The usefulness of nitrogen vacancy (NV) centers in diamond is augmented by a low defect and impurity density in the surrounding host material, and applications benefit from the ability to control the position of the NV centers. Herein, a process to create NV centers on single-crystalline diamond microstructures by chemical vapor deposition (CVD) is presented. Pyramidal structures with \{111\} side facets are formed during the intrinsic overgrowth of dry chemically etched cylindrical pillars on a substrate with \{100\} surface orientation. A thin nitrogen-doped epitaxial layer is deposited on top of the pyramids resulting in the creation of NV centers exclusively on the \{111\} pyramid side faces. Optically detected magnetic resonance (ODMR) and spin echo measurements reveal preferential alignment of the NV centers in a single \{111\} direction and a T_2 time of 55 μs. The T_2 time of the NV centers is limited by the surrounding substitutional nitrogen (P1 center) concentration of [P1] = 5 ppm. A low density of other paramagnetic spin noise is detected by double-electron electron resonance (DEER) measurements.

1. Introduction

The negatively charged nitrogen vacancy (NV) center is a point defect in diamond which exhibits an optically accessible spin system with formidable coherence times under ambient conditions. As a consequence, there has been steady development around NV centers, recently turning from fundamental research toward technological applications.\(^[1-3]\)

The most popular use case is the measurement of magnetic fields by detecting the Zeeman splitting of the electronic ground state triplet with optically detected magnetic resonance (ODMR).\(^[4,5]\) Owing to its minute size, the NV center can be used to measure magnetic fields on the nanometer scale, e.g., originating from currents in microelectronic circuits or magnetic nanostructures. This is achieved by including NV centers into diamond tips which are then mounted to an atomic force microscope (AFM) and scanned across the circuit.\(^[6-8]\) The electronic spin of the NV center can also be used to sense and polarize nuclear spins in its vicinity.\(^[9,10]\) Polarized nuclear spins in biological molecules can then act as contrast agent in MRI systems to facilitate the detection of cancer.\(^[9,11-13]\) The aforementioned applications benefit from three key competencies: the creation of optically and mechanically functional structures,\(^[14]\) the selective placement of NV centers,\(^[15]\) and aligning the NV centers’ axes in one direction.\(^[16]\)

The characteristics of NV centers can often be enhanced by creating functional structures on the diamond surface. Cylindrical pillars of a few 100 nm diameter and single digit micrometer height act as waveguides increasing the amount of collected photons from the NV centers.\(^[14,16-18]\) Using these pillars as a probe tip of an AFM makes it possible to bring the NV center close to the source of the magnetic fields of interest. Typically, diamond tips with NV centers at the apex are created by shallow implantation of nitrogen into the substrate followed by an etching step.\(^[8]\) However, it has been found that both the implantation\(^[19]\) and the etching processes\(^[20,21]\) are detrimental to the properties of the NV center such as the coherence time, thus limiting the magnetic sensitivity. Both of these processes can be avoided by producing the tips using bottom up CVD growth. The growth process has to be preceded by an
etching step to create precursor structures on the diamond substrate to enable lateral growth. The shape of diamond crystals growing in a CVD process can be controlled to a limited extent by the CVD process parameters and is usually described by a geometric growth model. A set of parameters ($\alpha$, $\beta$, and $\gamma$) is calculated by relating the different growth velocities in the {111}, {110}, {113} to the growth velocity in the {100} crystal direction. The bottom-up growth process allows for structures not feasible with etching techniques, particularly the creation of sharp edges as are required for the usage as AFM tips. NV centers are introduced into the epitaxially grown diamond by addition of nitrogen into the CVD gas mixture. During the CVD growth most of the incorporated nitrogen is included into the diamond lattice substituting carbon atoms to form P1 centers, while only a small amount ($\approx 1\%$) usually ends up in the NV configuration. These CVD-grown NV centers typically exhibit longer coherence lifetimes than their counterparts created by implantation and annealing. The axis of an NV center is defined by the two neighboring diamond lattice sites that the NV center occupies and can be directed in the four permutations of the (111) directions in a cubic crystal. The NV centers introduced into the diamond lattice during CVD growth can be created with their axes aligned in the same direction. The degree of alignment is dependent on the substrate surface orientation. No alignment is found for growth on {100} surfaces, whereas the degree of alignment can range from 73% on {113} up to 99% on {111} surfaces. Theoretical investigations present possible mechanisms for the formation of NV centers during CVD growth on {111} surfaces. When diamond growth proceeds in a step flow mode and a nitrogen atom is included into one layer there is an increased probability that the lattice site directly above that nitrogen atom stays vacant during the completion of the subsequent layer. As only the projection of the magnetic field vector onto the NV axis is detected, a high degree of alignment is beneficial for measurements of magnetic fields with ensembles of NV centers. If three of the four possible projections are ruled out due to alignment of the NV centers, a higher signal to noise ratio and higher readout contrast will enhance the sensitivity of magnetic field measurements. In this report, we demonstrate the selective placement of aligned NV centers by overgrowing previously etched structures in a nitrogen-doped PECVD process.

