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Effect of ultraprecision polishing techniques on coherence times of shallow nitrogen-vacancy centers in diamond

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ABSTRACT

We investigate the correlation between surface roughness and corresponding T_2 times of near-surface nitrogen-vacancy centers (~10 nm/5 keV implantation energy) in diamond. For this purpose we compare five different polishing techniques, including both purely mechanical as well as chemical mechanical approaches, two different substrate sources (IIa Technologies and Element Six) and two different surface terminations (O- and H-termination) during nitrogen-vacancy forming. All coherence times are measured and compared before and after an oxygen surface treatment at 520 °C.

We find that the coherence times of shallow nitrogen-vacancy centers are surprisingly independent of surface roughness.

1. Introduction

Quantum nanosensing has recently become a very promising application of diamond devices due to a specific quantum sensor: the nitrogen-vacancy (NV) center. A single center embedded few nanometers beneath the diamond surface is sufficiently sensitive to record nuclear magnetic resonance spectra of nanoscale samples [1,2]. This technique of "nanoscale NMR" has led to numerous applications including the conformation analysis of ice [3], as well as the detection and spectroscopy of atomically thin layers [4] or even single proteins [5]. Simultaneously, NV centers in scanning probes have enabled imaging of antiferromagnetic domains [6] and nanodiamonds containing NV defects have enabled temperature measurements in living cells [7,8]. As many signals decay steeply with the sensor-sample distance (cubically for a single spin), NV centers have to be located very close to the diamond surface for sensing applications. Although it is possible to implant optically stable NVs at a depth of only 1.1 nm, the resulting electron spin T_2 times are reduced more than tenfold compared to NVs in the bulk [9,10] for reasons that are not fully understood to date [11,12].

As a consequence, much effort has been spent on improving coherence by better surface preparation: thermal oxidation, as will be investigated in our study, can improve the T_2 time, although its impact varies considerably (improvement of effective T_2[1] from ~10 μs to ~50 μs in ref. [5], ~15 μs to ~18 μs in ref. [17]). Oxidative etching [9,18] and plasma etching [19,20] seem to reliably create shallow NVs from deeper implantations while maintaining relatively good coherence times. While O–, H– and F-terminations have been tested without success [21], promising calculations on N-terminations [22–24], as also considering different surface orientations of the diamond [24], could not be confirmed experimentally yet. However, simply covering the diamond with glycerol is reported to increase T_2 from 28 μs to 132 μs [12][2]. Complementary approaches aim to influence the coherence properties during or before NV center creation: Shallow NVs created in a delta-doping process can have coherence times $T_2 > 100$ μs [25], although this result is not easily repeatable [14,26]. Growing a thin layer of SiO_2 before implanting the nitrogen ions does not increase the coherence time [27]. However, growing a thin layer of boron-doped diamond before vacuum annealing and removing it afterwards has been reported to improve T_2 up to 180 μs for shallow NV centers [28].

Intuitively, the surface morphology is another parameter which may affect the local electric [12] and magnetic [15,21] field noise, which are likely origins of the observed decoherence. So far, no systematic study of influence of the surface geometry has been reported. It is known that different polishing techniques can yield surface roughnesses varying by two orders of magnitude [29], with the best results approaching

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[1] To ease comparison, all T_2 times in this paragraph have been corrected for their implantation depth and dynamical decoupling [13] order, assuming a d^2 rise of T_2 with surface distance d [14] and a $N^{1/2}$ scaling with the number of decoupling pulses N [14–16].

[2] *rms* value estimated from R_a value via the following equation: $rms \approx 1.1\ R_a$.

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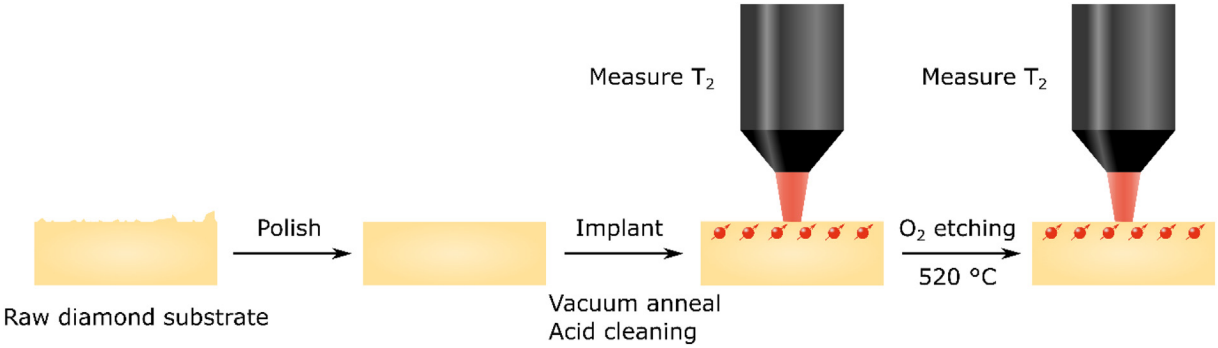

Fig. 1. Investigating the correlation between surface geometry and the coherence time T_2. A set of diamonds is subjected to different polishing techniques and subsequently doped with NV centers by ion implantation, vacuum annealing and acid cleaning. For each diamond, the NV spin coherence time T_2 is measured before and after a 520 °C thermal oxidation step.

smoothness on the atomic level [30–32].

