Nitrogen-vacancy (NV) centers have a great potential for quantum sensing. The spin of individual NV centers can be controlled and read out at ambient conditions by microwave and optical excitation[1]. Many applications have already been demonstrated, such as imaging magnetometry[23] and the recording of NMR spectra from molecular-size samples[24]. Furthermore, small local temperature differences[25] and the movements of mechanical resonators[26] can be measured.

For quantum sensing, close proximity of the NV center to the sample is crucial, which is only achieved for “shallow” NV centers located few nanometers beneath the diamond surface. A high control of the NV-surface distance can be achieved by implanting nitrogen atoms at low (keV) energies, followed by an annealing process to form NV centers. However, the resulting centers feature significantly reduced $T_2$ times ($10-100\mu s$) and a low (1%) conversion yield between implanted nitrogen atoms and NV centers. This has been attributed to the formation of divacancies and higher order complexes, which compete with the NV formation and can act as paramagnetic defects or charge traps[9].

By introducing a boron doped sacrificial layer in proximity to the implanted nitrogen layer, during annealing, $T_2$ times and the shallow NV center yield could be improved[9]. This phenomenon is explained by an increased hole density, leading to a positive charging of single vacancies, thus suppressing the formation of divacancies due to the repelling coulomb forces. Recently, a significant improvement in the formation yield (from 2% to over 60%) was achieved by directly n-doping the diamond with co-implanted phosphorous, oxygen or sulfur[20]. This success has been attributed to the same mechanism.

Both diamond doping and removal of a sacrificial layer are technically challenging and hence inaccessible to many laboratories. We therefore investigate whether similar effects can be achieved by technically simpler and noninvasive methods, in particular surface transfer doping and UV illumination.

Surface transfer doping is a method to induce a thin doped layer close to the diamond surface. It typically employs H-termination of the diamond to favor transfer of electrons across the surface into adsorbed electrolyte[11], molecule[12] or metal electrode[13], inducing p-doping close to the surface. This technique has already been employed to control the charge state of defects close to the surface[14,15].

Here we aim to replicate the same effect by forming a nickel junction on O-terminated diamond as well as a palladium junction or aluminum oxide junction on H-terminated diamond. In contrast to previous work, we cannot employ a bare H-terminated surface, as it would not be stable during the annealing. Figure 1 summarizes the effects schematically.

For a coating of O-terminated diamond with nickel (Fig. 1a), the Fermi level of nickel is situated above the valence band, forming a junction between both materials, electrons will therefore diffuse into the diamond, to form a thermal equilibrium. This leads to the formation of a band bending within the diamond. The junction exhibits a Schottky barrier height $\Phi_B = E_F - E_V$, at the interface, between 1.1 eV and 1.7 eV[13]. Hence, vacancies in close proximity to the surface will be forced into the $V^0$ state. Neutral vacancies are known to diffuse faster than $V^+$[16,19], but are also believed to be more prone to clustering.

A H-terminated diamond surface induces an even stronger shift of the Fermi level, owing to the negative electron affinity $\chi = E_C - E_{va} \approx -1.3 eV$ of H-terminated diamond[20]. A junction with the metal palladium will shift the diamond Fermi level near the surface into the valence band, forming a thermally stable Ohmic contact with $\Phi_B = E_F - E_V = -0.15 eV$. This will discharge vacancies close to the surface into the positive charge state $V^+$, possibly creating electrostatic repulsion between them[9].

A similar situation is expected for an interface between diamond and the insulator aluminum oxide Al$_2$O$_3$, where a p-doped hole gas has been observed[22,23] and has been explored...
for power electronics in recent experiments. The exact spatial dependence of band bending depends on several unknown parameters, in particular the dominating species and concentration of defects in the aluminum oxide as well as the concentration of defects at the interface. Hence, no exact value for the barrier height can be given, making this case less well controlled than the metal contacts.

As a possible noninvasive and simple method to charge lattice defects, we investigated the effect of laser irradiation during the annealing process. We irradiated the diamond with a wavelength of 405 nm (3.06 eV). This is above the threshold required for $V^0 \rightarrow V^-$ conversion (reported to be 2.88 eV), but below the threshold for the inverse process (3.15 eV), implying that it will bias population towards the negative charge state. However, this effect might compete with random changes of the charge state induced by thermal excitation or by migrating charges from laser ionization of other defects.

I. METHODS

For this study, four IIa electronic grade (100) diamonds from Element Six Ltd. were used (size 2 mm × 2 mm × 0.5 mm, $[N] < 5$ ppb $\pm 9 \times 10^{14}$ cm$^{-3}$, roughness Ra $< 5$ nm).

