Sample fabrication and metrological characterization of single-photon emitters based on nitrogen vacancy centers in nanodiamonds

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Abstract
Quantum metrology requires a stable single-photon emission and a high single-photon purity. Since nitrogen vacancy (NV-) centers provide both features at room temperature, they are promising candidates for the application in this field [1, 2]. The knowledge about a suitable sample preparation technique is crucial, because the quality of the single-photon emission strongly depends on the sample purity and on the spatial resolvability of the emitters. This work presents the comparison and optimization of various sample fabrication techniques of nitrogen vacancy center doped nanodiamonds on standard cover glasses. The preparation is followed by a comparative characterization of the centers of the various samples. The sample fabrication includes the removal of contaminants on the cover glass surface. This was carried out by using peroxymonosulfuric acid (piranha solution, H2SO5) in comparison to the commercially available lye Hellmanex III (by Hellma Analytics). After cleaning the cover glasses, volumes of various nanodiamond dilutions were applied via spin coating. In subsequent steps, the nanodiamonds themselves were cleaned with peroxymonosulfuric acid, too, to remove contaminants resulting from the manufacturing process, e.g. graphite. The samples were analyzed by using a confocal laser scanning microscope with an oil immersion objective. Single-photon purity was determined by measuring the second order correlation function with a Hanbury Brown and Twiss setup. Spectral analysis revealed the presence of NV−- and NV°-centers. It was shown that a suitable cleansing method has an immense impact on single-photon emission, as was proven by a comparative characterization of differently manufactured nanodiamonds.

1. Introduction
With the immense progresses made in quantum information technology, single-photon sources gain more and more importance in quantum optical applications [1, 2]. To supersede attenuated lasers, that can emit more than one photon per pulse [3], the nitrogen vacancy center, especially in nanodiamonds, is a promising candidate as a single-photon emitter [4, 5]. NV-centers provide a photostable emission even at room temperature thanks to the embedding of the defect centers in a stable carbon lattice and a short lifetime of the excited state of approximately 20 ns [6].

However, in most cases a reliable single-photon source is not created only by exciting the emitter. A suitable sample preparation technique is a crucial step for generating reproducible results. The nanodiamonds are placed on a substrate, in this case standard cover glass (Zeiss, 170 μm thickness) that has to be cleaned properly, beforehand, since a confocal inverse transmitted light microscope is used.

Besides many effects on the emission behavior of nitrogen vacancy centers in nanodiamonds as temperature [7], type and density of magnetic impurities [8, 9], magnetic or strain fields [10, 11], we only focus on the effects of surface cleaning, in particular cleaning the substrate and the nanodiamonds.
A specific surface treatment can enhance the surface attraction between the nanodiamonds and the cover glass [12]. Here we focus on the comparison of the results concerning the signal-to-noise ratio and single-photon purity after cleaning the cover glasses oxidatively with piranha solution and Hellmanex, respectively. Because of the nanodiamond fabrication process, graphite residues can remain in the dispersion. That may reduce the emission intensity of the NV-centers and therefore the signal-to-noise ratio. Removing these contaminants is a promising step on the way of establishing a single-photon source [13, 14]. As a part of this work, the nanodiamond dispersion was centrifugated in a piranha solution bath to prune them of graphite. In the following, the influence of changes in the sample fabrication procedure on the single-photon purity is demonstrated.

2. Experimental setup

The samples were measured using a self-built confocal microscope (figure 1). The NV-centers in nanodiamonds (Microdiamant, MSY 0–0.15 GAF, mean diameter 75 nm) were excited with a 532 nm second-harmonic Nd: YAG-laser (CrystaLaser LC, CL532–010, 10 mW). After enlarging and collimating the laser beam, it is reflected at a dichroic beamsplitter (Thorlabs, DMLP550), collected into an oil immersion objective (Nikon CFI Plan Apochromat Lambda, 60× Oil, NA = 1.4) and focused onto the sample, exciting just a small area of the sample. A continuous neutral density filter (Thorlabs, NDC-100S-4M) allows a fine tuning of the excitation power beforehand.

