


Contents

Table of Contents	i
List of Figures	i
List of Tables	ii
1 Crystal Quality of Nanodiamonds	1
1.1 Post-Processing Treatments	2
1.1.1 Annealing and Oxidation	2
1.1.2 Surface Treatment With Gas And Plasma	2
1.2 Raman Measurements	3
1.3 Transmission Electron Spectroscopy Measurements	5
Index	6

List of Figures

1.1	Raman spectrum of nanodiamond samples	3
1.2	TEM imaging of a single nanodiamond	5

List of Tables

Chapter 1

Crystal Quality of Nanodiamonds

Remark:

Das kapitel sollte nochmal ueberarbeitet werden. Vom logischem aufbau her ist es gut, ich hab aber den eindruck es gibt noch loecher die man stopfen sollte.

- In der introduction werden qualitaetsprobleme genannt und ein paar methoden die da helfen sollen. Hier muss noch kurz erwähnt werden warum die methoden helfen.
- In der ersten section sind annealing und oxidation zusammen. Im text steht aber nur was annealing oder? Falls oxidation dann erst in der naechsten section kommt, sollte man die ueberschriften ändern. Ich kenn mich halt nicht aus, d.h. das passt noch nicht.
- Was die surface treatments bewirken sollen bzw. wie die die qualitaetsprobleme minimieren? Da ist auch von shells die rede und ich hab keine ahnung was das fuer dinger sind. Hier fehlt auch noch was.
- Wenns um TEM messungen geht, dann ist hier auch von nanodiamond boundaries die rede. Hier sollte jetzt auch eine diskussion boundaries einfließen, bzw. was fuer effekte die haben koennen.

In this chapter we gauge the cristal quality of the nanodiamond samples examined in this thesis. In this context, crystal quality is a measure of how close the diamond crystal resembles its pristine form. Since we are interested in SiV centers, the presence of other lattice imperfections such as additional vacancies, impurities or the includion of graphite or amorphous carbon are detrimental. Superfluous imperfections negatively manifest themselves through photoluminescence spectra characterized by broad background florescence.

To improve crystal quality and to mitigate the mentioned effects the following methods are depoyed here: Annealing in a vaccuum, oxidation in air as well as surface treatments involving plasmas.

To study the effectiveness of these treatments we rely on Raman and TEM spectroscopy. The former is used to detect the presence of carbon in non-diamond phases, while the latter enables imaging of individual nanodiamonds revealing details in crystallinity such as crystal boundaries.

Hier fehlt
jew-
eils ein
kurzer
satz
was die
dinger
bewirken
sollen.

1.1 Post-Processing Treatments

1.1.1 Annealing and Oxidation

During silicon implantation the diamond lattice gets damaged by the penetrating ions. sp^2 bonds, carbon interstitials and vacancies disrupt the metastable equilibrium of the diamond phase. Hence, there is a tendency for damaged diamond to "tip over" to the thermodynamically stable form of carbon, i.e. graphite. At temperatures above about 500 °C, vacancies in the diamond lattice become mobile and diffuse towards the surface[?]. Literature suggests, that annealing at 900 °C for 1 h is sufficient to remove most of the damage following implantations, that however some damage remains even after annealing at 900 °C for 1 h. To reduce the damage in the diamond lattice, we anneal the implanted diamonds at 900 °C to 1200 °C for 3 h to 6 h in vacuum (10^{-6} Pa).

The surface of the nanodiamonds is contaminated with graphite and amorphous sp^2 hybridized carbon . The vacancies which diffuse towards the surface during annealing further increase the amorphous carbon content on the surface of the nanodiamonds []. We apply oxidation in an oven under ambient air at a temperature of 450 °C for 3 h to 6 h.

warum

1.1.2 Surface Treatment With Gas And Plasma

We wanted to know whether surface treatment with different gasses had an influence on the emission properties, so we treated them with hydrogen (H_2), oxygen (O_2), ozone (O_3) all both at room temperature and at 500 °C; and also with H_2 plasma. However, we found that most nanodiamonds treated in this way only showed luminescence which immediately bleached when illuminated with a cw 660 nm laser even at low excitation powers of 200 μ W, or no luminescence at all. We double-checked with a CCD-image of the surface to be sure that there are nanodiamonds in the focus. This bleaching occurred so quickly, that after a scanning no spectrum could be taken. The only samples which did yield spectra with measureable ZPLs were the ones treated with H_2 . However, also these SiV centers were not single ones. Therefore, we did not further investigate these samples.