The main processing steps to form the NV centers in the individual samples are summarized in Table I. The diamonds were acid cleaned (4 hours in a boiling H$_2$SO$_4$ : HNO$_3$: HClO$_4$ mixture) and implanted with $^{15}$N$^+$-ions (implantation energy 5 keV, ion fluence $5 \times 10^9$ ions/cm$^2$) at a 7° angle (Cutting Edge Ltd.). We expect an implantation depth of 10 nm.

The diamond samples $D_{NI}$, $D_{Pd}$ and $D_{AlOx}$ were oxygen terminated in an oxygen plasma (PS100-E, PVA TePla, $p = 1.4$ mbar, power 200 W) for 300 s. $D_{Pd}$ and $D_{AlOx}$ have been further fully hydrogen terminated by a hydrogen plasma in a microwave reactor (Astex, 15 min at 700 W ($D_{Pd}$) or 750 W ($D_{AlOx}$), temperature 700°C).

50 nm films of nickel or palladium were deposited onto $D_{NI}$ and $D_{Pd}$ by electron beam evaporation ($p < 10^{-6}$ mbar, deposition rate: 1.1 Å s$^{-1}$) on the O- or H-terminated diamonds, respectively. Atomic layer deposition was used to grow a 10 nm thick layer of aluminum oxide onto $D_{AlOx}$ ($T_{substrate} = 200$ °C, $p = 0.25$ mbar), with successive cycles of trimethylaluminum and water exposure. The diamonds were annealed in a vacuum of $\sim 10^{-6}$ mbar. After a 60 min heat up period, the diamonds were held for 225 min at 830 °C $D_{UV}$ was irradiated by a UV laser during the annealing process ($\lambda = 405$ nm, laser power $\sim 250$ mW, illuminated area $\sim 4$ mm$^2$).

After annealing, the nickel and palladium layers were removed by an aqua regia solution. The aluminum oxide layer was removed by hydrofluoric (HF) acid. To remove the graphite layer resulting from the annealing, all diamonds were acid cleaned, as described above. The H-terminated diamonds $D_{Pd}$ and $D_{AlOx}$ were finally O-terminated again.

The measurements of the spin properties of the NV centers were performed with a home-built confocal microscope. Excitation with a 532 nm laser and imaging were performed through an oil-immersion objective (NA=1.35). The emitted photoluminescence was filtered by a 650 nm long pass filter and measured by an avalanche photodiode. All measurements were performed at room temperature.

ODMR, Rabi and $T_2$ measurements were performed at a resonance frequency of 1.6 GHz, corresponding to a magnetic field $B = 45$ mT. Lorentzian curves were fitted to the data obtained by ODMR measurements. The $T_2$ time was measured by Hahn echo sequences with a rabi frequency of $\approx 9$ MHz. The data points were fitted to an ESEEM curve involving a stretched exponential decay, considering collapses and revivals induced by the $^{13}$C bath.

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Table I. Sample preparation details.

| Process              | $D_{NI}$ | $D_{Pd}$ | $D_{UV}$ | $D_{AlOx}$ |
|----------------------|----------|----------|----------|------------|
| Applied Material     | Nickel   | Palladium| Al₂O₃    |            |
| N-Implantation        | ✓        | ✓        | ✓        | ✓          |
| Piranha cleaning      | ✓        | ✓        | ✓        | ✓          |
| O-Plasma              | ✓        | ✓        | ✓        | ✓          |
| H-Plasma              |          |          |          | ✓          |
| Annealing             | 830 °C   | 830 °C   | 830 °C + UV | 830 °C    |
| Aqua regia            | ✓        | ✓        |          |            |
| Hydrofluoric acid     | ✓        | ✓        |          |            |
| 3-acid-cleaning       | ✓        | ✓        | ✓        | ✓          |
| O-Plasma              | ✓        | ✓        |          |            |
Figure 2. (a-d) Confocal fluorescence scans of the sampled regions. (e) Histogram of the fluorescence intensity $I(k)$ for $D_{Pd}$. A curve (black) consisting of two Lorentzians (yellow) was fitted to the histogram, distinguishing between individual and bunched NV centers. (f) Mean fluorescence intensity $I$ and NV-center yield $\eta$ of the respective samples.

