

UNIVERSITY ULM

MASTER THESIS

Optical Properties of Silicon Vacancies in Nanodiamond

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A thesis submitted in fulfillment of the requirements

for the degree of Master of Science

in the

Institute of Quantum Optics
Department of Science

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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:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

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Chapter 1

Motivation and Background

1.1 Quantum info processing and Qubit candidates

1.2 Silicon vacancy as a Qubit candidate

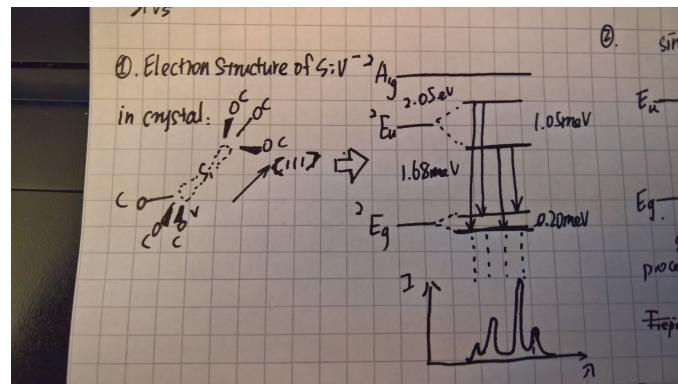


FIGURE 1.1

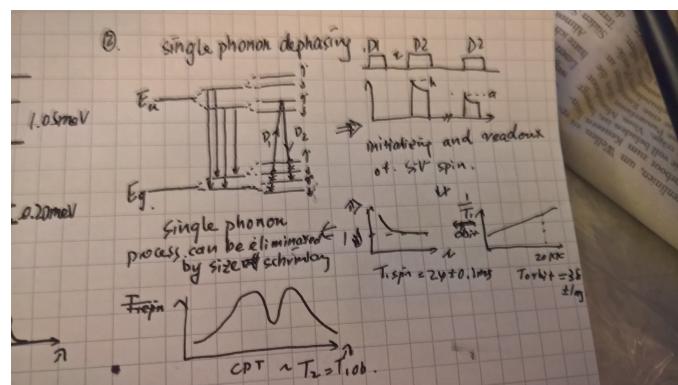


FIGURE 1.2

1.3 Silicon vacancies in nanodiamonds

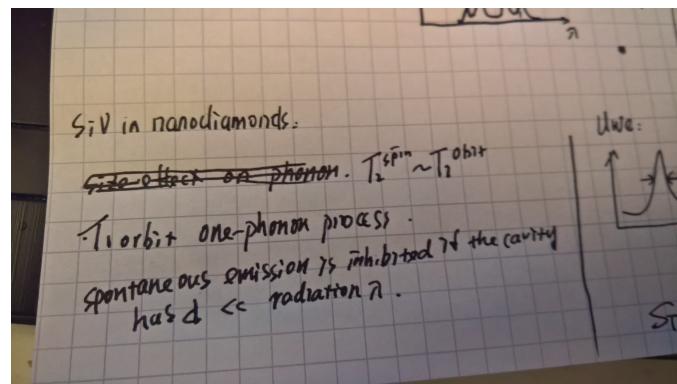


FIGURE 1.3

1.4 Motivation of the thesis, unsolved problem

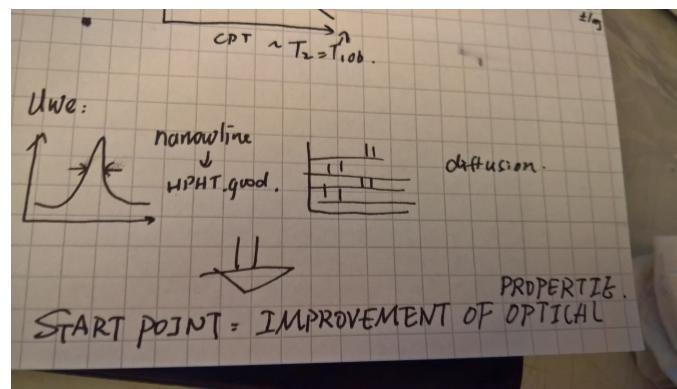


FIGURE 1.4

Chapter 2

Sample preparation and Experiment Apparatus

2.1 Information regarding the nanodiamond sample

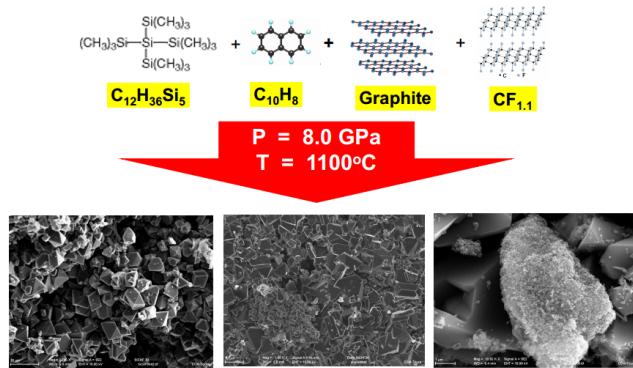


Fig. 1. SEM images of micro- and nanometer-sized Si-doped diamonds obtained as a result of high pressure high temperature treatment (HPHTT) of different mixtures of $\text{C}_{12}\text{H}_{36}\text{Si}_5$, C_{10}H_8 , $\text{CF}_{1.1}$ and graphite.

FIGURE 2.1

here is a paragraph about the fabrication of nanodiamond

After this the steps were the following:

1. Centrifuging at 2000rpm for 1 minute to remove the dirt. The liquid at the top was transferred to a new Eppendorf labeled "1st batch ND's". We suspect there to be not a lot of NDs as they are not soluble. These should be the smallest ones.
2. Diluting residues in Eppendorf with 1ml of microwater (the one behind the VWR) and then centrifuging at 1000rpm for 1 minute. The liquid part removed from this was named "2nd batch ND's".
3. Diluting residues again with 1ml of microwater. Centrifuging at 500 rpm for 1 minute. The liquid removed was called "3rd batch ND's".
4. Diluting residues again with 1ml of microwater. Centrifuging at 300 rpm for 1 minute. The liquid removed was called "4th batch ND's". This was the slowest possible centrifugation speed possible with this machine.
5. The residues after removing the liquid for batch 4 was called "residues after centrifuging at 300rpm for 1 min".



FIGURE 2.2

here is a paragraph about the separation of the nanodiamonds

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.

4 Chapter 2. Experimental approach of surpassing the spectral diffusion

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 emision 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 focues 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.

