

UNIVERSITY ULM

MASTER THESIS

Optical Properties of Silicon Vacancies in Nanodiamond

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Declaration of Authorship

I, John SMITH, declare that this thesis titled, "Thesis Title" and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
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- I have acknowledged all main sources of help.
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Chapter 1

Motivation and Background

1.1 Quantum info processing and Qubit candidates

The bit is the basic unit of information in computing and digital communications. A bit can have one value, which can be 1 or 0, that represents the logical states in a 2-level logic system. In modern digital computers, these two states exists as low and high voltages in highly integrated circuits. Just like bit for classical computing, qubit is the basic unit of information in QIP, which encodes 1 and 0 into 2 distinguishable quantum states. As the qubits behaves in the manner of quantum mechanism, it gives rise to the phenomena of superposition and entanglement, which enables the processing of massive number of calculations. Previous difficult tasks in classical computing such as simulation of quantum systems or factoring of numbers will be finished quick and efficiently by quantum computers.

For the realisation of quantum computer, the first priority is to find a fitting candidate as qubit. Five principles have been brought up for the candidates choosing by [Journal,name]:

1. A scalable physical system with well characterized qubits
2. The ability to initialize the state of qubits to a simple fiducial state
3. Long relevant decoherence times, much longer than gate operation time
4. A "universal" set of quantum gates
5. A qubit-specific measurement capability

Color centers are optically active impurities that are responsible for the colors in crystal that are transparent due to large band gap. Color centers are atom-like solid systems, with appropriate electronic structure and symmetry in crystal, they are the candidates for qubits. Additionally, it is practical to require a long enough coherent time for the operation regarding QIP.

Lots of research works has been done with NV^- , which has excellent spin properties at ambient condition, it has also been proved that it is possible to execute an all optical access to its spin.[reference from all optical paper]. Yet due to the transform of symmetry during the excitation process, NV^- has a big phonon side band following the ZPL. Moreover, the C3v symmetry leaves the color centre vulnerable towards the environment electric field, resulting in spectral diffusion, which is caused by the flipping of charging state. These disadvantages has reduced the generation rate of coherent photon generation rates and limit the development of NV-quantum networks[Lachlan paper].

1.2 Silicon vacancy as a Qubit candidate

SiV is considered as the next promising qubit candidate after NV. It has irresistibly excellent optical properties, and is also possible to achieve an all optical intallizaiton, read out and coherent preparation.

SiV^- has a D_{3d} symmetry with the symmetry axis along the $<111>$ crystal direction. The color center consists of a substital Silicon atom and a carbon vacancy. Due to the size difference between Silicon atoms and carbon atoms, it is expected that the Silicon atom will sit between 2 lattice site instead of on a lattice site[Goss etal, Gali and Maze,]. The inversed symmetry offers SiV^- extra shield from the environment small electric field.

Experimentally it is observed that the SiV^- has outstanding optical properties, 70% of its fluorescence couples into a sharp ZPL of 1.68eV. At cryogenic temperature this ZPL can be resolved with a fine structure of 4 lines. These four lines are signed to the electronic transitions between the ground state and the first excited state of SiV^- . Theoretical calculation based on the group theory and ab initio method offers us a model of the SiV^- electronic structure with a ground state of 2 folded degeneracy and even parity, a first excited state of 2 folded degeneracy of uneven parity and a second excited state of none degeneracy with even parity.[Goss etal] This calculation fits the observation as only the electronic transition between levels of different parity is allowed, due to the -1 parity of photons, thus only the 4 transitions between the first excited state and the ground state would be allowed, as signed to the 4 line structure of ZPL. Since this is a E to E transition, no dramatic symmetry change has been involved, less phonon would be involved in the relaxation, which fits the observation of the sharp ZPL with small phonon side band.

Lachlan et al showed the probility to read out and coherently prepare electronic spin in individual SiV^- centers via resonance excitation. The SiV^- was first initialized by resonantly pumping the spin-flipping transition D1 that is weakly allowed due to the off axis residue of the magnetic field, this is done with applying a laser pulse that resonant to transition D1. After a dark interval the spin state was read out using a laser pulse on the cycling transition D2. The leading edge peak from D2 pulse will decrease with the increase of dark interval approaching an minimum. From which the spin relaxation time T1 has be calculated as $2.4 \pm 0.2\text{ms}$. With the similar pulse measurement, the orbital T1 has been measured as $38 \pm 1\text{ns}$. The fact that the orbital T1 is much shorter than spin T1 indicates that the orbital relaxation is highly spin conserving, as the electron phonon interaction should be. The temperature dependency measurement reveals that the orbital rate increase linear with the temperature until 22K, which indicates a single-phonon mechanism of orbital relaxation.[Lachlan et al, and 30-32 from the paper]

Further CPT was carried out by tuning the pump laser to transition D2 while scanning across the transition D1 using the probe laser. The spin coherent time was then measured to be $35 \pm 3\text{ns}$. This short coherence time is likely to be connected to the dephasing caused by the rapid orbital relaxation.

Practically, as mention before, a qubit candidate ideally need to have long enough coherent time for the implementation of operation and read

out, in this sense, the short coherent time of SiV^- drew it back from being an competitive qubit candidate.

Several ideas of acquiring longer coherence time has been taken into consideration. While most of them can be classified into two main approaches: avoid orbital relaxation caused electron spin dephasing by accessing the orbital spin in Si^{29} or eliminate the single phonon that has been involved in the orbital relaxation.

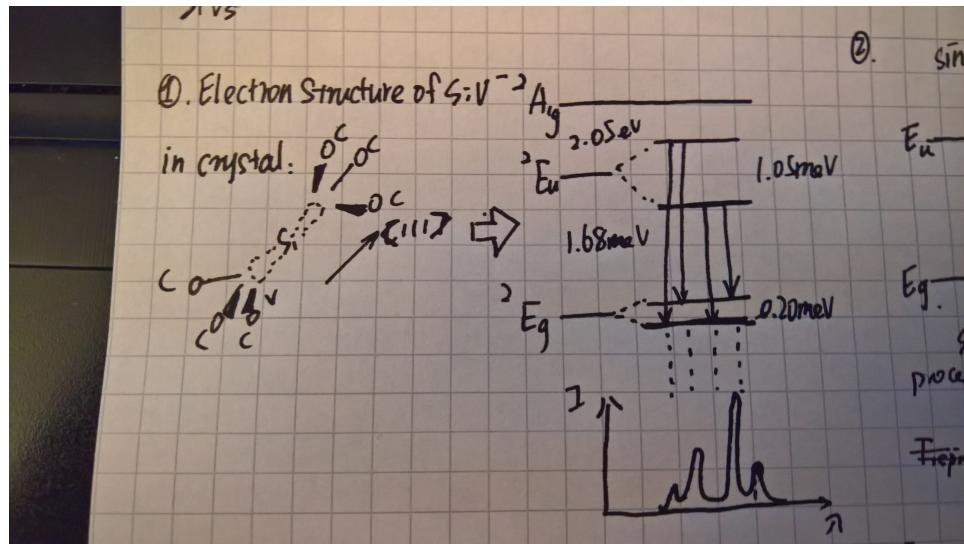


FIGURE 1.1

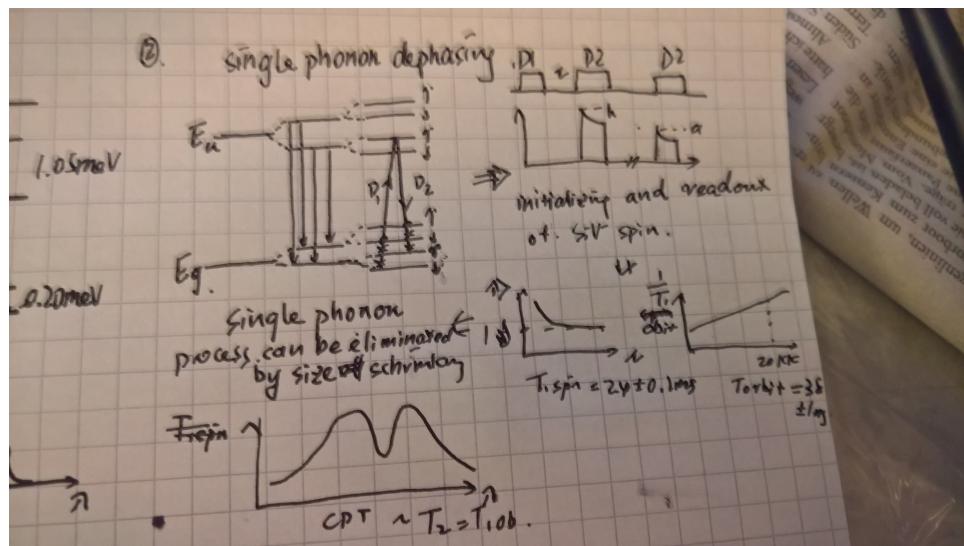


FIGURE 1.2

1.3 Silicon vacancies in nanodiamonds

As mentioned, one vital problem to solve if we want to use SiV^- as a qubit is that, the coherent time has been limited by the rapid orbital relaxation. And this is caused by the transition between the degeneracies of ground