II. RESULTS AND DISCUSSION

A. Fluorescence properties

Figure 2a–d shows the confocal fluorescence images of representative regions on the respective samples. We will analyze these images with regard to (i) the distribution of fluorescence intensity of the individual NV centers, (ii) the density of NV centers, i.e. the N → NV conversion yield, and (iii) the background fluorescence intensity $I_B$. Luminescence peaks (NV centers) are identified by points, which are maxima within a $0.3 \mu m \times 0.3 \mu m$ environment and have a luminescence well above the background. The fluorescence intensity $I(k)$ of individual NV centers is calculated by subtracting the background luminescence from the respective peak luminescence $I_{max}$ according to $I(k) = I_{max} - I_B$. The resulting distribution of intensities (Fig. 2e) is bimodal, which we attribute to individual (low-count rate peak) and multiple, bunched (high-count rate peak) NV centers within a confocal volume. This distribution was fitted to two Lorentzian peaks. In order to calculate the overall yield $\eta$, a linear model was established, relating $N/N_0$ and $a_2 = A_2/(A_1 + A_2)$ using synthetic data obeying Poisson statistics, with the true number of NV centers $N$, the number of identified peaks $N_0$ and the respective integrated areas of the Lorentzian curves $A_i$. The mean fluorescence intensity $I$ of the NV centers was determined by the center of the fitted low-count rate peak, the second peak is ignored for the analysis of $I$. The result of this analysis is presented in Table II and leads to the following results:

The fluorescence intensity is higher for the samples annealed under a metal coating (Ni and Pd) than for the samples annealed under Al$_2$O$_3$ coating and UV illumination. This hints towards a higher stability of the NV$^-$ charge state in the metal-coated samples. Since our detection optics are selective for NV$^-$, discharging into the neutral NV$^0$ state would manifest itself as a reduction of fluorescence intensity.

The yield $\eta$ of NV center creation follows a similar trend. $\eta$ is given by the ratio of the density of formed NV centers to the density of implanted nitrogen atoms. In relation to $D_{Ni}$ and $D_{AlOx}$ the yield is increased by 85% for $D_{Ni}$ and by 70% for $D_{Pd}$ to $\eta > 5\%$, as shown in Fig. 2f. Thus, by discharging V$^-$, an increased NV center yield is approached.

Bunching of NV centers is correlated to the charge state of vacancies. The ratio $R = a_2/a_2_{Poisson}$ relates the amount of bunched NV centers in the measured samples (Fig. 2f) to the expected number from Poisson statistics. While annealing, the NV centers are dominantly in the negative charge state NV$^-$. However, the vacancies may change their charge state due to surface doping, as they are in closer proximity to the surface. $D_{Pd}$ promoting positively charged vacancies (V$^+$), has a 70% increase of bunches compared to calculations (Tab. II). Vacancies may be attracted by existing NV$^-$ centers, enhancing the formation of new NV centers in close proximity to other NV$^-$ centers. In $D_{Ni}$, no deviation from the expected value is observed, hence a random formation is achieved, with vacancies being in the neutral state (V$^0$). The UV irradiated and Al$_2$O$_3$ covered diamonds have $R$ values well below 1, matching expectations for negatively charged V$^-$. We observe that the type of termination during the annealing process does not appear to influence the brightness of the NV centers, as long as the H-terminated samples are O-terminated again after annealing. After the annealing and acid cleaning process, the NV center luminescence intensities in $D_{Pd}$ and $D_{AlOx}$ were greatly reduced. In combination with a missing response on the microwave signal this suggests quenching of the NV centers into the neutral NV$^0$ state. After the final O-Plasma treatment, the luminescence intensity increased to a similar level as found for non H plasma-treated diamonds, recovering the NV$^-$ state.

Table II. Fluorescence properties of the NV centers. Mean intensity of individual NV centers $I$, background fluorescence $I_B$, NV conversion yield $\eta$ and ratio $R$ of bunched NV centers in the measurements to the number expected by Poisson statistics.

| $D_{Ni}$ | $I$ (kcps) | $I_B$ (kcps) | $\eta$ (%) | $R$ (1) |
|-------|---------|---------|--------|------|
| $D_{Pd}$ | 81 ± 14 | 15.3 | 5.61 | 1.00 |
| $D_{UV}$ | 69 ± 9 | 8.7 | 5.02 | 1.71 |
| $D_{AlOx}$ | 52 ± 20 | 10.2 | 3.05 | 0.57 |
| $D_{Ni}$ | 51 ± 13 | 1.9 | 2.89 | 0.77 |

Figure 2a–d shows the confocal fluorescence images of representative regions on the respective samples.
where each dot represents an NV center: (a) the contrast of the ODMR spectra, (b) the FWHM $\Gamma$ of the ODMR dips, as well as (c) $T_2$ times of individual NV centers. The measured values are uniformly distributed with rising values along the abcissa. Box plots of the measured $T_2$ times are shown in (d) for the respective diamonds. The gray box is limited by the 1st and 3rd quartile, thus including 50% of the data points. The black bar indicates the median of the distribution. $D_{\text{ref}}$ denotes the $T_2$ times of a previous study\cite{ref29} with NV centers formed by the standard annealing procedure.

