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Laser writing of coherent colour centres in diamond

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Optically active point defects in crystals have gained widespread attention as photonic systems that can find use in quantum information technologies [1,2]. However challenges remain in the placing of individual defects at desired locations, an essential element of device fabrication. Here we report the controlled generation of single negatively charged nitrogen-vacancy (NV^-) centres in diamond using laser writing [3]. Aberration correction in the writing optics allows precise positioning of vacancies within the diamond crystal, and subsequent annealing produces single NV^- centres with up to (45 ± 15)% success probability, within about 200 nm of the desired position in the transverse plane. Selected NV^- centres display stable, coherent optical transitions at cryogenic temperatures, a pre-requisite for the creation of distributed quantum networks of solid-state qubits. The results illustrate the potential of laser writing as a new tool for defect engineering in quantum technologies, and extend laser processing to the single defect domain.

The NV^- colour centre is one of an increasing number of point defects in wide band-gap materials such as diamond and silicon carbide that show promise as quantum light sources and provide an optical interface with coherent electronic and nuclear spins [4-11]. Realization of entangled networks for sensing or distributed quantum computing with these systems [12, 13] requires coherence of the optical transition, which some defects have displayed at cryogenic temperatures [7, 14]. With NV^- this coherent interface has been used to demonstrate spin-photon entanglement [15] and entanglement between distant spins [16].

To realise technological applications it will be necessary to integrate such colour centres with optical and electronic components by positioning them at desired locations with an accuracy of 10 nm – 1μm [17-20]. This presents a challenge, since most placement methodologies involve irradiation of the sample with electrons or ions creating residual damage to the crystal lattice and degrading the colour centre properties. Despite recent progress using advanced annealing recipes and low energy electron beams [21,22], new methods for placement of defects with minimal residual lattice damage are of significant interest.

Here we show that laser writing can be employed to generate vacancies in a crystal as a starting point for the formation of coherent colour centres. This method has several attractive features: the highly nonlinear process of laser writing [3] combined with appropriate aberration correction [23] permits vacancy generation with spatial resolution beyond the optical diffraction limit, at any depth in the diamond, without damaging the overlaying material, and the laser pulse energy can be tuned with high precision to control

the number of vacancies generated. We show that after applying this process to diamond samples in which nitrogen atoms are present at low concentrations, subsequent annealing produces single, high quality NV^- centres near the target locations.

The diamond samples were commercially available single crystals grown by chemical vapour deposition, with nitrogen density below 5 ppb (900 atoms per μm^3). Regions were chosen for processing in which 'native' NV centres were absent. Single writing pulses of wavelength 790 nm and duration 300 fs were delivered to each site in 25 × 20 square grids with a pitch of 5 μm at a depth of 50 μm. Along one axis of the grids, the pulse energy E_p was varied between 16.0 nJ and 61.8 nJ to generate incremental degrees of damage to the lattice. Along the other axis, 20 identical pulses were delivered to facilitate statistical analysis of the results for each pulse energy. The onset of lattice damage at low pulse energies is thought to occur by a 9-photon ionisation process [24] (see Supplementary Information), from which we estimate the resolution of vacancy writing to be 120 nm in the image plane and 500 nm axially (see Methods).

Figure 1a shows a photoluminescence (PL) image of a grid immediately after laser writing. E_p increases from the bottom to the top of the image. Visible fluorescence was produced from sites that had been exposed to pulses with $E_p > 31$ nJ (red line), and the PL spectra (Figure 1b, lower trace) confirmed the presence of photo-generated neutral vacancies (GR1 centres). We estimate that around 10^7 vacancies are generated by the pulse energy E_1 (see Methods).

Figure 1c shows the PL image of the same grid after annealing (see Methods). Fluorescence was observed at several sites for which $E_p < E_1$ indicating the formation of new colour centres. Spectroscopy revealed that all fluorescence from sites up to $E_2 = 36.4$ nJ (green line) was from NV^- centres, with characteristic zero phonon line (ZPL) at 637 nm and broad phonon sideband (figure 1b, middle spectrum). GR1 fluorescence was no longer observed, suggesting that the majority of the vacancies had been removed as a result of the anneal step [25]. Neutral NV centre (NV^0) ZPL signatures at 575 nm were also absent, further signifying low vacancy concentration (see Supplementary Information). Features created with $E_p > E_2$ showed broad-band fluorescence (figure 1b upper trace), suggesting that the damage created at these sites exceeded the threshold for graphitization during the anneal [26].

