 MHz when the cavity is tuned on resonance which is approximately consistent with an enhancement of 1.7 of the decay rate. This figure was reproduced from "Srivatsa Chakravarthi, Nicholas S. Yama, Alex Abulnaga, Ding Huang, **Christian Pederson**, Karine Hestroffer, Fariba Hatami, Nathalie P. de Leon, and Kai-Mei C. Fu. Hybrid integration of gap photonic crystal cavities with silicon-vacancy centers in diamond by stamp-transfer. Nano Letters, 23(9):3708–3715, May 2023." [17]

3.3.3 Device tuning⁸

When cooled to 10 K, the cavity mode of the devices are blue-detuned from room-temperature by ~ 5.5 nm due to the temperature dependence of the GaP index. Utilizing the 532 nm off-resonant excitation at the cavity center (Fig. 3.7(a)), we can monitor the cavity mode and SiV ZPL transitions at the output grating. Typical spectra shows four bright lines near 737 nm corresponding to the characteristic A–D transitions for SiV [42], together with a number of faint detuned lines associated with strained single SiV centers. The cavity mode can be red-shifted by injecting xenon gas into the sample chamber. The xenon condenses on the sample, increasing the effective index of the cavity mode and resulting in a controlled resonance shift as demonstrated in Fig. 3.7(b). The maximum range of the xenon-induced red-shift is 1.9 nm. Although all 28 intact devices from the stamped array exhibit cavity resonances, only the nine devices having resonances within 3 nm of 737 nm are utilized for xenon tuning measurements (Fig. 3.7(c)). For all nine devices, we are able to observe significant increase in PL on resonance for a range of SiV transitions from blue to red detuned with respect to the ensemble A–D lines (Fig. 3.7(b); other devices in SI.4).

To facilitate coupling to single SiV transitions and for ease of cavity-mode identification, we focus on a device with isolated blue-detuned SiV transitions. We select device-3 with $Q_{\text{Dia}} = 4,100$ which exhibits the maximum increase in PL of all devices. For this device, the cavity mode is tuned through two pairs of SiV ZPL denoted P-1 and P-2 (Fig. 3.7(c-e)). In order to quantify the SiV-cavity coupling we first perform time-resolved PL measurements while tuning the cavity over P-1 and P-2. We excite at the cavity with pulsed excitation at 704 nm (500 μ W average power, 2 ps pulse width and 80 MHz repetition rate) and collect PL

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through the output grating, thus filtering only the cavity-coupled SiV. We then spectrally filter the PL via a spectrometer (0.2 nm bandwidth, centered on P-1 or P-2) and detect the PL with an avalanche photodiode. A low-intensity continuous-wave (20 μ W) 532 nm laser is added to help stabilize the negative SiV charge state (SI.6 [17]). By fitting the temporally resolved PL (Fig. 3.8(a,c), see SI.8 [17] for details), we observe a reduction of the lifetime on resonance by a factor of

$$\frac{\tau_{\text{off-res}}^{\text{P-1}}}{\tau_{\text{on-res}}^{\text{P-1}}} = 1.7 \pm 0.1, \quad \frac{\tau_{\text{off-res}}^{\text{P-2}}}{\tau_{\text{on-res}}^{\text{P-2}}} = 3.0 \pm 0.1.$$

A plot of the lifetime as a function of cavity detuning (Fig. 3.8(b,d)) exhibits a Lorentzian lineshape, with a linewidth that is broader than the cavity resonance (FWHM $\approx$ 0.17 nm). This is consistent with the broadening expected due to the contributions from the two SiV transitions comprising each pair (with separation of about 0.06 nm and 0.08 nm for P-1 and P-2 respectively).

Next, we perform photoluminescence excitation (PLE) spectroscopy to characterize the optical linewidths off and on cavity resonance. The SiV is resonantly excited via a low-power tunable diode laser which is scanned over the ZPL transition under consideration while the phonon sideband PL is collected ($\lambda > 760$ nm) from above the cavity (as this emission is not resonant with the cavity). We observe distinct and consistent lines corresponding to ZPL P-1 (Fig. 3.8(e-h)) and P-2 (SI.5 [17]) by exciting either through the input grating or directly on the cavity. To maintain constant excitation intensity at the SiV during the scan, we select the latter configuration. Between different SiV centers, the excitation power was varied from 100 nW to 1 μ W to optimize the signal-to-noise while minimizing SiV ionization. Additionally, a low-intensity blue LED and/or 532 nm pulse enabled consistent re-pumping of the SiV (SI.5 [17]).

We focus on ZPL P-1 due to the larger tuning range of the cavity. Fig. 3.8(e) shows a series of PLE scans over ZPL P-1 with the cavity red detuned by approximately 0.7 nm. Two bright lines are observed to be separated by about 25 GHz, consistent with the separation measured in PL. The off-resonant lifetime of ZPL P-1 measured in Fig. 3.8(a) was determined to be $\tau_{\text{off-res}}^{\text{P-1}} = 1.94 \pm 0.06$ ns which corresponds to a lifetime-limited linewidth $1/2\pi\tau_{\text{off-res}}^{\text{P-1}} = 82 \pm 0.4$ MHz. The additional broadening of the lines is understood to be a result of a combination of homogeneous phonon-broadening (limit of ~ 250 MHz at 10 K [48]) and spectral diffusion. Because the broadening due to pure lifetime reduction is expected to be $(1/2\pi\tau_{\text{on-res}}^{\text{P-1}}) - (1/2\pi\tau_{\text{off-res}}^{\text{P-1}}) = 60$ MHz, we focus on the highlighted line near 5 GHz as it is significantly narrower than the other line near 30 GHz. While performing PLE scans centered on this line, we tune the cavity from the original red-detuned position into resonance (Fig. 3.8(g,h)). We measure a modest broadening of the overall linewidth by $\Delta\Gamma = 95 \pm 66$ MHz which is consistent with the estimated broadening via the lifetime measurements.

3.3.4 Purcell enhancement and cooperativity⁹

The lifetime and linewidth measurements can be utilized to determine the Purcell enhancement and cooperativity of the SiV-cavity system. The SiV-cavity system can be modeled as an open system where the cavity is a purely additive decay channel with cavity loss rates $\kappa \equiv \omega/Q$ and defect loss rates γ (including both radiative and non-radiative channels outside of the cavity). A Jaynes-Cummings Hamiltonian with single-photon Rabi frequency g describes the SiV-cavity interaction (SI.7 [17]). If we consider only contributions to γ which describe population decay (i.e. ignore pure dephasing) and assume that the system is in the “bad-cavity” regime ($\kappa \gg g, \gamma$), we may define the Purcell enhancement F as the multiplicative increase in the decay rate of the desired transition [29],

$$F \equiv 1 + F_P \left(\frac{\vec{\mathbf{E}} \cdot \vec{\mu}}{|\vec{\mathbf{E}}_{\max}| |\vec{\mu}|} \right) \frac{(\kappa/2)^2}{(\kappa/2)^2 + \delta^2} . \quad (3.3)$$

Here $\vec{\mathbf{E}}/|\vec{\mathbf{E}}_{\max}|$ is the unit-normalized mode electric-field profile, δ is the SiV-cavity (angular) frequency detuning, and $\vec{\mu}/|\vec{\mu}|$ is a unit vector in the direction of the transition’s dipole moment. The constant $F_P \equiv (3/4\pi^2)(\lambda/n)^3(Q/V)$ is the well-known Purcell factor for a cavity with mode volume V at wavelength λ/n [75].

Further assuming that the emitter’s proximity to the cavity does not substantially modify γ , we can determine the ratio of the off-resonant ($\delta \rightarrow \infty$) and on-resonant ($\delta = 0$) lifetimes τ to be given by

$$\frac{\tau_{\text{off-res}}}{\tau_{\text{on-res}}} = 1 + \frac{4g^2}{\kappa\gamma} . \quad (3.4)$$

Comparing Eq. 3.4 to Eq. 3.3 enables estimation of the resonant Purcell enhancement via

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the relation

$$F = 1 + \frac{\gamma}{\gamma_{eg}} \left(\frac{\tau_{\text{off-res}}}{\tau_{\text{on-res}}} - 1 \right), \quad (3.5)$$

where γ_{eg} is intrinsic spontaneous emission rate of the relevant transition. The factor γ_{eg}/γ is an intrinsic (cavity-independent) property of the emitter and may be estimated from the quantum efficiency η , Debye-Waller factor DW , and ZPL branching ratio ξ as $\gamma_{eg}/\gamma = \eta \cdot DW \cdot \xi$ (SI.7 [17]). Taking conservative estimates of $\eta = 0.3$ [7], $DW = 0.7$ [68], and $\xi = 0.325$ [114] provides an upper-bound of $(\gamma_{eg}/\gamma)_{\text{max}} \approx 0.126$, and thus a lower bound on the Purcell enhancement F_{min} of P-1 and P-2. Using the measured lifetime data (Fig. 3.8) we find

$$F_{\text{min}}^{\text{P-1}} \approx 11, \quad F_{\text{min}}^{\text{P-2}} \approx 30$$

which are within the range of feasible Purcell enhancement (Fig. 3.5(f,g)).

Additionally, the cooperativity C of the SiV-cavity system can be defined as $C \equiv 4g^2/\kappa(\gamma + \gamma_d)$ where γ_d is the pure-dephasing rate. Using the total off-resonant linewidth $(\gamma + \gamma_d)/2\pi = 588 \pm 32$ MHz and lifetime-limited linewidth $\gamma/2\pi = 82.0 \pm 0.4$ MHz, we are able to estimate the cooperativity of the P-1 transition under consideration as

$$C^{\text{P-1}} = \frac{\gamma}{\gamma + \gamma_d} \left(\frac{\tau_{\text{off-res}}}{\tau_{\text{on-res}}} - 1 \right) = 0.10 \pm 0.01. \quad (3.6)$$

Reducing the temperature to eliminate the thermal photon broadening beyond the lifetime limit is expected to reduce the total linewidth to $(\gamma + \gamma_d)/2\pi \approx 420$ MHz. Provided the other broadening mechanisms are temperature independent, this would result in a cooperativity of $C_{0\text{K}}^{\text{P-1}} \approx 0.14$. If the SiV linewidth was lifetime limited (i.e. no pure dephasing), then the maximum expected cooperativity for P-1 is given to be $C_{\text{max}}^{\text{P-1}} = 0.7 \pm 0.1$. Similarly for

P-2, assuming the pure depahsing is of similar magnitude ($\gamma_d/2\pi \approx 506$ MHz), we estimate a cooperativity of $C^{P-2} \approx 0.35$, increasing to $C_{0K}^{P-2} \approx 0.45$ below the thermal-broadening limit, and with a maximum value for a lifetime-limited linewidth of $C_{\max}^{P-2} = 2.0 \pm 0.1$.

Although the SiV studied here do not have lifetime-limited linewidths, similar ranges of broadening were observed in other implanted SiV that were not coupled to devices (SI.5 [17]). This suggests that a sample with improved defect linewidths could potentially achieve cooperativities $C > 1$ with little modification to the fabrication process. Additionally, since current devices are operating near the design limit, higher Q can be achieved with further design optimization. Relaxing the design limit on the minimum PhC hole dimension from $h_x = 70$ nm to 60 nm leads to an increase of Q by a factor of 5. Additionally, stamping of the cavity along the $\langle 110 \rangle$ crystal axis or utilizing a diamond with $\langle 111 \rangle$ surface orientation could result in improvements to the coupling coefficient by up to a factor of 4. This indicates that $C \gtrsim 10$ can be achieved in hybrid device geometries despite the low refractive index contrast. This regime is promising for applications such as optical spin readout [83], quantum-optical switches and tunable single-photon sources [93], and quantum repeaters [26].

3.3.5 Photonic crystal cavity outlook

The results from the photonic crystal cavity demonstrate both the promise of the GaP-on-diamond architecture and the unsolved problems regarding the color centers themselves. Even though the SiV⁻ are far less sensitive to spectral diffusion than NV⁻, it is still a significant, observable effect that limits the cooperativity of the devices. Since the diamond surface was never exposed to plasma, and the SiV that were under bare-diamond showed similar line broadening, a deeper understanding of the intrinsic sources of the remaining spectral diffusion is needed. This is the focus of Chapter 4, which seeks to identify the contributions to the spectral diffusion associated with the ion implantation and annealing,

the diamond surface, and the charge re-pump. In addition, new techniques to functionalize the diamond surface are needed to minimize charge instability, the focus of Chapter 5. Furthermore, identifying other defect charge states that may be less sensitive to spectral diffusion and ionization may be needed, along with other ways to dynamically engineer the charge environment, the subject of Chapter 6.

3.4 Conclusion

In this chapter we studied working GaP-on-diamond photonic structures integrated with color centers, and demonstrated that this platform offers the unique ability to decouple the challenges of photonic design and fabrication from the challenges of forming shallow color centers with ideal properties, all using scalable techniques. It is clear that there is still much to be done in this field, but these early results suggest that one must seriously consider charge and optical stability as very serious design constraints in any technology hoping to leverage color centers.

Fortunately, the GaP-on-diamond platform is extremely versatile; most of the exciting emitters in diamond are compatible with GaP due to GaP's large bandgap. For example the SnV^- which has recently received a lot of attention due to spectral stability and long spin coherence times emits at 620 nm which is still compatible with GaP. Furthermore, the scalability of high-quality, wafer-scale GaP growth is an active area of research. The GaP used for both photon extractors and photonic crystal cavities is grown using molecular beam epitaxy, an expensive technology to scale. However, doping GaP with boron, B-GaP, can be utilized to lattice match to silicon. Early material characterization on optical devices fabricated from B-GaP membranes [111] demonstrated quality factors approaching those needed for high cooperativity photonic crystal cavities.

Furthermore, we have barely scratched the surface in this work of the full capabilities of

the GaP-on-diamond platform, and it is the hope of the author that future advances in the material quality of GaP and in the preparation of color centers can leverage many of the exciting capabilities involving acoustics and non-linear frequency conversion for devices not yet conceived.

Chapter 4

SURFACE, IMPLANTATION, AND LASER-INDUCED OPTICAL INSTABILITY

4.1 *Introduction*

In this chapter, our goal is to identify optical instabilities in color centers formed via ion implantation and annealing that are caused by sources intrinsic to the diamond itself, without additional complications due to the fabrication of photonic structures. As we demonstrated in the previous Chapter 3, we have demonstrated that we can decouple the fabrication of our photonics from the treatment of our diamond due to the stamp-transfer. Thus it is critical to identify the remaining sources of spectral diffusion and charge instability, in order to mitigate these.

In Sec. 2.4.3, we discussed the physical origin of spectral diffusion, the stochastic Stark shift of a color center's optical emission due to fluctuating electric fields. These fluctuating electric fields originate from nearby ionizing charge traps, which can be exacerbated by strain. We also discussed in Sec. 2.4.4 several ways that color centers could be ionized, including direct photoionization of the color center being studied, or ionization via capture of free charge carriers.

Published results by van Dam et al. [103] and Kasperczyk et al. [50] determined that color centers that possess high optical coherence created by N^+ implantation and annealing are predominantly formed by implantation-induced vacancies diffusing and combining with native nitrogen deeper in the diamond. Prior to the work presented in this chapter, it is unclear what limited the optical coherence of the shallow color centers formed from the im-

planted ions. Two possibilities were charge traps associated with the surface of the diamond or charge traps related to unwanted defects formed from the ion implantation and annealing process.

Since ion implantation is currently the only reliable way to form color centers deterministically close to the surface, it is not obvious how to isolate these two potential sources of charge traps. Furthermore, PLE on current color centers relies on some mechanism to recharge a defect after ionization. This is usually in the form of optical excitation, such as green illumination, which results in photoionization of defects another potential source of spectral diffusion.

One possible solution to isolate the effects of surface traps and implantation damage is to prepare two identical diamond substrates and modify the acceleration voltage, and thus the implantation depth. Then, through careful characterization of the spectral diffusion of many color centers one could determine if the depth of implantation is correlated with the spectral diffusion. However, this wouldn't produce 'identical' samples, and thus wouldn't give a conclusive answer to our question. Modifying the acceleration voltage not only affects the depth of color centers, but also the amount of damage and the location of the ion relative to that damage. It may be that shallow color centers exhibit more spectral diffusion not from the surface, but because the ion ends up in close proximity to the damage it produces.

The solution we investigated is to keep the dose and depth fixed, and only change the angle of implantation. Thus the number of vacancies produced and the shape/distribution of those vacancies is identical, but the ion will be closer to the surface in the case of a high angle implantation. In order to isolate the effect of the green charge re-pump from the surface and implantation effects, we utilize only a conditional charge re-pump, i.e. we wait until the defect has bleached and is no longer detected before attempting a charge re-pump.