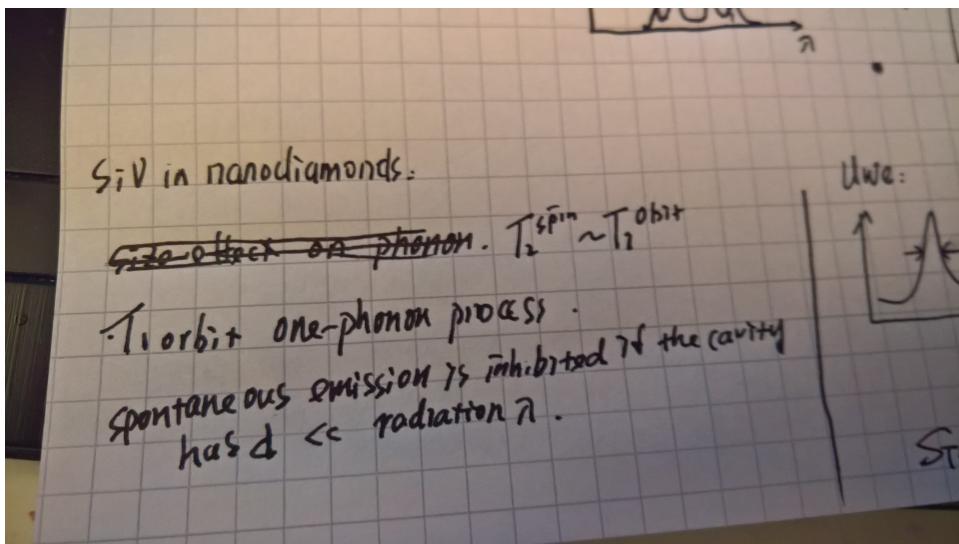


FIGURE 1.3

state which was driven by a single phonon. The elimination of such phonon is an direct approach towards the solution.

Spontaneous emission is inhibited if the cavity has characteristic dimensions which are small compared to the radiation wavelength [Daniel Kleppner 1981]. As in our case to eliminate the emission of phonon that couples into the splitting of ground state in SiV⁻ 47 GHz, nanodiamond of the size that is smaller than the half wavelength of this transition phonon wavelength (around 125nm) is desired.

Currently 3 major techniques are employed in the field of nanodiamond fabrication: denotation, CVD, and HPHT, while the exotic atoms can be mixed in the beginning or implanted via ion implantation. While the denotation method produced highly defective diamonds and ion implantation introduces inner strain, for the SiV containing nanodiamonds, HPHT method and CVD method are the top choices.

The principle of CVD method is to disintegrate the CVD fabricated diamond film, while the HPHT method initialize an phase transition of carbon at high temperature and high pressure. Previously, comparison between the PL spectra of silicon doped polycrystalline diamond films obtained by the CVD method and diamond single crystals grown at a pressure of 6 GPa from a nickel melt at 1500°C has been carried out, and demonstrates that the HPHT diamonds carries narrower SiV⁻ ZPL lines than CVD fabricated ones[C. D. Clark 1995]. As in the department of nanodiamonds, the narrowest SiV⁻ ZPL that has been measured by far, which has a corrected width of 206MHz, that is almost of the excitation state life time limit, is also from the HPHT method fabricated nanodiamond.

1.4 Motivation of the thesis

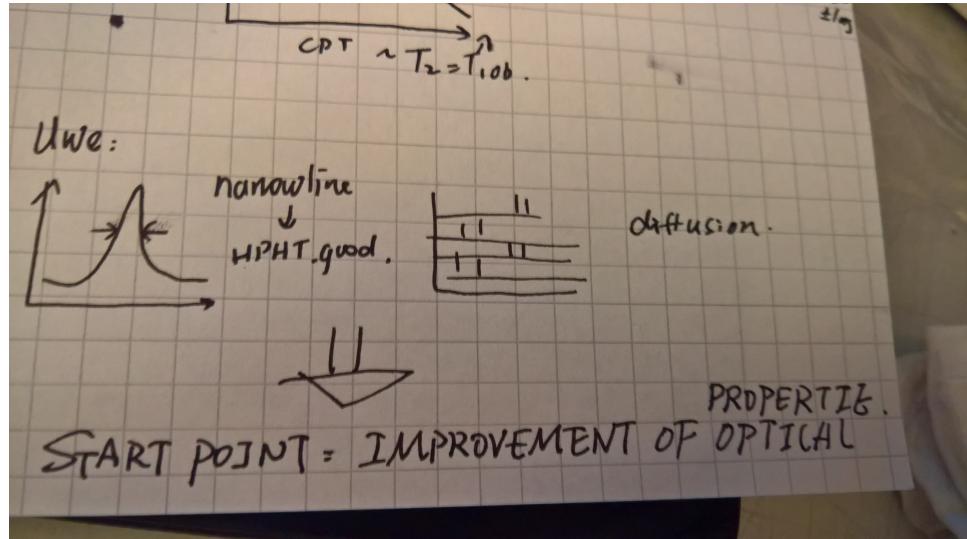


FIGURE 1.4

The motivation of looking into SiV^- in nanodiamonds is to acquire longer coherent time by eliminating the phonon that is responsible for the transition between the fine splitting of the ground state. Yet the obstacle on our way of justifying this approach is that, the optical properties of SiV^- in nanodiamonds are not as outstanding as it is in bulk diamond. Blinking and spectral diffusion, especially spectral diffusion has stopped us from further life time measurement.

The mechanism behind the spectral diffusion is yet not clear, our first guess is to connect the enhancement of spectral diffusion in nanodiamonds with the surface condition, due to the high surface to volume ratio of nanodiamonds.

Our target of this thesis is to improve the optical properties of nanodiamonds, more specifically, to suppress the spectral diffusion via methods of surface treatment, enabling further measurements including but not limited at orbital/spin T_1 and coherent population trapping, and finally to test out the possibility of acquiring a longer coherent time via the elimination of the single phonon process.

In the synthesis procedure of HPHT nanodiamonds, due to the surface absorption of nitrogen on ingredients, NV can be introduced. N atoms act as a n-type dopant, an electron donor in the diamonds. Due to the different dopant density on the surface and in crystal, to match chemical potentials at the surface and in the bulk, charge builds up on the surface depleting the donor charges a depth into the bulk and bending the bands accordingly.

The width of this depletion layer can be calculated with the equation

$$D = \sqrt{\frac{2\psi V(0)}{qN_D}},$$

where ψ is the dielectric constant, $V(0)$ is the band bending and N_D is the concentration of dopant. As in our case, the concentration of Nitrogen is not clear but expected to be low, thus resulting in broader depletion layer. With a typical moderate dopant concentration of $10^{-16}/\text{cm}^3$, the width of depletion layer is calculated to be 80nm[Diederich,1998]. As mentioned before, to inhibit the generation of 47 GHz phonons, the diameter of the diamonds need to be smaller than 125nm, and there is a high chance that

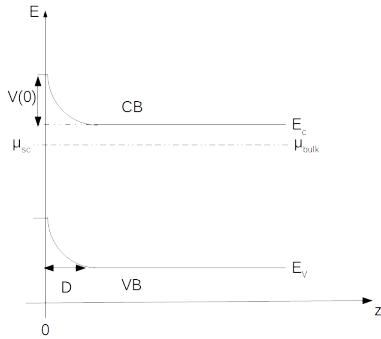


FIGURE 1.5: A sketch describing the band-bending of n-doped diamond. Since the chemical potential of the surface and the doped bulk area need to match up with each other, a depletion layer is formed, the bands (CB: conducting band, VB:valence band) bends towards up near the surface.

