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Quantum technologies in diamond enabled by laser processing

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Abstract

Integrated photonic circuits promise to be foundational for applications in quantum information and sensing technologies, through their ability to confine and manipulate light. A key role in such technologies may be played by spin-active quantum emitters, which can be used to store quantum information or as sensitive probes of the local environment. A leading candidate is the negatively charged nitrogen vacancy (NV⁻) diamond color center, whose ground spin state can be optically read out, exhibiting long (≈ 1 ms) coherence times at room temperature. These properties have driven research towards the integration of photonic circuits in the bulk of diamond with the development of techniques allowing fabrication of optical

waveguides. In particular, femtosecond laser writing has emerged as a powerful technique, capable of writing light guiding structures with 3D configurations as well as creating NV complexes. In the following Perspective, the physical mechanisms behind laser fabrication in diamond will be reviewed. The properties of waveguides, single- and ensemble-NV centers will be analyzed, together with the possibility to combine such structures in integrated photonic devices, which can find direct application in quantum information and sensing.

The existence of stable, fluorescent, and spin-active color centers has made diamond a promising platform for quantum photonics. In particular, its negatively charged nitrogen-vacancy (NV^-) color center has unveiled long spin coherence times (≈ 1 ms) even at room temperature¹, making it an appealing system for quantum applications. The NV^- center, which appears intrinsically in both natural and synthetic diamond, results from the replacement of two adjacent sites of the diamond carbon lattice by a nitrogen and a vacancy. The electronic ground state of such a complex forms a spin triplet, which can be polarized under green excitation and exhibits a zero-phonon line (ZPL) at 637 nm wavelength². Optical spin readout can be achieved through measurement of the fluorescence signal due to spin dependent non-radiative decay paths, which make one spin state brighter than the others³. Moreover, NV^- centers in diamond can be called into play for sensing applications, being sensitive to magnetic and electric fields through the Zeeman and Stark effects, respectively. Measurement of strain⁴, temperature⁵ and magnetic fields⁶⁻⁸ at the nanoscale with high sensitivity have already been demonstrated, with compelling applications in the biological sciences^{9,10} as well as in other fields^{11,12}.

The implementation of such systems requires the ability to create NV^- centers in a controlled way, with high precision and a desired density, from single color center to high density ensembles. Additionally, it is desirable to fabricate optical waveguides, to enable strong light-matter interaction and to link and spatially address NV^- centers. Indeed, this is a very challenging task due to diamond's extreme hardness and chemical resistance. Conventionally, this has been addressed through plasma etching^{13,14}, ion implantation¹⁵ or ion beam assisted lift-off¹⁶, all invasive techniques which inevitably degrade the quality of the diamond surface and consequently device performance, as summarized in Table I. A solution to such problems has recently been found in femtosecond laser writing of photonic structures^{17,18}, benefiting from the localized bulk modification due to nonlinear absorption of focused ultrashort pulses^{19,20}. In this way, direct writing of 3D integrated optical circuit has been demonstrated^{21,22}, with the possibility to create NV^- color centers in a controlled manner, while retaining their high-optical and spin coherence²³. In this Perspective, first the physical mechanism behind the fabrication of optical waveguides in bulk diamond will be explained. Subsequently, the integration of such waveguides with NV^- centers will be analyzed and in particular, results on the creation and interaction of single-color centers within optical waveguides

will be presented. Finally, the creation of ensembles of NV^- centers with a desired density will be shown, together with a proof-of-concept application given by a sensing device capable of magnetic field and temperature sensing. An outlook of the perspectives of the technique will underline the future developments for the described devices in terms of complexity and functionality, toward a fully integrated laser written photonic device in diamond.

TABLE I. Comparison of Femtosecond Laser Writing with other techniques for waveguides fabrication and NV^- center formation.

