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## Highly photostable NV centre ensembles in CVD diamond produced by using N<sub>2</sub>O as the doping gas

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### ABSTRACT

High density Nitrogen-Vacancy (NV) centre ensembles incorporated in plasma assisted CVD diamond are crucial to the development of more efficient sensing devices that use the properties of these luminescent defects. Achieving high NV doping with N<sub>2</sub> as the dopant gas source during diamond growth is however plagued by the formation of macroscopic and point defects that quench luminescence. Moreover, such NVs are found to exhibit poor photostability under high laser powers. Although this effect can be harnessed to locally and durably switch off NV luminescence for data storage, it is usually undesirable for most applications. In this work the use of N<sub>2</sub>O as an alternative doping source is proposed. Much higher amounts of the doping gas can be added without significantly generating defects which allows the incorporation of perfectly photostable and higher density NV ensembles. This effect is believed to be related to the lower dissociation energy of the N<sub>2</sub>O molecule together with the beneficial effect of the presence of a low and controlled amount of oxygen near the growing surface.

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Point defects in diamond and in particular the nitrogen-vacancy (NV) centre are among the most studied solid-state systems for applications in quantum technologies that promise to bring significant breakthroughs in computing, simulation, communication and sensing. NV's electronic spin state can indeed be manipulated with ms coherence time at room temperature.<sup>1,2</sup> For example, shifting of the NV centre's spin states with an applied magnetic field can be optically detected under resonant microwave radiation leading to promising magnetic sensors<sup>3,4</sup> or spectrum analysers<sup>5,6</sup> combining both a high spatial resolution and an extremely high sensitivity. One powerful approach to achieve this, relies on NV centre ensembles located in a layer near or at the surface since the signal to noise ratio and hence the magnetic sensitivity increases with  $N_{NV}^{1/2}$  where  $N_{NV}$  is the number of luminescent defects involved in the measurement<sup>7</sup>. Creating a high density of NVs with controlled spatial distribution while preserving their good coherence properties is thus an important challenge.

NV centres in diamond can be created by implantation of  $N^+$  ions followed by annealing above a temperature at which vacancies are mobile and can combine with nitrogen in the crystal.<sup>8</sup> In this case high NV densities can be locally achieved (up to  $10^{18} \text{ cm}^{-3}$ ) and accurate positioning on the surface or in-depth by changing the implantation energy is possible. However, implanting close to the surface (10 nm range) requires low implantation energy which results in a low creation yield of NVs. In addition, this technique may result in a reduced coherence time due to the generation of other defects during implantation that cannot be completely annealed out.<sup>9</sup> On the other hand native NV centres can be uniformly embedded into diamond layers during Chemical Vapour Deposition (CVD) leading to much longer coherence times. The CVD technique is versatile and allows stacking layers with different isotopic purity and thickness opening the way to complex structures.<sup>10</sup> By combining nitrogen doped CVD layers and  $He^+$  bombardment after growth to generate vacancies,  $1 \times 10^{17} \text{ NVs/cm}^3$  (0.6 ppm) have recently been obtained.<sup>11</sup> So far the highest densities were reported for type *IIb* High Pressure High Temperature (HPHT) diamonds that were proton irradiated leading to  $2 \times 10^{18} \text{ NVs/cm}^3$  (11 ppm) but at the expense of significant line broadening.<sup>12</sup> Reaching high NV concentrations by using in situ doping of CVD films alone remains in fact quite difficult but would be desirable in order to create a flexible platform that aims at exploiting NV centre properties for magnetometry.