SiV in nanodiamonds will lie in side or close to the band bending area, which may be the cause of spectral diffusions.

It is expected to flatten the band bending by inhibit the surface charge accumulation. In this thesis, 2 methods are applied.

First is to remove the graphitic defect by aerobic oxidation. Aerobic oxidation is a good method for surface purification and initialization. Research on denotation diamonds shows that, with the temperature between 375°C to 450°C , the removal of Sp^2 [Osswald,2006]. After 2h of aerobic oxidation at 575°C , the surface structure of HPHT NDs is very similar to bulk single crystals where hydroxyl and possibly ethers are the dominant functional groups[Wolcott 2014]. Aerobic oxidation with elevated temperature can cause the size reduction of nanodiamonds. It has been reported that the average height reduction rate of individual crystals was $10 \pm 1 \text{ nm/h}$ at 600°C , $4 \pm 1 \text{ nm/h}$ at 550°C and less than 1 nm/h at 500°C from aerobic oxidation. Since graphitic defects on the surface of diamond are possible electron trap candidate[J. Ristein, Diamond Relat. Mater. 9, 1129 (2000).], it is possible to lower the surface charge via aerobic oxidation.

The second method is to achieve negative electron affinity via Hydrogen termination, due to the electrostatic effect of the dipole moment p of the heteropolar $\text{C}^- \text{H}^+$ bonds. As most of the reducing agents would rather form different types of hydroxyl groups on the surface than replace the surface groups with C-H bond, only the direct reaction with elemental hydrogen enables the formation of C-H bond as surface termination. Hydrogen plasma has been applied to bulk diamond and diamond thin film as a method to achieve full coverage of hydrogen termination as well as to nanodiamond powers[Yeap Langmuir 2009].

Chapter 2

Sample preparation and Experiment Apparatus

2.1 Sample information

The nanodiamonds that are used as sample in this project was synthesised from a trinary mixture of naphthalene ($C_{10}H_8$), highly fluorinated graphite ($CF_{1.1}$) and Tetrakis(trimethylsilyl)silane($C_{12}H_{36}Si_5$) at a pressure of 8 GPa and a temperature of 1100°C. These nanodiamonds carry optically active SiV and NV. The presence of NV is the result of spontaneous doping from the synthesis procedure, more specific, is due to atmospheric nitrogen adsorbed on the surface of naphthalene powder.

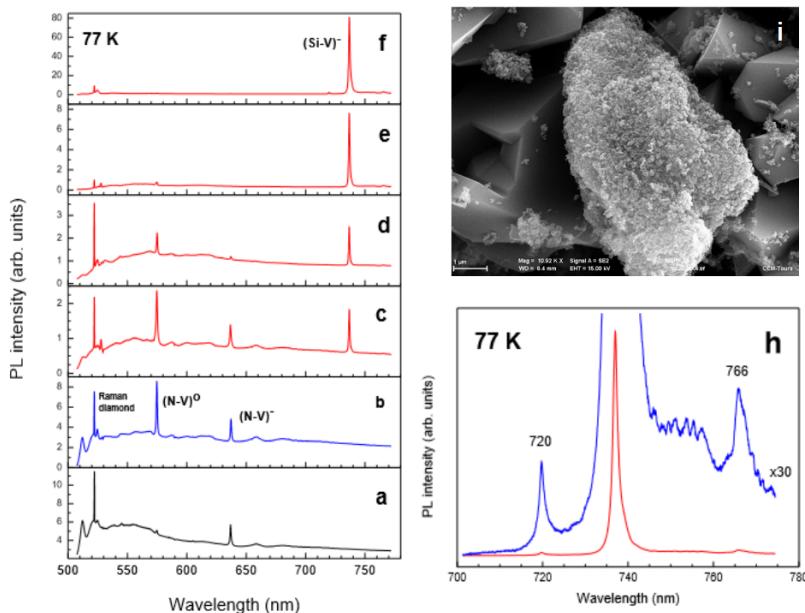


FIGURE 2.1

To obtain cleaner and more size-refined nanodiamond, the sample was then centrifuged and divided into 4 batches following the condition in table 2.1. in between each step, the residue was re-dispersed in 1ml of microwater. The average size of the nanodiamonds in batch 1 is expected to be the smallest, and the ones in the 4th batch are expected to have the largest size.

TABLE 2.1: Centrifuging conditions for nanodiamond size selection

Batch Number	Centrifuging Condition
1	2000rpm 1min
2	1000rpm 1min
3	500rpm 1min
4	300rpm 1min

2.2 sample preparation

2.2.1 preparation of the substrate

IIa diamond as substrate To choose a proper substrate for the nanodiamond sample, a few principles need to be considered.

1. Low background fluorescence. It is always vital to obtain a decent signal to noise ration in any kind of measurements. As for our case, the emission(fluorescence) from silicon centers are the target, thus we would love to lower the back ground fluorescence as much as possilble.
2. Good heat conductivity at low temperature. From previous calculation done by Uwen Jantzen, we know that the temperature difference ΔT between the bottom of the substrate and nanodiamonds(which are spin coated on the surface of the substrate) can be estimate as $\Delta T = \frac{\sigma \cdot d \cdot T^4}{k}$, where σ is the Stefan–Boltzmann constant, d is the thickness of the substrate and k is the thermal conductivity. To resolve the fine feature of silicon vacancy ZPL, we want to characterise the nanodiamond sample at a temperature that is lower than 30K for spectrometer and 10K? for PLE.
3. No distracting spectral features. Some misleading peaks from the emission of the substrate would be the least wanted when we want to character a sample spectrally. In many cases, this is related to the raman-scattering of the photons, which highly depends on the crystal structure of the substrate. This scattering process alters the energy of the incident photons by shifts of concrete values and sometime can introduce peaks that are misleading or distracting.
4. Refractive index. Inam et al calculated the relative emission rate for radiating dipoles near an interface between two dielectrics with FDTD simulation. The result demonstrates that in both of the cases, when the dipole lies perpendicular and parallel to the substrate, the emission rate from a interface with lower relative refractive index is always higher than that from a interface with higher relative refractive index. And to increase the emission rate, a substrate with lower refractive index would be prefered.

Previously, taking these principles into consideration, my colleges have already ruled out a couple of materials, for instance, glass/quartz(distraction

raman shift lines) and Sapphire(also a distracting raman shift line, and impurity induced emission that calls for extra attention when picking the optical filters). Now the temporary choice has landed on IIa type diamond, which has a low impurity density(resulting in low background fluorescence intensity), relatively low refractive index(2,4 to 2,7), good thermal conductivity($\Delta T = 4,17 \cdot 10^{-2} K$) and a raman shift at $1332 cm^{-1}$ that causes no distraction on our observation.

Focused Ion Beam milling In order to make it more convenient to trace the nanodiamonds, markers were curved onto the surface of the IIa type diamond substrate, this work was done by Uwe Jantzen during his master's thesis period. As is shown in the fig.[], the focus ion beam bombards the surface of diamond away and leaves behind markers that are visible in optical microscopy images and SEM images, as well as confocal microscopy images. But the impact of ion may also introduce new defect into the substrate, which will be discussed later.