We are able to identify whether NV centers are formed from implanted ions or native

nitrogen by implanting with a rare isotope of nitrogen, ^{14}N . The unique hyperfine coupling of the NV electron spin to the nuclear spin provides a mechanism to determine if NV centers we investigate are formed from nitrogen incorporated into the diamond lattice during growth (^{15}N) or from implantation (^{14}N). Neither the ODMR measurement that registers the isotope, nor the development of automated PLE measurements is a central focus of this thesis. Details of the automated PLE can be found in Appendix B of [16].

4.2 *Experiment*¹

4.2.1 *Samples*

In our primary study, to elucidate the effect of the surface on the optical properties of implanted NV centers, we utilize two identical chemical vapor deposition diamonds samples A and B (Element Six, electronic grade, $\text{N} < 1 \text{ ppb}$, $\text{B} < 1 \text{ ppb}$), with $\langle 100 \rangle$ surfaces. As purchased, the diamond surfaces are polished to less than 1 nm RMS surface roughness. Both samples are processed identically unless stated otherwise. First, we etch away $\approx 5 \mu\text{m}$ from the surface using plasma reactive-ion etching to remove polishing damage [18]. We take the following precautions to avoid micro-masking that is a common occurrence during diamond etching: At each step the diamonds are cleaned in a boiling 1:1:1 mixture of H_2SO_4 , H_2NO_3 and HClO_4 at 260°C for one hour to remove organic contaminants and graphitic carbon [18]. A sapphire carrier wafer is utilized to prevent silicon contamination of the diamond surface during the etch [53]. We utilize a two step Ar/Cl plasma (physical etching via sputtering) followed by O_2 plasma (chemical etching via oxidation) process to remove any deposited material that may result in micro-masking. The total etch duration is 45 min of Ar/ Cl_2 and 20 min of O_2 etching. Post processing, both diamonds have nearly identical surface

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morphology with sample A (B) exhibiting 0.63 (0.43) nm RMS roughness (Fig. 4.1a).

We implant both samples A (B) with ^{15}N at identical energies and effective beam dosages of 85 keV and $3\text{e}9\text{ ions/cm}^2$. The implantation angle for samples A and B are 7° and 85° respectively. We model the effect of the different ion incidence angles on the implantation profile using the Stopping and Range of Ions in Matter (SRIM) code [119]. For sample A (B), the average depth of the ^{15}N atoms is 100 ± 20 (21 ± 13) nm below the surface. Although the effective beam dosage is the identical for both samples, approximately 41% of the incident ions are back-scattered for sample B. This back-scattering is a geometric consequence of rotating the damage profile relative to the surface, such that some of the scattered ions escape the diamond surface. Hence the final ^{15}N density in sample B is predicted to have 60% the density of sample A.

The samples are vacuum annealed at $< 1.4\times 10^{-7}$ mbar, 1100°C for two hours with long ramp times as described in Ref. [18, 103]. This is followed by a short two hour anneal at 435°C under O_2 flow to oxygen terminate the surface and stabilize the negative charge state [?, 112] of the near-surface NV centers.

In addition, we characterize four supplemental diamond NV implantation samples (C-F) to support the reproducibility of the primary study. These diamond substrates have identical specifications (Element Six, electronic grade) but are sourced from different growth runs. Pre-implantation, all samples are processed as detailed in this section. The specifics of implantation/annealing conditions for each sample are provided in the table accompanying Fig. 4.4.

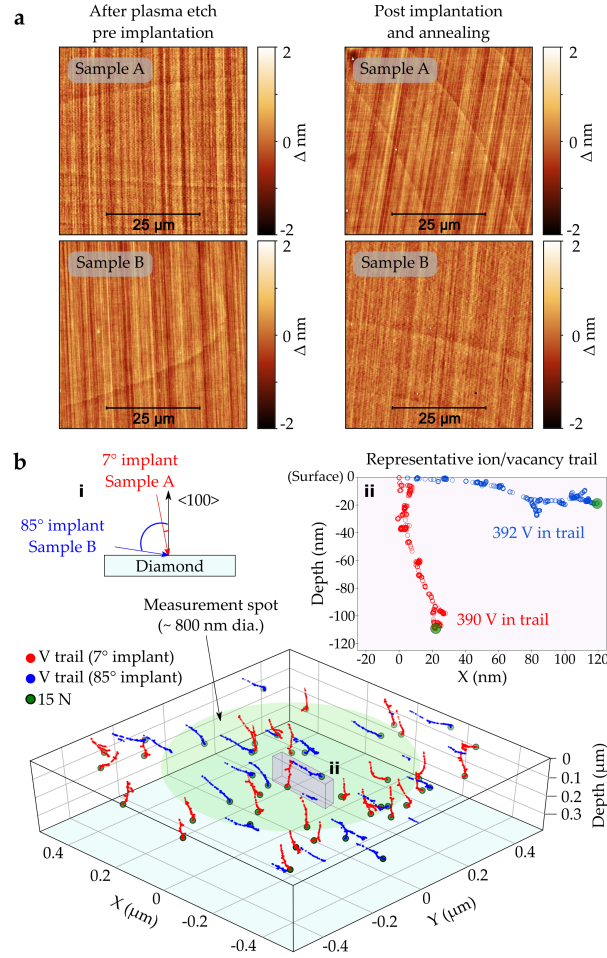


Figure 4.1: Diamond surface preparation and simulations of implantation conditions: **a.** Morphology of the diamond surface measured by atomic force microscopy. The RMS surface roughness for sample A (B) was measured to be 0.63 (0.43) nm before implantation and 0.56 (0.30) nm after implantation and annealing. **b.** A simulation of the implantation profile obtained by SRIM for sample A (red, 7°) and sample B (blue, 85°) showing the damage trails and final positions of implanted ¹⁵N atoms. The green circle represents our excitation laser spot. Note that the implantation yield is low (<5%), hence within an excitation spot there is a small probability each trail results in a NV center upon annealing. **Inset i.** Illustration of the implantation geometry. **Inset ii.** A cross-section of the simulation showing the ion damage trails for the two implant angles. Total vacancies generated per ion is similar for both the implant angles. However on sample B, some ¹⁵N atoms are lost due to ion scatter out of the surface. This figure reproduced from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

4.2.2 Measurements

A confocal microscope comprising a 532 nm DPSS laser and 60X (NA=0.7) objective lens is used to scan over $80 \times 80 \mu\text{m}^2$ areas using a piezo stage. A polarizing beamsplitter with an automated half-wave plate is used in the excitation path to preferentially excite a given NV orientation.

To identify the nitrogen isotope associated with each NV center, we use optically-detected magnetic resonance (ODMR) spectroscopy. For an NV in the $m_s = \pm 1$ ground spin-sublevel, reduced photoluminescence (PL) is observed upon off-resonant excitation due a small likelihood ($\approx 20\%$) of relaxation through the dark inter-system crossing transition [36, 102] (dotted line, Fig. 4.2a).

Low-temperature NV^- PL spectra under CW 532 nm excitation provides the inhomogeneous distribution of the ZPL transition (Fig. 4.5) arising from variations in the local strain and electric field environment of individual centers. The NV charge state ratio (NV^-/NV^0) is also recorded as a function of the excitation intensity for a subset of centers [16]. Additionally, high resolution photoluminescence excitation (PLE) spectroscopy provides insight into the optical coherence and temporal spectral stability of individual NV centers. In PLE measurements, a narrow-band tunable laser is scanned across the NV^- ZPL while collecting the NV^- phonon-sideband PL (650 nm to 800 nm) (Fig. 4.2e). The resonant laser and accompanying 2.9 GHz sidebands simultaneously drive the $\{m_s=0, m_s=\pm 1\} \rightarrow \{E_x, E_y\}$ transitions [88, 100, 33].

From the PLE spectra we collect statistics on the ZPL single-scan linewidth as well as the scan-to-scan variation in the ZPL frequency. During PLE we can sometimes observe a loss of the NV^- PL signal due to ionization to the NV^0 state; to reinitialize into the NV^- charge state we apply a short low power 532 nm re-pump pulse (50 ms) between scans (as indicated by the green markers in Fig. 4.2f). The interval between re-pump pulses is an

additional indicator of the stability of NV^- charge state.

4.3 Correlated ODMR and PLE spectroscopy²

On sample A, ODMR was performed on 32 NV centers with 26 centers identified as ^{15}NV , one as ^{14}NV ; remaining five NVs could not be conclusively identified. Similarly, on sample B, ODMR was performed on 38 NV centers with 27 centers identified as ^{15}NV , two as ^{14}NV ; the remaining nine NVs could not be identified. The observed total NV density for sample A (B) is $1.2/\mu\text{m}^2$ ($0.3/\mu\text{m}^2$) corresponds to an implantation conversion yield of 4 % (1 %). For both these samples, no grown-in NVs were observed in a $80\mu\text{m} \times 80\mu\text{m}$ area at a depth of $50\mu\text{m}$ implying very low native N_s density [27]. Considering the natural abundance of ^{15}N (0.4 %) and the $^{15}\text{NV}/^{14}\text{NV}$ ratio r for both samples ($r_A = 26$, $r_B = 13.5$), it is clear that for our diamond substrates and implantation conditions that NV formation incorporating implanted nitrogen is favored.

First let us consider sample A. The single NV low-temperature ZPL spectra under off-resonant 532 nm excitation is typically spectrometer resolution limited ($\Delta\lambda = 0.021\text{ nm}$). PLE spectroscopy reveals that both ^{15}N and ^{14}N centers typically exhibit near lifetime-limited linewidths. A sequence of laser scans over a span of ≈ 10 minutes (each scan is 4 to 8 s in duration) gives us a median linewidth of $< 60\text{ MHz}$ for 12 out of 16 centers (Fig.4.3a). This linewidth is computed by individually fitting each scan to a Lorentzian. The laser intensity is set between 30 to 60 nW with a scan rate of 1 to 2.5 GHz/s. A linewidth power dependence measurement was performed on two centers to ensure that the observed linewidths are not significantly power-broadened in our intensity range. The PLE results are summarized in Fig. 4.3a; the solid boxes mark the fitted linewidths between first and third quartile. This

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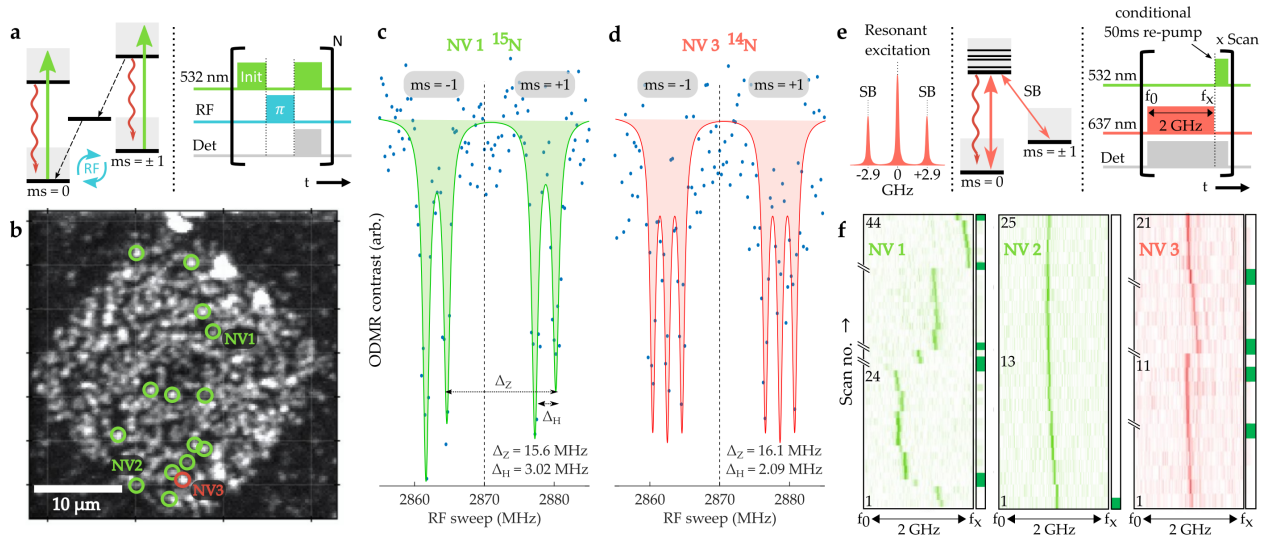


Figure 4.2: Correlated NV ODMR (RT) and PLE ($T < 12\text{K}$) measurements on sample A: **a.** Pulsed ODMR scheme utilized to identify the N isotope. Laser and radio-frequency (RF) pulses are generated by an acousto-optic-modulator and RF switch, respectively. (Laser power 0.8-1.0 mW, spot diameter $\sim 800\text{nm}$.) Pulses and photon collection are triggered by a programmable pulse generator. **b.** Confocal PL map of the implanted region with the measured NV centers indicated by their isotope (green ^{15}N , red ^{14}N). **c.** ODMR spectra for the marked NV incorporating implanted ^{15}N . **d.** ODMR spectra for the marked NV incorporating grown-in ^{14}N . **e.** Resonant excitation (PLE) scheme utilized for characterizing the optical coherence of the marked NV centers. Sidebands at 2.9 GHz are added (using an electro-optic modulator) to the scanning resonant laser to counteract optical spin pumping. Upon detection of an NV^- to NV^0 ionization event (indicated by lack of NV^- PL) a 50 ms off-resonant green re-pump is used to reset the NV charge state. **f.** Time traces of PLE scans measured at 10.5 K for three NV centers. Off-resonant re-pump between scans are indicated by green squares along the right column, this induces large spectral jumps in many ^{15}NV centers (e.g. NV 1). The '\n' markers along the scan axis indicate discarded scans where no NV PL is observed. The PLE traces for ^{15}NV centers typically show long periods of spectral stability between re-pump pulses. This figure reproduced from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

interquartile range is an indicator of spectral diffusion ($\Delta\nu$) of the NV ZPL during a single resonant laser scan (on the timescale of ms).

Additionally, by tracking the ZPL frequency between scans, we can characterize the long

term spectral stability (on the timescale of s). We calculate this spectral variation ($\Delta\omega$) by recording the change in ZPL frequency between subsequent scans (Fig.4.3b). Here, we emphasize that an off-resonant re-pump pulse is only applied when no NV PL is detected (i.e. NV^- has ionized to NV^0) emulating emerging NV quantum networking protocols [74, 45]. The median spectral variation is typically < 100 MHz, for long periods (60 to 300 s) between re-pumps. We observe that most ^{15}NV centers experience large spectral jumps (≈ 500 MHz) after an off-resonant re-pump pulse. These jumps occur in 95% of the re-pump events. In Fig.4.3b, the blue markers indicate re-pump triggered spectral jumps. This is the only metric where we see a clear advantage for the ^{14}NV also observed on sample A (Fig. 4.3, red). It is unclear at this time if the re-pump triggered perturbation originates at the surface (with the single ^{14}NV lying deeper within the sample) or from local implantation damage. Nevertheless, it may still be mitigated with the use of a low-power resonant NV^0 re-pump pulse [94].

Sample B reveals a different story, the low-temperature ZPL spectra under off-resonant 532 nm excitation for individual NV centers is much broader (0.02 to 0.25 nm;). Given that the lattice damage profile is similar to sample A, this spectral broadening could be attributed to rapid fluctuations of surface charges effectively Stark-tuning the NV centers within the exposure duration of the spectra. Such rapid ZPL fluctuations make resonant 637 nm PLE measurements very challenging. Of the six NV centers randomly sampled, only three showed PLE signal. All three NV centers (two ^{15}N and one ^{14}N) exhibit broad median linewidths (0.5 GHz to 1.2 GHz) and increased spectral variability (Fig. 4.3).

Finally, we confirm that the NV^- charge state is preferred across the full range of optical powers (15 to 600 μW of 532 nm excitation) for both samples A and B (Appendix C of [16]).