One sample showed shells around the nanodiamond after oxidizing in air. We attribute this effect to a contamination in the oven. When we illuminated these nanodiamonds in the SEM for several moments, the shell went away. We therefore deduced that the shell is organic material. To get rid of the shells on the whole sample, we treated it with oxygen-argon plasma for 3 min¹. After the first treatment, the shells were smaller, but not gone. So we put them into the oxygen-argon plasma again for 3 min, however, the shells were bigger than before any treatment. We tried another approach to get rid of the shells with ozon treatment for 4 h at 360 °C. Before ozon treatment there the diamond Raman line and other Raman lines visible. After surface treatment, more lines appeared and all of these other lines got more intense. There are probably organic contaminations on the sample in which functional groups got introduced by the ozon treatment. We did not further investigate this sample and defined it as broken.

¹Treatment performed by J. Schmauch, group of R. Birringer, Saarland University

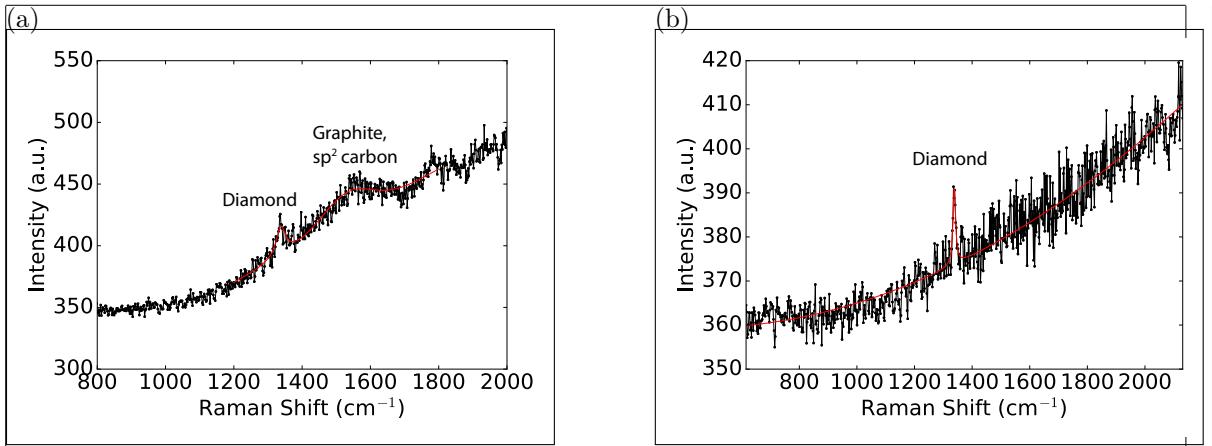


Figure 1.1: Raman measurements, black: data, red: fit. (a) Raman measurement before oxidation, sample insitu70. The diamond Raman peak is situated at 1338 cm^{-1} . The broad feature around 1600 cm^{-1} corresponds to the graphite G-band. (b) Raman measurement after oxidation, sample insitu70o. The G-band has vanished, indicating removal of graphite and amorphous sp^2 hybridized carbon.

1.2 Raman Measurements

Raman spectroscopy of various samples gives insight to crystal quality and surface contamination. Raman scattering is the inelastic scattering of a photon $\hbar\omega_i$ on a molecule or crystal lattice in the initial state $|i\rangle$ with energy E_i . The molecule of cristal transitions into a higher energy state E_f and the scattered photon with frequency ω_s looses the energy $\Delta E = E_f - E_i = \hbar(\omega_i - \omega_s)$. Therefore, energy from is exchanged between the photon and the excited matter, changing the rotational or oscillation energy of the involved molecule or the oscillation energy, i.e. phonons of the crystal lattice. The Raman shift is typically referenced in wavenumbers. It is calculated by:

$$\Delta\omega = \left(\frac{1}{\lambda_{ex}} - \frac{1}{\lambda_R} \right) \quad (1.1)$$

As every solid exhibits characteristic phonon modes, Raman spectroscopy is used to identify the contributing elements of a solid, hence in our case determine the purity of the diamond and identify contamination with sp^2 bonded and amorphous carbon, and graphite. Also, the Raman spectrum changes under the influence of stress in the sample, providing a way to investigate the stress in the sample with opical means.