here is a sketch of how Ga-ion bombards the surface of substrate

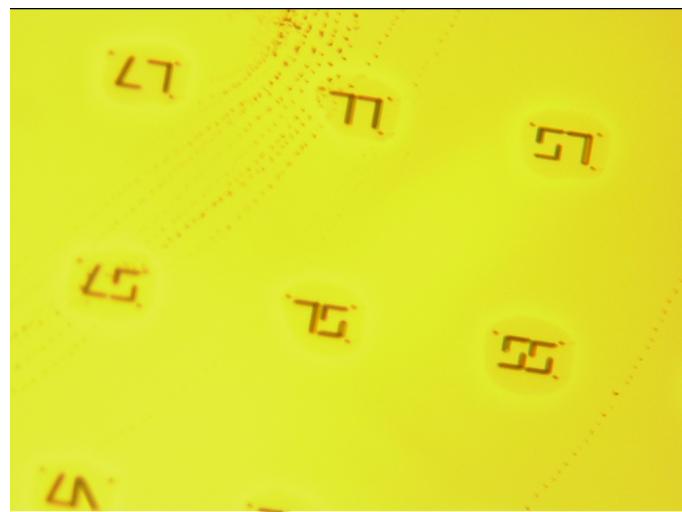


FIGURE 2.3

here insert image of markers, optical, sem and confocal

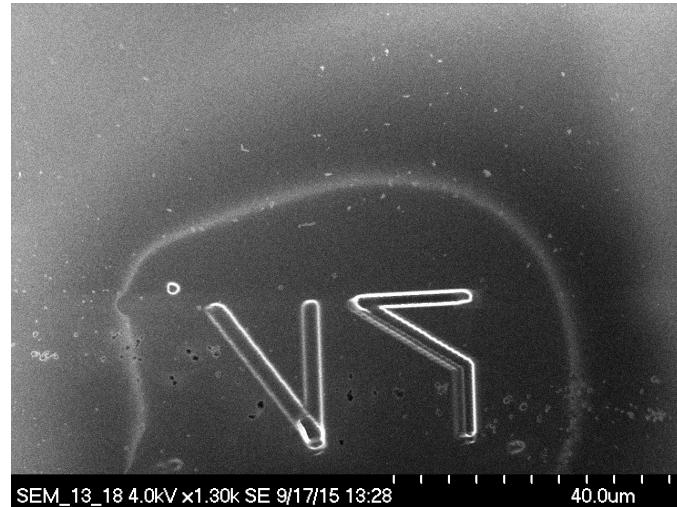


FIGURE 2.4

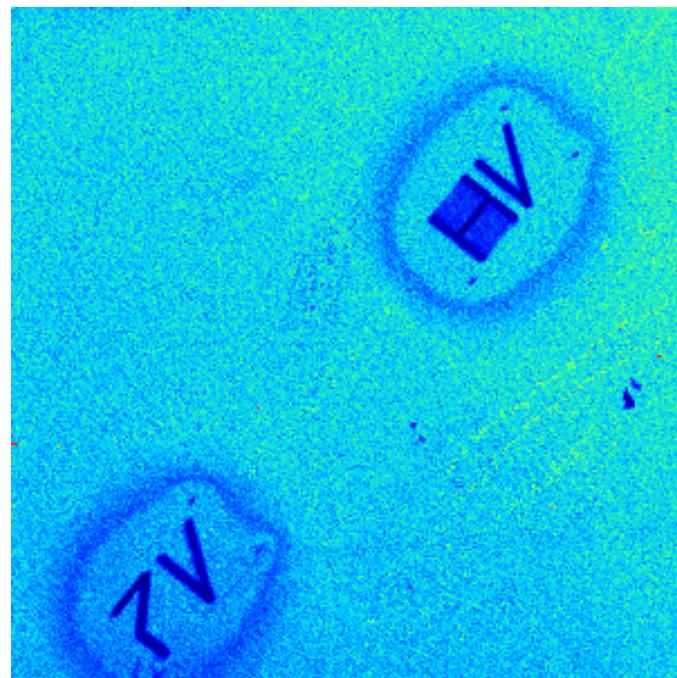


FIGURE 2.5

2.2.2 spin-coating of the sample

theory of spin coating

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 this procedure, 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.

Additionally, I want to emphasize that, when choosing the spin coating method, the properties of the nanoparticles is always one of the most important thing to take into consideration. Throughout my project, with the help of Andrea Kurz, several combination of these factors had been tried out:

1. 2. 3.

here we need a list of different program of spin coating that we have tried,with indexxxxx

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.

here insert a sketch of how we do acid cleaning After assembling the setup, we initialize the reaction by heating the mixture to a temperature where bubbles form. The substrate would stay inside the boiling tri-acid mix for 4h. 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.

here insert image of before and after cleaning substrate, optical image, confocal image

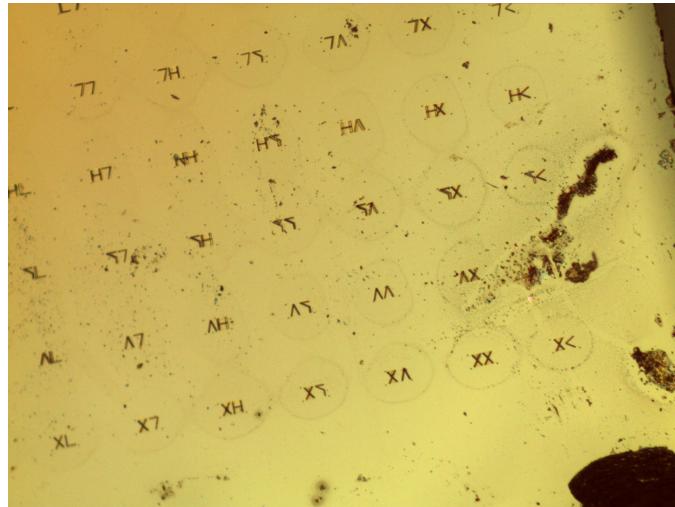


FIGURE 2.6

fig. the comparision between before and after acid boiling(need to be inserted later).

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.

Following the optical path, we start from the first part, the laser source.

As has been mention almost countless times, silicon vacancy is our focus of investigation. 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, 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.(expend) 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.

