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We demonstrate activation of bright diamond single photon emitters in the near infrared range by thermal annealing alone, i.e., without ion implantation. The activation is crucially dependent on the annealing ambient. The activation of the single photon emitters is only observed when the sample is annealed in forming gas (4% H\textsubscript{2} in Ar) above temperatures of 1000 °C. By contrast, no emitters are activated by annealing in vacuum, oxygen, argon or deuterium. The emitters activated by annealing in forming gas exhibit very bright emission in the 730-760 nm wavelength range and have linewidths of \(\sim\)1.5-2.5 nm at room temperature. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4821630]

Diamond single photon emitters have great potential in a range of quantum applications including quantum key distribution, quantum information, biolabelling, and quantum sensing. To date over 500 fluorescent emitters in diamond have been identified, although most of these have not demonstrated measurable single photon properties.

Identified diamond-based single photon emitters include the Nitrogen Vacancy (NV) complex centers, Silicon Vacancy (SiV), Ni/N related (NE8), Ni/Si related, and the centers recently identified as Cr-related defects. Additionally, there are several single photon emitters for which there is no clear structure or composition. These emitters vary in emission wavelength, linewidth, brightness and photostability. Because it is possible to identify particular emitters using confocal microscopy and to manipulate samples using “pick and place” technologies, in the future it should be possible to choose a particular emitter for a particular task, even if they occur at very low concentrations.

The formation of single photon emitters (particularly the NV centers) is usually accomplished by ion implantation followed by thermal annealing. Alternatively, centers can be fabricated via growth in a CVD reactor by the addition of specific gases to the growth mixture, or incorporation of impurities from the substrate on which the CVD film is grown such as in the case of Ni related centers. Many of the more promising new centers are found in very low densities in the sample, and are typically found by chance, rather than design. For this reason, it can be extremely difficult to identify precisely which steps in the growth process actually give rise to a novel defect center. It is even more difficult to differentiate between native centers that might be present but remain unobserved due to their very low concentration and centers that have been activated by the fabrication conditions, for example, by ion implantation.

Traditionally, thermal annealing has primarily been used to repair lattice damage after impurity implantation into diamond. In the case of vacancy related centers, vacancies become mobile during the annealing and diffuse towards impurity sites where they form defect complexes such as SiV.
and NV which are known to be optically active single photon emitters.\textsuperscript{15} Much attention has been paid to optimizing the annealing temperature in vacuum\textsuperscript{16} in an attempt to maximise the conversion rate of implanted species into optically active emitters. Much less attention has been given to the effect of the other annealing ambients. By contrast, the importance of the annealing ambient on the luminescence properties of other semiconductor systems including Si nanocrystals,\textsuperscript{17} InGaAs quantum wells,\textsuperscript{18} and Ga thin films\textsuperscript{19} is well established. In many cases, H\textsubscript{2} is known to play an important role in removing surface defects that act to quench luminescence\textsuperscript{17, 20} and indeed also stabilizing the diamond structure.\textsuperscript{21}

Here we present a systematic study of the formation of low-density, high brightness color centers with properties similar to those previously identified as Cr-related.\textsuperscript{9, 10, 22, 23} We show that the formation of these centers in single crystal diamond does not depend on ion implantation, but rather on the annealing ambient (forming gas, 4\% H\textsubscript{2} in Ar). Our results strongly suggest that a low density and unknown impurity in the diamond is being activated by the forming gas. These results highlight the need to understand the precise physical and chemical effects of annealing ambient on diamond, especially in the optimisation and discovery of new single photon emitters.

The diamond samples used in these experiments were N < 1 ppm B < 0.05 ppm ⟨100⟩ Type IIa diamond (Element Six Ltd. Product Ref. 145-500-0275-01). Although the impurity levels of these diamonds have been measured for N and B, the impurity levels of other trace elements are unspecified. Before and after each fabrication procedure, the samples were analysed using a home built confocal microscope (detailed in Ref.\textsuperscript{22}) with a Hanbury-Brown-Twiss interferometer for single photon time autocorrelation experiments. A 684 nm CW laser diode was used to excite the emitters with a pump power of \( \sim 1.5 \text{ mW} \), as measured at the back of a 100×, 0.95 NA objective lens.

We investigated the role of the annealing ambient by subjecting samples to 1 h furnace annealing in vacuum, argon, oxygen, deuterium, and forming gas. The results of the experiments are summarized in Table I. As an example, Figure 1(a) shows a confocal map of a 65 × 80 \( \mu \text{m}^2 \) area of a single crystal diamond (Sample 3 in Table I), before any processing of the material. Although there are many fluorescent areas, none of these areas exhibit single photon emission as measured by autocorrelation experiments. Figure 1(b) shows a confocal map of the same area as Figure 1(a) after a one hour forming gas anneal (4\% H\textsubscript{2} in Ar) at 1000°C. A large background fluorescence is observed as a result of the annealing process due to some surface contamination which may contribute to an inability to identify emitters. The sample was subsequently cleaned using a sulphuric acid and sodium nitrite mixture,\textsuperscript{24} which removes surface contamination and sources of fluorescence [Figure 1(c)] and reveals the existence of a newly activated single photon emitter whose spectrum is shown in Figure 1(d) with a Zero Phonon Line at (ZPL) at 752 nm.