$N_2$  is the most common intentional dopant for creating NVs in diamond. At concentrations as low as parts per million (ppm), nitrogen impurities in the gas phase are known to dramatically accelerate CVD diamond growth rates.<sup>13,14</sup> Possible explanations are the lowering of the energy barrier that needs to be overcome to incorporate C atoms in the lattice or nucleate the next diamond layer, or the reduction in the diffusion of carbon-containing species that improves their anchoring at the surface.<sup>15,16</sup> There is however no consensus on the chemical species responsible for this catalytic effect. Radicals such as CN, NH or atomic nitrogen (N) have all been monitored in the plasma by optical emission spectroscopy.<sup>17,18</sup>  $N_2$  is one of the most stable molecules with triple nitrogen-nitrogen bonds that require 9.8 eV for breaking apart. Despite the use of high plasma power densities (pressure > 150 mbar and microwave power > 2 kW) only a moderate fraction of about 0.5 % of  $N_2$  is actually dissociated. In such conditions nitrogen doping efficiency is poor with most of it being substitutional to a carbon atom ( $N_s$ ).<sup>19</sup> NV centres typically represent a low fraction of  $10^{-2}$  to  $10^{-3}$  of the total nitrogen content in the crystal.<sup>20</sup> Due to the stability of  $N_2$  molecules and issues related to the presence of large amounts of nitrogen in the gas phase, directly incorporating high NV densities is very challenging. In this paper we report on the use of  $N_2O$  as an alternative doping source and found that much larger amounts can be added to the gas phase

while keeping good morphologies, leading to higher NV densities that possess improved properties and photostability.

The effect of large N<sub>2</sub> additions to the gas phase during growth is particularly obvious when a high thickness of several hundreds of micrometres of N-doped material is required as illustrated in Fig. 1. With a few tens of ppm of nitrogen, NV<sup>0</sup> and NV<sup>-</sup> emissions at 575 and 637 nm respectively appear as illustrated on the photoluminescence (PL) spectra of Fig. 1a using a 488 nm laser as the excitation line. Their intensity normalized to the diamond Raman peak however does not scale linearly with the amount of nitrogen added and exhibits saturation (or quenching) for concentrations around 100 ppm under our growth conditions.<sup>21</sup> Besides, for thick freestanding layers, an increasing absorption in the UV extending to the visible range is observed as N<sub>2</sub> concentration is increased<sup>22</sup> (Fig. 1b). With 100 ppm of N<sub>2</sub> in the gas phase the diamond grows brownish possibly because of the presence of vacancy clusters,<sup>23</sup> while an undoped crystal of similar thickness is almost uncoloured (Fig. 1e). It should be noted that the brown colour can be partly removed by a HPHT annealing (typically 7 GPa, 2200 °C) due to a rearrangement of point and aggregated impurities that are causing this colouration.<sup>24</sup> Above a few tens of ppm, N<sub>2</sub> also promotes the formation of extended or unepitaxial defects during growth.<sup>25,26</sup> A polycrystalline rim is for example formed on the thick diamond crystal presented in Fig. 1d (40 ppm N<sub>2</sub>) as compared to an undoped film (Fig. 1c). PL images were obtained using near band-edge UV light with a *DiamondView*<sup>TM</sup>. Green luminescence from the HPHT substrate (H3 centres) can be seen in the centre together with a red colouration indicative of NV emission and a bright blue luminescence from the polycrystalline defects at the edges. On the other hand, the undoped sample shows only dim blue luminescence and clean edges. It should be mentioned that for much higher levels of nitrogen (> 500 ppm) and under our high power conditions, it is almost impossible to grow a thick single crystalline layer. Because of these defects that prevent growth or quench luminescence, obtaining films with a high NV density using N<sub>2</sub> as a doping gas is particularly difficult.