The background fluorescence intensity $I_B$ indicates the concentration of optically active lattice defects within the diamond and surface contamination. This value varies among the samples between 1.9 kcps ($D_{\text{AlOx}}$) and 15.3 kcps ($D_{\text{Ni}}$). The particularly low background fluorescence of $D_{\text{AlOx}}$ might show a reduced defect concentration. Alternatively, the HF acid cleaning, which is necessary to remove the Al$_2$O$_3$ layer, might have removed further surface contamination, resulting in a reduced fluorescence of the nearby surface.

### B. Spin properties of the NV centers

Figure 3 shows the distribution of relevant spin properties, where each dot represents an NV center: (a) the contrast of the optically detected magnetic resonance (ODMR) signal $A_{\text{rel}}$, (b) the ODMR linewidth $\Gamma = (\pi T_2^{-1})^{-1}$, and (c,d) the spin coherence times $T_2$. This analysis generates the following insights:

Fig. 3 illustrates that the observed ODMR contrast varies between the investigated samples. The NV centers of $D_{\text{AlOx}}$ and $D_{\text{Pd}}$ show the highest ODMR contrast, which is about 50% larger compared to $D_{\text{Ni}}$ and $D_{\text{UV}}$. This is different from the behaviour observed in fluorescence properties, where $D_{\text{Ni}}$ and $D_{\text{UV}}$ showed a comparable behaviour. Which seems to be due to the fact that the ODMR contrast is increased by several factors, most prominently a high stability of the NV$^-$ state ($D_{\text{Pd}}$) and a narrow ODMR linewidth ($D_{\text{AlOx}}$).

The linewidth $\Gamma$ of the ODMR spectra (Fig. 3b) is representative for the spin dephasing time $T_2$. The linewidth $\Gamma$ is smallest for $D_{\text{AlOx}}$, corresponding to the longest $T_2^*$ times. In addition, $D_{\text{AlOx}}$ and $D_{\text{Pd}}$ show the narrowest distribution of $\Gamma$. This suggests that the presence of a hole gas during annealing (or the oxygen plasma for removal of the hydrogen termination) improves $T_2^*$. Roughly 25% of the NV centers in $D_{\text{Ni}}$ have a substantially increased linewidth $\Gamma$.

To relate the distribution of $T_2$ times, we included the $T_2$ values reported in a previous study\cite{ref29} for a diamond sample (denoted here as $D_{\text{ref}}$) that was prepared using the standard annealing procedure (Fig. 3d). The median values of $T_2$ (corresponding to the $T_2$ values at 50% in Fig. 3c) and indicated by black bars in Fig. 3d) vary only in a small range between 12 $\mu$s ($D_{\text{Ni}}$) and 17 $\mu$s ($D_{\text{AlOx}}$, which also had the longest $T_2^*$). However, the tails of the distributions vary between the samples. For example, the upper quartile of the respective samples is moderately increased for $D_{\text{Pd}}$ and halved for $D_{\text{Ni}}$ in comparison to the three other samples. Both, the relatively large ODMR line broadening $\Gamma$ and the relatively narrow upper quartile of the $D_{\text{Ni}}$ sample suggest some source of magnetic impurities. We speculate that even after the final etching process, a small concentration of residual nickel atoms with a strong magnetic moment could remain on the diamond surface, reducing the dephasing and coherence time of nearby NV centers. Nevertheless, as can be seen in Fig. 3d, in all samples the top 10% of NV centers have similarly long $T_2$ values in the range between 59 $\mu$s and 78 $\mu$s. This shows that a small population of comparably robust NV-centers exists in all investigated samples and that surface transfer doping and UV illumination fail to induce a similarly striking effect as previously reported\cite{ref30}.

III. CONCLUSION

In summary, we investigated UV illumination and surface transfer doping as novel tools to temporarily dope a diamond during the formation of implanted NV centers by annealing. As its most salient conclusion, our study reveals that these tools have a weaker effect on the conversion yield and the spin properties than doping by growth or co-implantation, however the effect is non-negligible. The properties vary only by a factor of two within the small set of samples, but has been reported to improve by a full order of magnitude by other methods. Nevertheless, we draw the following conclusions:

Coating the diamond by metals (nickel or palladium) improves the yield by a factor of two, and partially induces super-Poissonian bunching of NV centers (palladium). It also improves fluorescence intensity, hinting towards a higher stability of the NV$^-$ charge state. The spin dephasing time $T_2^*$ improves significantly for an Al$_2$O$_3$ coating and slightly for a palladium coating, evidenced by a narrow ODMR linewidth, suggesting an effect of transfer doping or a final plasma step. In contrast, the coherence time $T_2$, arguably the most important figure of merit, is affected least strongly by our treatments. We observe a slight improvement for palladium coating and a clear reduction for nickel coating. The latter could be due to residual magnetic adsorbents or clustering of vacancies. Finally, UV irradiation has no effect on $T_2$ times and
seems to degrade fluorescence intensity as well as $T_2^*$. 

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Data available on request from the authors.

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