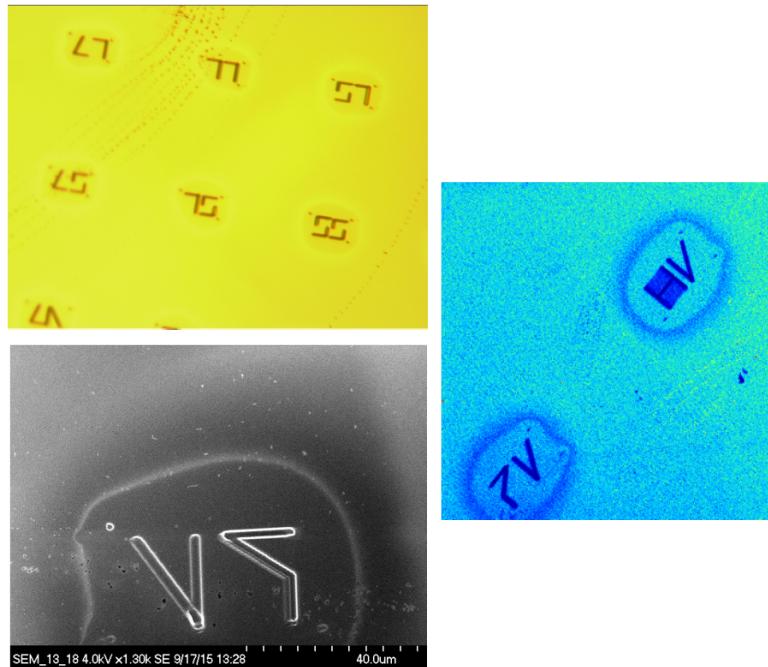


FIGURE 2.2: Pictures of markers obtained from FIB, which are placed following the order of numbers. They are visible in optical microscopes, confocal microscopes as well as SEM

2.2.2 spin-coating of the sample

spin-coating theory

Spin coating is the method of sample preparing that mainly contains 2 steps:

first, the preading of the liquid. In this step, certain volume of liquid containing the particle that we want to coat with is dropped on the surface of the substrate, driven by the centrifuging force from the rotational movement of the substrate, the liquid would be spread evenly on the surface.

Next, the evaporation of the 'solvent'. While the sample stage rotates, the 'solvent' (In our case is not a real solvent, since nanodiamonds never really desolve.) would evaporate, leaving the particle/molecules that are wanted to be coated on the substrate.

In the spin coating session, a few factors we find important.

1. spin speed: generally the thickness of the liquid layer t is proportional to the inverse of the angular velocity w squared $t \sim \frac{1}{\sqrt{\omega}}$, higher speed would help with forming a more uniform layer, yet this also means a smaller volume of solution, which would lead to lower density of nanodiamonds on the surface. On the other hand, with lower speed, the probability of aggregation would increase, which is also what we want to prevent.

2. volume of the 'solution': larger volume means longer drying time, which would increase the probability of aggregation and losing nanodiamonds, while smaller volume leads towards lower density of nanodiamond and more difficulty when trying to drop it with a pipette.

3. type of solvent: The type of solvent, viscosity and boiling point are important for the dispersion of nanoparticles inside solution, the spreading of the solution while spin coating and the rate of evaporation.

4. surface condition of the substrate. High contact angle is an obstacle towards the spreading of the solution, high roughness or inappropriate surface group of the substrate can result in poor wettability from the solution.

Acid cleaning

To make sure that the NDs dispersion can evenly spread and eventually settled on the substrate, a smooth, clean and hydrophilic surface is important.

Acid boiling is a very practical way of diamond substrate cleaning. As it is called, the diamond will be boiled in a mixture of three strong mineral acids: sulfuric acid, nitric acid and perchloric acid. This mixture has very strong ability of oxidizing.

After assembling the setup, we initialize the reaction by heating the mixture to a temperature where it mildly bubbles. The substrate would stay inside the boiling tri-acid mix for 4h. After the acid boiling, the sample should be removed from the flask and rinsed with pure water, after which a rapid blow dry with clean air is compulsory. The mixture of strong mineral oxidizing acid can remove most of the adhesions on the surface of diamond substrate, leaving a clean hydrophilic surface. This oxidizing procedure will lead to the formation of carbonyl and carboxyl groups. One thing that worth notice is that, although via acid boiling, most of the attachments on the surface can be removed, there is still very high chance to introduce other contaminations from the water, and air while the sample is still wet. So a rapid blow dry after the rinse is highly recommended, and if the acid cleaning is not operated in clean room, it is very important to clean the sample a second time via acetone boiling and ultrasonic bath in the clean room.

spin-coating practice

Throughout the project, with the help of Andrea Kurz, several combination of these factors had been tried out on different samples.

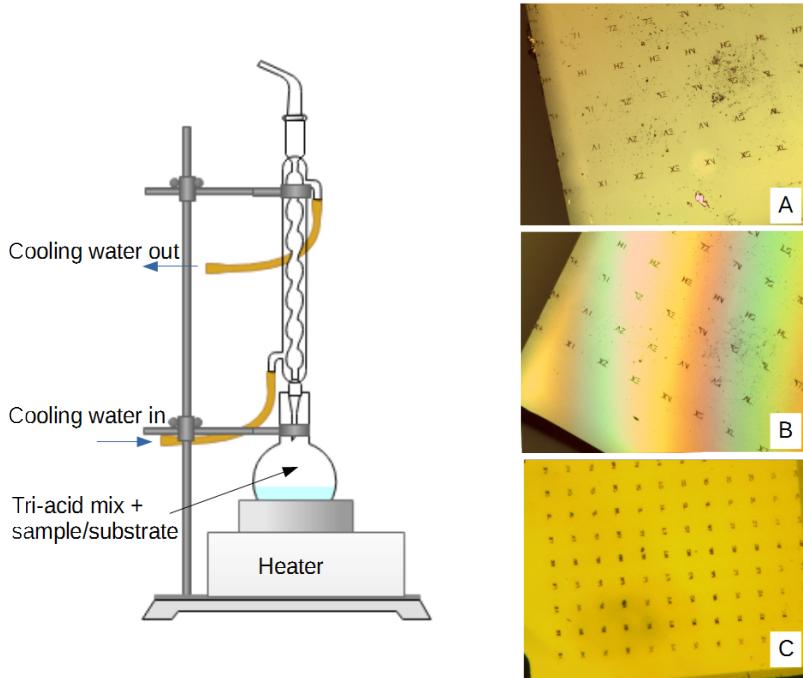


FIGURE 2.3: a) setup up of acid cleaning. b)substrate 207 before cleaning. c) substrate 207 after acid boiling. d) acid cleaned substrate 207 after acetone boiling in the clean room.

I. 35ul Chloroform with 1ul of nanodiamond, take 2ul of this kind of mixture and drop it on the substrate in one time. The spin speed is 5000rpm and the duration is 40s.(Sample 1506,1507)

II. 30ul Chloroform with 1ul of nanodiamond, 2ul of mixture, apply in one time, 5000rpm and 40s.(Sample 1508,1509)

III. 30ul Choloroform and approximately 120ul of water with 1ul of nanodiamond, 2ul of mixture, apply in one time, 8000rpm and 40s.(Operated on substrate207 and found no SiV⁻ signal later.)

IV. 30ul Choloroform and approximately 120ul of water with 1ul of nanodiamond, 10ul of mixture, apply in 5 times, each time 2ul, after each application, spin with the speed of 5000rpm and duration of 40s.(sample 1510,1512)

All the 3 methods other than method III produced samples with SiV⁻ containing points of interest. But among them, the method IV offers the highest SiV⁻ density.

2.3 Experiment Apparatus

The initial Setup The setup can be coarsely separate into laser source, confocal microscope(with APD and spectrometer as detector), flow cryostat and vaccum pump 4 parts, they are all sketched in Fig. 2.4.

While the absorption spectrum shows the highest off resonance absorption around 530nm[need check need find reference paper], the ZPL of silicon vacancy lies around 737nm. Acknowledged of such information, we choose to use green laser of wavelength 532nm as the laser source for photoluminescence spectrum and Titan Sapphire laser with the ability of scanning

around 737nm as the laser source of photoluminescence excitation. These two methods will be more detailed written about in the following paragraphs. The lasers are coupled into the same photonic crystal fibre, which guides the beam towards the optical table.

The second part is the confocal microscope, which is a very useful tool for imaging of samples that emits fluorescence, such as SiVs. Compared with fluorescence microscope, as sketched in Fig. 2.5, the confocal microscope uses a pair of convex lens and a pinhole that conjugates to the lens to achieve the increase of resolution and signal to noise ration. In the setup, there are two possibilities of signal detection, controlled by a flipping mirror, we can choose to count the photons with a pair of APD, or record the spectrum with a spectrometer. As the resolution of fine splitting of SiV ZPL needs to be measured in low temperature, the motorized sample stage is placed in a flow cryostat, the objective lens is also inside the cryostat. As the name mentioned, the decrease of temperature in this cryostat is achieved by the flow of cold, boiling liquid Helium, a transfer line connects the Helium dewar and the inlet of the helium cooling circulation inside the cryostat. The sample sits right on the cold finger, with proper method of mounting and substrate, the temperature can be brought to as low as 3.5K(need to check).