	Femtosecond Laser Writing	Other Techniques
Waveguides	<ul style="list-style-type: none"> • Easy single step, 3D fabrication^{17,18} • Type II fabrication of waveguides with stress-induced guiding between damaged laser-formed tracks¹⁷ • Single mode guiding by tailoring core size for specific wavelengths (13 μm @ 635 nm, 19 μm @ 1550 nm, 30 μm @ 2.4 μm, 60 μm @ 4.8 μm)^{24,25} • Easy coupling with optical fibers • Variable depth in the bulk of diamond □ from 12 μm to $\approx 200 \mu\text{m}$²⁴ • Not possible to fabricate surface photonics for quantum sensing • Modest refractive index increase between waveguide region and bulk ($\approx 10^{-3}$)¹⁸ • Not possible to write nm dimension structures • Only TM polarization guiding possible¹⁷ unless depressed cladding geometry adopted¹⁸ 	<ul style="list-style-type: none"> • Main alternatives: Nanolithography, Focused Ion Beam (FIB), Reactive Ion Etching (RIE) • Multi-step fabrication techniques involving more complex processing of diamond • Sub-μm core dimensions possible: □ possibility to create nanocavities and resonators^{28,29} □ hard to couple with optical fibers • Superficial modifications □ < 50 μm depth¹⁵ • Demonstrated complex structures through Nanolithography and RIE^{28,30} • Different and complex fabrication setup for each application
NV^- centers	<ul style="list-style-type: none"> • Deterministic single NV^- formation with realtime confocal fluorescence <u>feedback</u>²⁶ • Localized within 600 nm in the focus²⁶ • Possibility to form ensembles of NV^- with controlled density • Demonstrated integration with other laser written components²⁷ 	<ul style="list-style-type: none"> • Main <u>Alternative</u>: Ion Beam Implantation • Randomly distributed single/double NV^- within the focal volume³¹ • Localized within tens of nm laterally³² • Ensembles of NV^- with controlled density³³ • Damage of the crystal along the focused beam direction • Exotic color centers (ex. SiV^-)³⁴

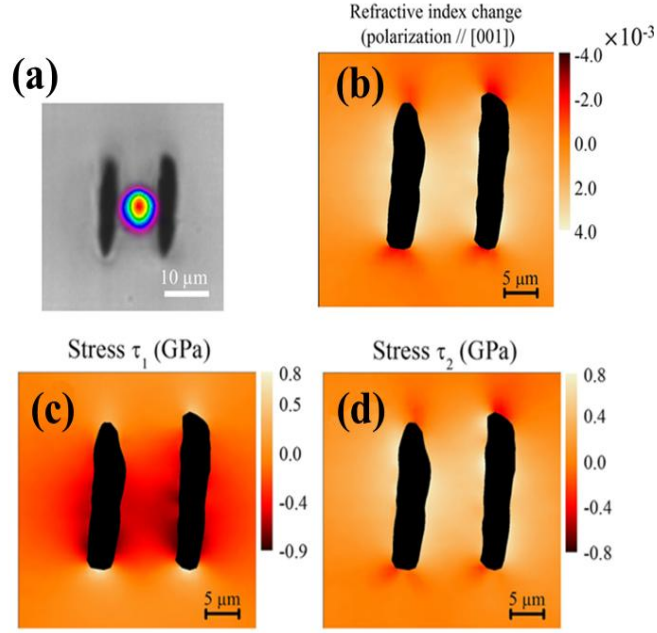


FIG. 1. (a) Optical microscopy image of a type II waveguide in diamond with overlaid the measured optical TM mode confined between the tracks. (b) Map of the refractive index profile. (c) (d). Maps of the horizontal and vertical components of induced stresses (named as τ_1 and τ_2 , respectively) in the waveguide from the Raman peak shift.

The use of ultrashort laser pulses to modify the internal structure of transparent materials has become an established technique over the last twenty years. The material modification due to focused femtosecond lasers pulses can assume different properties depending on the absorbed energy at the focal volume³⁵⁻³⁸, in addition to other properties such as translation velocity, polarization, repetition rate, wavelength, beam shape, focusing condition and pulse duration. In crystals, femtosecond laser irradiation generally produces a decrease in refractive index at the focal volume, caused by the creation of lattice disorder, leading to a lower density of the lattice. It has been demonstrated that it is still possible to achieve guiding of light in the bulk of crystals if two parallel lines separated by several micrometers are fabricated, confining the optical mode between these barriers, where the refractive index is higher (type II modification)^{17,38}. In Fig.1(a) it is shown how the TM mode of a red CW-laser can be confined within two laser-written tracks in diamond. *Sotillo et al.* showed how the guiding of the TM optical modes is related to the structural modification of the material³⁹. In Fig.1(b) a map of the refractive index