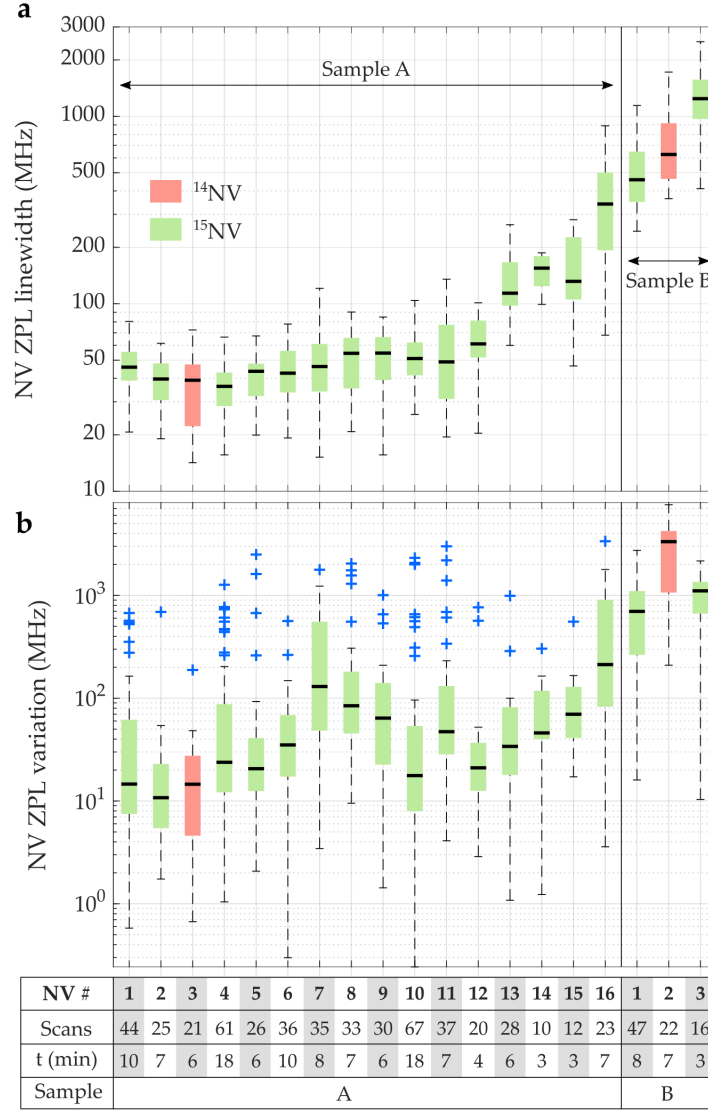


Figure 4.3: Photoluminescence excitation characteristics of measured NV centers on samples A and B: **a.** The fitted Lorentzian FWHM distributions for each observed NV. The color box and black marker represent the interquartile range and median linewidth respectively. The total number of scans and measurement duration comprising each distribution is recorded in the accompanying table. The PLE traces for NV centers 1 to 3 are also shown in Fig. 4.2f. **b.** The distributions of the scan-to-scan change in the center frequency of the fits, representing spectral variation. Off-resonant re-pump pulses are only applied when NV ionization is detected. On average, there are six re-pump events over a measurement duration of 10 min. The blue markers indicate large spectral jumps after re-pump pulses. This figure reproduced from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

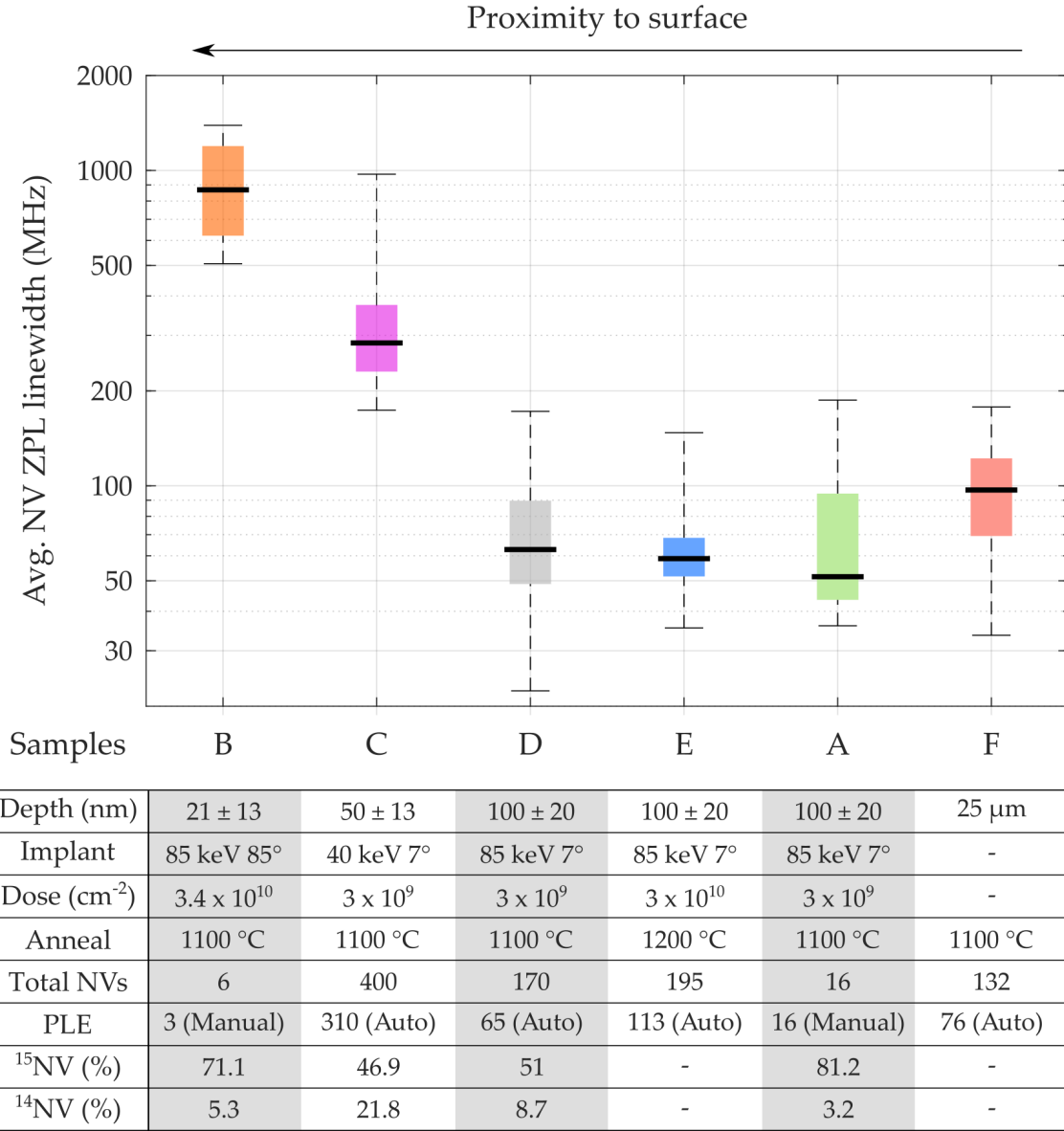


Figure 4.4: Automated ODMR and PLE measurements are performed on four additional samples (C to F). We are not able to track the NV centers between ODMR and PLE with the automated protocol. ODMR ¹⁵NV/¹⁴NV ratio suggests predominance of ¹⁵NVs across all implanted samples. Similar to the previous dataset (Fig. 4.3), the average linewidth for each individual NV is computed as the mean FWHM obtained by fitting each of the 30 frequency scans to a Lorentzian. Automated PLE scans performed on deep grown-in NVs (25 μm from surface, sample F) are used as a reference. This figure reproduced from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

4.4 Automated spectroscopy³

To corroborate the data from our primary samples (A, B), we present automated ODMR, PLE and low-temperature off-resonant PL spectroscopy datasets on four other samples (C to F). Our automation procedure allows us to sample hundreds of NV centers, however we are unable to track individual NV centers between PL, PLE and ODMR datasets. Details of the automated measurement protocol are provided in Appendix B of [16].

First, let us consider samples D and E with similar implant conditions (^{15}N , 85 keV 7°) to sample A. Uncorrelated ODMR measurements on sample D show most centers are ^{15}N . The measured average ZPL linewidth distribution (Fig. 4.4) of hundreds of NV centers, tracks well with the dataset from sample A, indicating reproducibility of narrow-linewidth ^{15}NV centers. In the ideal case, the linewidth of NV centers created through ion implantation and annealing would be equal to the linewidth observed in background NV centers distributed throughout the sample. No background NV centers could be identified in either samples (A, B) and a low density prohibited automated measurements in samples (C, D, E). Automated PLE measurements on native NV centers $25\text{ }\mu\text{m}$ within sample F, a similar electronic-grade sample that has undergone high-temperature annealing (with no implantation), serve as our reference. From the data presented in Fig. 4.4, the average NV linewidth distribution of all the 85 keV, 7° implant samples are in agreement with the reference sample.

Next, we examine the shallow implantation samples. The average ZPL linewidth distribution in Fig. 4.4, shows that both the shallow NV samples C (40 keV 7°) and B (85 keV 85°) exhibit decreased optical coherence. This is despite the fact that initial implantation damage for sample C is significantly lower compared to samples A, D and E (85 keV 7°). We can use the average number of vacancies (V) generated per implanted ion trail as an analogue

³This section reproduced from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

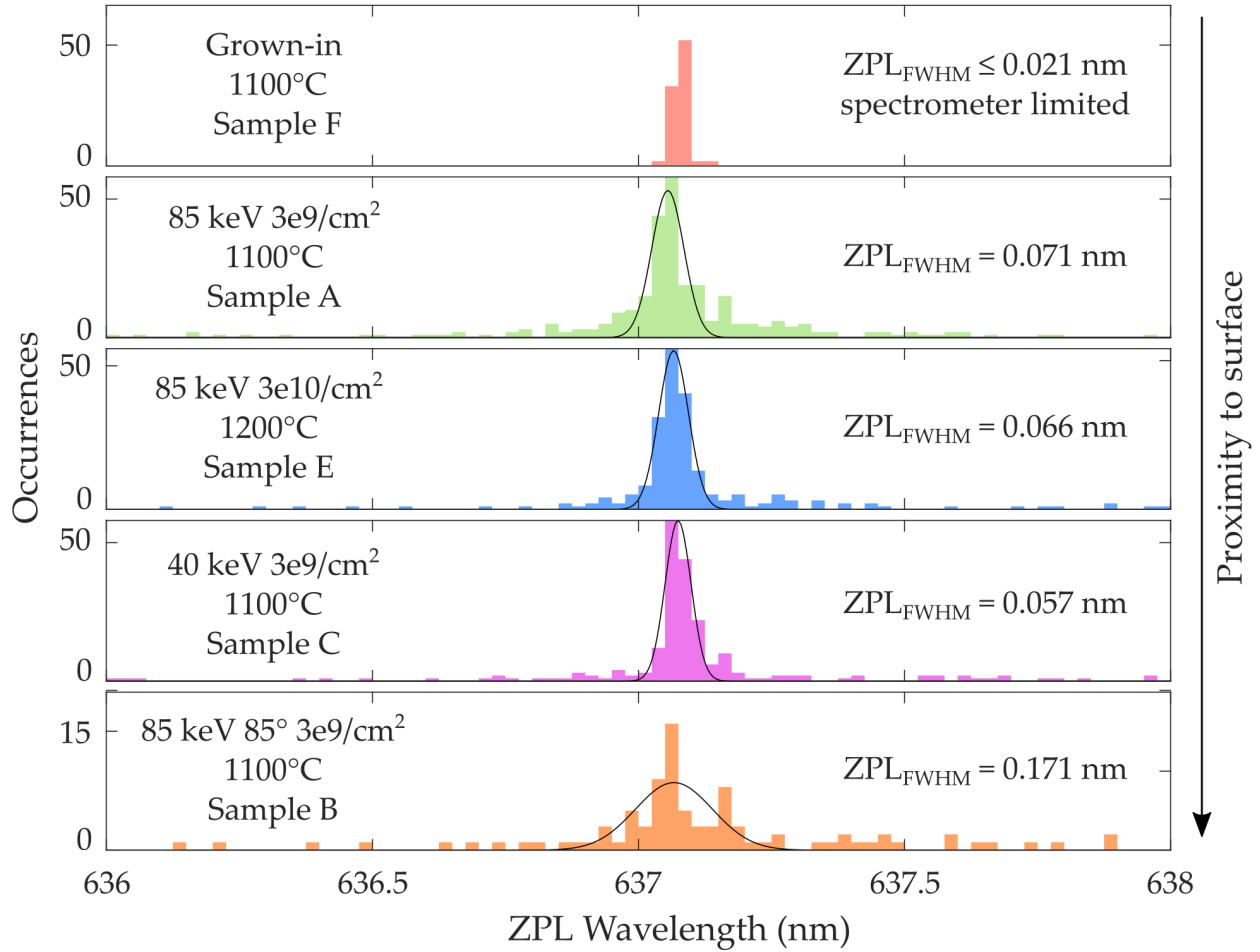


Figure 4.5: The NV ZPL inhomogeneous distribution. The histogram is generated by recording the center wavelength of all peaks observed with 532 nm excitation from locations within an implantation region (except the grown-in reference NV centers) on the respective samples. Note that no distinction is made of the different transitions associated with the NV excited state spin sublevels. The bin size is 0.025 nm, and the spectrometer resolution is 0.021 nm. The histogram data is fitted to a Gaussian to extract the full-width half max (FWHM) of the distribution. Sample B show an obvious deviation from other samples. This figure reproduced from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

for local lattice damage. From SRIM [119] simulations, sample C incorporates 203 V/ion whereas samples A, B, D and E incorporate 390 V/ion. This provides further evidence that

the broadening seen for the shallow implants is unrelated to the implantation damage at these energies and dosages and instead is a result of charge traps associated with the surface.

In addition, low-temperature PL spectra (off-resonant excitation) from a large number of NV centers provides the inhomogeneous ZPL distribution (Fig. 4.5). Regardless of the variations in the total implant damage ($\text{V}/\mu\text{m}^3$), the inhomogeneous NV ZPL distributions are similar for samples A, C and E (Gaussian fit FWHM = 52.5 GHz, 42.1 GHz and 48.8 GHz respectively). The grown-in NV centers exhibit a narrower ZPL spread (FWHM ≤ 15.4 GHz, spectrometer resolution limited). Finally, the ZPL distribution for sample B is much broader (FWHM = 126 GHz) than any of our other samples. A comparison suggests that there is still a small amount of residual strain remaining in the implantation samples.

4.5 Conclusion⁴

Lattice damage from the ion-implantation process introduces localized perturbations of the defect environment. Our result with the 85 keV 7° implant samples indicates much of this damage can be annealed out for an ^{15}NV created directly from an implanted nitrogen. We observe that ^{15}NV centers exhibit long periods of spectral stability, wherein their spectral characteristics are akin to optically coherent grown-in NV centers. The implanted ^{15}NV and grown-in centers exhibit comparable median optical linewidths. However, we do see distinct advantages for grown-in centers in terms of behavior under off-resonant green re-pump and inhomogeneous ZPL distribution. For ^{15}NV centers, green re-pump pulses used to reinitialize the NV charge state introduce large spectral variation (≈ 500 MHz). This behavior hints at why our ^{15}NV linewidths are qualitatively different from van Dam *et al.* [103] and Kasperczyk *et al.* [50]. They utilize re-pump pulses every scan, which we can see would cause linewidth

⁴This section adapted from "Srivatsa Chakravarthi, **Christian Pederson**, Zeeshawn Kazi, Andrew Ivanov, and Kai-Mei C. Fu. Impact of surface and laser-induced noise on the spectral stability of implanted nitrogen-vacancy centers in diamond. Phys. Rev. B, 104:085425, Aug 2021." [16]

broadening into GHz. In fact, an analysis considering only the PLE scans immediately after the re-pump pulse indicates our results in Sample A are consistent with the 400 nm 400 keV ^{15}N implanted sample in van Dam *et al.* Further studies are necessary to pin down the source of the re-pump triggered variation, however we can make certain inferences. Since these large spectral jumps are strongly correlated with the re-pump, we know it is related to the photoionization of some other defect in the vicinity of our studied color center, and not the movement of free carriers in the dark. Since it is more significant for shallow color centers than bulk color centers, the ionizing defects responsible are either associated with the surface or the ion implantation. Nevertheless, for the ^{15}NV centers, observation of long periods of spectral stability between re-pumps shows promise for the implementation of quantum networks with integrated photonic devices.

Further, we show that this optical stability rapidly degrades with increasing proximity to the diamond surface, corroborating measurements by Ref. [85] of NV centers in thin diamond membranes which showed strong correlation of reduced NV spectral stability with decreasing membrane thickness, not accompanied by a change in the NV strain environment. Ref. [85] suggests that the additional NV dephasing may be attributed the Ar/ Cl_2 plasma etch process even for micron-scale thick samples. Our past work has seen a similar effect on implanted centers [14], as we discussed in Chapter 3. Indeed, Ref. [54] show that $\approx 1\text{ }\mu\text{m}$ thin diamond membranes with improved diamond surface quality (etched by a soft graded O_2 plasma) can host NV centers with narrow linewidths.

Our conclusions fit into a larger narrative regarding the source of degradation of other properties near surfaces as well, such as charge state. Shallow color centers are extremely sensitive to the chemical treatment of the surface, as we discussed in Chapter 6 and prior works [41, 32]. In extreme cases, the preferred charge state can be NV^0 and PLE becomes impossible without continuous re-pump. This motivates novel techniques for precise surface

functionalization and characterization, which is the focus of Chapter???. Furthermore, it also motivates the use of other color centers that not only possess small sensitivities to electric fields but can also be excited without photoionizing, and have small carrier capture cross-sections. One potential candidate is SiV^0 , which we will discuss in Chapter??.