To reach cryogenic temperature, it is vital to cut off the heat exchange between the sample and the world out side the cryostat, since air and stainless steel(the material of the cryostat wall) can both conduct heat, a UHV condition need to be meet. In our setup, it is realized by the pumping system of a back pump and a turbo pump. The back pump pre-pumps the pressure until it meets the working condition for turbo pump.

With the mentioned setup, we are able to characterise the sample with following basic methods.

Photoluminescence Photoluminescence detects the emission after the absorption of photons. In our case, we use the 532nm laser to excite the sample, which would bring the SiV^- to the second excited state, while the electronic transition between 2 energy levels of the same parity is not allowed, it is possible to conduct the transition between such kind of 2 energy level via the creation and annihilation of phonons, thus it will be the 4 transitions between the first excited state and the ground state that we are expect to record in the spectrum .

The resolving power of a grating in a spectrometer depends on the width of the grating, the centre length to be resolved and the geometry of the use condition. In our setup, a resolution of 16GHz can be achieved, which is capable of observing the 4 line structure in SiV^- ZPL, but not enough to resolve a peak with the width of the lifetime limit.

PLE When PL excites the sample with a laser of single wavelength to obtain the information about multiple emissions, PLE, on the contrary, excites the sample with various wavelength and monitors the photon emission from the side band to characterise a single transition. The resolution of PLE depends on the resolution of laser, with the Matisse Titan-Sapphire

laser(linewidth of 50kHz), it allows us to resolve single electronic transmission in SiV⁻ with life time limited line width, as well as to obtain better signal to noise ratio.

time resolved PL spectra With such high resolution, it is extremely time consuming monitoring the spectral diffusion of a width up to 1nm. To help characterise the spectral diffusing behaviour of SiV⁻, we improvised the time-resolved PL spectra. By stacking the sequentially taken spectra in the order of time, we can visualize and estimate the spectral diffusion in a more coarse but convenient way.

Departing from the initial setup, a few alternations have been done during the project, which would be discussed in detail in the following up contents.

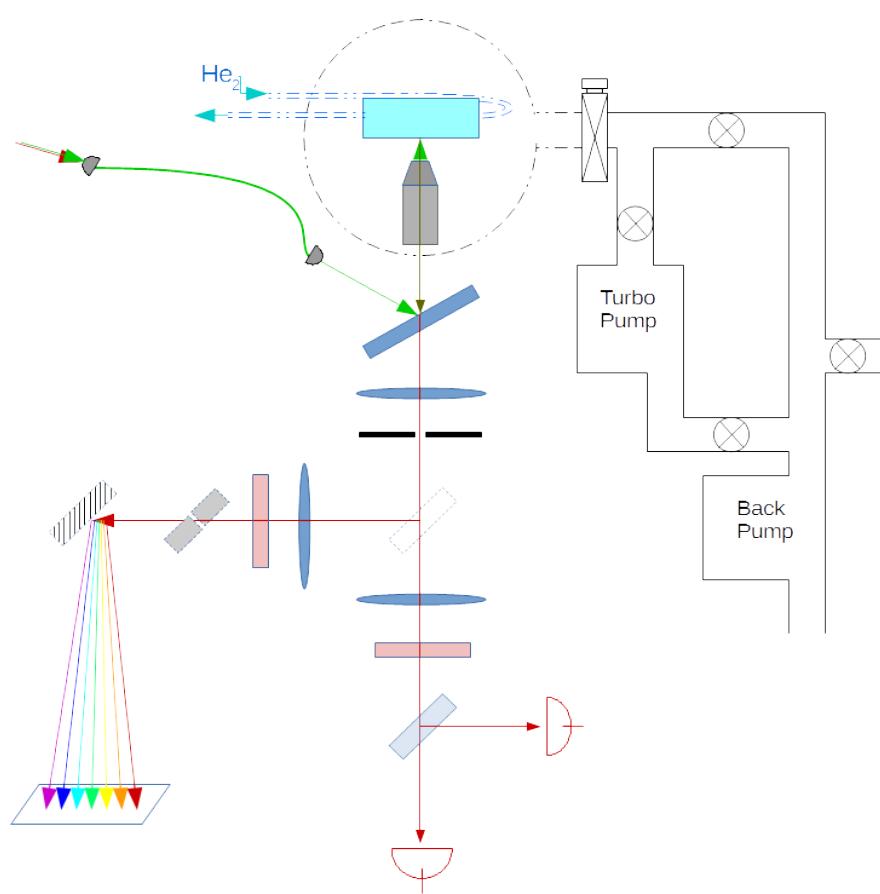


FIGURE 2.4: A sketch of the initial setup.

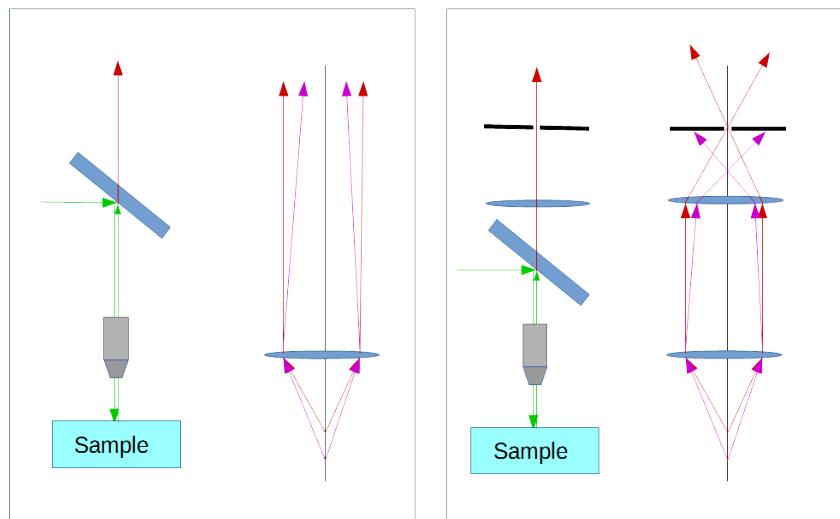


FIGURE 2.5: A)In a typical fluorescence microscope, the back ground fluorescence will also be collected. b)In the confocal microscope, with the help of a lens conjugating pin hole, a large fraction of the fluorescence from non-focus plane will not get through by the pinhole.

Chapter 3

Surface treatments

3.1 Oxidation

Room temperature oxidization is a common way of nanodiamond purification. With different oxidizing temperature, different types of impurities can be removed from the surface of the nanodiamond, ranging from water and physisorbed organic impurities, amorphous carbon, and graphitic shells and ultimate the sp^3 phase of diamond[T.Gaebel,2010]. After the oxidation, carbonyl and carboxyl groups are formed on the surface[Petrakov,2012]. Several paper have mentioned temperature choices for oxidation aiming at impurity removal. During the master's thesis period, 2 different oxidation has been examined.

3.1.1 first Oxidation

As reported, it is possible to achieve the removal of sp^2 carbon without any oxidation on sp^3 carbon via aerobic oxidation with temperature between $375^\circ C$ and $450^\circ C$. With temperature lower than $500^\circ C$, the size reducing rate of nanodiamond is lower than 1nm/h . As our first treatment, we carried out a two step oxidation on sample 1508 and 1509, to achieve the complete removal of graphitic defect on the surface and light oxidation on the surface. Sample 1508 was spin coated with nanodiamond batch2, sample 1509 was spin coated with nanodiamond batch1.

The aerobic oxidation is carried out in a tube furnace and it is done with the help of Markus Mohr. The tube furnace consists of a glass tube connected to the room atmosphere and heating coils around the glass tube. The glass tube can be slide in or out of the heating coils. We put our sample inside a ceramic sample holder and put the holder into the glass tube carefully, after the temperature has been raised to $460^\circ C$, the glass tube was slide into the heating coils. The sample was oxidized at $460^\circ C$ for 90min,then $480^\circ C$ for 40min. After the Oxidation, the glass tube was slide out and the sample stayed inside the tube until it reached room temperature.