change in proximity to the laser-written tracks shows a reduction of the refractive index inside the tracks and at their apex, while a relative refractive index increase is produced in between the two parallel lines, where Δn was calculated to be about 3×10^{-3} ⁴⁰⁻⁴². From an analysis of the Raman peak shifts and change of intensity of the Raman signal at the modification⁴³⁻⁴⁴, a map of the stress components along two perpendicular directions of the crystal lattice has been developed (Fig.1(c-d)). The results show amorphization and the transformation of sp^3 -diamond bonding into sp^2 bonding in the laser written lines. As a consequence of this density reduction, stress is exerted between the lines which depends on the crystal lattice direction: along the horizontal direction the stress is compressive (Fig. 1(c)), whereas in the vertical direction, a shear tensile stress is established (Fig.1(d)). This explains why only the TM mode can be guided by the type II waveguide in diamond¹⁷, being parallel to the tensile stress component which experiences a refractive index increase, while the TE mode lies along the compressive stress component where it experiences a refractive index decrease.

For practical implementation of quantum systems or high-spatial-resolution sensing devices, it is not sufficient to confine and guide light through waveguides. Deterministic placement of NV^- centers is also necessary. In 2013, it was shown how femtosecond laser pulses focused slightly above the surface of optical grade diamond can induce the formation of NV^- centers through surface ablation⁴⁵. A further step was taken by *Chen et al.*, demonstrating on-demand and high-quality single NVs written in the bulk of electronic grade diamond, with nitrogen concentration of < 5 ppb, using femtosecond laser writing with a spatial light modulator (SLM) to correct for aberrations, followed by high-temperature annealing²¹. This is achieved by formation of vacancies within the focal volume when femtosecond laser pulses with energies below the amorphization threshold are focused in the bulk of diamond. The high temperature annealing mobilizes the vacancies, which eventually are captured by substitutional nitrogen impurities to form NV centers^{22, 26}. The spin coherence times of laser induced NVs are shown to be comparable with those implanted by ion beams²⁶. The development of this powerful technique overcame near surface fabrication limitations related to previous works, also providing an alternative to ion implantation^{27, 39, 46}, the most common technique for color center creation, but which can lead to significant damage of the diamond lattice.

A challenging task for the development of integrated photonic circuits is related to the integration of the color centers with the optical waveguides⁴⁷⁻⁴⁹. Recently, the possibility to write single NV^- centers in electronic grade diamond coupled to an optical waveguide has been demonstrated⁵⁰. The fabrication consisted of three steps. Firstly, a Type II waveguide was written in bulk diamond at a depth of 25 μm using the second harmonic of a regeneratively amplified Yb:KGW system (Pharos, Light Conversion), with a 515 nm wavelength, at a repetition rate of 500 kHz with 0.6 nJ pulse energy and 0.5 mm/s