The spectrometer is

As the resolution of fine splitting of SiV ZPL needs to be measured in low temperature, the motorized sample stage and objective lens are placed in a flow 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.

here inserts a picture of our flow cryostat, from out and in side. This is the flow cryostat, whose main body is a vaccum chamber with

here insert a sketch of the cryo4 setup Confocal + Cryostat, Green laser + Red laser, spectrometer, apd, pic

PL Photoluminescence spectra is one of the most efficient way of finding silicon vacancies. In this measurement, we use green laser of 532nm to excite the Silicon vacancies from ground state to

PLE resonance excitation of optical transition. Resolution limited by scanning step of laser. Observing phonon side band with apd. range of scanning: limited by laser, small.

time resolved PL spectra Tracing PL spectra over time, show the diffusing behaviour of lines, characterisation methods: excitation polarisation: width of diffusion. Cross- correlation over time.

We recorded and noticed that the diffusion, whose range can up to 1nm, is far beyond the capability of PLE.

Chapter 3

Experimental approach towards the improvement of optical properties of silicon vacancies in nanodiamonds via surface treatment

3.1 Oxidation

Effect of 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

method As reported, oxidation of sp^2 carbon already starts at $400^\circ C$, while the size reducing rate of diamond phase remains neglectable when the temperature is lower than $500^\circ C$. So it is an obvious choice to settle down the oxidation temperature at somewhere close to $500^\circ C$ when the maximum removal of sp^2 phased carbons and the minimum lost of the diamond body(sp^3 phased carbons). Inspired by Elka Neu's paper,here insert a sentence explaining why we choose the two step oxidation program.

setup The aerobic oxidation is carried out in a tube furnace that is offered by the ?? institute 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 is slid able. We put our sample inside a ceramic ?bowl? and put the bowl into the glass tube carefully, after the temperature has been raised to ? $460^\circ C$?, the glass tube would be slide into the heating coils. After the Oxidation, the glass tube would be slide out and the sample would cooled inside the tube until room temperature.

pre-characterisation Before the oxidation, we tried to characterise the sample with several different methods based on our confocal microscopy setup.

1. RT poi mapping

First we take a scan with green laser and record the fluorescence with an APD, which offers us a confocal microscopy image of the surface of the sample, then the photoluminescence spectra of the bright spots are taken, those ones with a sharp peak at 737nm are saved as points of interests and their positions are saved as region of interest for the reference of further examine.

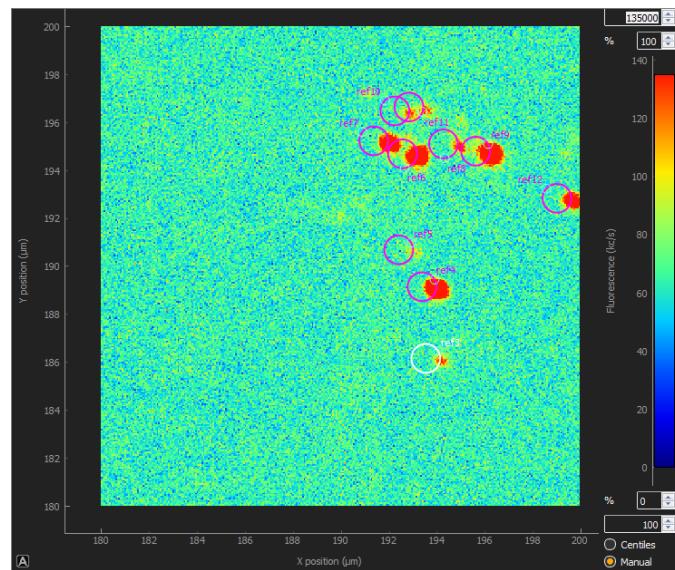


FIGURE 3.1

2. SEM imaging of nanodiamonds

3. Cryogenic measurements PLE

The sample is attached to an cold finger and the placed inside the cryostat, after UHV condition has been achieved, we start the helium transfer, which would brought the temperature of the sample down to 4.8K. We re-found the points of interests that has been confirmed with SiV like spectra and excited it with 532nm green laser to double check 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, 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. 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 also brought difficulty in the measurement of orbital T1, since we always need to initialize the obital states with green laser, and this spectral shift/jump/diffusion that is related to the application of green laser can result in the fail of hitting the resonant wavelength, while it is technically difficult to refind the line and adjust the wavelength of the resonance laser coordinately.

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 betweenn spectra over time.