Before the oxidation, the samples was first mapped with a room temperature setup that resembles fig. 2.4, but without vaccum pump and cryostat. To make a map of SiV^- containing points of interest, it was first taken, a scan with green laser while the fluorescence was recorded by APD, which offers us a confocal microscopy image of the sample, then the photoluminescence spectra of the bright spots were taken, coordinates of those ones with a sharp peak at 737nm saved as points of interests for the reference of further examine.

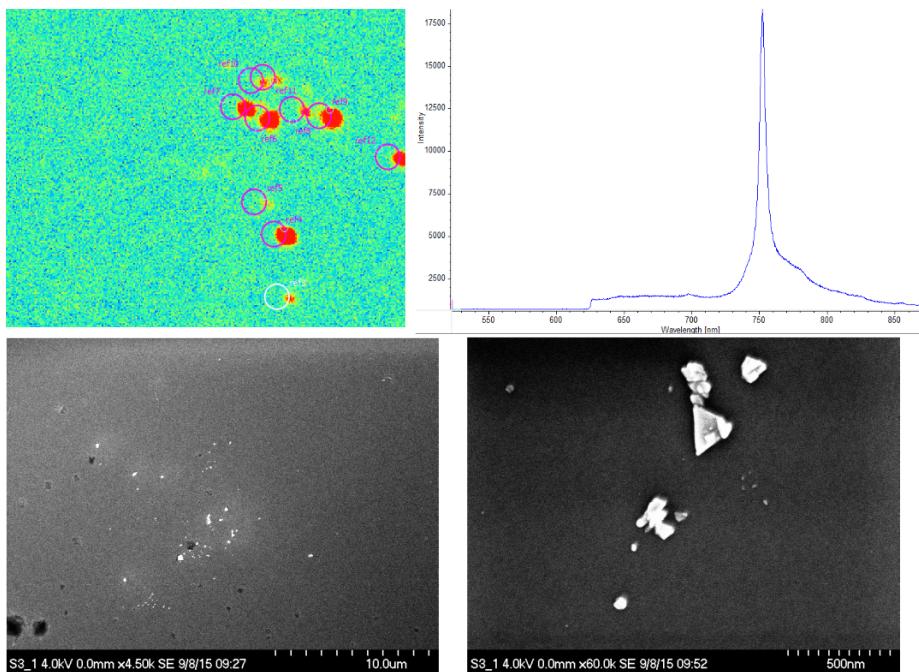


FIGURE 3.1: A)confocal image of a region of interest. The bright spots with circle markers are points of interest. B)Room temperature spectrum of a poi recorded by spectrometer. C)the roi in SEM. D)ref10 and 11 in SEM.

Once the map was acquired, we bring the samples to the electron microscope center and observed the regions of interest with SEM. SEM showed that, sample1508 contains more big single crystals that are larger than 300nm and clusters, while sample 1509 contains more single crystal with under 200nm sizes. This proved that the size selection via centrifuging has worked.

The samples was then attached to an cold finger and the placed inside the cryostat, after UHV condition has been achieved, the helium transfer was started, which would brought the temperature of the sample down to 4.8K. Most of the mapped pois are refound. Excitation with 532nm green laser double checked the existence of SiV. After the confirmation, it has been tried to carry out a resonance excitation with Titan Sapphire laser, when observing a few points of interest next to marker 5A in sample1509, it was noticed that while scanning the red laser across the line with the help of very low amount of 532nm for repopulation, a spectral diffusion of 6GHz in 15Min has been observed. To exclude the possibility of instrumental error, PLE has been operated on the bulk diamond sample with also SiV inside, where no spectral diffusio has been observed(Fig. 3.2). It has also been noticed that the increase of green laser power can cause more severe spectral drift/jump. In a case when the power green laser is brought up for a better refocus, the line has shifted totally out of the range of the spectra scan, and didn't recover in 10min. This observation brought difficulty in the measurement of orbital T1, since we always need to initialize the obital states with green laser, and this spectral diffusion that is related to the application of green laser can result in the fail of hitting the resonant wavelength, since it is technically difficult to refind the line and adjust the wavelength of the resonance laser coordinately.

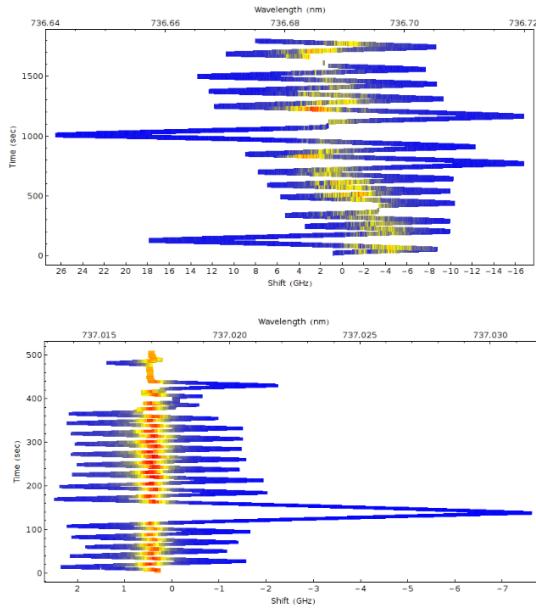


FIGURE 3.2: PLE scan over time on A) ref5A_014 from sample1509 and B) a SiV⁻ site from bulk diamond sample 33b. No significant spectral diffusion been found in bulk diamond sample, which exclude the possibility of instrumental error.

4. time-resolved PL spectra.

After the obeservation that is mentioned in the last paragraph, we want to study more about this spectral diffusion behaviour that is associated with the green laser. We learned that the sudden jump/diffusion when more green power is applied can be larger than 20GHz, maybe it is possible to resolve it with the higher resolution grating of spectrometer.

To observe the diffusion with a spectrometer, we introduced time-resolved photoluminescen spectrum, which has been detailed described in the chapter development fo a way to estimate the spectral diffusion.

Due to the technical problem, our motorized sample stage can not move ideally in the vertical direction anymore, which has limited our region that is observable. This time we refind the ROI around the marker 4C. And recorded the time-resolved spectrum. A session is set to be 30 spectra taken consecutively. At first, to feel the long term diffusing better, 3 sessions, with a refocus after each, are undergone for each points of interests. Since the green laser induced line jump in PLE is gets wider when raising the green laser power, we excite the sample with 500uW power in front of the objective lens to obtain more diffusion. As a result, line diffusion up to 1nm

has been observed.

Follow up we decrease the input power to examine the expectation that the level of this spectral diffusion is proportional to the excitation power.

To estimate the level of spectral diffusion, we compared the time resolved spectra in following ways: the mean linewidth, histogram of wavelengths and cross-correlation between spectra over time.

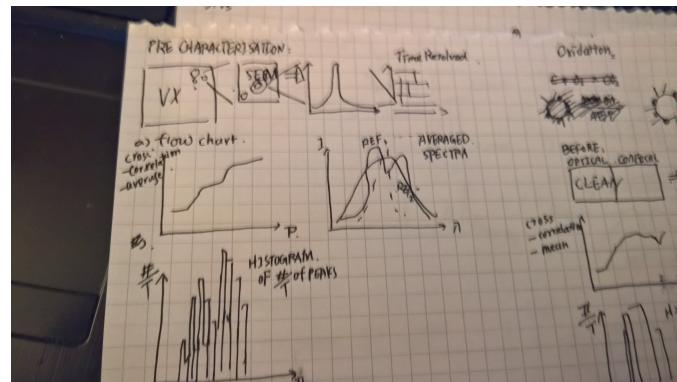


FIGURE 3.3

post-oxidation characterisation

1. Optical microscopy check The first thing we found after the oxidation is that, the surface of our sample turned very dirty. We are yet not certain about what the contaminations are, are they intrinsic or are they external. A possible deduction is that, the contamination comes from the glass tube of tube furnace, that the residues of previous treatments has attached to the inner surface of the tube and evaporized again, depositing on the surface of our sample. Further improvement of oxidation operation has been done in our second oxidation test, and will be mentioned in the next part of the thesis.

2. Refound poi with RT setup Huge amount of bright spots can be seen in the confocal image when we excite the sample with 532nm green laser. There's no Silicon vacancy like spectra found in these bright spots. We re-find our points of interests next to the marker 4C. The photoluminescence spectra shows much higher intensity than before the oxidation.

3. Cold spectra and PLE After the confirmation of points of interests, the sample was transferred into the flow cryostat and the helium flow brought the temperature down to 4.8K.