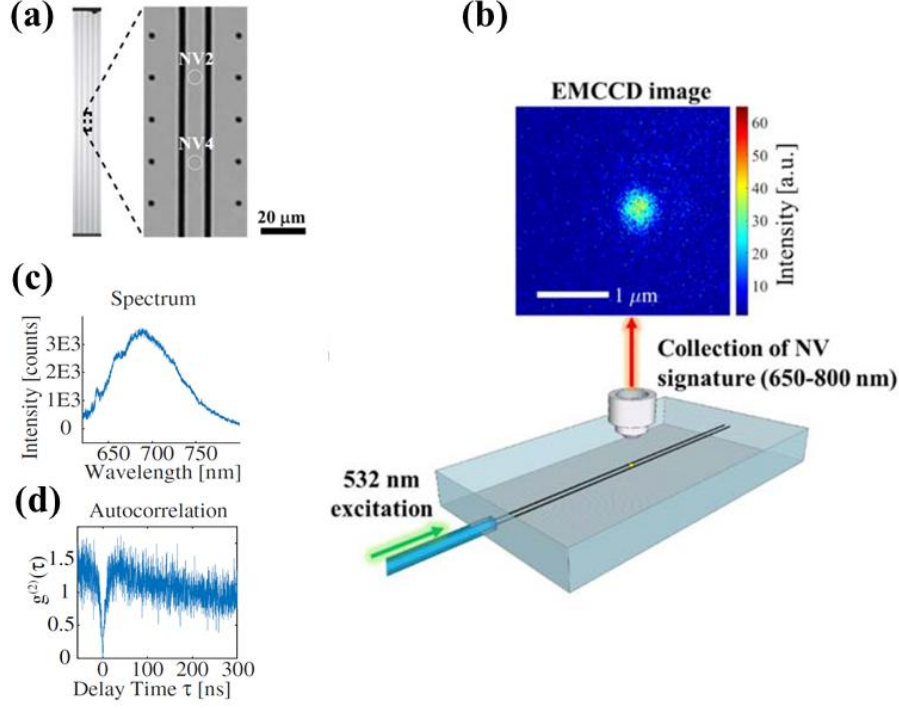


FIG. 2. (a) Overhead optical microscope image of the 2 mm long waveguide, with a zoom-in of the central 80 μm containing the NV centers 2 and 4 (NV2, NV4). (b) schematic of the experimental setup for the characterization of the color centers and their coupling with the waveguide. (c) PL spectrum displaying NV ZPL at 637 nm. (d) NV intensity autocorrelation confirming single-photon emission.

scanning speed. A separation of 13 μm between the two laser-written tracks was used to optimize single mode propagation of 637 nm radiation corresponding to the ZPL of the NV^- center emission. Secondly, the same femtosecond laser system was used for single-pulse exposures within the waveguide to induce vacancies in the diamond lattice. To study the reproducibility of the experiment, five identical single-pulse exposures separated by 20 μm were performed at the center of the tracks defining the optical waveguide, with an energy of 28 nJ per pulse. Next, the sample was annealed for 3 hours at 1000 $^\circ\text{C}$ in a nitrogen atmosphere to induce the formation of the NV^- centers and anneal out other detrimental vacancy complexes⁵¹. Importantly, this did not compromise the previously written waveguide, in contrast to studies in other materials where the high temperatures treatment caused the lattice to recover its initial structure⁵². Figure 2(a) shows an overhead optical microscope image of the waveguide- NV^- optical device. The fabricated device was characterized using a 532 nm excitation laser focused either through a microscope objective or through single-mode fiber that was back-coupled to the waveguide. The emitted light was then detected from the other end of the waveguide or from overhead as shown in Fig.2(b). The single NV formation probability, including trials in other waveguides, was estimated as $(31 \pm 9)\%$, consistent with the Salter group's initial work. The NV placement accuracy was estimated to be $\sim 1 \mu\text{m}$, larger than the 600 nm value that was previously reported, due to the larger focal volume provided by the femtosecond writing setup. Fig.2(c) shows the emission

spectrum from one of the NV^- centers at room temperature, showing the characteristic ZPL at 637 nm and the broadband phonon side band (PSB), while Fig.2(d) shows the second-order intensity autocorrelation chronogram $g^{(2)}(\tau)$, confirming single-photon emission. Laser written waveguides allowing excitation and fluorescence collection from precisely located and single-photon NV^- emitters resulted in a simple device opening the way towards more complex systems, necessary in the field of quantum information.