We now detail efforts in growing thinner layers of about 10 μm with NV ensembles using the highest possible N<sub>2</sub> concentration before reaching saturation (100 ppm under our conditions). Previously, we have shown that reducing the growth temperature is an efficient way to increase NV luminescence.<sup>27</sup> Therefore the structure presented in Fig. 2a was prepared with the top layer grown with 100 ppm of N<sub>2</sub> and a temperature reduced from 890° C to 810 °C in order to promote the formation of NV centres (Sample A). After growth, luminescence was observed with a scanning confocal microscope that uses a 532 nm laser (Fig. 2b and set-up in Fig. S1 of supporting information file). Inserting an appropriate pinhole in a secondary image plane allows collecting the luminescence from a limited volume of the sample (typ. 1 μm<sup>3</sup>) and drastically removing the background signal. By comparing with the PL intensity measured from a single NV centre, NV density could be estimated to roughly 10 ppb (i.e. 10<sup>15</sup> NVs/cm<sup>3</sup>) which is a fairly high value leading to bright emission. Optically Detected Magnetic Resonance (ODMR) spectroscopy was also carried out. It aims at detecting the Zeeman shifts of the spin levels under an applied magnetic field only by optical means. Four pairs of resonances corresponding to a random orientation of NV centres along the 4 different <111> axes are visible (Fig. 2d). This is expected for growth on a (100)-oriented substrate contrary to growth on (110), (113) or (111) diamonds that lead to preferential orientation of 50, 73 and 97 % respectively.<sup>28,29,30</sup> Each resonance shows a characteristic triplet due to additional hyperfine splitting of the spin energy levels due to interaction with the nuclear spin of <sup>14</sup>N.<sup>31</sup> Their full width at half maximum (FWHM) was found to be 0.58 MHz (Fig. 2e). This is a low

value, comparable to that obtained with single NV centres in high quality CVD diamond with continuous ESR spectroscopy<sup>32</sup> and consistent with NV centres having good coherence properties.

The photostability of NV centres was then evaluated by scanning the sample with a higher laser power of 5 mW. Surprisingly this led to a strong (nearly 50%) and long lasting bleaching of PL emission (Fig. 2c). One possible mechanism is a change in the charge state due to the loss of one or several electrons from the emitting NV<sup>-</sup> centres that might be recaptured by adjacent defects.<sup>33</sup> This trapping was fully reversible since a scanning with an intermediate laser power of 0.5  $\mu$ W was sufficient to generate photo carriers and fully reconvert NV centres to their negative charge state, thus recovering the initial PL intensity (see Fig. S2 in supplementary information). In a recent paper, Jayakumar et al. have explored the dynamics of NV photoionization using type *Ib* HPHT diamonds that contain large amounts of nitrogen.<sup>34</sup> Luminescent patterns could be written and erased using excitation at different wavelengths (green and red). They were able to model their time evolution by considering the diffusion of photo-carriers that convert NV centres back to their negatively charge state. In our case a similar behaviour was observed but with a single wavelength at different excitation powers. Similarly to Dhomkar *et al.*<sup>35</sup> we used this property to realize a simple data storage experiment by writing a luminescent pattern into the diamond (see Fig. S2 in supplementary information). It was confirmed that the created patterns were still visible even after 24 hour time interval. The precise nature of these defects is yet to be investigated but a possible candidate is the nitrogen-vacancy-hydrogen (NVH) defect which is present at relatively high concentrations in nitrogen-doped CVD diamonds. Khan et al. have for example reported long-lasting charge transfer between NVH and surrounding defects leading to photochromism reversible through heating or UV exposure.<sup>22</sup> This ability to switch on and off luminescent regions of the crystal on demand might be of interest to create memories based on this material or to locally generate arrays of NV centres. If close enough, those centres could be coupled via the dipolar magnetic interaction and be used as a quantum register. Nevertheless for the purpose of creating dense NV ensembles for magnetometry applications, this low photostability is an important drawback.

The addition of N<sub>2</sub> together with appropriate growth conditions can lead to relatively dense ensembles of NV centres. However further increasing NV density is particularly challenging due to the appearance of defects that compromise the photostability of luminescent centres. As an alternative we propose the use of nitrous oxide (N<sub>2</sub>O) as a doping source during growth. N<sub>2</sub>O is a non-toxic non-flammable gas. It is a strong oxidizer used in the semiconductor industry available with a high purity for the deposition of silicon dioxide from SiH<sub>4</sub>/N<sub>2</sub>O mixtures.<sup>36</sup> The energy required to dissociate this molecule in the plasma (4.6 eV) is much lower than N<sub>2</sub> leading to a higher amount of atomic nitrogen at the growing surface together with atomic oxygen. Thin films similar to sample A were grown but with 500 ppm and 2000 ppm of N<sub>2</sub>O at 900 °C (samples B and C) for the top layer. An additional sample (sample D) was prepared with 500 ppm N<sub>2</sub>O at 800 °C to maximize NV density.