A wide field lens situated before the dichroic beam splitter can be flipped into the exciting light path. Combined with a flippable mirror afterwards, reflecting the emitted light onto the camera chip of an sCMOS-camera (Hamamatsu, Orca-Flash 4.0 LT), a visualization of the emitting centers is allowed. For sample scanning the sample is mounted on a piezoelectric translation stage (Physik Instrumente, P-563.3CD with controller E-727). This allows a fine adjustment over 300 μm in each direction.
The emitted light is collected through the same objective and transmitted through the dichroic beamsplitter, since the fluorescence has another wavelength than the excitation.

Afterwards the emission passes a set of edge filters and is then focused through an objective onto a single-mode optical fiber (Ø 9 µm), that forms the pinhole of the setup [16]. The pinhole is situated in a conjugated focal plane according to the object plane, indicating the confocal character of the setup [17].

The single-mode fiber also functions as the connection between the single-photon source and the devices and setups needed for further characterization. For that, a single-photon avalanche diode (SPAD) (Laser Components, COUNT series) detects the emitted photons and a second one of identical type is used as part of time correlation measurements, the Hanbury Brown and Twiss-setup, to determine the single-photon purity. The fiber can be connected to a spectrometer (Horiba Jobin Yvon, iHR320), too, to measure the emitted spectrum and to reveal the presence of an NV− or NV0-center, respectively.

For time correlation measurements, the detectors are connected to a time-correlated single photon counting device (TCSPC; Swabian instruments, Time Tagger 20). It measures the time delay τ of detection events between the SPADs. The delay times τ are collected in a histogram and subsequently normalized according to the equation [2]

\[ g^{(2)}(\tau) = 1 + c \tau e^{-\frac{\tau}{\tau_1}} + c \tau e^{-\frac{\tau}{\tau_2}} \]  

resulting in the second order correlation function \( g^{(2)}(\tau) \). The index 2 describes the lifetime \( \tau \) and amplitude \( c \) of the excited state and the index 3 those of the shelving level, a metastable energy state [2]. This function parametrizes the probability for detecting one single photon at one detector at the time \( \tau \) after another one has arrived at the first detector after a delay time \( t + \tau \) [6]. For an ideal single-photon source a value of \( g^{(2)}(\tau) = 0 \) is expected, assuming a delay time of 0 ns. That means, there is a probability of 0, that two photons arrive simultaneously at both detectors [1, 18].

Admittedly, there is no ideal single-photon source [3, 4]. So, there is only the option to approach towards a \( g^{(2)}(\tau) \)-value as close to 0 as possible. And for that, a specified sample fabrication procedure is one prerequisite.

3. Sample fabrication techniques

The sample preparation includes the removal of contaminants on the cover glass surface, that are used as a substrate for the nanodiamonds as well as the application of the nanodiamonds. However, the methods shall not only clean the surface but also enhance the surface attraction between the nanodiamonds and the cover glass. According to that, the glass slides show a hydrophilic character after the cleaning procedure since hydrophobic functional groups are converted to hydrophilic by adding hydroxyl groups (OH) [12, 19].

3.1. Cleaning procedure

3.1.1. Peroxymonosulfuric acid

Hydrophilicity is achieved by using peroxymonosulfuric acid, also called piranha solution [12, 19]. In our work, therefore we mixed three parts 96% sulfuric acid (H₂SO₄) with one part 30% hydrogen peroxide (H₂O₂). The hydrogen peroxide is slowly given into the sulfuric acid, the reaction is exothermic with smoke emission. When the reaction has started, the cover glass is inserted into the solution and kept in there for ten minutes. During this time, the solution was continuously stirred using a stirring rod.

When treated with piranha solution, the silicon dioxide surface of the cover glass is hydroxylated owing to the insertion of hydroxyl groups. Siloxane bonds on top of the cover slip are cracked resulting in hydrophilic silanol groups [20].