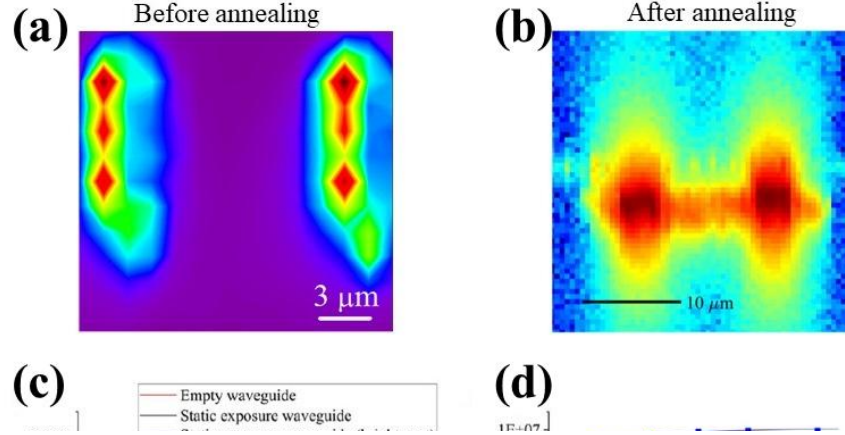
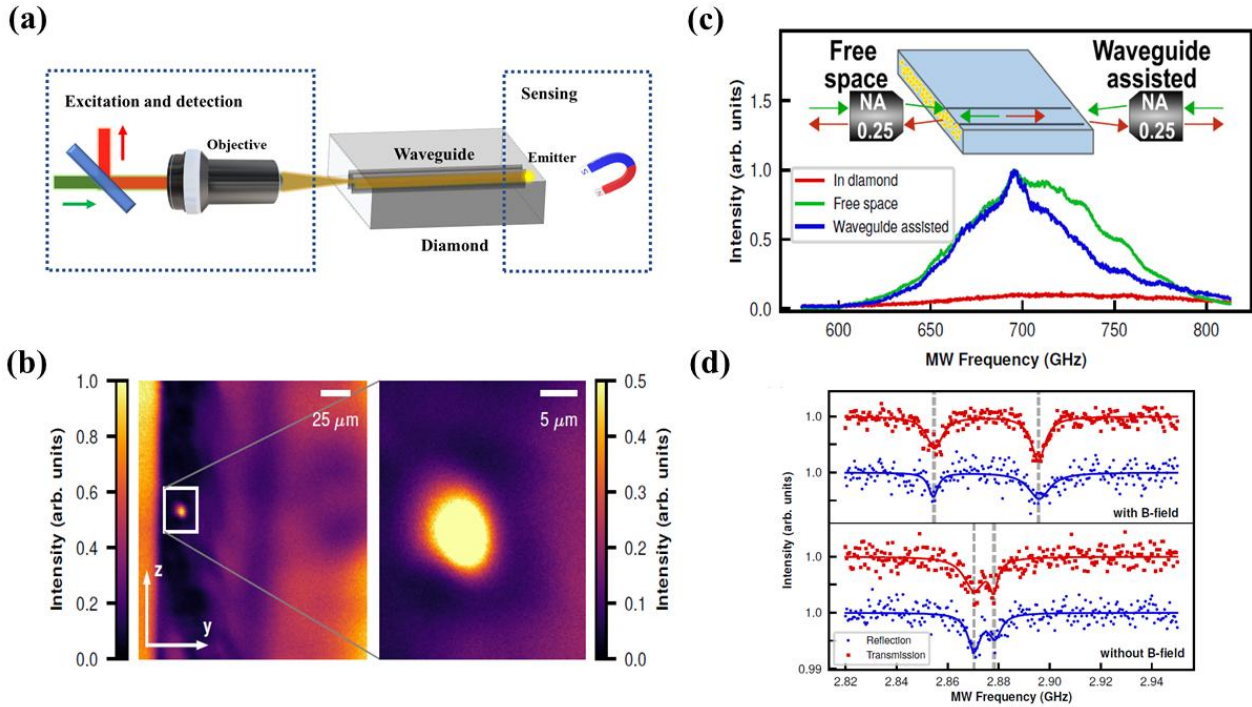


FIG. 3. Photoluminescence confocal cross-section of ‘empty’ waveguide and modification lines written in HPHT sample before (a) and after (b) annealing. PL spectra (c) and Power dependent PL (d) from ‘empty’ waveguide, ‘static exposure’ waveguide and from a bright spot corresponding to a static exposure.

Room temperature quantum sensing is one of the main applications of color centers, due to the susceptibility of their spin states to electric and magnetic fields^{8,10,53-56}. Single NV^- centers have been used to show nanoscale spatial resolution surpassing the resolution of the optical fluorescence microscopes used for measurement, with the intrinsic low sensitivity related to the use of a single NV^- center increased by averaging over many measurements. When nanoscale spatial resolution is not required, the sensitivity or the measurement speed can be increased through the use of NV^- center ensembles, as already shown through high density NV^- centers in bulk diamond⁵⁴. It has been demonstrated that the sensitivity of such devices scales as $M^{-1/2}$ ⁵⁷, where M is the number of color centers in the ensemble. This can be achieved by either increasing volume of NV^- centers or the density of sampled NV^- centers, while not compromising on their spin coherence time. Ensembles with several NV^- densities in CVD and HPHT grown diamond with higher intrinsic nitrogen content have been studied⁵⁸⁻⁶¹ to optimize the sensitivity without a reduction of the spin coherence time of the system. *Clevenson et al.*