At 4.8K we recorded the time-resolved photoluminescence spectra of different incident beam power with an excitation wavelength of 532nm.

After the first oxidation, we learned that due to the inner strain of photonic fibre, the incident beam can not preserve a static polarisation. To stable the polarisation, we used a polarising beam splitter with a LC noise eater behind it. This would fix the polarisation at vertical direction.

The spectra appeared to be different from before oxidation, the most obvious change is the increase of the luminescence intensity, another observation is the broaden of the peaks and the decrease of peak number per spectra. The broadening can be caused by the misalignment of the spectrometer or the poor contact between the sample and indium, or between the sample mount and the cold finger.

We recorded the time-resolved PL spectra, in data proceeding of post characterisation, we noticed some slow diffusion, that is not obvious when only one session is taken. So we decided to take 2 session per poi and 90s per session.

Due to the external sourced contamination, a few poi has gained a very noisy background, which leads to none ideal result.

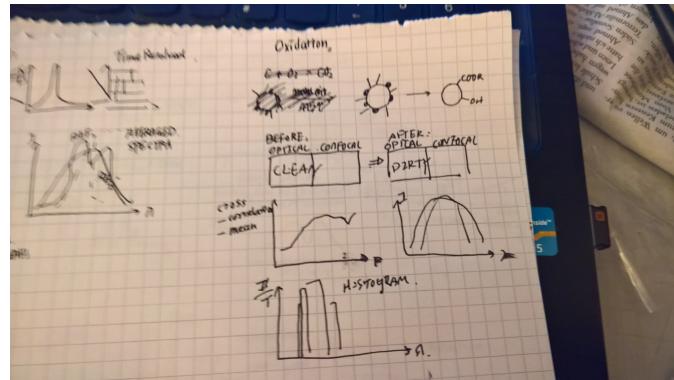


FIGURE 3.4

3.1.2 second Oxidation

method As is mentioned before, the optical properties of SiV in bulk diamond is extraordinary. Most importantly, the spectrodifusion that we have observed in nanodiamonds has never been seen in bulk diamonds. In the first oxidation, it seems the removal of graphitic impurity didn't help with the stabilization of emiision lines. In this second oxidation, we decided to used a higher temperature to acquire a surface with groups that imitates the bulk diamond. As reported by [paper], after 2 hours of aerobic oxidation at $575^\circ C$, ... here insert a sentence of the surface groups of nanodiamonds. To increase the chance of finding smaller nanodiamonds that would fit into a cavity and decrease the chance of getting clusters of nanodiamonds, this time we chose to use nanodiamond of the first batch. These nanodiamond are spin coated on the substrate following the method II(the index, can be change).

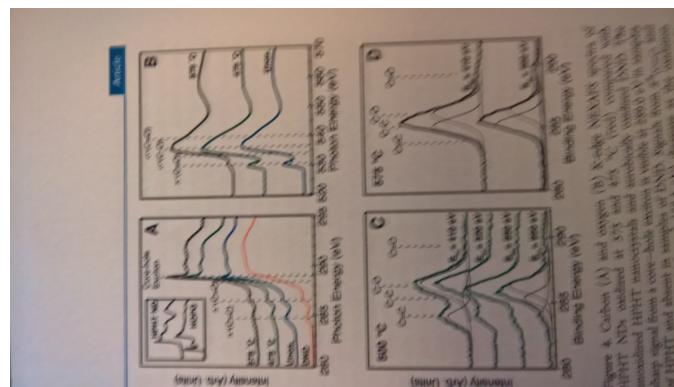


FIGURE 3.5

Figure 4. Carbon (A) and oxygen (B) XPS spectra of (C) Kondo insulator species of SPHT NDs oxidized at 5% and 4% weight fraction. (C) The corresponding XPS spectra of NDs spin-coated onto a substrate at 200 μm thickness oxidized from a cone-hole etching in air at 575 $^\circ C$ for 2 hours. The binding energy of the H2PFT and absent in samples of NDs at 284.5 and 288.5 eV referring to the C1s peak.

Taking the experiences of last oxidation into consideration. This time we introduce flowing inert gas (helium) to flush away the potential contaminations during the cooling process. This can also prevent the result to be affected by the humidity of the air. We found out the extinction rate of polarising beam splitter is not ideal, so this time we used a Clan Thompson polarisation filter instead.

Before Oxidation 1.Optical microscopy observation

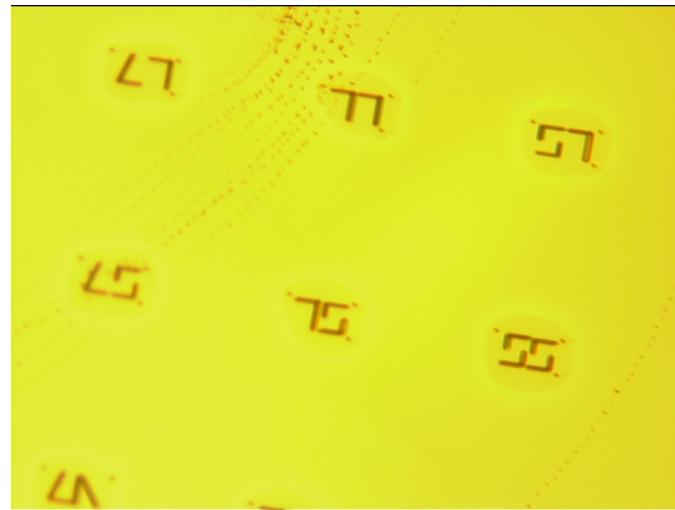


FIGURE 3.6

THIS IS NOT THE RIGHT FIGURE NEED CHECK THE SERVER We observed the sample after the spin coating with optical microscopy, the surface appeared to be relatively clean, little amount of contamination has been observed, but is acceptable.

2.Mapping of SiV^- with room temperature setup.

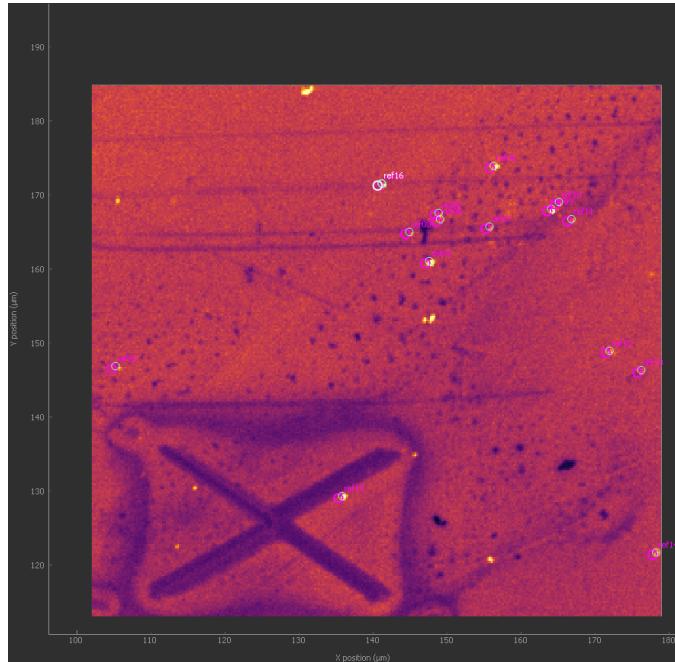


FIGURE 3.7

Once again, we explored the sample with the same room temperature confocal microscopy setup. With the help of spectrometer, we find a few points of interest with a emission spectrum that resembles SiV^- .

3. Cold time-resolved PL and exitation polarisation

As has been mentioned in last chapter, it is suspected that the incident polarisation can affect the spectral behaviour of SiV. We added in the excitation polarisation measurement and recorded the time resolved photoluminescence spectra of 2 different excitation polarisation that are perpendicular to each other. This is achieved by putting a motor-driven half-lambda plate after the noise eater. Due to short time scheme from this measurement we decided to fix the input power at [?need to check], which is the lowest power that can offer most of the points of interest's a decent signal to noise ratio.