Photon autocorrelation measurements (see Methods) were carried out for each of the sites with $E_p < E_1$ to determine the number of NV^- present. Figure 2a shows a typical dataset revealing a dip at $\delta t = 0$,

characteristic of a single colour centre. A histogram of the $g^2(0)$ values from all sites measured is shown in figure 2b. Two populations emerge, one with $g^2(0) < 0.32$ and another with $0.32 < g^2(0) < 0.65$, which we attribute to the presence of one and two colour centres respectively. A few sites showed $g^2(0)$ between 0.65 and 0.9, which we attribute to the presence of three colour centres. Figure 2c shows a spatial map of the NV^- populations per site, and figure 2d shows the row statistics versus writing pulse energy. At E_p = 25.7 nJ 9 out of 20 sites revealed a single NV^- corresponding to a probability of (45±15)% consistent with the statistical optimum of 37%. The total number of NV centres per row (black squares) reveals a systematic trend for more to be generated at higher pulse energies, but with a region of deviation from this trend spanning five rows, attributable to non-uniform nitrogen distribution in the sample.

From the PL image the location of each NV^- in the image plane can be determined to within <100 nm. Figure 2e shows a magnified image of a section of the NV^- array with a superimposed grid showing the nominal target positions. A histogram of the measured displacements of the NV^- from the target points (see Methods) is shown in figure 2f. The displacements measured are significantly larger than the predicted radial distribution of laser-generated vacancies, suggesting that diffusion of vacancies during the anneal stage determines the spatial distribution of the NV centres. The solid line is a fit of the 2D distribution function $f(r) = Are^{-r^2/r_0^2}$ where r is the radial displacement and A and r_0 are fitting parameters, corresponding to the isotropic diffusion of vacancies (see Methods). r_0 was found to be 196 ± 20 nm, consistent with the expected thermal diffusion length (see Supplementary Information). Based on this distribution, 61% of the NV centres fall within r_0 of the target position in the image plane. In the axial direction the positioning accuracy is expected to be lower, around 700 nm, due to the elongated shape of the vacancy generation volume (see Methods).

Photoluminescence excitation (PLE) spectroscopy (see Methods) was used to probe the ZPLs of the NV^- at T = 4.2 K, and reveals examples of colour centres with highly coherent transitions. Figure 3a shows a selection of PLE scans from three NV^- centres, revealing widths of 13.5 ± 0.3 MHz, 12.0 ± 0.7 MHz, and 27.5 ± 1.2 MHz. The two narrowest lines are consistent with the Fourier transform limit of 12.4 ± 0.1 MHz for an NV^- centre in bulk diamond based on a fluorescence relaxation time of 12.8 ± 0.1 ns (see Supplementary Information). Of 50 NV^- measured, 25 showed clear PLE signals, seven with line widths

below 30 MHz and four under 20 MHz. Repeated scans of one of these colour centres (Figure 3b) revealed only small fluctuations in peak position producing an inhomogeneously broadened line of width 16.1 MHz. After prolonged (~30s) excitation the NV^- centre ionized to NV^0 and an optical repump was required to restore the negative charge state. The repump pulse ionized other defects in the vicinity of the NV centre, changing the local electric field and shifting its transition energy by about 70 MHz via the Stark effect (Fig. 3c). Such shifts can be suppressed by using a repump tuned to 575 nm [21, 27], or corrected using dynamic stabilization techniques [28].

Figure 3d shows the measured single-scan line widths (solid circles) and repump-broadened line widths (open circles) for the NV^- centres measured from the two samples, plotted against the energy of the laser writing pulse used. Although a wide range of line widths is observed for each pulse energy setting and the narrowest line widths displayed in sample A are around 60 MHz, the narrowest line width identified across both samples increases systematically with increasing pulse energy (indicated by the blue dashed lines), suggesting that residual damage may limit the homogeneous line width at progressively higher pulse energies. Birefringence and Raman scattering measurements revealed evidence of residual stress only at sites corresponding to pulse energies well above E_2 (see Supplementary Information).

Finally, we measured the electron spin properties of the written NV^- using optically detected magnetic resonance. Hahn echo measurements (see Methods) showed T_2 times typically between 30 and 80 μs (Figure 4a), while one NV^- centre showed T_2 >100 μs. Such coherence times are comparable with those reported for NV^- implanted in similar diamond material using ion beam methods [29]. No correlation was observed between the optical line width and spin coherence, although it is worth noting that the NV^- centre with the longest T_2 also showed a narrow ZPL width of 27.5 MHz (NV1 in figure 3).