identified an optimal NV^- density of $2 \times 10^{16} \text{ cm}^{-3}$ (0.1 ppm)⁶². In agreement with previous studies, high density NV^- center ensembles have been written in HPHT diamond through single static exposures followed by thermal annealing and their integration within a waveguide has been characterized²². Arrays of ‘empty’ waveguides together with ‘static exposure’ ones (containing arrays of nine single 100-nJ static exposures uniaxially separated by 2 μm) were written in HPHT diamond at a depth of 18 μm . During annealing, NV^- s are generated throughout the waveguide mode due to the diffusion of vacancies from the modification lines, as can be seen from the confocal microscope images of Fig.3(a-b). Fig.3(c) shows PL spectra acquired after annealing from the ‘empty’, ‘static exposure’ waveguides and from a bright spot corresponding to a static exposure in the waveguide. In all three cases, the characteristic ZPL of the NV^- center can be identified, confirming NV^- creation. In addition, the static exposure waveguides show enhanced signal as well as additional features, for example the strong contribution of a line at 575 nm corresponding to the neutral NV^0 ZPL. It was possible to estimate the density of the ensembles from the power dependent PL saturation measurements of the considered waveguides compared to the signal collected by a single NV^- center in another sample (Fig.3(d)), resulting in a $1.1 \times 10^{15} \text{ cm}^{-3}$ value (corresponding to 6 ppb) in the ‘empty’ waveguide, and up to $1.4 \times 10^{15} \text{ cm}^{-3}$ (8 ppb) in the ‘static exposure’ one. It has been estimated that these densities would permit a magnetic field sensitivity of $1.5 \text{ nT Hz}^{-1/2}$ or an electric field sensitivity of $2.4 \text{ V cm}^{-1} \text{ Hz}^{-1/2}$, which are comparable to those allowed by current state-of-the-art systems^{57,61} and which could be further improved by optimization of the laser fabrication parameters.

A first demonstration of a device combining laser written waveguides arrays with shallow ion implanted NV⁻ center ensembles for temperature and magnetic field sensing has recently been reported by *M. Hoese et al.*⁶³. Such a system combines the sensing capabilities of NV⁻ ensembles with the photon routing properties of optical waveguides, separating the optical access to the NV centers from the object to be sensed and allowing non-invasive field detection from biological and chemical samples (Fig.4(a)). This is an advantage compared to confocal microscopy as the waveguide platform is fully integrated and can be scaled to many channels which are laterally separated. The device was fabricated by laser-writing type II optical waveguides in depths ranging from 5 to 25 μm below the diamond surface, followed by shallow implantation of nitrogen ions into the front facet of the waveguides, which resulted in NV⁻-ensemble creation after annealing at 1000 $^{\circ}\text{C}$. NV⁻ center spin state measurement was performed via room temperature optically detected magnetic resonance (ODMR)⁶⁴. Off-resonant 532 nm laser excitation and NV⁻ center fluorescence collection coupled through a 0.25 NA objective from the end facet of the waveguide is fully compatible with the placement of biological or chemical samples. A confocal scan of the end facet of the sample in Fig.4(b) shows a clear waveguide mode corresponding to remote NV⁻ excitation and fluorescence detection. A comparison of the spectra in Fig.4(c) confirms that the waveguide-assisted spectrum resembles that of the



directly collected free space fluoresce from the NV⁻ ensemble. The ODMR sensing performance of an ensemble was studied by monitoring the fluorescence while applying a swept microwave (MW) field to the sample and varying external magnetic field. Upon application of a magnetic field, an increased splitting between the two characteristic dips in fluorescence is

observed when measured both in the free space and waveguide assisted configurations (Fig.4(d))^{39,53,65}. Such a change in the splitting can be directly linked to the applied magnetic field^{66,67}, which is detected with a precision better than 6 μT with this device configuration. Furthermore, in a typical 30 min CW-ODMR measurement, sensitivities up to 36 $\mu\text{T Hz}^{-1/2}$ (for confocal detection) and 62 $\mu\text{T Hz}^{-1/2}$ (for detection after waveguide transmission) have been reached, which can be improved when using lock-in⁶⁸, pulsed ODMR or Ramsey spectroscopy techniques⁶⁹. Finally, the device works reliably over more than a 20-hour period with a minimal measurement time below 40 seconds and has been shown to be working also as a temperature sensor, by exploiting the temperature-dependence of the zero-field splitting (ZFS).