The laser microscope images of Fig. 3a-c show that all samples have a smooth morphology without any unepitaxial defects indicating that the presence of relatively high amounts of N<sub>2</sub>O did not significantly impact the growth in contrast with what is observed when using N<sub>2</sub>. Bright emission from NV centres is confirmed on the spectra of Fig. 3d obtained with a 473 nm excitation line. From the intensity of PL images acquired with a confocal scanning microscope (not shown here), it was possible to estimate NV densities to 15, 40 and 70 ppb of NV<sup>-</sup> for samples B, C and D respectively. These concentrations are significantly higher than those obtained for sample A (10 ppb) for which only a limited amount of N<sub>2</sub>

could be added in order to preserve the surface morphology. This is favourable to the development of devices that exploit luminescence from NV ensembles such as magnetic sensors and imagers.<sup>31</sup> It should be added that by submitting the samples to an additional post-treatment such as He or electron bombardment, to convert part of  $N_s$  into NV, much higher densities could be achieved. Four pairs of resonances were found in the ODMR spectra indicating that NV centres were randomly oriented as expected for (100)-orientation. The FWHM of the characteristic triplet (Fig. 3a-c) was estimated to around 0.9, 1.6 and 1.4 MHz for samples B, C and D respectively. This increase in the inhomogeneous linewidth roughly scales with the NV density although slightly thinner resonances are observed for the sample with highest doping. Widening of the peaks is usually indicative of a higher stress in the crystal or higher spin bath density. Therefore to improve the performance of magnetic devices based on NV centres, one needs to find a compromise between a higher NV density and longer coherence time of the ensembles.

In order to assess the nitrogen doping efficiency with different dopant sources, we performed Secondary Ion Mass Spectroscopy (SIMS) analysis on sample A (100 ppm  $N_2$ ) and another diamond layer (sample E) grown under similar conditions as B (2000 ppm  $N_2O$  and high temperature). Details of the analysis conditions and depth profiles are presented in the supplementary information file (Fig. S3). Tab. 1 shows the measured and calculated values. Although the nitrogen doping efficiency is an order of magnitude higher with  $N_2$ , the proportion of NV to the total N amount is improved with  $N_2O$ . It is possible that the presence of oxygen limits the incorporation of N in the crystal. However much higher amounts of this gas can be added without deteriorating the crystalline quality thus allowing reaching higher NV densities.

*Tab. 1. Concentration of N and NV measured in samples grown with different dopant gas sources.*

	<b><math>N_{total}</math> by SIMS (ppm)</b>	<b>NV density by PL (ppb)</b>	<b>N doping efficiency</b>	<b>NV doping efficiency</b>	<b><math>NV/N_{total}</math></b>
<b>A - 100 ppm <math>N_2</math></b>	14	10	0.140	$1 \times 10^{-4}$	<b><math>7.1 \times 10^{-4}</math></b>
<b>E – 2000 ppm <math>N_2O</math></b>	35	40	0.017	$2 \times 10^{-5}$	<b><math>1.1 \times 10^{-3}</math></b>

The most interesting finding though is the high photostability of NV ensembles produced by doping with  $N_2O$  during growth. Fig. 3e shows PL emission under low and high laser scanning powers (250 nW and 5 mW) for sample C. No change in NV emission intensity was observed in contrast with sample A that showed strong bleaching of the luminescence. This result was confirmed for the other 2 samples (B and D). Defects that contribute to the change in NV charge state through trapping and detrapping of carriers have therefore a much lower density here. It is unclear what the reason for this improvement was but the different chemical species produced near the growth surface could lead to a different mechanism of nitrogen incorporation in the crystal. In particular the presence of atomic oxygen through the dissociation of  $N_2O$  could have a beneficial effect by etching away unwanted defects as already reported for intentional additions of  $O_2$ .<sup>37</sup> Using  $N_2O$  is indeed a very efficient way to bring a low amount of oxygen near the growth surface together with the nitrogen dopant.