In summary, we show that femtosecond laser writing of vacancies into diamond can be used to produce optically coherent NV^- colour centres at desired locations. The sub-micrometre positioning accuracy achieved is sufficient for placing NV^- centres in optical structures such as multimode waveguides, whispering gallery resonators [18], or under solid immersion lenses [16]. The demonstrated accuracy is limited by the diffusion of vacancies during annealing, and further improvement may be achieved using a higher nitrogen concentration in the starting material and an adjusted the anneal recipe. In particular, high precision depth positioning may be achieved by combining laser writing of vacancies with delta doping of a

thin layer of nitrogen-rich material during growth [30]. The adaptive optics used for aberration correction would also allow colour centres to be positioned under microstructured surfaces. Beyond quantum photonic devices, the ability to write large and detailed 2D or 3D arrays of NV^- defects may find use in magnetic field imaging systems [31]. The laser writing technique demonstrated here for NV centres may be straightforwardly applied in conjunction with the writing of sub-surface waveguides [32] and electrodes [33], and can adapted for the generation of other colour centres and point defects in other wide band gap materials.

Methods

Samples and processing

The samples used were 'electronic grade' single crystal plates from Element Six Ltd, with (001) crystal orientation and nitrogen concentration < 5 ppb. Laser writing of vacancies was performed using a regeneratively amplified Ti:Sapphire laser (Spectra Physics Solstice). The optical layout for the laser processing is shown in Figure S4a. The laser beam was expanded onto a liquid crystal phase-only spatial light modulator (SLM) (Hamamatsu X10468-02), which was imaged in a 4f configuration onto the back aperture of a 60× 1.4NA Olympus PlanApo oil immersion objective. The diamond sample was mounted on precision translation stages (Aerotech x-y: ABL10100; z: ANT95-3-V) providing three dimensional control. An LED illuminated transmission microscope provided visualisation of the sample during processing. Prior to the objective the laser pulse was linearly polarised and had a duration which was measured to be 250 fs using an intensity autocorrelator (APE Pulsecheck). The pulse duration at focus will be slightly increased due to dispersion in the objective lens. To optimise the aberration correction, the phase pattern displayed on the SLM was adjusted to minimise the pulse energy needed to produce visible fluorescence at test processing positions of similar depth in the sample.

The resulting point spread function in the diamond was assumed to be a Gaussian beam with the cylindrically symmetric intensity distribution

$$I(r,z) = I_0 . \frac{1}{1+\left(\frac{z}{z_R}\right)^2} . e^{-\frac{2r^2}{w_z^2}}$$

where $w_z = w_0\sqrt{1+\left(\frac{z}{z_R}\right)^2}$ is the beam width at axial displacement z, w_0 is the beam waist and z_R is the Rayleigh range. Based on the numerical aperture of the objective lens we estimate that $w_0 = 297$ nm and $z_R = 852$ nm. These correspond to FWHM in the radial and axial directions for the photon intensity of $d_1 = 350$ nm and $L_1 = 1704$ nm respectively, corresponding to a focal volume of $\frac{\pi}{4}d_1^2 L_1 = 0.16$ μm^3. Single pulse energies for vacancy generation at the desired sites were controlled using a rotatable half-wave plate in conjunction with a Glan-Laser polariser and measured before the microscope objective lens. The full list of pulse energies is given in table S1.

Positioning and number of vacancies

The vacancies generated at low pulse energies where single NV centres are produced are thought to result from multi-photon ionisation (MPI) (see Supplementary Information), in which energy is delivered to the diamond material as a result of multi-photon absorption prior to electronic relaxation. The nonlinearity of the absorption process is expected to lead to vacancy generation within a region smaller than the focal volume determined by the field intensity $I(r,z)$. The distribution function for the absorption of *y* photons is $I^y(r,z)$, and the corresponding radial and axial dimensions (FWHM) are given by $d_y = w_0\sqrt{\frac{2ln2}{y}}$ and $L_y = 2z_R\sqrt{2^{\frac{1}{y}}-1}$. Assuming y = 9 [24] results in estimates of $d_9 = 117$ nm and $L_9 = 482$ nm. The volume over which vacancies are generated is therefore estimated to be $\frac{\pi}{4}d_9^2 L_9 = 5.2\times10^{-3}$ μm^3.