Chapter 5

LASER-ASSISTED SURFACE FUNCTIONALIZATION

*5.1 Introduction to Fermi level engineering*¹

In previous chapters, we focused on quantum information applications of color centers, but color centers are also attractive platforms for quantum sensing due to their long spin coherence times and spin-selective optical transitions [108, 5]. For a given application, a particular charge state of the defect is required. As we discussed in Sec. 2.2.4, this charge state can be passively controlled by Fermi level engineering of the host crystal, typically through bulk impurity doping [76, 25, 84]. However, control over the Fermi level can be challenging in wide band gap semiconductors due to limits in dopability [104]. For quantum sensors and integrated quantum photonics, the defect must be close (nanometers to hundreds of nanometers) to the surface. This opens up an additional control knob, surface Fermi level engineering. Control over the surface Fermi level can be realized via active techniques such as gating [49, 90] or passive techniques such as chemical surface functionalization [41, 32, 117, 82]. Control over the surface termination is additionally attractive because it not only affects the defect charge state, it also affects defect spin [86] and optical properties [16]. This surface sensitivity indicates a pressing need for engineering atomically ordered surfaces with the desired electronic structure.

A large body of existing work in diamond surface science has focused on electronic ap-

¹This section adapted from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

plications [20]. Now, the impact of these surfaces on quantum point defect properties in diamond is receiving attention. We demonstrated in Chapter 3 the sensitivity of the charge and optical stability of color centers to the exposure of plasma. This was not surprising, as optical measurements have directly linked the ratio of fluorescence of near-surface neutral nitrogen-vacancy centers NV^0 and negatively charged NV^- centers to the degree of oxidation and hydrogenation [41, 32]. Later work has shown similar switching between the neutral SiV^0 and negatively charged SiV^- [117]. In both cases, the surface termination was switched in a binary fashion between an oxidized surface and hydrogenated surface. However a desired defect may require an intermediate termination. For example, in the case of SiV^0 , theoretical calculations of the formation energies suggest that near-surface SiV may not be in the desired neutral charge state for strongly hydrogenated or strongly oxidized surfaces [34].

To date, the primary method for determining the effectiveness of the surface treatment is typically the direct optical probing of the quantum defects, in particular when the device size is small (microns) [90] compared to standard large-area surface characterization techniques such as ultraviolet photoelectron spectroscopy (millimeters). In this work, we combine optical probing with conductive atomic force microscopy (C-AFM) and Kelvin probe force microscopy (KPFM) techniques. The scanning probe techniques work under ambient conditions, high vacuum, on fabricated electronic devices, and even under optical excitation, enabling measurements under practical experimental conditions. We find a strong correlation between the scanning probe measurements and the charge state and emission intensity of the quantum defects. We further utilize the method to study laser-assisted oxidation which provides controlled surface modification with optical spatial resolution. Finally, correlated measurements show a significant acceleration of oxidation of hydrogen-passivated surfaces in ambient conditions in the presence of implantation damage.

5.2 Sample preparation²

We implanted five chemical vapor deposition diamond substrates on the (100) surface (Element Six, ELSC grade), named A-E, with silicon and nitrogen. Samples A-D were preliminary samples used to verify the hydrogenation of our samples in the hydrogen plasma, and to study the behavior of our color centers at different depths. The preliminary measurements of these samples is discussed in Sec. 5.5. Sample E was implanted and annealed after initial characterization on the preliminary samples, at an intermediate depth but higher annealing temperature. The nominal nitrogen and boron substrate concentrations for all samples are specified as less than 5 ppb and 1 ppb, respectively. Prior to implantation, we etched the top 5 microns of each sample's surface in an Ar/Cl RIE plasma and oxygen plasma [16] to remove surface damage from polishing and prior implantation. We co-implant all samples with nitrogen and silicon at fluences of 10^{10} cm^{-2} and 10^{11} cm^{-2} , respectively. The acceleration voltage and mean depth of the N^+ and Si^+ are provided in Table 5.1 for each sample. We implanted at an angle of 7 degrees from normal through a TEM mask, resulting in implantation squares (Fig. 5.1(a)). The mean implantation depth for each sample is simulated by SRIM [119]. We chose the implantation depth such that the quantum defects lie in the band bending region of the surface, and thus are sensitive to surface terminations [41].

We utilized the implanted nitrogen to form NV centers, whose charge state is very sensitive to band bending and relatively well understood, whereas we used silicon for forming SiV in order to further our understanding of SiV charge state stabilization. We annealed samples A-D at 800 °C for 2 hours under vacuum (10^{-7} mbar), and sample E at 1200 °C for 2 hours under vacuum to mobilize the vacancies produced by ion implantation, form both

²This section adapted from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

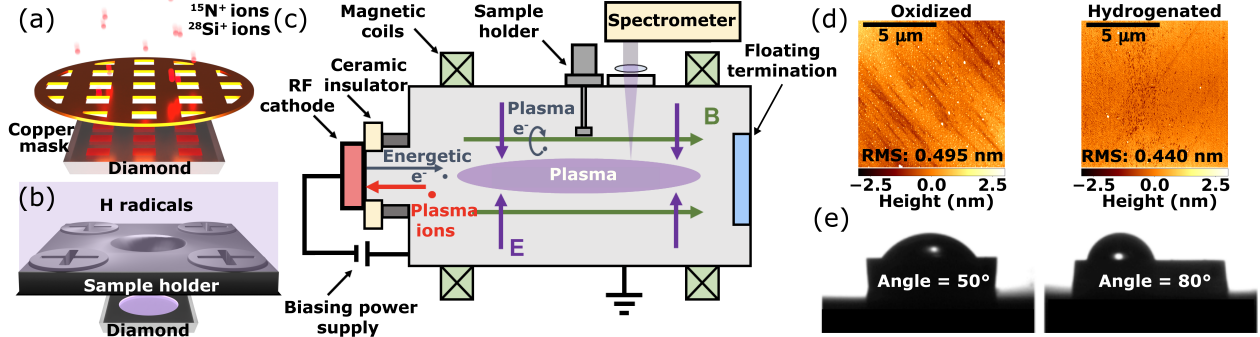


Figure 5.1: (a) Schematic of implantation geometry. The diamond substrate is implanted through a TEM grid resulting in squares of implanted nitrogen and silicon. The squares are $28\mu\text{m}$ ($90\mu\text{m}$) wide in sample A-D (E). (b) Schematic of the sample holder used in the plasma reactor. A large circular window on the diamond surface is exposed to the hydrogen radicals, while the edges are masked (c) Schematic of cold plasma reactor. (d) AFM topography measurements before and after the hydrogenation showing similar surface roughness for sample A and sample E. (e) Water wetting angle measurements before and after hydrogenation show the expected increase in hydrophobicity for sample A and sample E. This figure reproduced from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

NV and SiV centers, and to anneal out residual implantation damage. Following the vacuum anneal, we boiled the samples in a 1:1:1 mixture of sulfuric, nitric and perchloric acid for 1 hour and subsequently annealed at ambient pressure in oxygen at 465°C for 4 hours to form a starting oxidized surface [32].

Next, we exposed the sample surface to a cold hydrogen plasma treatment which was shown to achieve record hydrogen termination on graphene [118]. The exposure time for each sample is listed in Table 5.1. We mounted the sample in a holder which exposes a circular region of the sample to the hydrogen plasma, with the sample edges masked (Fig. 5.1(b)). In conventional direct-current (DC) and radio-frequency (RF) plasma processing reactors, high energy hydrogen ions generated at the plasma-substrate interface (so-called sheath)

Implantation Conditions					
Sample Name	N ⁺ Acceleration Voltage (kV)	Si ⁺ Acceleration Voltage (kV)	Mean Depth (nm)	Annealing Temperature (C)	Hydrogen Plasma Exposure (min)
A	10	19	15	800	30
B	10	19	15	800	60
C	50	91	60	800	30
D	50	91	60	800	60
E	18	34	25	1200	60

Table 5.1: Implantation and annealing conditions of the 5 samples

and energetic atoms generated due to charge-exchange collisions between ions and atoms can induce substantial damage by irreversible etching and sputtering. In contrast, the cold hydrogen plasma is generated by non-thermal electrons in crossed electric and magnetic fields, so-called cross-field or ExB plasma discharge (Fig. 5.1(c)). The sample is held beneath the confined plasma to expose the surface to hydrogen radicals (rather than ions). The electric field is directed inward, *i.e.* away from the substrate, preventing energetic ions from impinging on the substrate. AFM measurements confirm a similar RMS roughness before and after H treatment (RMS=Fig. 5.1(d)). Additionally, the sample surface becomes hydrophobic (Fig. 5.1(e)) which is expected for hydrogen passivation [20]. As we see in Sec. 5.5 and Sec. 5.7, this masking allows us to probe the continuous region between the oxidized and hydrogenated surfaces.

5.3 Oxygen and hydrogen terminated diamond surfaces

In order to understand why the surface termination is so important, we need to discuss how the surface termination modifies the Fermi level near the surface. Within the bulk of diamond is a periodic arrangement of carbon atoms each bonded to their 4 neighbors through sp^3 orbital bonding. At the surface the carbon is forced to adopt a different configuration,

known as surface reconstruction, to minimize the energy of the otherwise dense arrangement of dangling bonds. Different diamond surfaces (e.g. the $\langle 100 \rangle$ or $\langle 111 \rangle$ surface) have different exposed planes of carbon and many different chemical species can serve to terminate these dangling bonds. The study of surface reconstructions is complex, especially as there can be multiple co-existing surface reconstructions [20].

For the purposes of this work, it is not necessary to know the exact surface reconstruction. Instead we will merely designate the chemical species that participates in the surface reconstruction and the method by which this chemical species was incorporated. We discuss why surface reconstructions involving the same chemical species have similar properties. Still, the possibility of multiple co-existing surface reconstructions explains why not all oxidized or oxygen-terminated diamond has *exactly* the same properties.

There are many known ways to achieve oxidation of diamond, such as heating in oxygen, exposure to oxygen plasma, electrochemical oxidation, UV-ozone treatments which have all been characterized according to their oxygen incorporation [35]. Within the field of color centers, one of the most common treatments involves heating the diamond in an oxygen rich environment at 465°C for a few hours [32], which is how our samples are oxidized.

For hydrogen termination, there are several techniques as well. Synthetic diamond grown via PECVD already possesses a hydrogen termination due to the high concentration of hydrogen in the growth chamber [20]. Thus all of our CVD samples, A-E, started with a hydrogen termination before processing. More recently, it has been discovered that high temperature annealing of diamond in a molecular hydrogen rich environment results in hydrogen termination [91, 117]. However the most common technique is exposure of the diamond to a hydrogen containing plasma. In this work, we utilize a hydrogen plasma that was shown to achieve record hydrogen termination in graphene [118].

Even though this effect only modifies the surface of the diamond, the chemical termina-

tion can have dramatic consequences on the diamond's properties easily observable at the macroscopic scale. For example, oxidized diamond is hydrophilic and insulating while hydrogenated diamond is hydrophobic and conductive [20]. The reason why this termination has such a large effect on the diamond's properties is due to two factors. First the types and concentrations of surface traps will be different depending on the termination. Second the terminating chemical bonds are densely packed and roughly aligned in the same direction resulting in potentially large dipole moment densities.

Defects on the surface of a semiconductor have a large impact on the electrical properties. These defects can introduce states within the bandgap which can pin the Fermi level, just like defects within the bulk. It is a common problem in many semiconductors to have a Fermi level pinned mid-gap at the surface for precisely this reason. The oxidized diamond surface is believed to have a surface Fermi level pinned due to carbon atoms double-bonded to carbon atoms, so-called primal sp^2 defects [96]. Hydrogenated diamond has significantly lower concentrations of such defects [96].

The other major effect of surface reconstruction is the formation of a dipole layer. We can quantify this dipole moment density with a quantity known as the electron affinity. The electron affinity is defined to be the energy difference between a conduction electron at rest just inside the diamond and a free electron at rest just outside the diamond, as depicted in Fig. 5.2(a). The electron affinity is the energy barrier an electron in the conduction band would need to overcome to escape the diamond due to the surface electric dipole moment. In the case of oxidized (hydrogenated) diamond, carbon is less (more) electronegative than oxygen (hydrogen) and the electron affinity is positive (negative). Unfortunately, we do not have the ability to image the electron affinity directly in our work, but the values of the electron affinity for hydrogen and oxygen terminations are known from literature [41].

The electron affinity is an important quantity because it determines the direction of elec-

tron transfer when a material is brought in electric contact with another, for example when exposed to atmospheric adsorbates. We depict the hypothetical electron transfer that would occur between a doped semiconductor and an atmospheric adsorbate under the conditions of a large positive electron affinity or a large negative electron affinity in Fig. 5.2(b).

Another important quantity, closely related to the electron affinity, is the work function of a material. Just as the electron affinity is the difference in energy between an electron in the conduction band and at rest just outside the material, the work function is the difference in energy between an electron at the Fermi level and at rest just outside the material, also depicted in Fig. 5.2(a). The work function will always be positive, otherwise electrons would spontaneously be emitted from the material. The difference in two material's work functions is called the contact potential difference (CPD). The CPD is an important quantity because unlike the electron affinity, we can directly measure it, and it is very sensitive to the surface termination.

5.4 *Surface state-induced band bending*³

Surface state-induced band bending is the phenomena describing electron transfer between the bulk and surface of a semiconductor which generates a corresponding electric field and space charge region within the semiconductor. The samples studied in this work are high purity, n-type diamond substrates with a nominal nitrogen donor density less than 5 parts per billion, or $8.8 \times 10^{14}/\text{cm}^3$ (Element Six, ELSC grade). Due to the large ionization energy of the nitrogen donors, 1.7 eV [30], the intrinsic free electron density is negligible at room temperature. Therefore the space charge region inside the bulk of diamond is composed primarily of ionized nitrogen donors.

³This section adapted from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raites, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

The corresponding surface acceptor states are distinct between hydrogenated and oxidized diamond due to differences in two factors: the surface defect density, and the electron affinity. The difference in surface defect density was investigated in [96], which found that as-grown hydrogen terminated diamond had significantly lower concentrations of double-bonded carbon defects at the surface compared to samples prepared via various oxidation techniques. The higher surface density for oxidized diamond results in Fermi pinning that is predicted to lie in the 0.6 eV band between 1.8-2.4 eV [47, 96]. The electron affinity varies between -1 eV to 1.7 eV from fully hydrogenated to oxidized diamond [41]. The difference in sign of the electron affinity is attributed to the opposite polarity of C-H and C-O bonds whereas the large magnitude is related to the large electronegativity difference between carbon and hydrogen as well as between carbon and oxygen. For hydrogenated diamond, the magnitude of the negative electron affinity (χ_H) can be large enough that the valence band maximum lies above atmospheric acceptor states (μ_{atm}) [20]. Thus in addition to band bending from the ionized nitrogen donors, there will be band bending due to the electron transfer from the valence band to these atmospheric states.

We can estimate the depth d of the band bending region for the two terminations following Ref. [96] which is based on Mönch's [64] treatment of band bending in semiconductors with static ionized impurities and no minority carriers. For a uniform concentration of ionized nitrogen donors,

$$d = \sqrt{\frac{2\epsilon_d\epsilon_0 V_{bb}}{eN_d}}.$$

Here $\epsilon_d=5.7$ is diamond's relative permittivity, V_{bb} is the band bending height, and N_d is the nitrogen donor density. In hydrogenated diamond the Fermi level is pinned at the nitrogen donor level in the bulk and at the valence band maximum in the surface. Since the nitrogen donor level is 3.8 eV above the valence band [30], $V_{bb} \geq 3.8$ V resulting in a minimum $d = 1.65 \mu\text{m}$. For oxidized diamond the surface is pinned by the surface defects

at ≈ 2.4 eV, resulting in $V_{bb} \approx 1.4$ V, corresponding to $d = 1$ μ m. This depth represents the maximum depth over which one can control the charge state of a defect with surface functionalization and is significantly deeper than typical implantation depths for quantum sensing and information applications.

In Fig. 5.3(a) we illustrate how the charge state of the NV center varies with depth due to the band bending we just calculated. The formation energies of the NV center charge states are taken from [22]. The dominant charge state in each shaded region is labelled. Both hydrogenated and oxidized surfaces have the same Fermi level in the bulk, in the NV^- charge state region. In the hydrogenated case, the band bending results in the Fermi level crossing into the NV^0 regime for intermediate depths and NV^+ close to the surface. In Fig. 5.3(b), we can see that NV centers within the top 50 nm should all be positively charged and optically inactive. This is consistent with the lack of photoluminescence observed in our measurements immediately after hydrogen plasma exposure. On the oxidized side, the Fermi level remains very close to the boundary between negatively charged and neutral states in the top 50 nm.