In summary, we have explored the possibility to grow CVD diamond layers that contain a high density of NV ensembles on a (100) orientation. The amount of  $N_2$  that can be added to the gas phase is

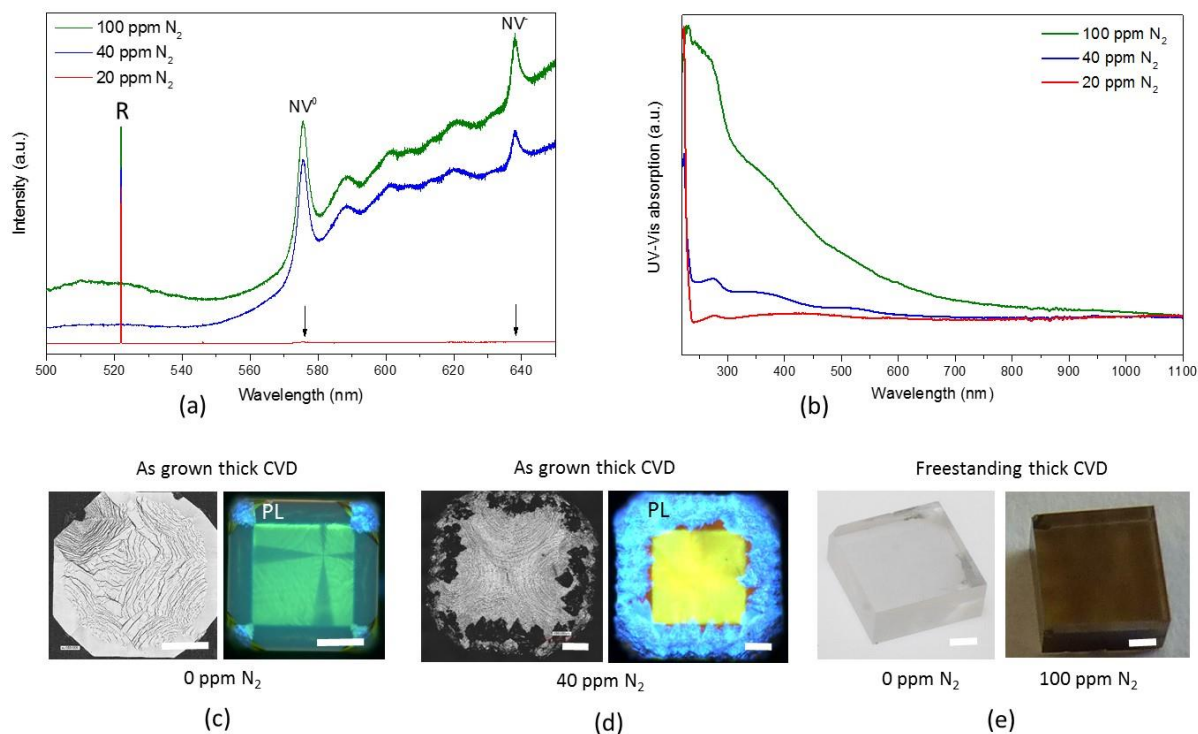
limited to a few tens or hundreds of ppm before the crystalline quality of the films is degraded leading to quenching of NV luminescence and defect formation. Despite the relatively high NV density obtained (10 ppb) the photostability is low, and under a high laser power, bleaching occurs. On the other hand the use of N<sub>2</sub>O as an alternative dopant gas source leads to much higher NV densities (up to 70 ppb) without impacting crystalline quality. Although inhomogeneous linewidth increases together with nitrogen concentration, the NV ensembles produced show perfect photostability. This result is possibly attributed to the higher dissociation efficiency of N<sub>2</sub>O in the plasma and the presence of a low amount of oxygen near the surface. The use of this alternative dopant could thus be significant for the purpose of creating highly NV-doped diamond layers with improved properties for applications in magnetic imaging and sensing. It would for example be relevant to couple this doping technique with growth on (111) or (113) substrates in order to achieve preferential orientations or to use an isotopically purified carbon source to further reduce linewidths.