In addition to that, the nanodiamonds can be pruned of residual graphite contaminants. Those sp²-hybridized carbon formations are very reactive, so that they can be removed effectively by oxidative reactions. When removed, the signal-to-noise ratio can increase [13, 14, 19]. Contaminations with sp²-hybridized carbon modifications also have an impact on the charge state of defect centers close to the surface resulting in an increase of the amount of NV− - centers [20]. Since NV-centers close to the surface are removed, the detection of deeper generated centers is improved enhancing the signal resolution [21]. So finally, an oxidation of the nanodiamond surface should result in a functionalization and, after all, a surface homogenization [19].

3.1.2. Hellmanex

Compared to the sample preparation carried out with piranha solution, samples consisting of nanodiamonds on cover glasses cleaned with the commercially available lye Hellmanex (pH-value = 12) were fabricated. It removes particle contaminants from the cover glass surface and since it contains specific surface-active substances, Hellmanex prevents new contaminants from attaching on the cover slip.
A greater fabrication success after the application of Hellmanex compared to piranha solution was expected because Hellmanex leaves the surface more negatively charged. The reason for that is the more negative zeta-potential and therefore the electrokinetic attraction force increases, presumably resulting in a higher amount of attached nanodiamonds [12].

3.2. Application of nanodiamonds

The nanodiamonds were applied via spin coating technique. This means, that a diluted amount of nanodiamonds is deposited onto the cover slip. The cover slip is rotated with a few thousand rounds per minute resulting in a rotational spreading out of the solid and liquid components. Because of the high rotational forces, the solvent evaporates and leaves the particles separately distributed on the cover glass surface [21].

In this work, we applied different rotation speeds, acceleration values and process times to approach to the, in our opinion, best suited parameter combinations for separately distributed nanodiamonds. The final values promise a high signal-to-noise ratio since the density of emitting centers, assuming one center per diamond, is low enough to yield a high single-photon purity.

4. Experimental results

4.1. Progresses made in the sample fabrication process

This chapter presents selected results showing the improvements made. In the beginning the results after cleaning the cover glasses with piranha solution are presented.

Once the cover slips were cleaned as described in section 3.1 with piranha solution, they were deposited in deionized water, until the nanodiamonds are applied. Gaseous nitrogen was used to dry the cover glasses. Before applying, each used nanodiamond dilution kept in a reaction tube was left in an ultrasonic bath filled with water at 60 °C for 15 min.

In figure 2 the results of one sample (PNV004), that was prepared without spin coating, are displayed, to illustrate the emendations made afterwards.

The sample scan in figure 2 shows a high density of emitters, resulting in a just as high background emission intensity and a signal-to-noise ratio of 3:1. Spectral analysis revealed the existence of an NV−-center. These centers are more suitable to be used as an emitter in a single-photon source since they stay stable in their charge state unlike NV0-centers, that can switch to a negatively charged state [22].

The intense background is reflected in the second order correlation function with $g^{(2)}(0) = 0.36$. The emitter lifetime calculation revealed a value of $\tau_2 = 30.6 \text{ ns}$ for the excited state.
To achieve a more homogeneous emitter distribution on the cover glass surface, spin coating was applied. In the presented case, the glasses were cleaned also in a 2% Hellmanex dilution. The results can be seen in figure 3.

Further fabrication optimization steps including tuning the rotation speed and acceleration revealed the best parameter combination with a speed of 2000 rpm, an acceleration of 50 rpm s$^{-1}$ and a process time of 2 min. To produce the sample HNV011 with the results shown in figure 3, a 1:100 diluted dispersion of nanodiamonds in deionized water was applied on top of the cover glass. The acceleration process started first and then the dilution was pipetted, to ensure that the particles will be distributed and are not staying in the center of the cover glass.