We therefore investigated the influence of different polishes on the coherence time T_2 of shallow implanted NVs. We applied different polishing methods to a set of 10 diamonds, subsequently implanted NV centers, and performed Hahn echo [33] measurements before and after a 520 °C thermal oxidation step (Fig. 1).

2. Material and methods

One electronic grade single-crystal CVD diamond with a scaife-polished (100) surface and dimensions of $2.0 \times 2.0 \times 0.3\,mm^3$ was bought from IIa Technologies Pte. Ltd., referred to as substrate 1. We measured a surface roughness of *rms* = 2.07 nm by AFM with clearly visible polishing grooves (Fig. 2b), consistent with the manufacturer's specification of *rms* < 5.5 nm^2. We will refer to this sample as sample Std3.

All other diamonds investigated have been laser-cut from three single-crystal electronic grade CVD diamonds with a scaife-polished (100) surface from Element Six Ltd. (145-500-0389), referred to as substrates 2A through 2C. Since our study focuses on the effect of surface roughness, no additional treatment was applied to reduce potential subsurface defects.

Two diamonds (referred to as Std1 and Std2) were chosen to keep the manufacturer's original scaife polish, with an rms roughness of roughly 1 nm (see Table 1 for details) and clearly visible polishing grooves in AFM (Fig. 2a).

Two samples (Scf1 and Scf2) were subjected to a different scaife polish (Almax easyLab), resulting in surface roughnesses of *rms* = 2.42 nm (Scf1) and 1.07 nm (Scf2, Fig. 2f) with visible polishing grooves.

One diamond (H1) was treated by hydrogen plasma (15 min in the Seki Technotron quartz tube reactor of an ASTEX microwave plasma system, power 750 W, pressure 50 mbar, flow 100 sccm, temperature 700 °C). While this had no effect on roughness (Table 1), termination-induced lattice charging during annealing could affect the NV creation process [28].

Two samples (Cmp1 and Cmp2) were processed in a recently developed chemical mechanical polishing (CMP) process employing a fluid of silica nanoparticles [30,34]. On these samples we observe point-like defects rather than grooves, and one of them shows a significantly reduced roughness of *rms* = 0.51 nm (Cmp2, Fig. 2d). This latter result varies, with Cmp1 showing roughness of *rms* = 2.68 nm, presumably owing to local variations in substrate properties.

Finally, two samples (UV1 and UV2) were polished by another recently developed CMP process, based on a UV-light-induced photochemical reaction [31]. While there are comparably high debris-like defects on both resulting surfaces, they are extremely smooth for the most part. The clean areas provide roughnesses of *rms* = 0.44 nm (Uv1) and *rms* = 0.56 nm (Uv2, Fig. 2e).

After polishing, all diamonds were implanted with $^{15}N^+$-ions with an implantation energy of 5 keV and an ion flux of 10^{10} ions/cm^2 under an angle of 7° (CuttingEdge Ions, LLC). Subsequently, all diamonds were annealed in a vacuum chamber at 900 °C for 4 h and then boiled for three hours in an acid mixture (1: 1: 1 – H_2SO_4: $HClO_4$: HNO_3). The resulting NV centers are expected to be ~10 nm deep according to previous Monte Carlo simulations and measurements [28,35,36], which is in good agreement with the measured low T_2 times. Photoluminescence measurements in a typical confocal setup for NV centers [37] confirmed the successful formation of NV centers with an average density of 1 NV/μm^2. ODMR measurements did not show splitting due to strain effects.

We measured coherence times on single NV centers in every sample by a Hahn echo measurement in a magnetic field of 400–600 G along the NV axis. In order to check for a potential improvement by thermal oxidation [5,19], we performed each measurement twice, once after acid cleaning of the diamond and once after an additional etching step at 520 °C in air atmosphere (Heraeus RO 7/50). This etching step has been calibrated beforehand on sample Scf2 as will be described below. Both Hahn echo measurements were performed on the same NV centers.

Measurements were performed in a microscope with widefield illumination and camera detection, allowing us to simultaneously probe all ~100 NV centers in an area of $10 \times 10\,\mu m^2$ (Camera: Princeton ProEM-HS: 512B_eXcelon3, laser power: 500 mW) The widefield beam was shaped from a Gaussian profile into a homogeneously illuminated square profile by a holographic phase plate TOPAG GTH-4-2.2-532.

3. Results and discussion

In order to find proper parameters for the thermal oxidation, four treatment steps were successively applied to diamond Scf2 after the vacuum anneal: acid cleaning as described above, 4 h thermal oxidation at 465 °C in a pure oxygen atmosphere [5], 1 h thermal oxidation at 520 °C and finally 1 h thermal oxidation at 560 °C in air. After a further oxidation step at 580 °C in air, the fluorescence signal of some NV centers was quenched and the remaining NV centers showed pronounced blinking, prohibiting continued Hahn echo measurements. We therefore conclude that etching of the surface beyond few nanometers only occurs at a threshold temperature above 560 °C, while annealing at lower temperature mostly affects surface termination. The samples were placed in a Piranha solution (3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2) at ≤100 °C for 30 min immediately before and after each treatment. The distribution of T_2 times after each treatment is shown in Fig. 3.

While the median value, as a measure of the collective properties of the examined NV centers, could be increased from initially 12 µs to 19 µs after the 560 °C step, the maximum values decreased from 60 µs to 45 µs. Since the results from the 520 °C treatment are very similar to