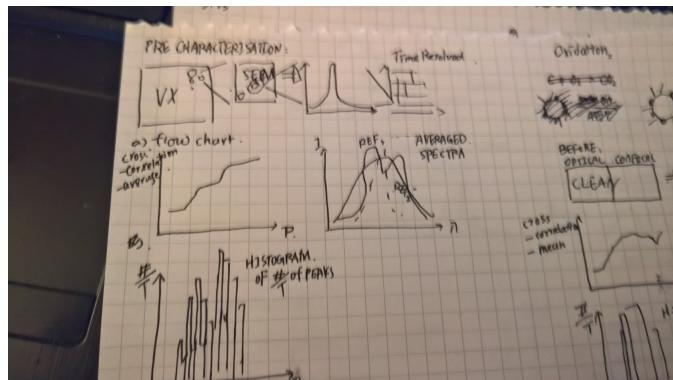


FIGURE 3.2

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.

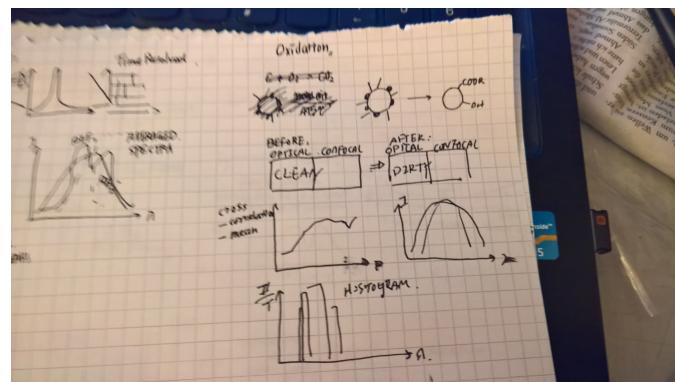


FIGURE 3.3

Analysis After the oxidation we noticed an increased intensity of emission, both background and the 737nm line. The number of lines per spectrum has decreased, while before the oxidation, fine lines ranging from

3.1.2 second Oxidation

method As is mentioned before, the optical properties of SiV in bulk diamond is extraordinary. Most importantly, the spectrodiffusion 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°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).

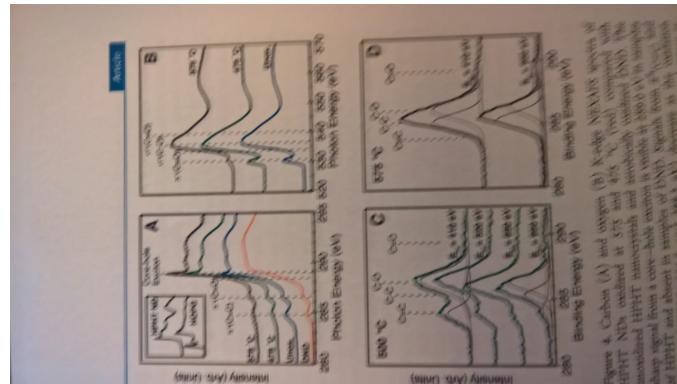


FIGURE 3.4

Taking the experiences of last oxidation into consideration. This time we introduces 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

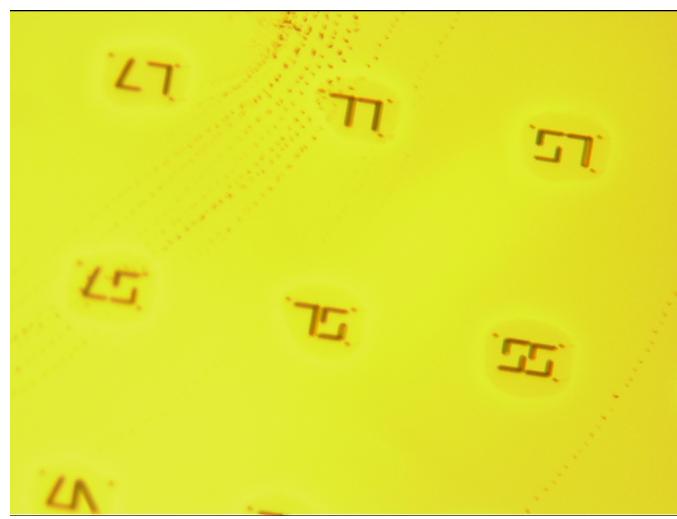


FIGURE 3.5

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.