As a result of the homogeneous emitter distribution and the successful removal of contaminants using Hellmanex, the signal-to-noise ratio was increased to 6:1. Hence, the second order correlation function yields a lower value of \( g^{(2)}(0) = 0.2 \). For the considered emitter the excited state lifetime is \( t = 9.12 \) ns. So, for both observed defect centers the lifetime does not correspond to the time in literature with \( t = 20 \) ns [6].

A side effect of nanodiamond production are graphite residues covering the particle surface and, therefore, reducing the signal intensity [13, 14]. As no more background emission reduction could be achieved tuning the spin coating parameters, the potential of cleaning the nanodiamonds themselves was observed. Graphite residues can be removed oxidatively using piranha solution [19]. On that account, 200 \( \mu l \) of the original nanodiamond dispersion were mixed with 10 ml of piranha solution. After the reaction took place, 200 \( \mu l \) of that solution were diluted with 10 ml deionized water and centrifugated afterwards for 3 min at 3500 rpm. The nanodiamonds deposited on the bottom of the falcon tube, the supernatant could be discarded. The diamond pellet was resuspended in deionized water again and the centrifugation process was repeated until a neutral pH was measured.

20 \( \mu l \) of that dispersion were applied on a Hellmanex cleaned cover glass via spin coating, adjusting the parameters 2000 rpm, acceleration 50 rpm s$^{-1}$, process time 5 min. The results of the sample PHNV04 are depicted in figure 4.

The signal-to-noise ratio was increased to values of 10:1. But the procedure caused many diamond clusters resulting in multi-photon emission since sp$^2$-hybridized carbon modifications prevent nanodiamonds from clustering [19, 20, 24]. In that case just one emitter revealed at least a non-classical character with a second order correlation function of \( g^{(2)}(0) = 0.44 \) at a delay time of \( \tau = 0 \), but not clearly indicating a single-photon or two-photon emission. The calculated lifetime of the excited state resulted in \( \tau = 14.3 \) ns.

Those values close to \( g^{(2)}(0) = 0.5 \) are more likely a result of two or more NV-centers with various emission intensities, diverse surface effects or additionally existing different structured defect centers.
4.2. Direct comparison and characterization

At least two identically prepared samples, but consisting of different nanodiamonds, were characterized and their results compared. For simplification, they are called sample 1 (Microdiamant, HNV011) and sample 2 (Diamond Nanotechnologies, HNV013) in the following.

For both samples, the cover glasses were cleaned with 2% Hellmanex and 10 $\mu$l of equally diluted dispersions with deionized water were spin coated on top.

Figure 4. (a) Laser scan of the sample PHNV04 measured in the confocal setup. The cover glass was cleaned with piranha solution as well as the nanodiamonds. (b) Second order correlation function of the marked emitter at zero delay time with $g^{(2)}(0) = 0.44$. (c) The existence of an NV$^-$-center was proven by the depicted normalized spectrum.

Figure 5. Measurement results of sample 1. (a) Scan of sample 1 (HNV011) obtained with the confocal measurement setup. (b) Second order correlation function of sample 1: $g^{(2)}(\tau) = 0.24$. (c) The normalized spectrum proved the existence of an NV$^-$-center. (d) Intensity in counts per second of the analyzed NV-center as a function of the excitation power (532 nm). Red: total amount of counts per second; blue: counts per second only emitted by NV-center; black: background.
The samples were compared according to their signal-to-noise ratio, the distribution of the nanodiamonds on the surface, the single-photon purity, their spectra, and the emitters’ saturation behavior. The results of the observed samples are depicted and compared in figure 5 (HNV011) and figure 6 (HNV013).

For saturation measurements the excitation power was gradually increased while the emission intensity in counts per second was recorded. Assuming a linear correlated background, the total count rate was calculated using a mathematical model following the equation:

\[
N_{\text{count}} = \frac{N_{\text{sat}}}{1 + \frac{P_{\text{sat}}}{P}} + mP,
\]

where \(N_{\text{count}}\) denotes the number of counts per second, \(N_{\text{sat}}\) the saturation count rate, \(P_{\text{sat}}\) the excitation power at \(\frac{N_{\text{sat}}}{2}\), \(P\) the excitation power and \(m\) the factor describing the linear background increase. The resulting fit parameters are summarized in table 1.