Fig. 5.3(b) illustrates the relationship between work function, electron affinity, and CPD. Although the CPD appears as a small potential difference on this scale, this is relative to diamond's large band gap of 5.5 eV. The approximately 300 mV CPD signal between the two different surfaces is relatively large and easily resolvable in FM-KPFM, even under ambient conditions.

In Fig. 5.3(c-d) we provide similar diagrams for the SiV states using the formation energies calculated in Ref. [34]. We note that for promising defect species like SiV^0 and SiV^- , an intermediate termination between hydrogenation and oxidation may be desired.

Fig. 5.3 is a schematic illustration to highlight the role of the work function and electron affinity in the CPD measurements. We do not measure the electron affinity directly, however

as Fig. 5.3(b) illustrates, the change in the electron affinity from a hydrogenated to oxidized surface is given by $\Delta\chi = \Delta E_F + \Delta W$. Using the estimated surface Fermi levels from above, we estimate $\Delta\chi=2.1$ eV which is slightly less than the 2.7 eV one would expect from the reported electron affinities of -1 eV and 1.7 eV for hydrogenated and oxidized diamond. This discrepancy could be due to a Fermi level that is deeper in the valence band than we conservatively predicted on the hydrogenated side, or a reduced electron affinity magnitude on either termination due to long term exposure to atmosphere.

5.5 Optical investigations of color centers under oxidized and hydrogenated surfaces

In this section, we will demonstrate our ability to consistently hydrogenate samples without etching of the diamond substrate, and the effect of hydrogenation we observe on the PL of NV and SiV centers. Fig. 5.4 shows sample A-D, whose parameters are provided in Table 5.1. The samples were originally annealed in oxygen gas at 465°C for 4 hours to form the oxidized surface. After initial characterization, they were exposed to a hydrogen plasma.

Fig. 5.4 shows wetting angle measurements and AFM scans performed before and after the hydrogen treatment described in Ref. [118], revealing a change from a variety of hydrophilic surfaces to a consistently hydrophobic surface. No evidence of plasma induced roughening is present.

Fig. 5.4 shows confocal images taken on samples A-D after the oxygen anneal revealing bright squares consisting of NV and SiV fluorescence on all 4 samples. The square pattern is due to a TEM grid which masked the samples during implantation, resulting in an easy identification of background surface fluorescence and fluorescence due to formed defects. After hydrogen termination the shallowest samples show no PL, while some PL can be observed for defects 60 nm below the surface. These measurements are in complete agreement with earlier work [41].

During the hydrogen plasma treatment, the sample mount only exposed a circular window of the diamond to the plasma. Confocal scans and spectra were taken of sample A at the edge of this window revealing a continuous range of PL intensity, over 270 μms . Not only was the intensity varying, but the ratio of $\text{NV}^0:\text{NV}^-$ changes. Three spectra taken from three squares are shown in Fig. 5.5.

These measurements were taken at 12 K, such that the ZPL of each species are sharp lines on the broad wavelength scale shown. The ZPL intensities are integrated and normalized by the raman intensity for each of the squares shown in the confocal, and are plotted in Fig. 5.6. This shows the clear charge state tuning of the surface from NV^+ , which is optically inactive, to NV^0 in intermediate hydrogenated regions, to NV^- in the oxidized region that was protected from the plasma.

These results demonstrate our ability to hydrogenate our samples, and optically detect differences between the oxygen and hydrogen termination through optical measurements. Next we will discuss another surface-sensitive measurement that will provide an additional way to characterize the two different surfaces.

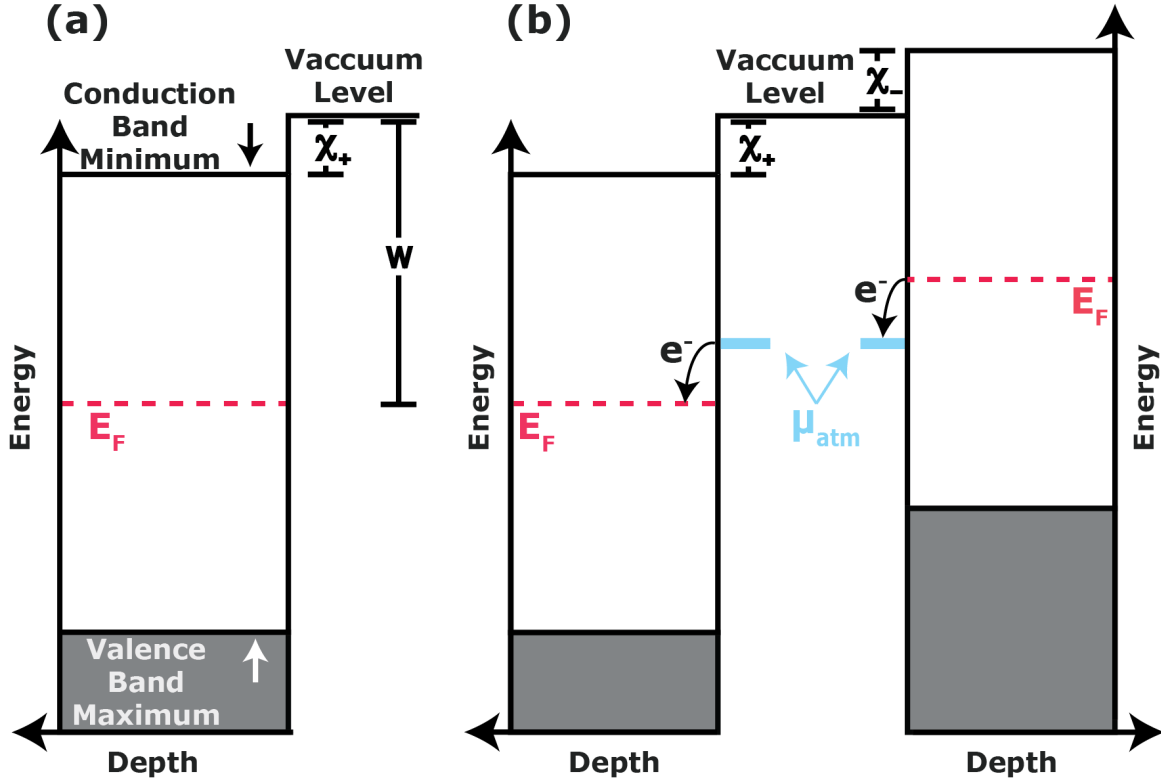


Figure 5.2: **a.** Simplified band structure of a hypothetical semiconductor with a Fermi level deep in the bandgap. The electron affinity is denoted χ_+ for the case $\chi_+ > 0$ and the work function is denoted W . **b.** Simplified band structure of two semiconductors with identical doping, but differing electron affinities. The chemical potential of the atmospheric adsorbate is denoted μ_{atm} . The diagram indicates the electron chemical potentials before contact of the semiconductor and atmospheric adsorbates, and thus before formation of the band-bending region. The left semiconductor has a positive electron affinity, χ_+ , resulting in a Fermi level lower than the atmospheric adsorbates chemical potential. Thus upon contact, electrons will be transferred from the atmospheric species to the semiconductor. The right semiconductor has a negative electron affinity, χ_- , resulting in a Fermi level higher than the atmospheric adsorbates chemical potential. Upon contact electrons will be transferred from the semiconductor to the atmospheric species.

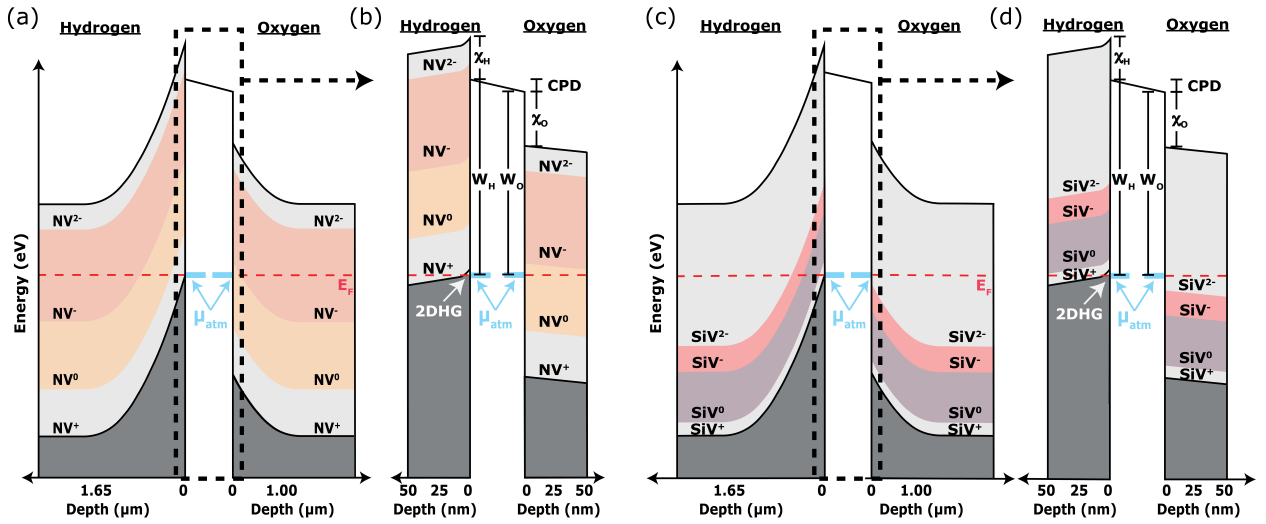


Figure 5.3: (a) Extended band bending diagram for NV centers in diamond using formation energies calculated in [22]. (b) band bending diagram for NV centers within the top 50 nm of the surface. (c) Same as (a) but for the SiV formation energies calculated in [34] (d) Same as (b) but for the SiV levels. This figure reproduced from "Christian Pederson, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

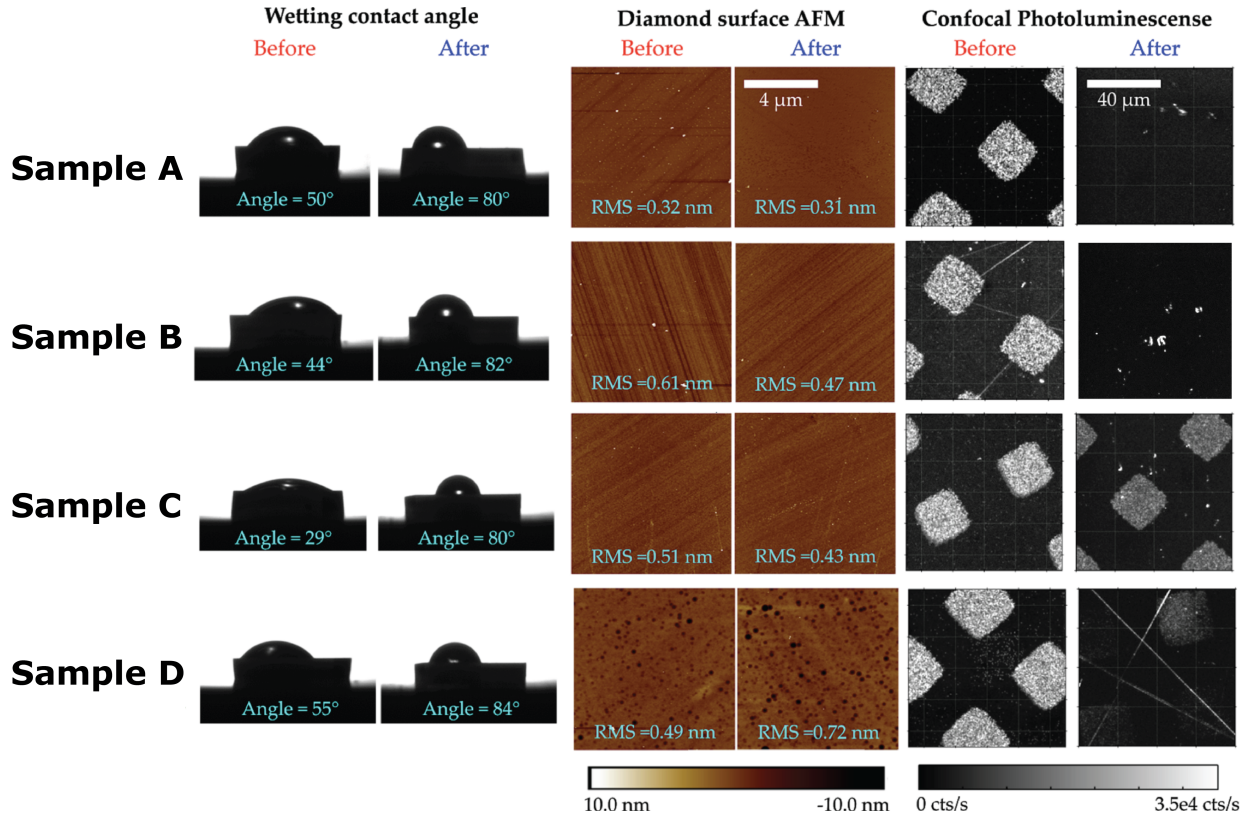


Figure 5.4: 4 diamond samples, samples A-D, implanted with nitrogen and silicon at average depths of 15 nm and 60 nm go through 30 mins and 60 mins of hydrogen plasma described in [118]. Wetting angle measurements demonstrate a change from hydrophilic to hydrophobic. AFM scans demonstrate similar surface roughness before and after treatment. Confocal scans shows a complete loss of PL that is strongest for the shallower samples.

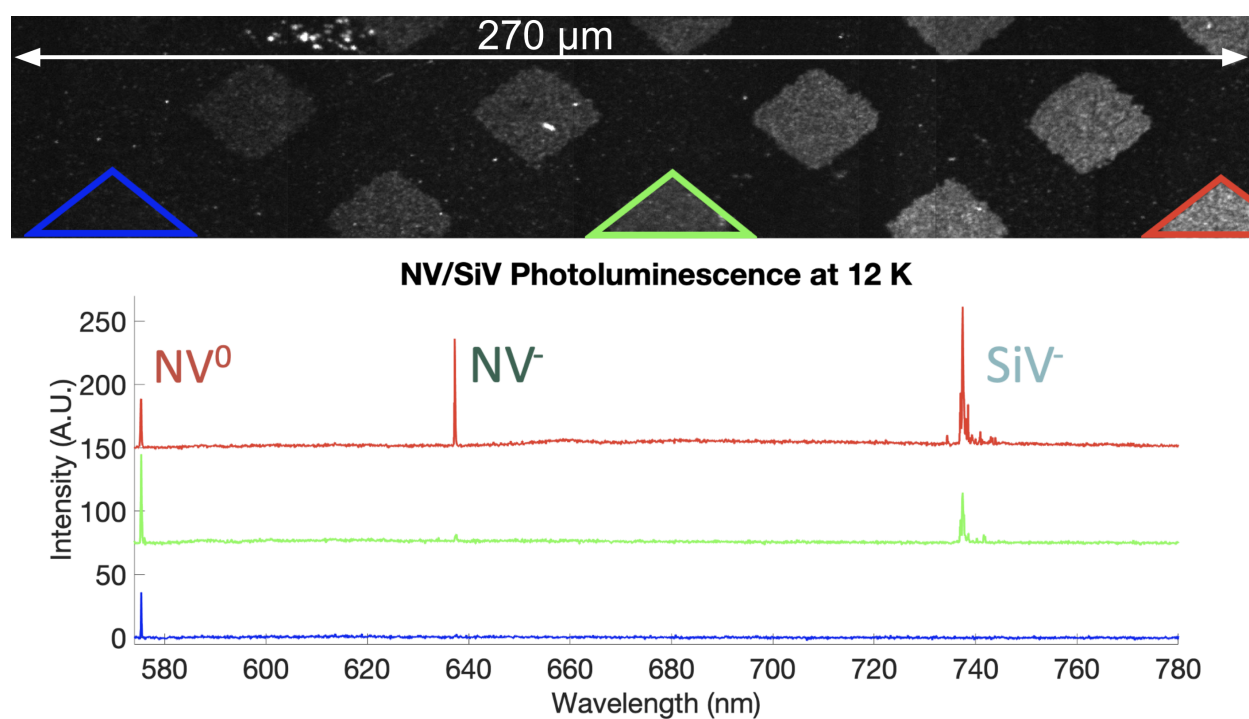


Figure 5.5: Spectra taken at 3 locations along the edge of the exposed H plasma region are shown. ZPLs corresponding to NV^0 , NV^- , and SiV^- are marked.