### **Supplementary Material**

Information is given about the growth procedure for the nitrogen-doped CVD diamond samples as well as the photoluminescence and ODMR set-ups used for estimating the NV density in the films. The emission stability of NV centres under various green laser powers is described leading to the possibility of writing and erasing luminescent patterns on the diamond surface. The SIMS analysis procedure is provided together with the depth profiles of samples A and E.

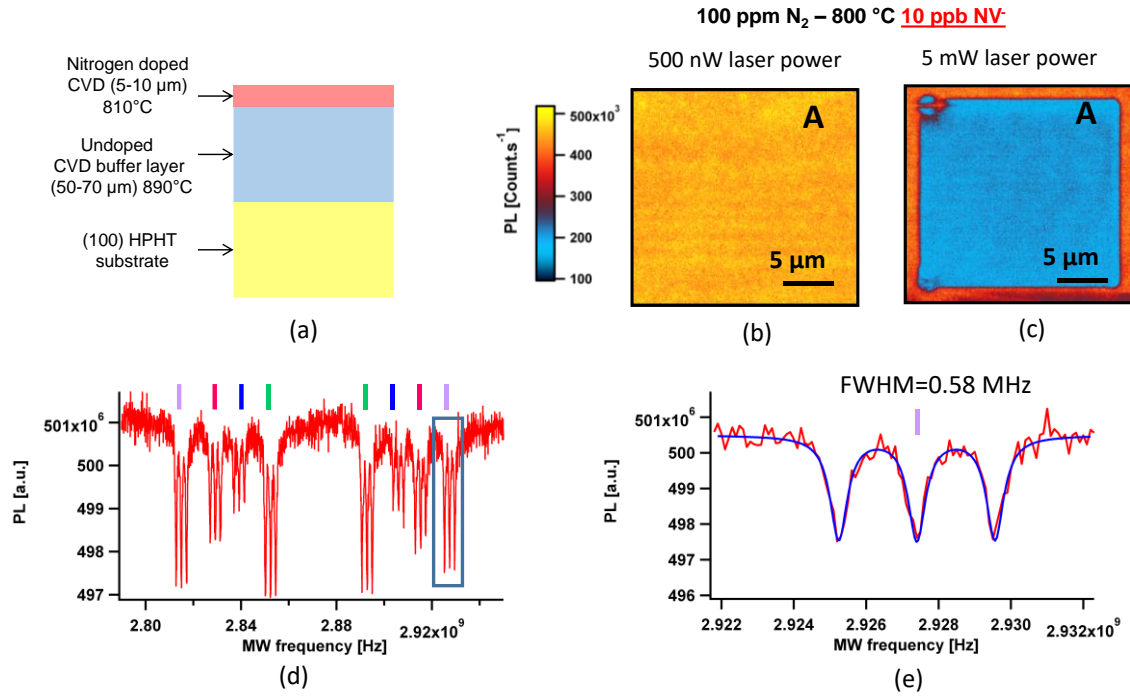
### **Acknowledgements**

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*Fig. 1. Effect of the addition of N<sub>2</sub> on the growth of thick CVD diamond films. (a) Room temperature Raman/PL spectra (488 nm laser) of thick films (around 1 mm) grown with 20, 40 and 100 ppm of N<sub>2</sub>. Spectra were normalized to the Raman peak (labelled as R) and vertically shifted for clarity. (b) UV-Vis absorption of the same freestanding CVD films showing an increasing absorption at higher nitrogen doping. (c) and (d) laser optical and PL images (DiamondView<sup>TM</sup>) of thick CVD films on their substrates grown with 0 and 40 ppm of N<sub>2</sub>. (e) Optical images of freestanding thick CVD crystals grown without and with 100 ppm of N<sub>2</sub> for which brown colouration is visible. Scale bars are 1 mm.*