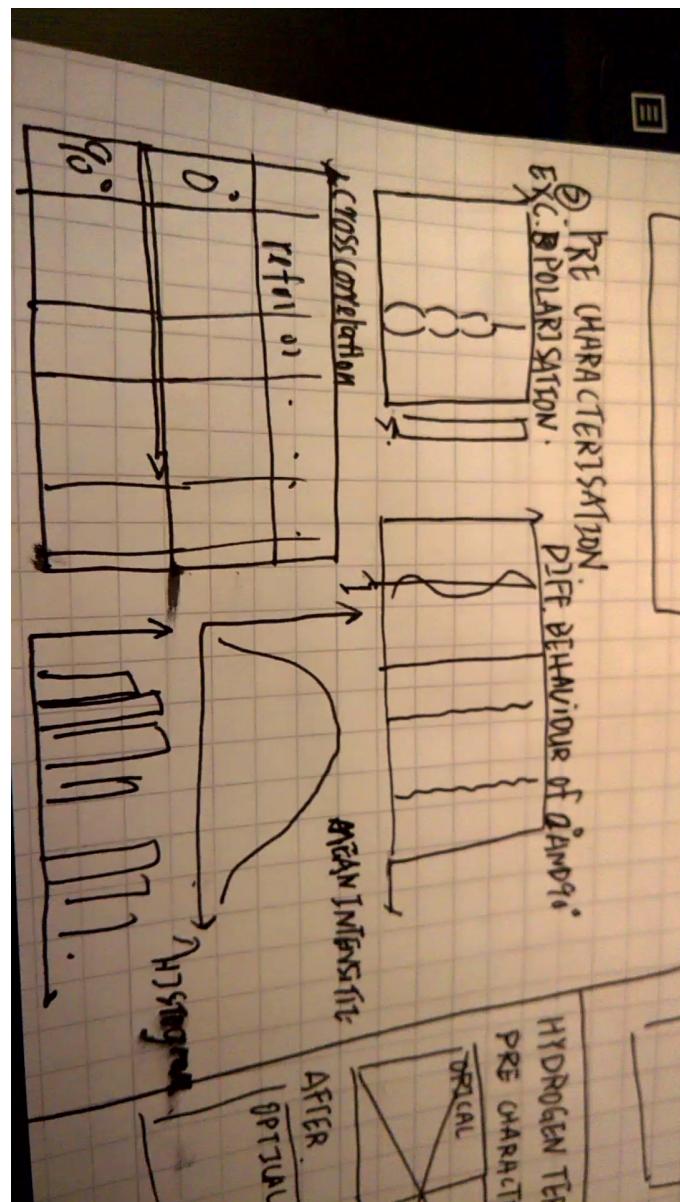


FIGURE 3.8

After Oxidation 1. Optical Microscopy observation.

After the Oxidation, we found the surface not as dirty as the last Oxidation. It seems a cleaner tube and flowing gas flushing do have helped suppressing the surface contamination introduced by the tube furnace. 2. Room temperature mapping

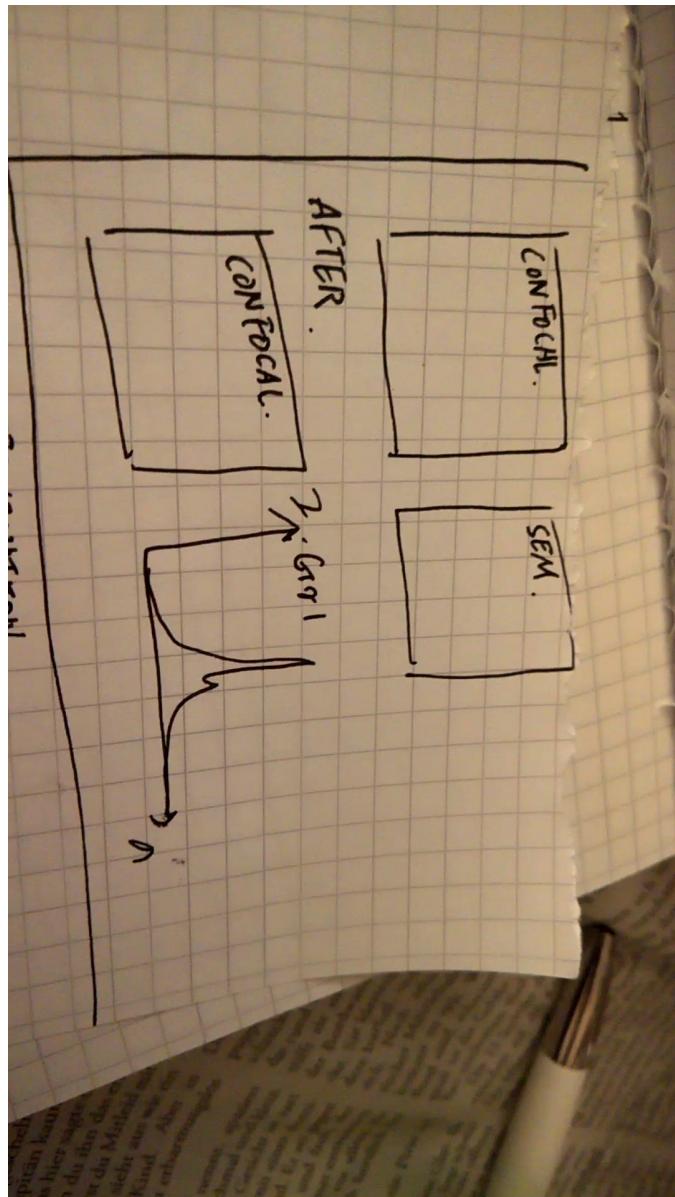


FIGURE 3.9

Analysis Comparasion if possible: different behaviour pre treatment between two batches Possible reason: losing NDs due to Helium flow while cooling, GR1 getting closer to the surface due to oxidation caused size/thickness reduction.

3.2 H termination

Effect of H termination

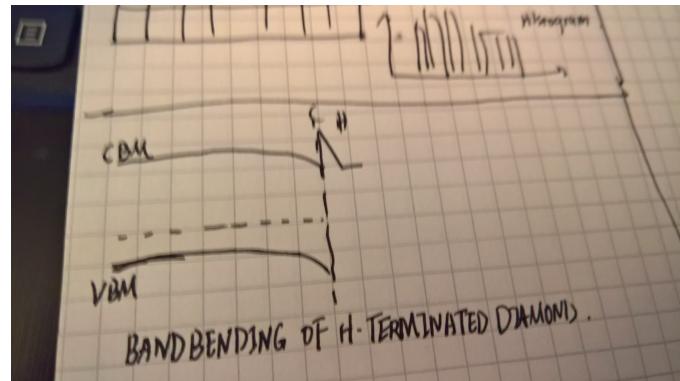


FIGURE 3.10

method Plasma treatment, setup, apparatus. ASK OSCHDI TO SEND THE PARAMETERS

why no pre characterisation Conditions for Plasma treatment. Vacuum and clean surface.

After H termination Confocal image, optical image, excitation polarisation, time resolved PL with different incident polarisation.

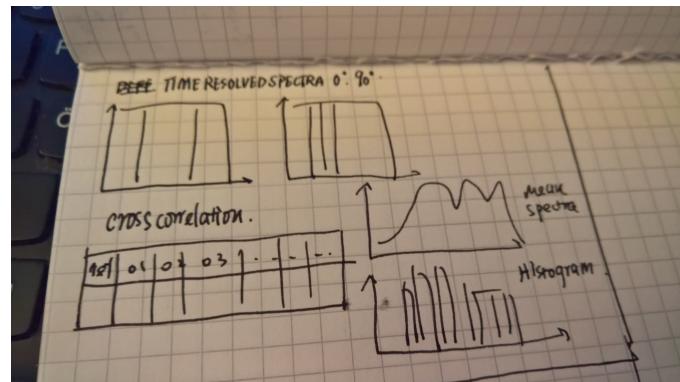


FIGURE 3.11

Analysis Within the instrumental limit of spectrometer, the spectral diffusion has been significantly suppressed. Possible reason.

Chapter 4

Conclusion and outlook

4.1 The road so far

Initial motivation

Development of a method to estimate the spectral diffusion

Surface treatments and their effects

4.2 Probabilities in the near future

PLE

life time measurement

comparasion of different surface group -OH and graphitic patch

better method for size selection porous/gel system, chromatographic way of size selection

relation between surface geometry and spectral behaviour

Appendix A

Appendix Title Here

Write your Appendix content here.