2. Sample Preparation

The process is based on a single crystalline HPHT substrate with {100} surface orientation obtained from Element Six Ltd. A lithography and O$_2$ ICP etching process as described previously produces cylindrical micropillars of 2.2 $\mu$m height and diameters between 300 nm and 5 $\mu$m as depicted in Figure 1a. The overgrowth is carried out in a custom built ellipsoidal diamond CVD reactor with a microwave frequency of 915 MHz and 15 cm diameter deposition area. We use a two-step recipe with 0.5% CH$_4$ diluted in H$_2$ with natural abundance of 1.1% $^{13}$C for both steps. An intrinsic growth step with a duration of 2 h is followed by a nitrogen doped step of 1 h duration for which N$_2$ with natural isotopic distribution is added to the gas mixture yielding

Figure 1. a) SEM image of micropillar after the etching process. b) SEM image of a CVD overgrown micropillar with the shape of a truncated pyramid. Scale bars indicate a length of 1 $\mu$m. c) Model of the truncated pyramid with its components: substrate and etched micropillar (yellow), pyramid after intrinsic overgrowth (gray), N-doped coating on the pyramid (green). d) Rendering of topographic AFM data of a complete pyramid grown on a pillar with 300 nm diameter. The pyramid has a height of 2.1 $\mu$m above the substrate surface, approximately 50° side wall angle and 150 nm tip radius.
a N/C ratio of 3333 ppm in the gas phase. The total gas flow is kept constant at 2000 sccm and a pressure of 120 mbar. An applied microwave power of 13 kW results in a substrate temperature of 825 °C throughout the process. All gases except for N₂ are purified in a Pd cell prior to feeding to the reactor.

3. Results and Discussion

The shape of the resulting structures was analyzed with SEM and atomic force microscopy using an AFM tip with a half cone angle of 10° to ensure correct imaging of the steep slopes. The SEM images and AFM measurements displayed in Figure 2a, b, d show that overgrowing the etched cylinders in a CVD process results in structures with a shape of complete and truncated pyramids. A model of the truncated pyramids resulting from the overgrowth of the etched pillars is given in Figure 2c. The pyramids exhibit smooth top and side faces. An AFM measurement of the pyramid surfaces reveals reproducible angles for the side faces of approximately 50° against the {100} substrate surface, which is close to the theoretical value of 54.6° for {111} surfaces.

From the SEM images, it could be determined that the diameter of the overgrown, etched pillar is the only factor deciding over completion or truncation of the pyramids. Pyramids grown on the same pillar diameter are of uniform shape and size. Only pyramids grown on the smallest diameter of 300 nm appear complete and exhibit a tip radius of approximately 150 nm similar to commercial NV containing diamond AFM tips. It is expected that the tip radius of the pyramids can be reduced further by fabricating micropillars with smaller diameter or sharper apexes. The feasibility of CVD grown diamond tips with a tip radius of only a few nanometers has already been demonstrated.