The number of vacancies produced is estimated from the graphitisation threshold, reported as 10^{22} cm^{-3} [27], which over the volume calculated above suggests that 5.2×10^7 vacancies were produced with the 36 nJ pulse energy. Assuming a 9-photon process then provides an estimate of 10^7 vacancies at the GR1 visibility threshold, and ~10^5 at the lowest pulse energies to produce NV centres.

Annealing

Annealing was carried out in a tube furnace (Elite Thermal Systems TSH16/50/180-2416). The diamonds were placed in an alumina boat and buried in a sacrificial diamond grit (Element Six Micron+). Prior to annealing the furnace was purged with dry nitrogen boil-off to minimize oxidization and graphitization of

the diamond surface. Annealing was then carried out for 3 hours at 1000 degrees Celsius, a temperature that is known to allow healing of the diamond lattice through removal of most of the extended lattice defects [26]. Details of the optimisation of the annealing process are provided in the Supplementary Information.

During the annealing, vacancies are assumed to diffuse isotropically following the 3-dimensional diffusion equation and bind with substitutional nitrogen atoms distributed randomly in the lattice to form stable NV colour centres. To facilitate comparison between the measured radial distribution of NV centres and a simple model, we assume that the initial vacancy distribution is elongated to an infinite extent in *z*, whereby the resulting distribution of NV centres relative to the focal position after an anneal time *t* will be

$$n_{NV}(r) = Are^{-r^2/4Dt}$$

where *A* is a constant and *D* is the diffusivity. This approach neglects 'end effects' of the initial vacancy distribution but provides a good first approximation with which to analyse the positioning data.

Photoluminescence (PL) and NV position measurements

PL imaging was carried out using a home-made scanning confocal microscope and spectroscopy with a 500 mm spectrograph (Acton SpectraPro 500i) fitted with a back-illuminated CCD camera (Princeton Spec-10 100B), with > 90% quantum efficiency across the wavelength range of interest. Excitation was performed using a frequency-double YAG laser (λ=532 nm) with a maximum power delivery to the sample of 4 mW. A laser clean-up filter is used in excitation, combined with a 540 nm dichroic beam splitter and a 532 nm blocking notch filter in the collection optics. When recording a PL image, a 650 nm long-pass filter is inserted in the fluorescence collection path to block the diamond Raman emissions (all filters were from Semrock).

The position in the image plane of each NV centre was determined from the PL images by fitting a 2D Gaussian surface to the measured intensity distribution. The spatial resolution of the microscope (~500 nm) combined with the intensity of the single NV fluorescence images (~10,000 counts) allows Gaussian fitting with a standard error in the position of the NV centres of between 50 and 100 nm. After subtracting a quadratic field distortion for the PL microscope, determined using a PL image measured pre-anneal, these

positions were compared with the uniform grid pattern locations targeted in the processing microscope (see Supplementary Information for supporting data).

Photoluminescence Excitation (PLE) measurements

For PLE measurements the sample was cooled to 4.2 K in a liquid helium bath cryostat. An external cavity diode laser (Toptica DL100) was scanned through resonance with the NV- zero phonon line at a wavelength of 637 nm, and the wavelength measured directly using a wavemeter (High Finesse WSU-30). No microwave modulation was applied, so the spin population time of the NV centres is very long and only the highly cycling upper branch $m_s = 0$ transition is observed.

Repump pulses were delivered from a frequency doubled diode-pumped solid state laser at 532 nm (CNI MGL-III-532), gated into 200 ms pulses using an acousto-optic modulator.

Photon autocorrelation measurements and data fitting

Photon autocorrelation datasets were measured using the Hanbury Brown and Twiss (HBT) method, using continuous wave 532 nm excitation at a power of 0.74 mW. The fluorescence was spectrally filtered using a 650 nm long pass filter. To establish the statistics for $g^{(2)}(0)$ in figure 2 the results were fitted by the standard function for the photon autocorrelation of a three-level system derived using coupled rate equations:

$$g^{(2)}(\delta t) = g^{(2)}(0) + 1 - c * \exp\left(\frac{-|\delta t|}{\tau_2}\right) + (c-1) * \exp\left(\frac{-|\delta t|}{\tau_3}\right)$$

where c, τ_2 and τ_3 are related to the inter-level rate constants, and $g^{(2)}(0)$ is a fixed background. No background correction was applied to the data prior to fitting. The solid red line in Fig. 2(a) is a least-squares fit of this equation to the measured data.