Raman measurements of the wet-milled nanodiamonds give insight to the issues of surface contamination, defects in the diamond lattice and strain in the lattice: Surface contamination like graphite and amorphous sp^2 hybridized carbon atoms cause additional peaks in the Raman spectrum. A high defect concentration may lead to both additional peaks, to a broadening of the first order Raman peak and a shift to smaller wavenumbers. Strain in the diamond broadens the first order Raman peak and causes a shift to higher wavenumbers [?, ?, ?]. For the Raman measurements the same layout of the setup described in ?? is used. As excitation lightsource, a 532 nm continuous wave diode laser is used (IO). It provides single (frequency) mode laser light, which is a prerequisite for Raman investigations. The beam-splitter is a dichroic mirror (DRLP645), the laser light is additionally filtered out with a 532

type

check
number

Notch filter in the detection path in front of the single mode fiber instead of the otherwise used longpass filter. With these adaptions, the combination of the confocal unit and the spectrometer serve as a Raman spectrometer. As the diamond Raman line is very narrow (xx), the 600 grooves/mm grating is used for a first overview; for more detailed measurements the 1200 grooves/mm and 1800 grooves/mm gratings are used.

Due to the low signal from a single nanodiamond, the Raman measurements are carried out at several areas on the sample insitu70 which are densely covered with nanodiamonds, hence taking measurements of clusters of nanodiamonds. The narrow peak in Figure 1.1a corresponds to the first order diamond Raman peak. The Raman shift of 1338 cm^{-1} compared to the literature value of 1332 cm^{-1} of pristine diamond [?] indicates the presence of strain in the diamond particles. Furthermore, the investigated Raman spectra show a broad peak with a Raman shift of about 1582 cm^{-1} (Figure 1.1a). This shift corresponds to the G-band due to amorphous sp^2 hybridized carbon atoms and graphite. The exact G-band position and linewidth is sensitive to parameters such as the clustering of the sp^2 phase, bond-length and bond-angle disorder, presence of sp^2 rings or chains, and the sp^2/sp^3 ratio [?].

Nanodiamond Raman spectra are considerably modified after oxidation in air at 450°C . To verify this, we perform Raman measurements on three different spots on a non-oxidized sample (insitu70), and for comparison on three different spots on a sample produced in the same process which is additionally oxidized. While the G-band peak is present in every measurement performed on the sample which was not oxidized, it is not present in any of the measurements performed after oxidation (Figure 1.1b), indicating successful removal of sp^2 hybridized carbon and surface graphite. The position of the diamond Raman peak is the same oxidized (insitu70o) and non-oxidized (insitu70n) samples, indicating no effect on strain in the diamond. On the other hand, the width of the diamond Raman peak is between 15 cm^{-1} and 30 cm^{-1} without oxidation treatment, but is only 9 cm^{-1} to 11 cm^{-1} after the oxidation process. A possible reason for a change of the width is improved crystal quality. This effect is also subject in the following paragraphs and will be explained in more detail there.

For comparison, measurements of the Raman line were also carried out on the implanted sample implanted250ao. These diamond particles are big enough to perform measurements on single nanodiamonds. We found one diamond Raman line at $(1308 \pm 5)\text{ cm}^{-1}$, one at $(1345 \pm 5)\text{ cm}^{-1}$ and one at $(1348 \pm 5)\text{ cm}^{-1}$ (given uncertainties are governed by spectrometer resolution). We have to distinguish two cases, a shift of the first order Raman line to higher versus lower wavenumbers than the first order Raman line of 1332 cm^{-1} in pristine diamond.

As mentioned before, a Raman shift of the first order Raman line to lower wavenumbers and a broadening of the Raman line indicates defects in the diamond lattice [?]. The Raman line at $(1308 \pm 5)\text{ cm}^{-1}$ exhibits a broad linewidth of $(25 \pm 5)\text{ cm}^{-1}$. Therefore both the position and the linewidth of the Raman line indicate that there are many defects present in the diamond. The other case is a shift of the first order Raman line towards higher wavenumbers. The shift of the first order Raman line to higher wavenumbers is attributed to strain in the diamond lattice. While under hydrostatic pressure, the triply degenerate first order Raman peak remains degenerate, under uniaxial and more complex stress configurations (biaxial stress, shear stress etc.) mode splitting occurs [?]. As the measured peaks at wavenumbers higher than the wavenumber in pristine diamond are broad, we attribute these peaks to stress configurations other than hydrostatic stress, where the mode splitting manifests itself in a broadening of the peak due to limited spectrometer resolution.