Quadratic top faces with {100} orientation are observed for larger pillar diameters. The top face of the truncated pyramid has an edge length that equals the diameter of the underlying cylindrical pillar. This finding is true for all pillar diameters on the sample indicating that the CVD growth proceeds rapidly until the volume of the truncated pyramid is filled and slows down significantly upon completion. Furthermore, growth on the {100} top faces is apparently suppressed under the described conditions. A more detailed description of the diamond growth in terms of the geometric growth model can not be given due to unquantifiable growth rates in {100}-direction and varying growth rates in {111}-direction depending on the underlying pillar diameter. The regular shapes and smooth surfaces of the pyramids as evidenced by the SEM images indicate a step flow growth mode on the {111} faces.

Figure 2. a) Confocal PL map on the substrate surface with pyramids on pillars with nominal diameters of 2000 nm (top) and 5000 nm (bottom). b) PL map perpendicular to the substrate surface along the line A–A marked in (a).
ODMR scans on four different side walls of one truncated pyramid. Individual scans are offset for better readability. The inset shows the location of the measurements as color-coded circles. The presence of only one pair of dips per pyramid side wall indicates a high degree of preferential alignment. Fits of the missing peak pairs stay within the noise and limit the degree of alignment to values between 91 ± 3%, 97 ± 3%, 94 ± 3%, and 99 ± 3% for the spectra from top to bottom and the respective pyramid side facets.

measurements on each of these lines show contrasts of up to 30% of the total fluorescence, which is the typical spin signal contrast for single NV centers on the utilized setup, also indicating alignment of the NV centers. The ODMR spectra were acquired with a microwave power corresponding to a NV electron spin Rabi frequency of about 5 MHz. This power leads to resonance lines with large contrast and allows for a reasonable amount of frequency points to be sampled. On the downside we are not able to observe the $^{14}$N-induced threefold hyperfine splitting of each individual resonance in this mode of operation due to power broadening. However, the $T_2^*$ time of these NV ensembles (see below) is sufficient to resolve the $^{14}$N induced hyperfine splitting. The alignment of the NV centers during CVD growth, especially for growth on (111) type surfaces where alignment ratios of up to 99% are reached, has been reported multiple times. Our results indicate that the step flow growth model and with it the mechanism for creation of aligned NV centers is also applicable when overgrowing structures with (111) surfaces on a (100) substrate surface.

The EPR spectrum in Figure 4a exhibits the characteristic hyperfine peaks of an ensemble of P1 centers in diamond where the magnetic field is aligned with the hyperfine tensor of one quarter of them (i.e., along a [111]-direction). To this end, the magnetic field was raised to about 570 G and aligned with the NV centers in the respective pyramid surface. By utilizing the DEER spectroscopy protocol the NV centers act as EPR detectors for P1 centers in their proximity. The resulting, narrow linewidth of the central line of 2 MHz FWHM is connected to a low concentration of paramagnetic defects in the host crystal material.

The peak at 1700 MHz in the DEER spectrum is used to determine the P1 substitutional nitrogen concentration. Observing the peak height while increasing the interaction time of the P1 electronic spins and the NV center electronic probe spins results a mono-exponential decay of the NV center coherence with a time constant $\tau = 16.5 \pm 0.3 \, \mu s$ as shown in Figure 4b. The inverse of the decay time constant $\tau$ divided by the interaction strength of $292 \, \text{kHz} \, \text{ppm}^{-1}$ and multiplied with a multiplicity of 12 for all P1 transitions yields a P1 concentration of $3.0 \pm 0.1 \, \text{ppm}$.