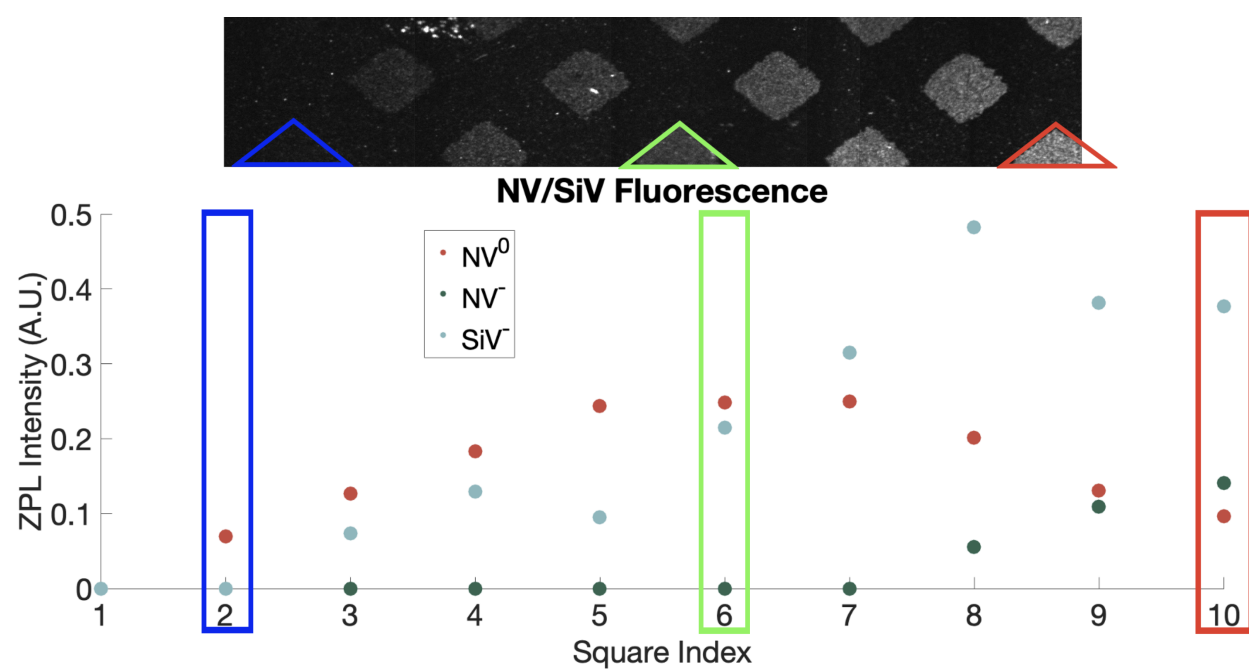


Figure 5.6: Integrated ZPL intensities at a point within each square along the edge of the exposed H plasma region are shown. The continuous conversion from NV^+ to NV^0 to NV^- are shown. SiV^- nearly monotonically increases across the scan.

5.6 *Kelvin probe force microscopy (KPFM)*

KPFM is a non-contact technique for measuring the work function of a material. It relies on the fact that an electric potential, the contact potential difference (CPD), exists between dissimilar materials in electric contact and thermal equilibrium with each other. This CPD exists because electrons will flow from the material that had the higher Fermi level before contact to the material that had the lower Fermi level before contact such that their Fermi levels are equal after contact. The actual amount of charge transferred is typically very small, but it can produce large potentials. KPFM is often performed utilizing the architecture of scanning atomic force microscopy to provide spatial imaging of these potentials. Although the measured signal is the CPD between the material and the conductive cantilever and not the work function of the material, the cantilever remains constant throughout the measurement. Thus careful calibration of the work function of the cantilever could be used to determine a precise value for the studied material.

5.6.1 *AM-KPFM*

Amplitude modulated KPFM (AM-KPFM) is the most common and simplest implementation of KPFM. In AM-KPFM, a weak AC voltage is applied to a conductive cantilever near the cantilever's resonance frequency. If there is a DC potential, i.e. a non-zero CPD, between the cantilever and the substrate, this electrical driving will induce oscillations in the cantilever. Applying a DC bias that is equal and opposite to the CPD will minimize the cantilever's driven oscillations. Using a scanning tip, the CPD can be spatially mapped over the sample.

AM-KPFM is the fastest imaging modality, but has limitations if the work function changes rapidly over the surface. This is because the entire cantilever is conductive, and so the DC bias that minimizes the oscillations is not just determined by the CPD at the sharp

tip but over the whole cantilever [62].

5.6.2 FM-KPFM

Frequency modulated KPFM (FM-KPFM) provides a way to measure potentials with much higher resolution by focusing on the effect of the electrostatic field at the tip of the cantilever. One effect of the CPD between the sample and the cantilever is that it slightly modifies the cantilevers resonant frequency. This tuning of the cantilever's resonant frequency depends on the electrostatic force gradient, which is strongest at the sharp tip of the cantilever [62]. In FM-KPFM, one images the CPD by mapping the DC bias that minimizes tuning of the cantilever's resonant frequency.

FM-KPFM is slower and noisier than AM-KPFM as it relies on two lock-in amplifiers. Nevertheless for our measurements, where the work function changes on a micron scale it is the preferred measurement.

5.7 Correlated PL, KPFM and C-AFM imaging⁴

Now that we have discussed the basic concepts of surface termination in Sec. 5.3, the theory of band-bending in Sec. 5.4, experimentally demonstrated the ability to oxidize and hydrogenate our samples in Sec. 5.5, optically detected the difference between the surfaces in Sec. 5.5, and discussed KPFM in Sec. 5.6, we are ready to discuss correlated measurements taken on samples A and E.

We performed confocal photoluminescence imaging and spectroscopy at STP to monitor the luminescence from the NV^0 , NV^- , and SiV^- . We excited and oxidized the samples with

⁴This section adapted from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

a 532 nm laser focused to a 500 nm diameter spot. The ratio of the NV^- to NV^0 luminescence is used to serve as a proxy for the Fermi level [41].

For KPFM and C-AFM measurements, we patterned the ground electrode onto the face of the diamond using e-beam evaporation through a shadow mask, and then wire bonded the electrode to a chip-carrier. The electrode consists of a 140-nm-thick gold layer deposited on a 10-nm-thick titanium adhesion layer. This lateral geometry allows both KPFM measurements and C-AFM measurements on the same area; the use of a backing plane electrode on a thick insulating substrate would prevent C-AFM measurements. We performed KPFM using both amplitude-modulated (AM-KPFM) and frequency-modulated (FM-KPFM) methods. FM-KPFM is sensitive to the electrostatic force gradient, rather than the electrostatic force as in AM-KPFM, and therefore yields better spatial resolution and a more accurate CPD, the difference between the work function of the sample and the tip. AM-KPFM is more efficient at scanning large areas quickly [62]. The absolute value of the contact potential difference measured in the KPFM signal is dependent upon the material and geometry of the tip. We performed all AFM measurements with an MFP3D AFM (Oxford Instruments) using metal-coated cantilevers (KPFM: BudgetSensors ElectriTap190-G cantilevers; C-AFM: BudgetSensors CONTG-B contact-mode cantilevers). We performed FM-KPFM using custom, publicly available code (<https://github.com/GingerLabUW/AFMSoftware>) written in Igor Pro, as in previous work [113]. We used a typical lift height of 10 nm during KPFM acquisition.

We perform correlated C-AFM, KPFM and PL spectroscopy around a narrow transition region between the oxygen and hydrogen termination transition (Fig. 5.7(a)). C-AFM measurements (Fig. 5.7(b)) confirm that the hydrogen-terminated surface on the right is conductive while the left oxygen-terminated surface is insulating. This provides further verification that the hydrogen termination has pushed the Fermi level into the valence band.

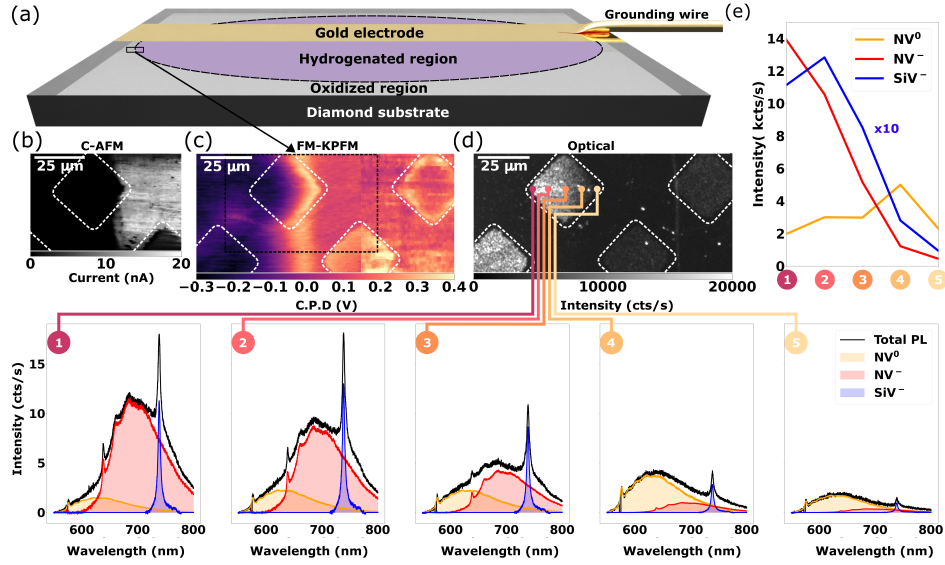


Figure 5.7: (a) Schematic of sample with electrode. (b) C-AFM image of sample A (15 nm depth) with a 5 V sample bias. (c) Stitched FM-KPFM image of sample A taken with a 10 nm lift height. A constant -70 mV offset is applied to the right scan to match the CPD in the overlapping region. (d) Confocal photoluminescence image of sample A obtained using 1 mW of 532 nm excitation. Spectra taken at 5 locations across the boundary are shown below using 0.8 mW at 532 nm. (e) Total PL intensity for the three defect charge states for the spots indicated in (d). This section reproduced from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. *Phys. Rev. Mater.*, 8:036201, Mar 2024." [71]

Additionally, a dramatic increase in resistance is observed above the implantation squares, suggesting either a loss of hydrogenation in these regions or increased scattering due to interactions between the holes and the residual implantation damage. Further measurements below support the former hypothesis.

FM-KPFM in Fig. 5.7(c) in the same region shows a 250-320 mV potential increase from the oxidized to hydrogenated surface. The size and sign of the change in surface potential

is similar to prior reports which range between 100-300 mV [97, 80]. Similar to the C-AFM data, one of the most striking features of the KPFM image is the ability to visualize the implantation squares. Additionally, we note that the CPD does not monotonically increase from the oxygen-terminated to hydrogen-terminated side, but rather has a maximum between the two regions. This behavior was observed even in the region that has not been implanted and will be discussed further below.

During photoluminescence imaging, we collected a spectral band of 653-815 nm which includes PL contributions for NV^0 , NV^- and SiV^- . The PL image shown in Fig. 5.7(d) shows bright PL emission under the oxidized surface, with very low fluorescence shown under the hydrogenated surface. Spatially resolved spectra across the square which lies on the termination boundary show that not only does the total intensity change (black spectra), but the relative contributions of the three defects, NV^- , NV^0 and SiV^- vary as well. We extracted these relative contributions by fitting the total spectrum to a weighted sum of the individual defect spectra (Fig. 5.7(d)). Fig. 5.7(e) depicts the change in PL intensity for the three defects across the termination. The PL from the negatively charged defects monotonically quench with hydrogenation, while the neutral NV^0 PL increases but eventually quenches at the highest exposure. These results are consistent with prior reports of NV luminescence after hydrogen plasma treatment which show NV centers can be left in the neutral or even optically dark positively-charged NV^+ state [41], dependent on the level of hydrogenation.

5.8 Optical control over the surface Fermi level⁵

In this section, we utilize KPFM to demonstrate that the hydrogen-terminated surface can be oxidized via laser irradiation in air. Fig. 5.8(a) depicts a confocal image of a hydrogen-terminated region in Sample A. Prior to imaging, we patterned a “W” on an implantation square using a 20 mW 532 nm laser in air focused to a 500 nm-diameter spot corresponding to an irradiance of 1.0×10^{10} mW/cm². The laser-exposed implantation square is visibly brighter, similar to the oxygen-terminated surface. AM-KPFM of the same region (Fig. 5.8(b)) reveals that the bright PL corresponds to a decrease in the work function. In AM-KPFM, due to contributions of the work function far from the sharp tip, this value likely represents a lower limit for the shift. These correlated measurements suggest that the level of hydrogen termination and thus the surface Fermi level can be tuned with laser irradiation. This result is consistent with the observation of diamond etching via laser-induced local oxidation which has been reported at much higher laser powers [79]. At the laser intensities used in this work, no etching is detectable via atomic-force microscopy. Finally we observe that the NV center responds to the laser-assisted oxidation as expected, showing a conversion to the desired negatively charged state, which is shown in Sec. I of the Supplemental Materials [71].

We tested the hypothesis that the oxidation can be continuously tuned using sample E. Fig. 5.8(c) shows a time trace of the PL intensity from SiV⁻ at a single excitation spot plotted under 30 mW (1.5×10^{10} mW/cm²) excitation. The increase in intensity is observed to saturate after around 15 minutes. This relatively slow process and the optical spatial resolution enable very precise control over the Fermi level. In contrast to sample A, the spectra taken on sample E after exposure show that SiV and not NV contribute to the

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majority of the signal. The lower formation yield of sample E NV centers is attributed to the higher annealing temperature [70].

We then exposed three 5x5 micron squares using the 30 mW (1.5×10^{10} mW/cm²) excitation, varying the exposure time to obtain 3 different oxidation levels. These squares overlap the edge of an implantation square, allowing us to study differences in the changes in PL and surface potential between implanted and non-implanted regions. As expected, the PL intensity only increases in the part of the square over the implanted defects (Fig. 5.8(d)), while the entire exposed square is modified in the KPFM image (Fig. 5.8(e)). The nonlinear response in the SiV⁻ PL intensity with laser exposure is used to estimate the exposure from the tuning curve (Fig. 5.8(c)). Similar to the “W”, we observe an increase in PL intensity and a decrease in surface potential. Spectra in Fig. 5.8(f) on the exposed squares confirm that the PL enhancement is coming from the SiV⁻.

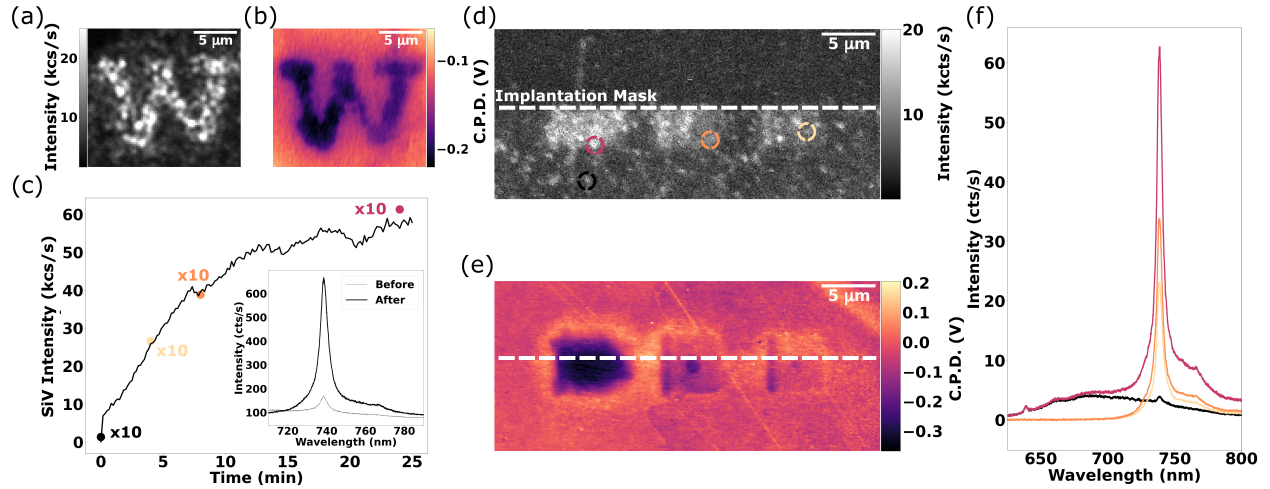


Figure 5.8: (a) Confocal PL image of sample A (15 nm) after laser-assisted oxidation. Laser-assisted oxidation is performed with 20 mW ($1.0 \times 10^{10} \text{ mW/cm}^2$) of 532 nm, while confocal imaging utilizes 1 mW ($5.1 \times 10^8 \text{ mW/cm}^2$) of 532 nm. The entire time of exposure was 10 hours. (b) AM-KPFM image of sample A after laser-assisted oxidation. (c) Time dependence of the SiV⁻ PL intensity on sample E (25 nm) using 30 mW ($1.5 \times 10^{10} \text{ mW/cm}^2$) of 532 nm excitation. Colored data points correspond to the SiV⁻ intensity from the 3 laser-assisted exposed regions. *inset*: Representative PL spectra taken at the start and end of the laser exposure used to determine total PL intensity. (d) Confocal image of three laser-assisted exposed squares on sample E using 1 mW of 532 nm excitation. The dashed white line denotes the implantation square boundary. PL background from deeper native NV is observed throughout the implantation square (lower half). (e) FM-KPFM image of the laser-assisted oxidized squares on sample E. (f) Photoluminescence spectra corresponding to the four marked regions in (d) and the colored data points in (c) obtained using 1 mW of 532 nm excitation. This figure reproduced from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raiteses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

5.9 Discussion and outlook⁶

In these experiments, KPFM and C-AFM, correlated with photoluminescence measurements, enable us to link the brightening of quantum defect luminescence to surface properties. This connection can be understood using the band bending diagram depicted in Fig. 5.9(a). Under both oxidized and hydrogenated nitrogen-doped diamond, electron transfer from nitrogen donors to surface acceptors results in an upward band bending. This upward band bending is more obvious over larger depths than the 50 nm depth shown in Fig. 5.9(a) and can be seen in Sec. II of our Supplemental Materials [71]. In the case of hydrogenated diamond, there is an additional upward bending contribution from the transfer of electrons in the valence band to atmospheric acceptors on the surface. This 'surface transfer doping' mechanism results in the conductive 2D hole gas [20] detected by C-AFM. It is also responsible for the pinning of the Fermi level near the valence band maximum. Under oxidized diamond, the electrons from the nitrogen donors are trapped at surface defects [96] pinning the Fermi level mid gap.