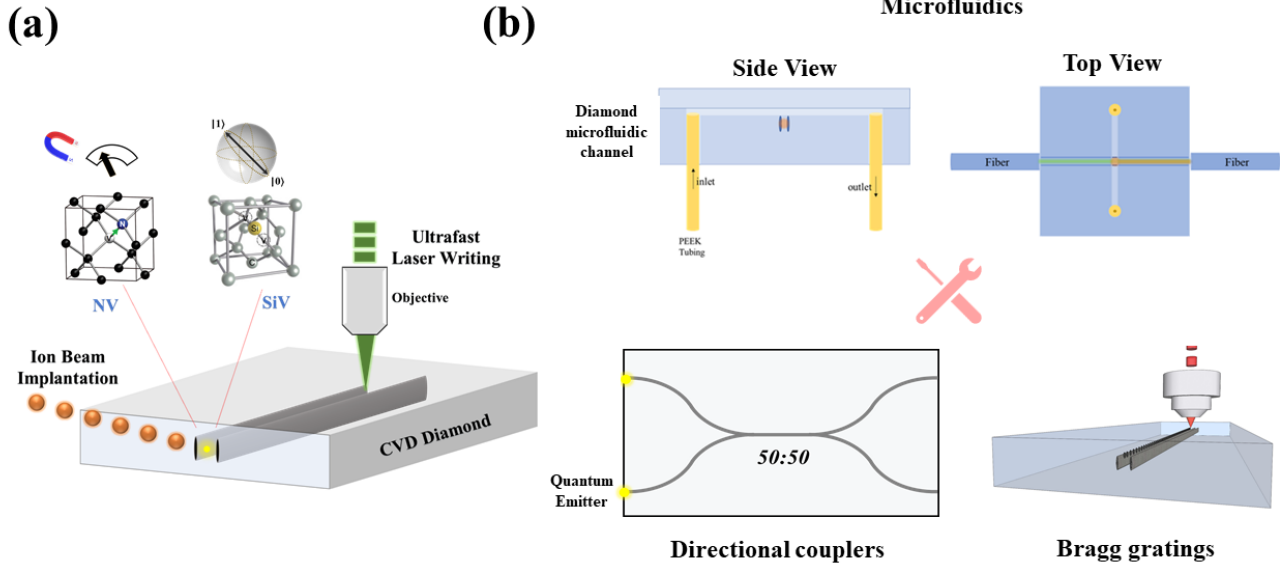


Fig 5. (a) Schematic overview of employing Ion beam implantation and ultrafast laser writing in diamond to create integrated photonic networks using NVs for magnetometry and SiVs for quantum information. (b) Schematic overview of engineering laser writing strategy to create integrated microfluidics, directional couplers and Bragg gratings.

Despite the first implementations of simple, proof-of-concept devices revealing the possibilities of laser written photonics in diamond, there is still large room for improvement for the fabrication of diamond-based devices in terms of waveguide quality, color center formation and integration between different techniques, which will allow the development of more complex photonic integrated circuits. On one side, the relatively large mode field diameter of laser-written waveguides inevitably leads to a low interaction strength on the single emitter level resulting in a rather low cooperativity. However, utilizing defect center creation on the waveguides side-facets enables to operate in a regime of high color center density within the field maximum of the waveguide mode. With such high-density ensembles of NV centers future quantum sensing tasks with high sensitivity come into reach, as already proved in the past sections. Furthermore, the device architecture facilitates the combination A resulting in a strong focus and a strong interaction strength on the single emitter level. Consequently, a large single-emitter cooperativity will give an opportunity to feed individual waveguides with single photons and with high efficiency, therefore paving the way towards on-chip operation on the single quantum level. In addition, techniques enabling a better control of the creation of NV^- centers are being tailored, where one could for example use laser pulses to increase the pool of electron donors (NV^-) by changing the charge state of neutral NV^0 s, as already demonstrated in diamond bombarded with ions and rich in defects⁷⁰. Quantum photonics in diamond will also benefit by employing laser writing to integrate other vacancy related color centers in diamond. Group IV centers such as the silicon vacancy (SiV, ZPL 738 nm) have superior spectral properties due to their inversion symmetry making them promising as a single photon source

for quantum photonics⁷¹. Integration of ion beam implantation techniques to implant SiVs and laser inscription to form photonic networks will enable devices for quantum optics applications⁷², as represented in Figure 5(a). Through a similar approach, devices based on other group IV color centers are being explored. These centers display a similar defect structure and opto-physical properties as those of the SiVs, the most promising being the germanium-related (GeV, ZPL at 602 nm), tin-related (SnV, ZPL at 620 nm) and lead-related (PbV, ZPL at 520 nm) color centers⁷³⁻⁷⁹.