The doping efficiency of this process amounts to 0.15%, which is two times higher than reported values in literature for growth on (111) substrates. A spin coherence time of $T_2 = 55 \pm 1 \, \mu s$ for the NV centers in the pyramid faces was determined with a Hahn-echo sequence. According to Bauch et al., the $T_2$ time is dominated by the dipolar interaction with the unpaired electrons of the nitrogen donor atoms above P1 concentrations of 1 ppm. A fit to their large set of $T_2$ and [P1] data was found to be $T_2, \text{expect} = 160 \pm 12 \, \mu s \cdot \text{ppm}^{-1}$.[41] The measured coherence time of $T_2 = 55 \pm 1 \, \mu s$ slightly surpasses the expected value of $T_2, \text{expect} = 32 \pm 2.4 \, \mu s$ calculated with the model, which supports the finding of a low concentration of additional paramagnetic defects. Influences of other crystal defects on the coherence times could not be detected at the present nitrogen concentration of $5.0 \pm 0.1 \, \text{ppm}$. The influence of $^{13}$C nuclear spins on the NV center Hahn-echo decoherence is negligible. The $T_1$ lifetime of
the observed NV ensembles was measured at $0.4 \pm 0.2 \mu s$ and was not corrected for magnetic field gradients, lattice strain inhomogeneities and temperature fluctuations and therefore falls short of the expected value of $2 \mu s$.[46]

4. Conclusion

We have presented the N-doped CVD overgrowth of the etched micropillars with diameters of 300 nm to 5 μm that resulted in regular, complete and truncated pyramids with (111) side faces and a (100) top face. The side length of the top faces equaled the diameter of the underlying micropillar so that pyramids grown on top of the 300 nm pillars have tip radii of 150 nm, which is comparable with conventional NV-containing diamond tips for scanning probe magnetometry.[8] It was found that the NV centers created during the CVD process have a high $T_2$ time of $55 \pm 1 \mu s$ and that 91 ± 3% to 99 ± 3% of the NV centers are aligned perpendicularly to the respective pyramid side face in which they are located. The $T_2$ time of the NV centers is limited by the surrounding P1 nitrogen concentration of 5.0 ± 0.1 ppm. The P1 limitation in combination with the narrow DEER linewidth is an indication for a high purity host crystal. Pyramidal structures increase the usable surface area of the substrate and aligned NV centers with long $T_2$ coherence times as presented in this report can help to facilitate the polarization of nuclear spins in biological molecules as NMR contrast agent. The separation of the four possible NV axis orientations into different locations is also advantageous for magnetometry applications. It could for example aid the construction of a vector magnetometer, as each of the four NV orientations can be read out with increased ODMR contrast. Future work will focus on improving the process by fabricating micropillars with smaller tip radii in order to create sharp pyramids enhancing the function as AFM probe tip. A thinner nitrogen doped layer will bring the NV centers close to the surface and closer to the sources of the magnetic fields of interest. The coherence properties and sensitivities of the CVD-grown NV magnetic field sensors could well be improved by investigating a larger range of the nitrogen concentration in the doped layer.

Acknowledgements

This work was supported by European Union’s Horizon 2020 research and innovation program under grant no. 820394 (ASTERIQS) and no. 820374 (MetaboliQs). A.G. acknowledges funding by the Carl-Zeiss-Foundation granted within the project SCHARF. A.M. acknowledges funding by the EU H2020 program under grant no. 765267 (QuSCo).

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.G. prepared the manuscript with support from P.K., conducted CVD growth and structural analysis of the samples. NV center analysis was done by N.S., A.M., and P.N. Lithography and ICP etching was conducted by C.G. and P.Q. P.K. supervised the project. All authors discussed the results and contributed to the final manuscript.

Data Availability Statement

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

Keywords

chemical vapor deposition (CVD) diamond growth, nitrogen vacancy centers, preferential alignment, quantum sensing

Received: July 9, 2021
Revised: September 7, 2021
Published online: October 5, 2021

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