The forming gas anneal and acid boil etch was repeated on multiple samples (Samples 1-3). Single photon emitters were found with similar average areal density of 2.5 × 10\(^5\) emitters/cm\(^2\) within the spectral window of interest of 720–900 nm. We did not observe any emitters below a depth of 1 \( \mu \text{m} \) for any of the samples. It is also important to note that the samples used in this

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Annealing environment</th>
<th>Annealing conditions</th>
<th>Density of single photon emitters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td>Forming gas (4% H\textsubscript{2} in Ar)</td>
<td>1 h, 1000°C</td>
<td>2.5 × 10(^5) cm(^{-2}) (25 emitters)</td>
</tr>
<tr>
<td>4-5</td>
<td>Forming gas ( (1 × 10(^{14}) e\textsuperscript{-}/cm(^2)) )</td>
<td>1 h, 1000°C</td>
<td>1 × 10(^5) cm(^{-2}) (5 emitters)</td>
</tr>
<tr>
<td>6</td>
<td>Vacuum</td>
<td>1 h, 1000°C</td>
<td>None detected</td>
</tr>
<tr>
<td>7</td>
<td>Forming gas (Sample 6)</td>
<td>1 h, 1000°C</td>
<td>9 × 10(^4) cm(^{-2}) (6 emitters)</td>
</tr>
<tr>
<td>8</td>
<td>Argon</td>
<td>1 h, 1000°C</td>
<td>None detected</td>
</tr>
<tr>
<td>9</td>
<td>Oxygen</td>
<td>1 h, 400°C</td>
<td>None detected</td>
</tr>
<tr>
<td>10</td>
<td>Deuterium (4% D\textsubscript{2} in Ar)</td>
<td>1 h, 1000°C</td>
<td>None detected</td>
</tr>
<tr>
<td>11</td>
<td>CVD hydrogen plasma</td>
<td>1 h, ( \sim 850 \text{ °C} )</td>
<td>None detected</td>
</tr>
<tr>
<td>12</td>
<td>Forming gas ( (1 × 10(^{17}) e\textsuperscript{-}/cm(^2)) )</td>
<td>1 h, 1000°C</td>
<td>None detected</td>
</tr>
</tbody>
</table>
FIG. 1. Confocal maps of the same ∼65 x 80 μm² area of a sample (a) as received, (b) after annealing in forming gas for one hour at 1000 °C and (c) after acid boil etching. One single photon emitter was observed for this particular area (circled and with a magnified view) which is not observed in either (a) or (b). (d) Spectral properties of the emitter with ZPL at 752 nm in (c).

experiment were purchased from different batches of diamonds, although all nominally within the same technical specifications provided by the supplier (Element Six Ltd. Product Ref. 145-500-0275-01). Three different batches were used with Sample 1 from one batch, Samples 4 and 5 from another batch and the rest of the samples from a third batch.

Figure 2 displays the spectral properties of 12 different single photon emitters with different ZPLs found in Samples 1-5 and 7 with emitters with different brightness observed and collected under the same conditions. The low concentration of emitters for Samples 1-5 and 7 which were prepared under different conditions, with the only commonality being the formation gas anneal, strongly indicates activation of an intrinsic trace element in the [N] <1 ppm samples. Indeed in previous studies, this class of emitters was never observed when higher purity [N] <5 ppb diamond was used as the starting material. The spectral range of the ZPLs of these emitters ranges from ∼730–760 nm. The emitters possess FWHMs of 1–2.5 nm at room temperature, which is narrow compared with other photon emitters observed: SiV (∼10 nm), Ni/Si(3–5 nm), and comparable to NE8 (∼2 nm), and Cr-related emitters. The previous measurements of Cr-related emitters were subsequently found to have been limited by the resolution of the spectrometer to 4 nm. In this work the spectrometer resolution was measured as <0.9 nm. The ZPL emitter wavelength, count rates (∼100–250 kHz), areal density, absorption, and emission dipole orientation of these emitters are consistent with the emission characteristics attributed to Cr-related emitters. The inset of Figure 2 shows the normalised time auto-correlation function $g^2(\tau) = \langle I(t)I(t+\tau)\rangle/\langle I(t)\rangle^2$ function for an emitter emitting at 748 nm with a value of $g^2(0) = 0.38$ confirming single photon emission. Bunching behaviour is observed which is consistent with a three level system. Both two-level and three-level emitters were found in previous Cr-implanted samples and have very similar correlation characteristics to the three-level emitters observed in Figure 2. The decay rate of the emitter was measured to be 1.3 ns, similar to those found for Cr-related defects by co-implantation of Cr⁺ and O⁺ ions.