*Fig .2. Optical properties of a thin film (sample A) grown with addition of 100 ppm of N<sub>2</sub> and a growth temperature of 800 °C. (a) Schematics showing the grown structure, (b) and (c) PL images obtained with a confocal scanning microscope (laser 532 nm) allowing estimating NV density and showing the poor photostability under high laser power. (d) ODMR spectra obtained under a magnetic field of 3 mT where 4 pairs of resonances are visible. (e) Zoom into one of the resonances highlighted by a square, where the characteristic hyperfine splitting is observed with a FWHM of 0.58 MHz.*

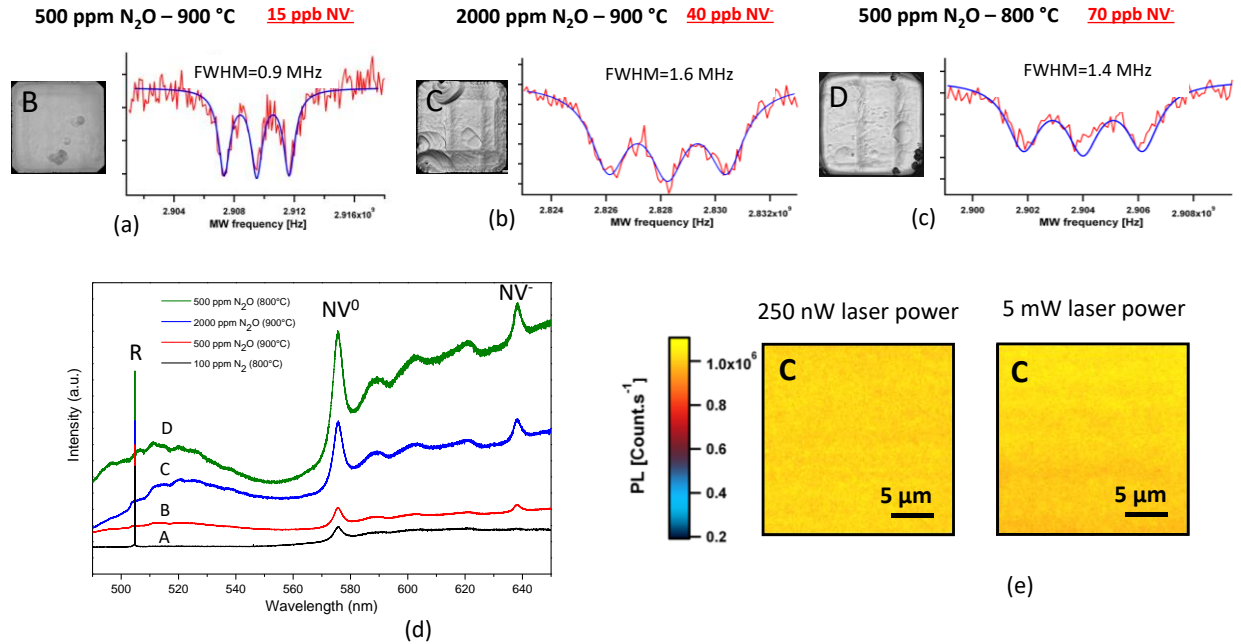


Fig. 3. (a)-(c) Laser microscope images of samples B, C and D grown with N<sub>2</sub>O addition and zoom into one of the hyperfine structures of the ODMR spectra showing the triplet and its linewidth. (d) Room temperature Raman/PL spectra (473 nm laser) for samples A, B C and D. Spectra were normalized to the Raman peak (labelled as R) and vertically shifted for clarity. The broader baseline around 520 nm originates from luminescence of the HPHT substrate underneath. (e) PL images obtained on sample C with a confocal scanning microscope (laser 532 nm) showing the perfect photostability of NV centres under higher laser powers.

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