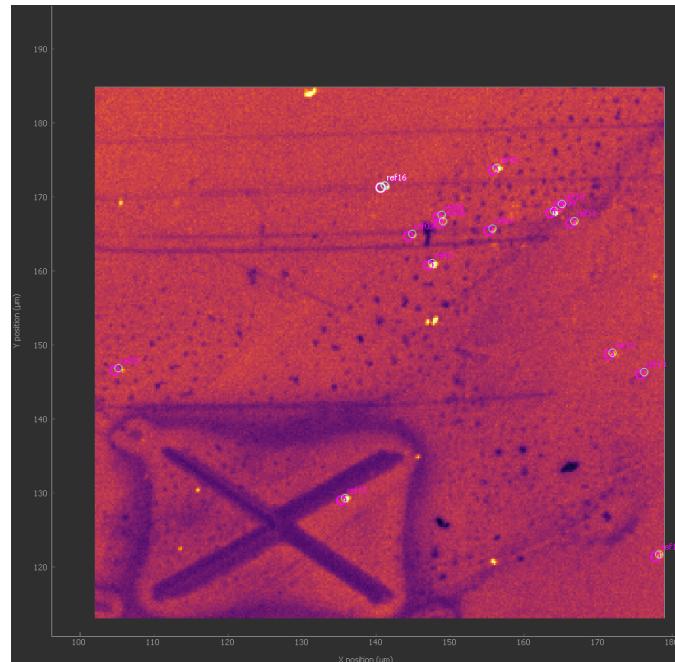


FIGURE 3.6

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 ration.