Annealing in non-reactive ambient such as vacuum (Sample 6) and argon (Sample 8) resulted in no emitters within the wavelength range of interest. An oxygen anneal (Sample 9) was performed at 400 °C. The low temperature limits surface oxidation. The oxygen annealed sample did not
FIG. 2. Spectral properties of 12 different intrinsic defects activated by annealing of diamond in forming gas found in Samples 1-5 and 7. The inset shows $g^{(2)}(\tau)$ for an emitter with the ZPL at 748 nm found in Sample 1 which shows bunching behaviour consistent with a three-level emitter.

yield any emitters. Oxygen is pertinent as previous implantation studies, where Cr and O were co-implanted, report an increased yield of emitters. It is somewhat surprising that annealing in deuterated forming gas (4% D$_2$ in Ar) (Sample 10) also did not result in any emitters. This result might be explained by the different kinetics between H$_2$ and D$_2$ on diamond surfaces. It has been suggested that the energy needed to break D$_2$ bonds is greater than that of H$_2$ which results in less diffusion of hydrogen/deuterium.

The diffusion of hydrogen into diamond has been studied extensively and has significant effect on emitter formation. For example, NV$^-$ fluorescence can be suppressed by hydrogen plasma treatment. This was attributed to the diffusion of the atomic hydrogen on the order of $\sim$100 $\mu$m below the single crystal diamond lattice. To study the effects of atomic as opposed to molecular hydrogen, Sample 11 was hydrogen plasma treated using a CVD reactor with a microwave power of 900 W, pressure of 150 Torr and a substrate temperature of 850 $^\circ$C with 99.999% H$_2$ gas and acid cleaned afterwards. No emitters were observed after the plasma treatment. This is surprising as the diffusion of energetic H$^+$ ions in a plasma environment should facilitate the diffusion into diamond more so than molecular hydrogen in a forming gas anneal. However, hydrogen plasma treatment is a harsh process and may etch the (001) surface of the diamond which inhibits efficient formation of emitters especially if the concentration of impurities near the surface is low.

For completeness, we performed a second anneal on Sample 6 in a forming gas ambient after this sample had previously been annealed in vacuum with no resulting emitters. After the forming gas anneal (Sample 7), single photon emitters were observed, albeit with a slightly lower density than for Samples 1-3 that were directly annealed in forming gas without being annealed in vacuum.

To explore the role of vacancies, we electron irradiated three different samples (Samples 4, 5, and 12). Prior to the annealing step, one of the samples was irradiated by 2 MeV electrons with a relatively high fluence of $1 \times 10^{17}$ e$^-$/cm$^2$ (Sample 12). The damage caused by the implantation resulted in strong broadband background fluorescence ($\sim$100 kHz). This was not diminished after annealing in forming gas and an acid boil etch, making detection of any isolated single photon emitters nearly impossible. Samples 4-5 were irradiated with 200 keV and 2 MeV electrons, both with a relatively low fluence of $1 \times 10^{14}$ e$^-$/cm$^2$. Subsequent forming gas anneals of these samples successfully activated single photon emitters with a yield of $\sim1 \times 10^5$ emitters/cm$^2$. The yield of emitters was found to be similar to samples which had not been electron irradiated. Hence it is unlikely that the introduction of vacancies plays any significant role in enhancing the activation of the emitters. The intensity of the emitters with similar ZPLs was quantitatively lower than in non-irradiated samples. This is most likely due to the damage caused to the diamond lattice during the irradiation process.
FIG. 3. (a) Histogram of the number of emitters observed with different ZPL’s in Samples 1-6 which yielded emitters after a forming gas anneal. (b) Histogram of the linewidths at room temperature of the emitters shown in (a) with no clear correlation between the emission wavelength and its linewidth.

A histogram of the number of emitters which exhibit single photon behaviour is shown in Figure 3(a) for Samples 1-5 and 7. The figure shows the distribution of ZPLs following a forming gas anneal with a majority of the emitters possessing a ZPL between 747.5 nm and 752.5 nm. This is similar to the distribution of emitters obtained by extensive Cr and Cr–O ion implantation experiments. Figure 3(b) shows the linewidths of the same emitters shown in Figure 3(a) with no clear correlations between the emission wavelength of the emitters and the linewidths. However, a majority of the emitters have very narrow linewidths between 1.38 nm and 2.13 nm, comparable to other narrow emitters found in diamond such as the NE8.