To summarize, there are two cases, one where the first order Raman line hints at many defects present in the diamond lattice and the other that leads to the assumption that the stress con-

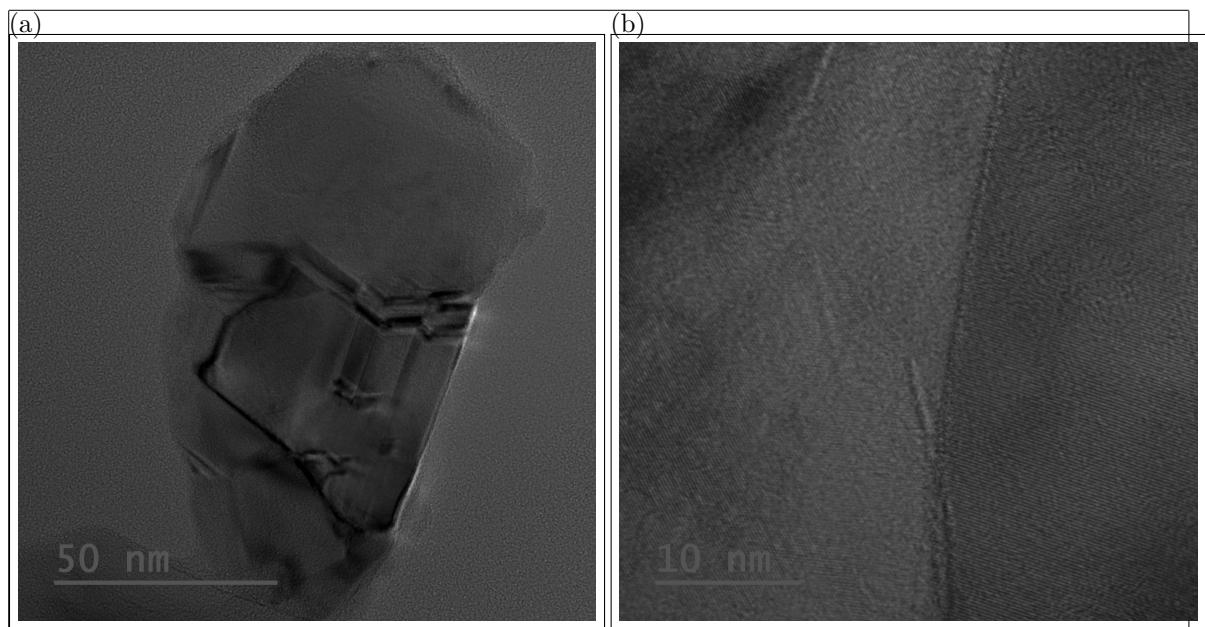


Figure 1.2: Transmission electron microscopy (TEM) pictures of sample insitu100. (a) Image of a single nanodiamond particle. Several crystal boundaries can be seen within the diamond particle. (b) Close-up image a diamond particle. The vertical line is a crystal boundary, to the left and right the more or less horizontal layers of one crystalline region can be seen.

figuration in the diamonds are uniaxial or more complicated stress configurations. In ?? we will show that both of these assumptions are consistent with the results from the measured photoluminescence spectra.

1.3 Transmission Electron Spectroscopy Measurements

Transmission electron microscopy (TEM, also sometimes conventional transmission electron microscopy or CTEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. During transmission electron microscopy a beam of electrons is transmitted through a sample, forming an image of the transmitted sample. Since electrons have higher de Broglie wavelengths than photons, a higher resolution is obtainable, allowing the surface of nanodiamonds to be resolved. Thus, the crystallinity of single nanodiamonds can be studied directly.

Using the sample insitu100, TEM were performed by J. Schmauch, group of R. Birringer, Saarland University. Smaller nanodiamonds would have been too small for the carbon grid which serves as a sample holder in the TEM, and might have fallen through the grid and bigger bigger particles would have been too big to be transmitted by the electron beam, making the imaging impossible. In Figure 1.2 there are TEM images, one of them exhibits a single diamond particle and the other is a close-up image of a crystal boundary. From Figure 1.2a it can be seen that the diamond particle contains several crystallites and crystal

1.3. TRANSMISSION ELECTRON SPECTROSCOPY MEASURED CRYSTAL QUALITY

boundaries. The edges of the crystallites are the sharp features within the diamond particle, the crystal boundaries the smoother features. In Figure 1.2b the crystal layers which are more or less horizontal and in more or less the middle of the picture there is a vertical line which is the edge of a crystallite. So it is clear that the investigated sample does not contain beautiful single crystal diamond particles, which means a reduction of the crystal quality of the diamond particles.

er nur
vermu-
tung