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Regarding the scans (figures 5(a) and 6(a)) one can see that the emitter distribution of sample 2 (HNV013, figure 6(a)) is more inhomogeneous compared to sample 1 (HNV011, figure 5(a)), indicating no successful spin coating in the sample fabrication process. That causes a higher signal-to-noise ratio in sample 2, being reflected in a low single-photon purity with \(g^{(2)}(0) = 0.41\) (sample 1; \(g^{(2)}(0) = 0.24\)). Additionally, a shift in the position of the zero-phonon line between the two emitters was observed (see figures 5(c) and 6(c)).

In contrast to the low single-photon purity of the emitter of sample 2, saturation measurements revealed a less amount of linear background emission contributing to the total count rate. This effect might be the outcome.
of the different nanodiamonds in that sense, that the diamonds in sample 2 can contain comparatively more than one NV-center or are affected by more inclusions and contaminants than sample 1, respectively.

5. Conclusion

Intense background emission caused by contaminants is one of the most limiting factors concerning a high single-photon purity of an NV-center as a single emitter. For that, a sample fabrication technique was developed, that reduces the background intensity. This work showed promising results towards signal enhancement and further realization of a single-photon source.

The sample fabrication procedure included the restless removal of contaminants from the substrate, in this case standard cover glasses. The results after an oxidative cleaning with piranha solution and with the commercially available tenside mixture Hellmanex were compared. Because the chemical composition of Hellmanex left the cover glasses more hydrophilic, such that the attraction forces between the surface and the nanodiamonds were enhanced, a higher number of emitters was established. Hellmanex removed contaminants from the cover glass surface more successfully than piranha solution did, resulting in a higher signal-to-noise ratio.

As a further cleaning step, the nanodiamonds were treated with piranha solution, too, to clear them of graphite residues and defect centers, that are located close to the diamond surface. A high signal-to-noise ratio from 10:1 showed the success of that procedure. Nevertheless, the single-photon purity was reduced significantly, since the nanodiamonds formed several clusters containing more than one NV-center. However, this enormous background reduction can lead to a nearly pure single-photon emission, when cluster formation can be prevented. When being used for detector calibration, this high single-photon purity would lead to significantly reduced measurement uncertainties [15]. It was shown that the prevalent oxidative cleaning method using piranha solution did not show better results regarding the signal-to-noise ratio and hence the single-photon purity compared to Hellmanex. Due to the higher pH-value and surface-active agents, the electrokinetic attraction between the nanodiamonds and the glass surface was increased as well as new contaminants were repelled from the more negatively charged surface [12]. Therefore, the sample fabrication technique is at least as crucial as the measurement itself. In the future, the preparation methods can be expanded for different emitters, e.g., single organic molecules, and other techniques as using dielectric structures.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Eisaman M D, Fan J, Migdall A and Polyakov S V 2011 Rev. Sci. Instrum. 82 071101
[2] Kurtsiefer C, Mayer S, Zarda P and Weinfurter H 2000 Phys. Rev. Lett. 85 290–3
[3] Beveratos A, Brouli R, Poizat J-P and Grangier P 2002 Bunching and Antibunching from Single NV Color Centers in Diamond Quantum Communication, Computing and Measurement ed P Tombesi and O Hirota 3 (Boston, MA: Springer) 261–7
[4] Jelezko F and Wrachtrup J 2006 Physica Status Solidi (A) 203 3207–25
[5] Beveratos A, Kühn S, Brouli R, Gacon T, Poizat J-P and Grangier P 2002 Eur. Phys. J.D 18 191–6
[6] Aharonovich I, Castelletto S, Simpson D A, Su C-H and Greentree A D 2011 Rep. Prog. Phys. 74 076501