Through the same fabrication technique microfluidic components^{23,80} will be produced and interfaced with complex photonics with nearby NV centers to enable efficient quantum sensing of biomolecules under flow conditions, as shown in Figure 5(b). The biocompatibility of diamond, the use of all-optical methods and the strong fluorescence of dense NVs are ideally suited for implementing lab-on-chip diagnostics. For example, paramagnetic reactive oxygen species and free radicals are involved in cell signaling, in the aging process and in pathological states. However, detection with conventional electron spin resonance does not afford sufficient sensitivity to study their synthesis and trafficking in a physiologically relevant environment. The Bifone group has demonstrated that coupled charge and spin dynamics in dense ensembles (> 5 ppm) of NVs are strongly affected by interaction with electron spins⁸¹, enabling the detection of paramagnetic species with ultrahigh sensitivity through relaxation measurements⁸². Indeed, the large number of detected photons from such dense ensembles of NV⁻ can dramatically reduce acquisition time, down to 10 ms, for detection of a few tens of unpaired electron spins per 1000 nm² of diamond surface. Importantly, incoherent detection of the evolution of polarized NV ensembles can be performed without microwaves and at ambient conditions, thus paving the way to applications in biological samples. Femtosecond laser writing shows great potential for realizing specific patterns of dense NVs in a diamond microfluidic chip, enabling all-optical detection of paramagnetic species.

On the topic of the functionalization of the devices and furthering the already demonstrated Y-splitters in diamond using laser writing²¹, realization of 3 dB directional couplers in diamond integrated with quantum emitters will allow the formation of complex photonic networks for single photon interference and Hong–Ou–Mandel experiments⁸³. Moreover, wavelength-selective reflective elements such as Bragg gratings at the visible wavelengths can be integrated in waveguide devices to improve the excitation and collection efficiencies from the quantum emitters²¹ (Figure 5(b)).

Indeed, laser writing has emerged as a promising fabrication platform for diamond integrated quantum photonics. From the first results of laser written diamond photonic networks in the year 2016^{17,18}, until now, more than 30 high-impact publications employing laser writing to form photonic networks, quantum emitters and microfluidics by various research

groups from around the world have endorsed the capabilities of laser writing for the future of quantum technologies. Currently, one of the main limitations of femtosecond laser writing in diamond with respect to other techniques is due the field's immaturity only over the past five years. In comparison, there has been significantly more research on ion beam lithography in diamond, a method that was pioneered in 1970s⁸⁴ (i.e. when ion beam irradiation was already a well-established technique in the semiconductor industry) and subsequently was successfully implemented for the fabrication of graphitic structures in this material for different applications (ohmic contacts⁸⁵, color center electrical stimulation⁸⁶, particle detection⁸⁷, metallo-dielectric photonics crystals⁸⁸, refractive index modulation⁸⁹, biosensing⁹⁰, etc.). However, a rapid development of new techniques and protocols in the framework of the laser fabrication of photonics circuits in diamond is justified by the numerous advantages of such a technique. With substantial advantages with respect to ion-irradiation based techniques⁹¹, it results as the most convenient and versatile technique for the bulk fabrication of waveguiding structures, making possible the reliable formation of advanced 3D photonic devices in the bulk of diamond with different geometries and at different depths, up to 200 μm from the crystal surface. In terms of color center creation, femtosecond laser writing has established itself as complementary method to ion beam implantation. The latter approach has the advantage of introducing foreign species into the diamond matrix to produce quantum emitters other than the NV^- center, at the expenses of introducing substantial "collateral damage" in the diamond structure resulting in mechanical stresses⁹² that affect the opto-physical properties of the color centers^{93,94}. Although femtosecond laser writing has thus far demonstrated lower performance in terms of lateral and vertical placement accuracy, it offers superior capabilities to ion implantation in terms of vertical depth range on color center fabrication, limited only by the working distance of the focusing lens. Furthermore, the low ratio of quantum-optically functional color centers per implanted ion is still one of the main obstacles for the ion beam implantation technique, making it largely unsuitable for the scalable fabrication of multiple-qubit devices, while in the case of laser induced creation of NV^- centers, unitary yield formation can be achieved. Overall, femtosecond laser writing in diamond has proven to be a powerful and versatile technique, allowing the implementation of integrated photonic circuits for both quantum information and sensing applications, through a simple and versatile setup. It has been demonstrated how NV^- centers can be created and combined with the guiding properties of optical waveguides to develop room temperature devices with unprecedented spatial resolution and sensitivities. In perspective, the research related to the femtosecond laser writing in diamond is still in an early stage and as already shown, the possible developments include the optimization of the existing devices to the implementation of more complex systems, which in the future will play a key role in several technological fields.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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