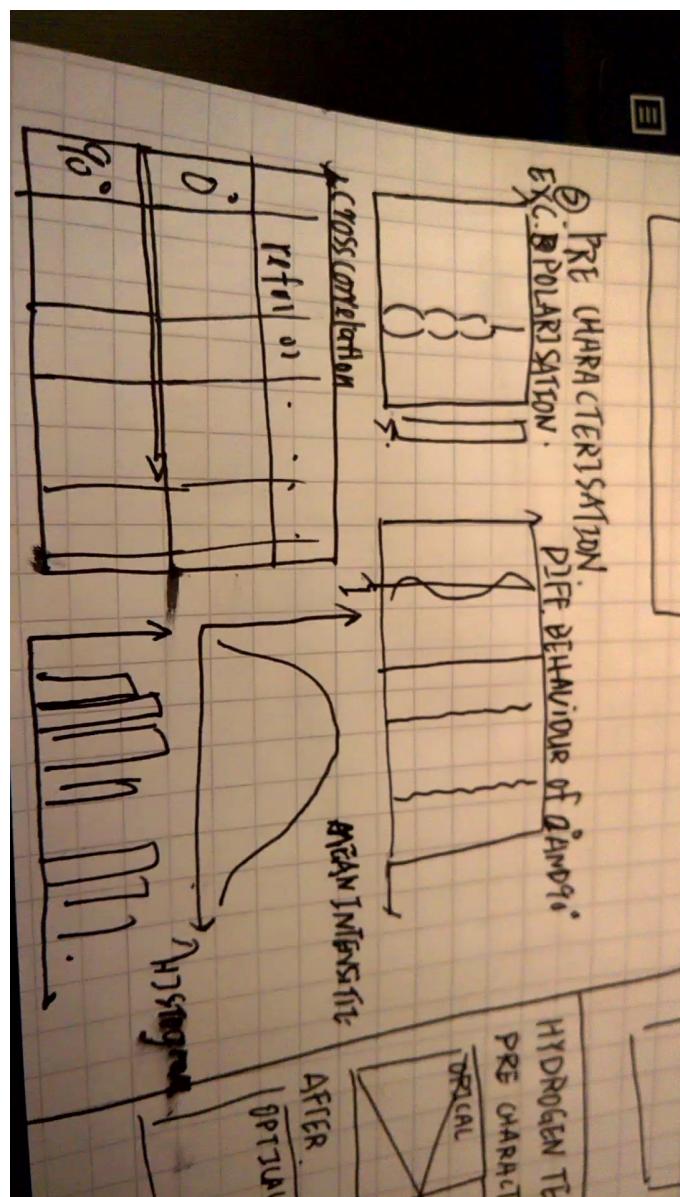


FIGURE 3.7

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

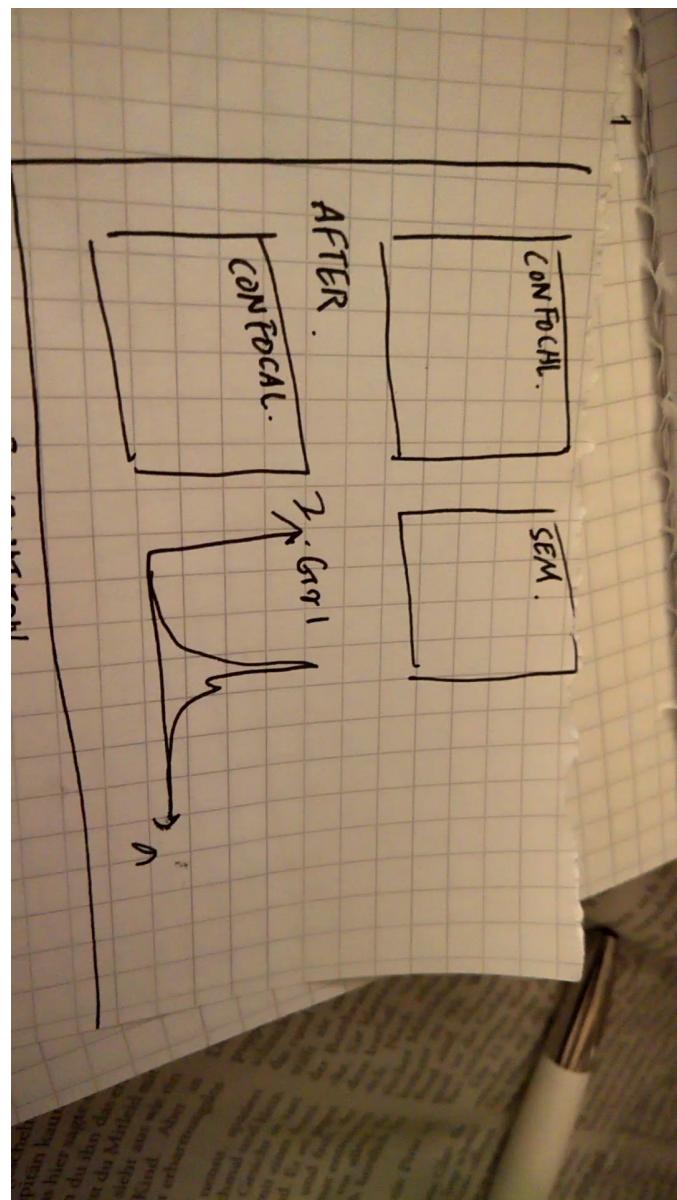


FIGURE 3.8

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 NEA, band structure of diamond. Reduction of surface.

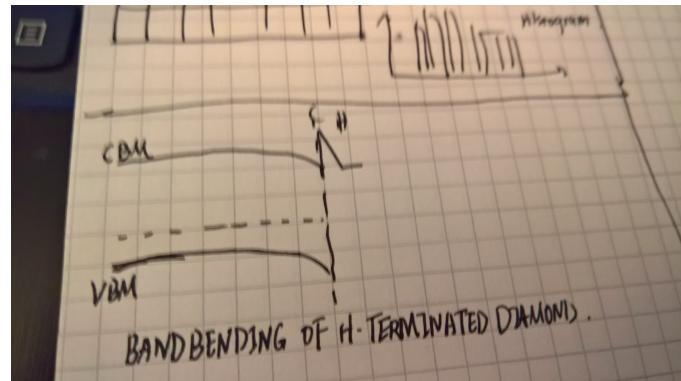


FIGURE 3.9

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

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

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

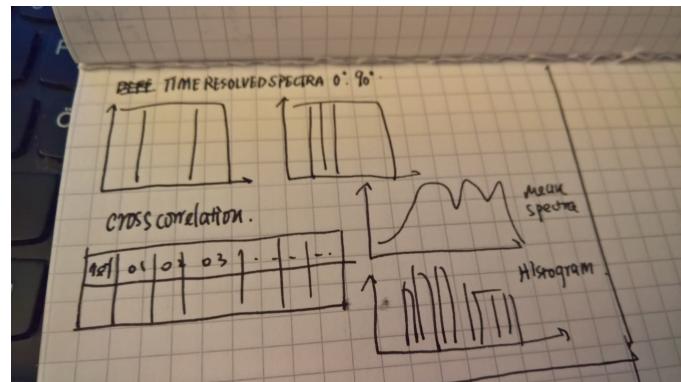


FIGURE 3.10

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.

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