Hahn Echo measurements

Hahn echo measurements ($\pi/2$-τ_0-π-τ_1-echo, see figure S8) were carried out on seven NV^- centres. For each measurement, an external magnetic field of 6.7 mT was applied and carefully aligned parallel to the NV^- centre axis. The splitting between the -1 and +1 fine transitions was large enough to ensure the individual driving of the -1 transition. The amplitude of the fluorescent echo signal was measured as a function of the

pulse separation. The time duration of the π/2-pulse was chosen to be 20 ns (40 ns for a π-pulse), determined by Rabi oscillation measurements on the 0 ↔ -1 transition. Therefore the bandwidth was larger than the splitting, allowing full excitation of the 0 ↔ -1 transition. A single Hahn echo measurement, i.e. iteration of τ_1 around the set value of τ_2, consisted of a few million iterations of the pulse sequence, and corresponds to about 3500 photon detection events. The signal was normalised to the equilibrium between the -1 and 0 state of the optical pulse. The Hahn echo decay was measured over the first decay and on the revival.

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Author contributions

YCC carried out the PL, HBT and PLE measurements with assistance from LW, PD, and SJ, and coordinated the work; PS performed the laser writing; SK performed the Hahn echo experiments with

supervision from JGR; AF, CS, BG and SI annealed the samples and performed birefringence and Raman imaging with supervision from GM and MN; JS and MB conceived and oversaw the project. All coauthors contributed to writing the manuscript.

Competing Financial Interests Statement

The authors have no competing financial interests

Figure 1 | NV^- colour centre generation using laser processing. **a**, Photoluminescence image of the 25 × 20 array immediately after laser processing (before annealing). The laser pulse energy increases from the bottom to the top of the image. The red line at pulse energy E_1 indicates the lowest energy laser pulse that produces visible fluorescence. The drop-off in intensity of features toward the edge of the array is due to field aberrations in the PL microscope. **b**, Typical spectra measured from points in fig 1a (lower plot), characteristic of GR1 (single vacancy) defects and from figure 1c below energy E_2 (middle plot) characteristic of the negatively charged nitrogen-vacancy (NV^-) centre, and figure 1c above energy E_2 (upper plot) characteristic of the radiation B-band. **c,** PL image of the same region of sample after the annealing process, showing NV^- emission from multiple sites processed with pulse energies both above and below E_1. The green line at pulse energy E_2 indicates the graphitization threshold.

Figure 2 | Statistics and positioning accuracy of NV generation using laser processing. **a**, Histogram showing the two-photon correlation function $g^{(2)}(\delta t)$ from a single NV centre; **b**, Histogram of $g^{(2)}(0)$ for the different laser processing sites, allowing identification of sites of single, double, and triple NV centre generation. **c**, Map of the number of NV centres generated at different sites. 'NV pair' refers to a double NV where the two defects are spatially resolved. **d**, Plot of the number of single (red), double or 'pair' (yellow), and triple (blue) NV's generated in each row of 20 sites as a function of laser pulse energy measured before the objective lens in the writing apparatus. The total number generated per row is shown in black. **e**, Magnified image of NV centre fluorescence relative to the laser processing grid. Red circles centred on the grid points are 1 μm in diameter. **f**, Histogram of the displacement in the image plane for the single NV centres measured after correction for field distortion in the PL microscope. The data are fitted with a cylindrical distribution function (see text).

Figure 3 | Spectral properties of single laser-generated NV centres at 4.2 K. **a**, Photoluminescence excitation (single sweep) of three different NV centres, with two showing Lorentzian peaks below 14 MHz in width. Full-width-at-half-maximum values from Lornetzian peak fits are given, with errors in parentheses; **b**, Colourscale map of repeated PLE spectra of NV3, showing a stable line over 70 laser

sweeps with an inhomogeneous line width of 16.1 MHz. **c**, Spectral jumping as a result of a 532 nm re-pump pulse required to restore the negative charge state upon ionization. Lower plots in b and c are aggregates of the consecutive sweeps in the colourscale images. **d,** Scatter plot of the single scan line width (solid circles) and repump-broadened line width (open circles) for the different energies of laser writing pulse. Data from samples A and B are shown as red and black circles respectively. The dashed blue line is a guide showing a trend to larger single scan line widths with higher pulse energies (see main text).

Figure 4 | Spin resonance properties of laser-generated NV centres at 300K. Hahn echo data for an NV centre created with pulse energy 19.6 nJ, fitted with the function $I(\tau) = y_1 e^{-(\tau/T_2)^n} + y_0$, where the exponent n is a free parameter and y_0, y_1 and T_2 are fitting parameters.