

UNIVERSITY NAME

DOCTORAL THESIS

Thesis Title

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in the*

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Department or School Name

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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.
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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

1.3 Silicon vacancies in nanodiamonds

1.4 Motivation of the thesis, unsolved problem

Chapter 2

Experimental approach of suppressing the spectral diffusion

2.1 sample preparation

2.1.1 preparation of the substrate

Ila 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 ratio 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 background fluorescence as much as possible.
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 estimated 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 characterise 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 an interface with lower relative refractive index is always higher than that from an interface with higher relative refractive index. And to increase the emission rate, a substrate with lower refractive index would be preferred.

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 focused 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

here insert image of markers, optical, sem and confocal

fig. ?.

2.1.2 spin-coating of the sample

theory of spin coating

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

1. Spreading 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.

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

In this procedure, 2 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 $t \sim \frac{1}{\sqrt{w}}$, 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 of 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 a obstacle towards the spreading of the solution, high roughness or inappropriate surface group of the substrate can result in poor wettability from the solution.

Throughout my project, with the help of Andrea Kurz, several combination of these factors had been has been tried out and in the end we landed on

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 practicle 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 ver 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 is mildly bubbles. The substrate would be 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 hydrphilic 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 fig. the comparision between before and after acid boiling.

Tri Acid boiling blabla. Expectation of the surface. Before after cleaning. Optical image. Confocal image.

2.2 development of a technology to estimate the spectral diffusion

Setup In order to resolve the fine structure of ZPL of SiVs, we need to observe the sample at low temperature, thus a cryogenic setup must be applied. Our setup is a typical confocal microscopy setup connects with a cryostat, which cools the sample with liquid Helium flow.

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 green laser + spectrometer. Instrumental limitation to resolution from spectrometer. See the sum of all Emission over exposure time. Observing ZPL and phonon side band.

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 be up to 1nm, is far beyond the capability of PLE.

2.3 Oxidation

Effect of Oxidation Size reducing, surface group changing, removal of Sp² carbon

2.3.1 first Oxidation

method According to the paper[Elka Neu], condition: . With the help from Markus Mohr. Setup : tube furnace, pic.

Before Oxidation Confocal image, SEM image, PL, time resolved PL, PLE. Power dependence.

After Oxidation dirty surface: Optical image, Confocal image, time resolved PL. Power dependence.

Analysis Reason for getting dirty surface. Behaviour of the lines: brighter, broader...

2.3.2 second Oxidation

method According to [] paper, higher temperature - total removal of Sp² carbon. Improvement of setup: to prevent contamination: cleaner tube, clean He flow when cooling. Improvement of characterisation: added in excitation polarisation, record the time resolved PL with 2 differently polarised incident beam. Smaller nanodiamonds: a earlier batch.

Before Oxidation optical image after spincoating, excitation polarisation: confocal image, histogram of the distribution of peaks. SEM image.

After Oxidation Confocal image of bright background. Gr1 center everywhere. Can't see pois.

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.

2.4 H termination

Effect of H termination NEA, band structure of diamond. Reduction of surface.

method Plasma treatment, setup, apparatus.

why no pre characterisation Conditions for Plasma treatment.

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

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

Chapter 3

Conclusion and outlook

3.1 The road so far

Initial motivation

Development of a method to estimate the spectral diffusion

Surface treatments and their effects

3.2 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

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