The charge state of the near-surface defects can be determined from the Fermi level through the calculation of formation energies. In Fig. 5.9(a) we illustrate the possible charge states of the NV center as shaded regions within the bandgap. The region that contains the Fermi level is the equilibrium state, thus for hydrogenated diamond, we expect the NV^+ state. In oxidized diamond, the charge state will depend on the density of the trap states and will lie within the NV^0 and NV^- bands [96].

Also depicted in Fig. 5.9(a) is the difference in CPD between the two surfaces. Both the Fermi level and electron affinity will change with surface termination, which can result in

⁶This section reproduced from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

a seemingly complex spatial dependence of the CPD. In Fig. 5.9(b), a horizontal line scan of the work function is shown across the hydrogenated-oxidized boundary. For simplicity, this scan is taken in a region with no implantation. An initial increase in the work function is observed as the diamond becomes oxidized, before finally dropping 250-320 meV below the hydrogenated level. This behavior can be understood by noting that the CPD has two contributions, the electron affinity χ_e and the Fermi level E_F . Specifically, the change in CPD over a material with a constant bandgap is given by $\Delta W = \Delta\chi_e - \Delta E_F$, where W is the work function, χ_e is the electron affinity, and E_F is the Fermi level measured from the valence band maximum. The electron affinity should monotonically increase as oxygen replaces hydrogen due to the opposite polarity of the two surface dipole moments. This increase can happen spatially across the surface due to masking, or over time by our laser-induced oxidation. The Fermi level also increases as the surface is oxidized; on a hydrogenated surface, it can lie as deep as 0.7 eV below the valence band [81], while oxidized diamond is believed to be pinned around 1.8-2.4 eV [47, 96] above the valence band. We utilize the upper estimate 2.4 eV for the oxidized Fermi level to explain our measurements, which is discussed in Sec. II of the Supplemental Materials [71]. The dependence of the Fermi level on the surface termination is more complicated than the electron affinity dependence as it also depends on electron transfer between the diamond and the surface wetting layer. We hypothesize that the initial increase in the work function is caused by a Fermi level that remains pinned near the valence band despite the increasing electron affinity.

The non-monotonic behavior of the CPD with oxidation results in some unique features in the KPFM images of laser-exposed and defect-implanted surfaces. In Fig. 5.9(c) a KPFM scan of the square with the largest laser exposure is shown. We observe a dark oxidized patch surrounded by a lighter halo. The work function of this halo is even higher than the surrounding unexposed surface. We attribute this halo to the Gaussian laser profile

which results in a weaker exposure at the edge of the square, combined with the CPD's non-monotonic dependence with oxidation. This effect is analogous to the boundary effect we observed in Fig. 5.9(b).

The non-monotonic CPD effect can also be used to explain two different characteristic behaviors observed at the surface of seemingly identical implantation squares. These squares have not received the laser oxidation treatment. As illustrated in Fig. 5.9(d), we observe an increase in work function over the entire surface of some squares, while others we observe only an increase in a halo around the square. For the halo squares, the interior may exhibit a slightly higher to significantly lower work function than outside the square. These results can be explained by accelerated oxidation of the diamond surface in ambient conditions due to implantation damage, even at the low implantation fluence in this study corresponding to one ion per $(30\text{ nm})^2$. Squares that are early in the oxidation process will have an all-positive surface, with the halo forming later in the process when the interior of the square becomes more oxidized. This implantation-induced acceleration is significant; only the implanted regions in sample A show signs of oxidation after 2 years in ambient conditions. More theoretical work is needed to elucidate the mechanism for accelerated oxidation given the importance of near-surface defects for quantum technologies.

In summary, we utilize correlated scanning-probe microscopy and photoluminescence to study surface oxidation of hydrogenated diamond surfaces. We continuously vary the hydrogenation/oxidation in two ways: by shadow masking an oxygen-terminated surface in a cold hydrogen plasma and by controlled laser-assisted oxidation. In both cases, we observe the non-monotonic increase in work function with oxidation. KPFM measurements are consistent with the observed charge state of quantum defects beneath these functionalized surfaces. Correlated measurements further uncover that the surfaces over implanted defects oxidize more quickly than pristine surfaces. Combined with knowledge of the electron affinity

of a surface, these results indicate KPFM can be a powerful, high-spatial-resolution technique to advance surface Fermi level engineering for charge stabilization of quantum defects.

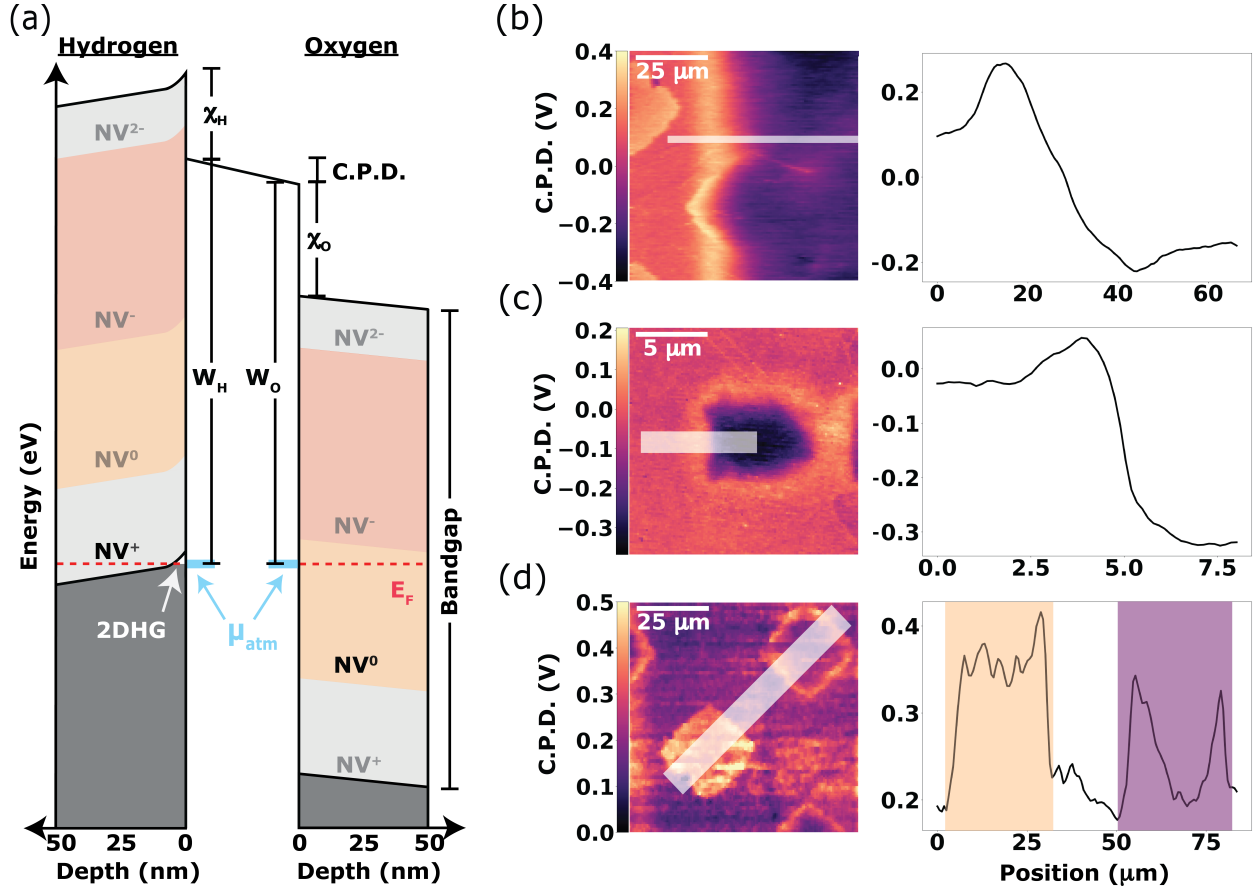


Figure 5.9: (a) Band diagram of the top 50 nm of hydrogenated and oxidized diamond surfaces using formation energies calculated in [22]. The Fermi level for hydrogenated diamond is located at approximately the valence band maximum where the 2-dimensional hole gas (2DHG) forms. The oxidized surface is shown pinned 2.4 eV above the valence band due to the presence of surface defects. (b) *Left*: FM-KPFM image depicting the boundary between the masked oxidized and hydrogenated diamond surface of sample A (15 nm). *Right*: Line scan across the unimplanted region, averaged over 2.5 microns. (c) *Left*: FM-KPFM image depicting the square created by the longest exposure to the laser on sample E (25 nm). *Right*: FM-KPFM line scan across the square's boundary, averaged over 1.5 microns. (d) *Left*: FM-KPFM image of two implantation squares of sample A after hydrogen passivation. *Right*: Line scan across the two implantation squares, averaged over 10 microns. The implantation squares are indicated by the shaded regions. This section reproduced from "**Christian Pederson**, Rajiv Giridharagopal, Fang Zhao, Scott T. Dunham, Yevgeny Raitses, David S. Ginger, and Kai-Mei C. Fu. Optical tuning of the diamond fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy. Phys. Rev. Mater., 8:036201, Mar 2024." [71]

Chapter 6

CHARGE NEUTRALIZATION VIA ABOVE-BANDGAP EXCITATION

6.1 *Introduction to charge neutralization*

In Chapter 5, we discussed a passive technique for controlling the charge state of color centers, surface functionalization. This technique relies on the fact that color centers close to the surface of diamond thermalize to a charge state determined by the Fermi level, and that we can control this charge state by chemically functionalizing the surface [32, 41, 117, 71]. However passive control of a color center is often insufficient; NV^- centers are observed to ionize to NV^0 even under oxidized surfaces as we saw in Chapter 4. Thus dynamic techniques, commonly optical charge re-pump schemes, are employed to reset the charge state. The most common re-pump scheme involves exposing the diamond to green ($\approx 532\text{nm}$) excitation, however we have shown in Chapter 4 that this exacerbates spectral diffusion.

The problems of charge re-pump are likely fundamental; as long as the desired charge state of a color center is charged then an opposite charge must be produced somewhere. If this charge does not travel sufficiently far away and is captured by a defect, it will be a source of spectral diffusion. Furthermore, charge re-pumping can directly ionize other defects within the optical spot, another source of spectral diffusion. One potential solution is to design a charge re-pump scheme that doesn't generate charged defects (e.g. NV^- , SiV^- , N^+), but rather neutralizes charged defects. Assuming we had a color center with a promising neutral charge state that we were interested in, our re-pump scheme would serve two purposes, to reset the charge state, and eliminate nearby sources of charge and thus spectral diffusion.

One plausible way to accomplish this involves the use of above-bandgap excitation, which can generate free charge carriers within the diamond. These charge carriers, due to Coloumbic attraction, have long-range attractions with oppositely charged defects, and may recombine at these defects. In fact, this highlights two potential benefits of neutral defects. First, they may be efficiently created in charge-free environments, and second, once created they have a lower chance of capturing charge carriers than ionized species.

There is existing evidence that above-bandgap excitation is effective at neutralizing charges. Work on samples highly doped with silicon and nitrogen show dramatic photochromism [13] after exposure to above-bandgap excitation. In fact, above-bandgap excitation was utilized in early work to generate SiV^0 [23]. Furthermore NV^- defects have been demonstrated to have exceptionally large hole capture cross-sections [56] attributed to the unscreened Coloumb potential, while NV^0 electron capture cross-sections were negligible [57].

However the existing body of work utilizing above-bandgap excitation exposed the entire sample for many minutes prior to the measurement and have yet to investigate it's potential as a dynamic technique compatible with quantum technologies. This is precisely the focus of this chapter, investigating above-bandgap excitation for dynamic charge control.

6.2 NV^0 and SiV^0 as case studies

Although NV^0 is typically not desired for quantum applications, the NV center is one of the only defects whose charge can easily be read out through optical spectroscopy. Furthermore, neutralizing NV^- implies neutralization of the compensating charge, assumed to be N^+ . Thus succesfully neutralizing NV centers would be important evidence that above-bandgap excitation can neutralize some technologically relevent defects.

A much more exciting color center to test the neutralization technique on is the SiV^0

charge state. Early experiments suggest that it may hold potential as a promising qubit [84]. For example, it possesses the inversion symmetry of the group IV-vacancy complexes, and has a ground state analogous to NV^- [38] resulting in low spectral diffusion and long spin coherence times respectively [84]. Furthermore, several works have already demonstrated a degree of success at generating SiV^0 using above-bandgap excitation [23, 13].

For our purposes involving charge and optical stability, it also has the advantage of emitting into a ZPL at 946 nm with efficient optical excitation at 830 nm due to bound excitonic transitions [116]. This is exciting because 830 nm (and therefore 946 nm) is energetically below the photoionization threshold of many known defects. This may provide a third protection against ionization, a much lower rate of carrier photogeneration.

There are also undesirable features of SiV^0 , for example the bright optical emission at 946 nm is known to peak in intensity at around 100 K, and freeze-out at low temperatures [23]. Spectra taken at 80 K and 10 K are shown in Fig. 6.1, demonstrating this freeze-out. This is attributed to a lower energy excited state, with a forbidden transition at 951 nm [38]. Another undesirable feature is the linewidth of the 946 nm emission line of ensembles remains broad, ≈ 1 nm in Fig. 6.1, even at 10 K. The origin of the broad ensemble linewidth is currently unknown, but could be due to a high susceptibility to strain.

Already a variety of techniques for generating SiV^0 exist, for example bulk doping [84], surface functionalization from hydrogen termination [117], and even conversion from SiV^{-2} using photogenerated carriers [115], but a direct, dynamic technique has yet to be demonstrated.