Although the density of activated emitters is low, the relatively clean background and the ability to observe the same region before and after annealing leads to the conclusion (see Table I) that the forming gas ambient is essential for their formation. The origin of these emitters is not clear, although it is reasonable to assume that they are activated when hydrogen diffuses into the sample and forms some sort of complex with a pre-existing impurity. As mentioned earlier, the emission characteristics of the observed emitters and the density of emitters are similar to those previously reported as being associated with Cr impurities in diamond in which bright, ultra-fast single photon emitters in the near-infrared regime ranging from 744 to 764 nm were observed.

In order to elucidate the role of implantation and annealing, a diamond sample was implanted using 300 eV Cr$^+$ and 120 eV O$^+$ with doses of $2 \times 10^{10}$ ions/cm$^2$ and $3 \times 10^{10}$ ions/cm$^2$, respectively. The ions were implanted into the sample resulting in four “quadrants” implanted with Cr$^+$, O$^+$ and a co-implantation region where both Cr$^+$ and O$^+$ ions were implanted. One quadrant was intentionally left unimplanted by the use of an aluminum mask. The energy of the Cr$^+$ and O$^+$ ions was chosen so that the end-of-range was the same at ∼140 nm as calculated by SRIM calculations. Figure 4(a) shows a confocal map of an area intersecting the three implanted and the unimplanted regions. The map shows large background fluorescence in the co-implanted
FIG. 4. Confocal maps of the same region for 300 keV Cr\(^+\) and 120 keV O\(^+\) implanted in type IIa [N]\(<\)1 ppm diamond. (a) After implantation. (b) Further treatment of (a) by annealing in 1000 °C forming gas and acid clean. The fluorescence collection window is 720 nm to 900 nm.

Cr\(^+\) and O\(^+\) area due to the damage caused by the implantation process and reveals polishing damage typical in these diamond substrates. The areas where only one species were implanted also exhibit large amount of background fluorescence but to a lesser degree than the co-implanted area. As expected, the unimplanted area shows very low background with (∼10 kHz) and shows importantly that the region was not contaminated in the implantation process. Due to the large amount of damage in the implanted regions, it was difficult to determine whether there were emitters in those regions. Extensive scanning in the unimplanted region over a 400 × 400 \(\mu\)m\(^2\) area did not reveal any emitters. Figure 4(b) shows a similar area as Fig. 4(a) after a 1 h, 1000 °C anneal in a forming gas ambient and acid cleaned which reduced background fluorescence to similar levels as the unimplanted region. Similar to previous experiments, single photon emitters attributed to Cr-related defects were found. Importantly however, in this study the emitters were found in all of the four quadrants including the unimplanted areas with an areal density of ∼10\(^5\) emitters/cm\(^2\), strongly arguing against any significant role of the implanted ions in the formation of the emitters. The experiment was repeated using the same implantation scheme on another sample with similar results.

Figure 5 shows the spectral properties of all the emitters found in each of the four regions over a specific 100 × 100 \(\mu\)m\(^2\) area. Emitters with very similar luminescence properties in terms of their ZPL and the associated linewidths can be found in the implanted regions and the unimplanted region. The inset of Figure 5(b) shows the \(g(2)(\tau)\) function of an emitter with ZPL at 748 nm showing three-level behaviour found in the unimplanted region. Rough estimates of the yield in each of the regions are measured to be ∼10\(^5\) emitters/cm\(^2\).

In conclusion, we have shown that the annealing ambient is a critical parameter in the formation of particular, bright fluorescent single photon emitters in diamond. This is likely due to the activation of native defects within the commercially available Type IIa [N] <1 ppm diamond. By annealing at a temperature of 1000 °C in forming gas, without the need for ion implantation, emitters with ZPLs between 730 and 760 nm were formed with densities ∼10\(^5\) emitters/cm\(^2\). We believe that due to near identical ZPLs, linewidths, and count rates that the emitters found in the implanted sample and the annealed samples to be of the same class. The emitters activated in the forming gas anneal are therefore identical to those found in previous Cr-related centres. Given the extremely low concentration of activated fluorescent emitters in the annealed samples, we assume either the concentration of the pertinent defects is low or the activation probability is small, or both. Annealing in other ambient conditions such as vacuum, argon, deuterium, and oxygen resulted in none of these single photon emitters being formed in our spectral region of interest. The role of vacancies in the activation process was explored and found to have no significant impact on the density of emitters. These emitters show promising properties for Quantum Key Distribution applications and understanding their composition and formation is therefore an important goal. Conversely, understanding that such emitters can be formed also highlights potential sources of background whilst working with other diamond optical centers, and hence minimisation of these emitters is also a goal. Finally, if an impurity in the as-grown material is indeed responsible for
these emitters, then our methodology may provide for a novel way to quantify these impurities at the single atom level. To illustrate this, we note that if the conversion yield of these emitters was 100%, and if they were single atom defects, then the concentration of the impurities would be around one part per trillion.

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