6.3 *Experimental setup*

In this work we will utilize two samples, one enriched with nitrogen and another enriched in silicon. The nitrogen-enriched sample is single-crystal diamond, and is commercially sold

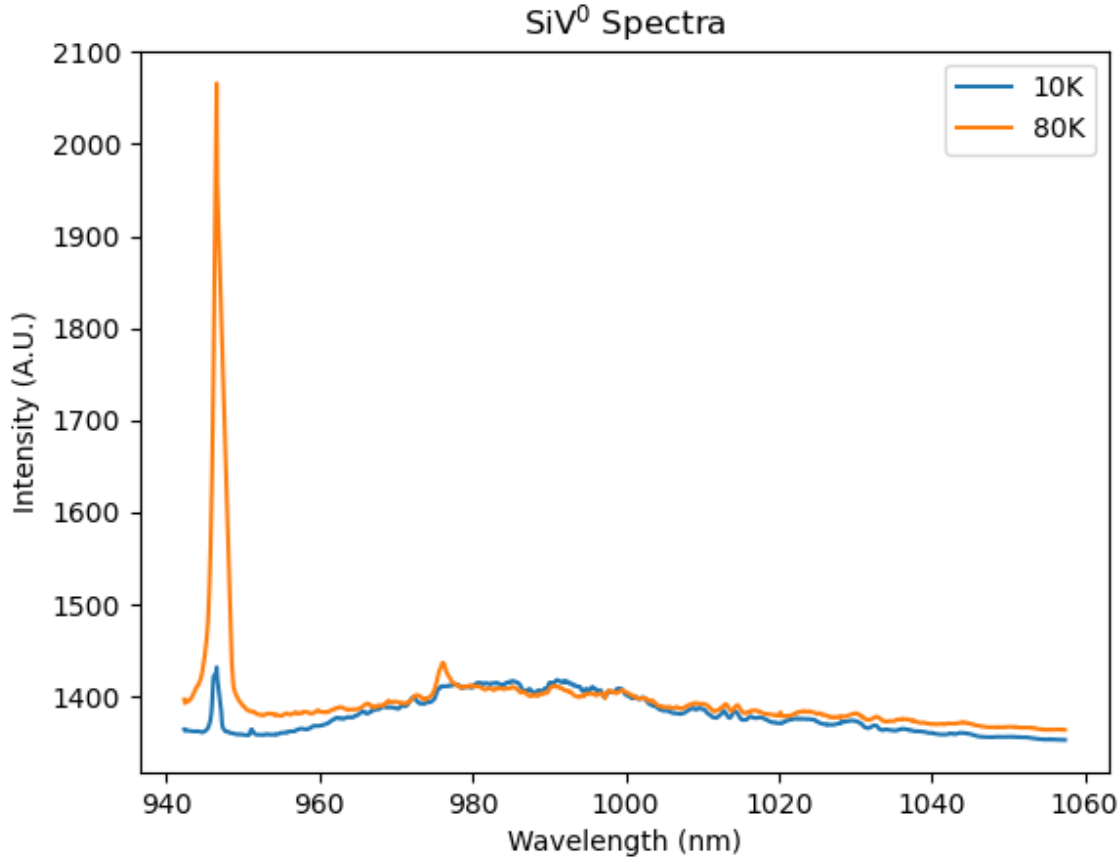


Figure 6.1: Spectra of SiV⁰ taken at 10 K and 80 K with 15 mW of 830 nm excitation showing the dramatic temperature dependence of the 946 nm line

by Element Six with a nominal nitrogen concentration below 1 ppm. The silicon-enriched sample is also a single-crystal grown by Element Six and contains approximately 0.1-0.4 ppm silicon. Both samples contain a high concentration of color centers, NV and SiV, such that an ensemble of centers are excited in the optical excitation volume.

The above-bandgap source is a deep-UV (DUV) pulsed excimer laser (Photon Systems) that emits ≈ 35 mW of 224.8 nm light during a pulse-width of 100 μ s, at a max repetition rate of 5 Hz. The DUV laser is focused onto the diamond through the cryostat window at

an angle as shown in Fig. 6.2.

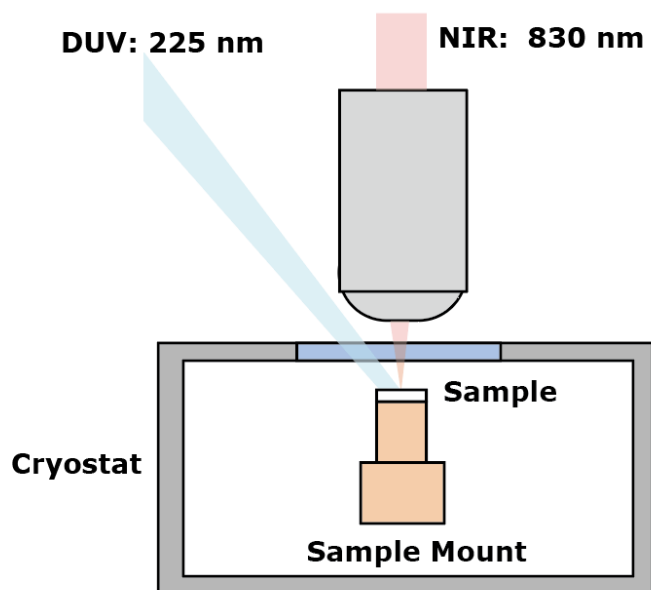


Figure 6.2: Schematic of excitation scheme. 35 mW of 225 nm excitation is focused at an angle through the cryostat window. An objective focuses the 830 nm (or 532 nm for NV/SiV⁻) excitation onto the sample, and collects the photoluminescence

6.4 NV measurements

In the case of the nitrogen-enriched sample at room temperature, the DUV laser modifies the spectrum of NV centers under continuous, weak ($10\text{ }\mu\text{W}$) green excitation. As we modulate the pulse rate of the DUV laser from 0 to 5 Hz, we observe that increased DUV exposure increases the signal from NV^0 at the expense of NV^- as shown in Fig. 6.3. The spectrum never reaches 100% NV^0 and is limited by the fact that the continuous green excitation rapidly converts any generated NV^0 to NV^- . Nevertheless it is clear that the NV^- charge state is neutralized by the DUV, and thus the compensating species, likely N^+ , is as well.

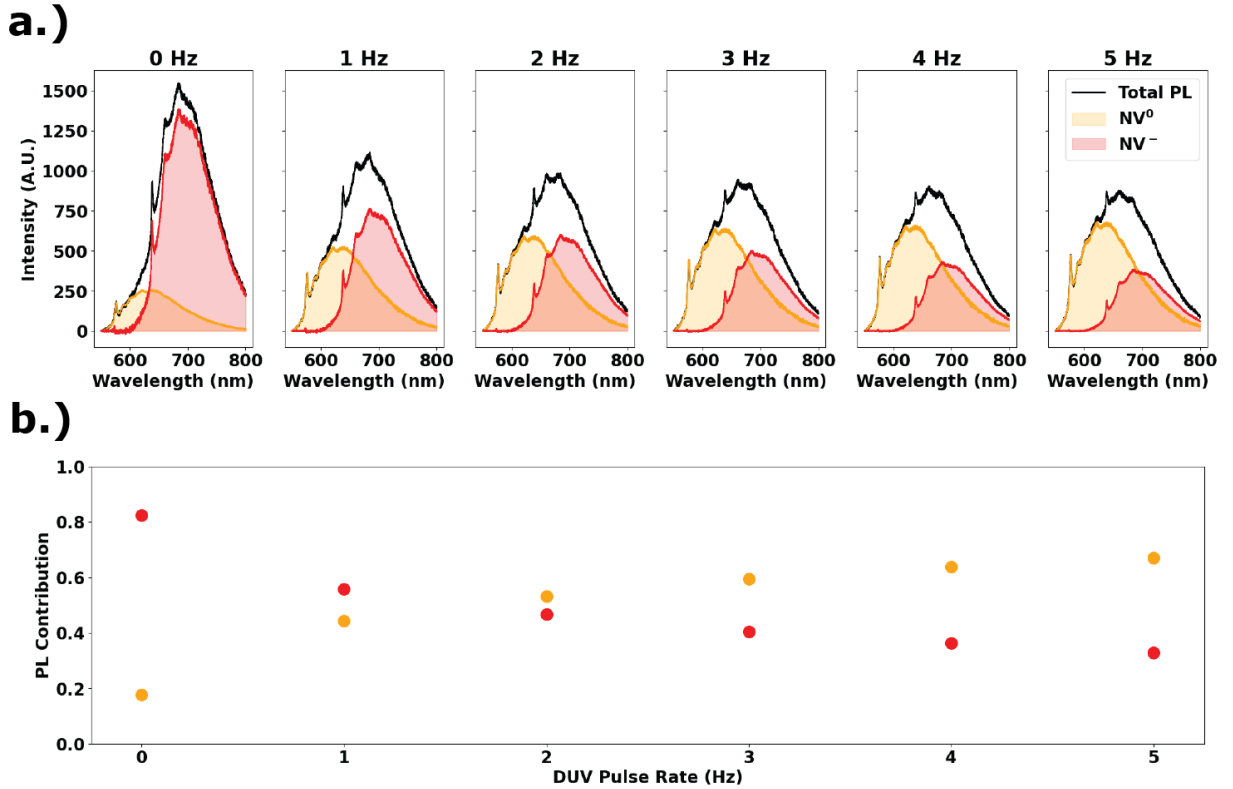


Figure 6.3: **a.** NV spectra taken with $10\text{ }\mu\text{W}$ of 532 nm excitation under increasing DUV pulse repetition rates. **b.** Fraction of the total PL attributed to NV^0 and NV^- .

6.5 SiV measurements

In the silicon-enriched sample, we are unable to directly detect the SiV^0 PL above 240 K due to non-radiative pathways. Instead, we perform time-resolved PL of the SiV^- in relation to the DUV pulse in Fig. 6.4. We observe a strong bleaching of the PL during the DUV pulse, with a recharge rate to SiV^- that depends on the strength of the green power.

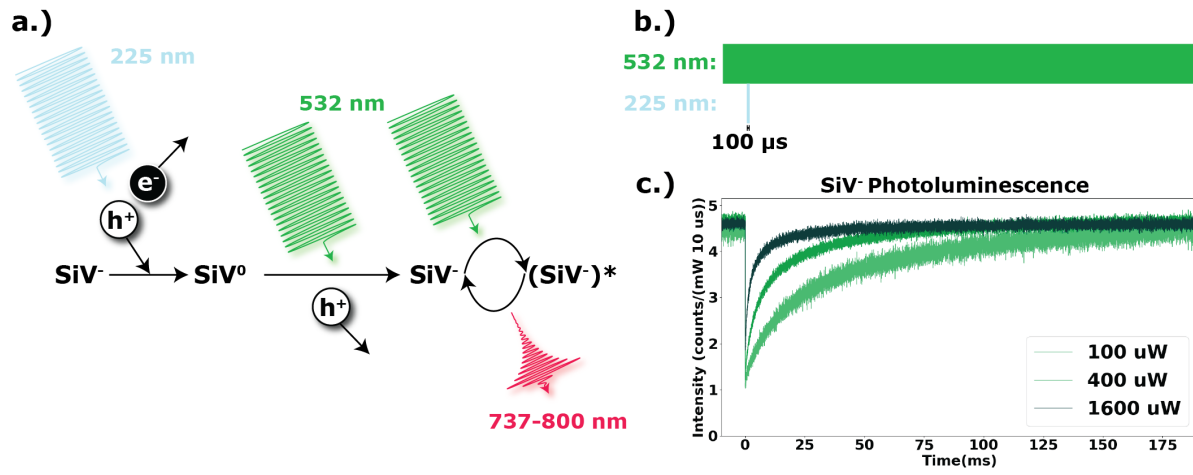


Figure 6.4: **a.** Illustration depicting the hypothesized charge dynamics. **b.** Pulse sequence of measurement **c.** PL trace normalized by power of green excitation

At lower temperatures, we perform spectroscopy on the SiV^0 PL using continuous 15 mW of 830 nm excitation. Due to the photostability of SiV^0 , we are able to take a 1-minute spectra after each 100 μs pulse until the SiV^0 signal saturates and integrate the ZPL counts. This was repeated 3 times, by resetting the SiV^0 population to a minimum SiV^0 population each time via 1 mW of 532 nm excitation for 1 minute. These results show promise for neutralizing SiV color centers dynamically at temperatures where quantum technologies operate.

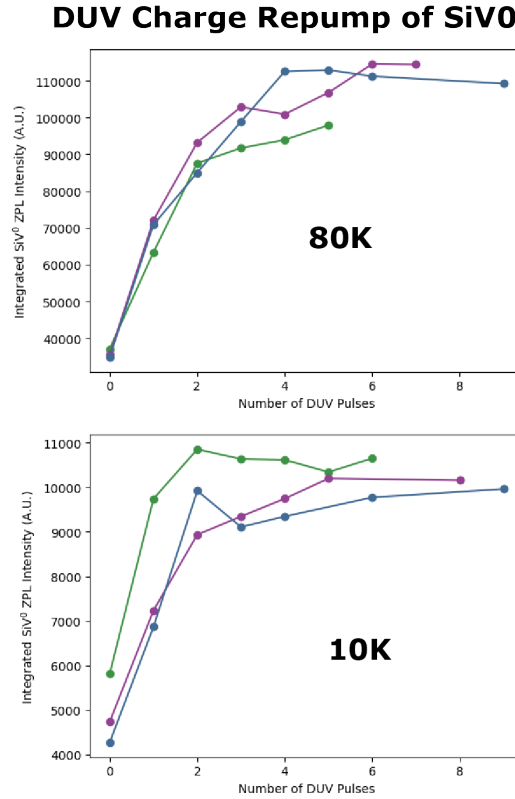


Figure 6.5: SiV^0 ZPL intensity as a function of the number of DUV pulses incident on the sample. Due to the temperature freeze-out, the intensity in the ZPL is weaker overall at 10 K compared to 80 K, but the number of pulses needed to saturate the SiV^0 population remains very similar. Three separate runs were performed at each temperature.

6.6 Conclusion

These results, although preliminary, show effective neutralization of the charged defects we can observe, NV and SiV, and whichever defect species are compensating their ionized charge states. Furthermore, in the case of SiV^0 , it seems continuous, strong excitation using 830 nm doesn't cause the continuous charge-cycling that is observed for a defect like the NV center. This is evidenced by the fact that we don't observe any bleaching of the SiV^0 emission. Ionization of SiV^0 to SiV^+ is energetically forbidden given the close proximity of the SiV levels to the valence band, requiring ultraviolet light to ionize through the conduction band. Ionization of SiV^0 to SiV^- may be possible through a 2-photon absorption process like that of the NV center, however we would expect this to show up as a bleaching since 830 nm excitation is below the excitation energy of SiV^- .

The ability to generate SiV^0 on demand and its apparent photostability add to the growing list of beneficial properties of SiV^0 for quantum technologies. Future work needs to be done to see how effective this neutralization technique works on implanted color centers, which are required for photonic integration, and whether the neutralization technique actually reduces spectral diffusion. Still, there are many potential color centers that may benefit from this relatively sample-independent neutralization technique, such as the other group IV-vacancy complexes whose neutral charge states have yet to be detected.

Chapter 7

OUTLOOK

In this thesis we have demonstrated improvements on several fronts for characterizing and improving charge and optical stability of color centers in diamond.

In Chapter 3, we demonstrated that fabrication induced damage to the diamond is a major source of charge and optical instability but that it can be avoided by decoupling the fabrication of photonic devices from the surface treatment of the diamond. Already there are many ways that the photonic crystal cavities could be improved. We could only study the coupling of single SiV^- that were significantly strained and thus de-tuned from the high-density ensemble. Lowering the implantation dosage of silicon would minimize implantation strain and damage, allowing us to study single SiV^- that better emulate the bulk. In addition, the SiV^- could be pre-characterized to identify the most promising color centers, followed by an aligned stamp transfer. Improvements in the design of the photonic crystal cavities could enable efficient out-coupling of single photons on chip, and improvements in e-beam technology may enable higher-Q devices and more reliable writing of the small feature sizes needed. Future developments in minimizing BGaP absorption would also drastically increase the scalability of the GaP-on-diamond platform.

In Chapter 4, we were able to identify that the surface of diamond, not ion implantation, is primarily responsible for the large spectral diffusion of shallow color centers. This indicated a pressing need for atomically clean surfaces, such as what has been achieved in silicon. We also discovered the role that re-charge pumps have on spectral diffusion, motivating better techniques of dynamically controlling charge state.

We demonstrated the ability to carefully functionalize surfaces using intense optical excitation in Chapter 5. Future work could investigate whether other surface terminations may be achievable via laser exposure in alternate atmospheres. This technique provides a way to functionalize tiny portions of the diamond without the aggressive treatments commonly used making it an attractive technique for complicated commercial device geometries. The resolution of the KPFM measurements could be improved by measuring under vacuum, and possibly even integrated with confocal microscopy for rapid correlated measurements. This could provide a significantly faster way to generate and characterize surface terminations, which could further our understanding of the physics of the diamond surface.

Finally, we showed that above-bandgap excitation is an effective mechanism for directly generating NV^0 and SiV^0 in Chapter 6. The SiV^0 showed promising features, such as continuous PL under excitation without charge cycling, which isn't the case for the more common color center charge states NV^- and SiV^- . Future work investigating the effect of charge neutralization on PLE measurements could determine if SiV^0 possesses the charge and optical stability needed for generating indistinguishable photons or forming quantum networks. In addition, the neutralization technique also provided a way to study the photoionization rates through time-resolved PL measurements, as we observed for SiV^- under green illumination. Future work could investigate the ability of this technique to other neutral group IV-impurity complexes that have yet to be observed.

It is not the claim of this thesis to have solved charge and optical stability of color centers in diamond, an extremely difficult challenge likely requiring a number of significant advancements in crystal growth, annealing treatments, surface science, device fabrication and color center choice. Instead, the goal has been to carefully identify the major sources of ionization and spectral diffusion through various optical measurements, and develop new tools for characterizing and mitigating these sources.

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