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Single-color centers implanted in diamond nanostructures

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\textbf{Abstract.} The development of material-processing techniques that can be used to generate optical diamond nanostructures containing a single-color center is an important problem in quantum science and technology. In this work, we present the combination of ion implantation and top-down diamond nanofabrication in two scenarios: diamond nanopillars and diamond nanowires. The first device consists of a ‘shallow’ implant (\textasciitilde 20 nm) to generate nitrogen-vacancy (NV) color centers near the top surface of the diamond crystal prior to device fabrication. Individual NV centers are then mechanically isolated by etching a regular array of nanopillars in the diamond surface. Photon anti-bunching measurements indicate that a high yield (>10\%) of the devices contain a single NV center. The second device demonstrates ‘deep’ (\textasciitilde 1 \textmu m) implantation of individual NV centers into diamond nanowires as a post-processing step. The high single-photon flux of the nanowire geometry, combined with the low background fluorescence of the ultrapure diamond, allowed us to observe sustained photon anti-bunching even at high pump powers.

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1. Introduction

The development of robust and practical quantum information processing systems is an important problem at the interface between materials science, photonics and atomic physics. Light-emitting defects (color centers) in diamond are increasingly attractive for their implementation in a solid-state platform. For example, color centers based on nitrogen [1]–[3], silicon [4], carbon [5], nickel [6] and chromium [7] impurities have been shown to generate non-classical states of light and emit single photons at room temperature, which is a critical resource for quantum optical communication systems. Of these defects, the nitrogen-vacancy (NV) center is very attractive since it can possess additional electron and nuclear spin degrees of freedom with long coherence times that act as a quantum memory for long-distance quantum communications [8, 9], quantum computing [10]–[14] and nanoscale magnetometry [15]–[17]. Efforts to identify other outstanding color centers in diamond are ongoing [18].

Practical implementations of these technologies require the integration of single-color centers into diamond photonic systems whose optical performance exceeds that offered by a homogeneous bulk diamond crystal. Towards this end, a variety of photonic devices are under development that: (i) enable efficient single-photon collection and overcome total internal reflection at the diamond–air interface and (ii) engineer optical properties such as fluorescence spectrum and lifetime of an individual NV center. Some of these devices are based on broad-band antenna [3, 19] or solid immersion lens [20] effects, while others are based on narrow-band cavity resonance enhancements [21]–[26]. Concurrently, there has been interest in engineering the spatial distribution of single-color centers in diamond via ion implantation on a large scale. Techniques based on blanket implantation at different dosages [27, 28], focused ion implantation [29] and implantation through nanoscale apertures [30, 31] have all been demonstrated to generate single-color centers in a bulk crystal. Future scalable quantum technologies will benefit from complete fabrication routines that combine diamond photonic device engineering with ion implantation of color centers at the single defect level.

In this paper, we demonstrate two complementary procedures that are widely applicable to quantum photonic devices based on diamond: implantation of single-color centers before and after top-down diamond nanofabrication. In section 2, we demonstrate the ability to generate large arrays of diamond nanopillars near the top surface of the diamond crystal via a low-energy, ‘shallow’ implantation of nitrogen followed by dry etching. This scalable fabrication technique could be used to facilitate the coupling of single NV centers to proximal nanophotonic devices in the future. In section 3, we demonstrate the ability to perform a high-energy, ‘deep’ implantation of nitrogen at a low density into large arrays of diamond nanowires that have been fabricated from a bulk crystal. An NV center in the nanowire acts as a high-flux source
Figure 1. Approach to isolate-implanted NV centers in large arrays of diamond nanopillars fabricated in a high-purity single-crystal diamond substrate: (a) start with clean type-IIa diamond, (b) low-energy nitrogen ion implantation plus annealing activate a thin surface layer of NV centers, (c) deposit electron beam lithography resist on the diamond surface, (d) electron beam lithography defines an etch mask, (e) reactive ion etching mechanically isolates individual NV centers in the device and finally (f) HF wet etch of the diamond reveals the structures.

of single photons due to an antenna effect that modifies its radiation pattern [3, 32], and the pure diamond host generates a low level of background fluorescence compared to previously demonstrated nanowire devices in type-Ib material. These combined effects enable photon antibunching to be observed at high pump powers, where single-photon count rates are maximized. In section 4, we discuss some natural extensions of these fabrication routines to future quantum photonic systems.

2. Fabrication and characterization of diamond nanopillars

Figure 1 shows our approach to realize the diamond nanopillar arrays studied in this experiment. First, high-quality electronic grade type-IIa diamond (element 6) grown in a chemical vapor deposition (CVD) chamber with low (<5 ppb) background nitrogen content was implanted with $^{15}$N ions at an energy of 14 keV and a dosage of $1.25 \times 10^{12}$ cm$^{-2}$. Stopping range of ions in matter (SRIM) calculations [33] project a nitrogen layer $\sim$20 nm below the diamond surface. Next, the sample was annealed at 750°C for 2 h in high vacuum ($<10^{-6}$ Torr) to mobilize vacancies and generate a shallow layer of NV centers. Arrays of circular shaped masks (XR electron beam resist, Dow Corning) with $\sim$65 nm radius were then defined on the top surface using an electron beam lithography tool (Elionix). An oxygen dry etch, whose conditions were similar to those described elsewhere [32], was applied for 1 min and generated $\sim$200 nm-tall pillars on the top of the diamond surface. Finally, the sample was placed in a hydrofluoric acid wet etch for approximately 20 s to remove the residual mask layer and then in a 1 : 1 : 1 mixture of sulfuric, nitric and perchloric acid at 400°C for $\sim$30 min to clean the sample. A scanning electron micrograph (SEM) of a typical nanopillar array is presented in figure 2(a).
Figure 2. (a) SEM image of the array of nanopillars of height \( \sim 200 \text{ nm} \) and radius \( \sim 65 \text{ nm} \). The inset shows a close-up of several pillars. (b) Confocal microscope image of a 10 \( \times \) 10 array of diamond nanopillars, with center-to-center spacing of 2 \( \mu \text{m} \) (c) Photoluminescence spectrum of the nanopillar circled in (b). The ZPL of this device, indicated by an arrow, is at \( \sim 634 \text{ nm} \). (d) Intensity autocorrelation function of the fluorescence emitted from the device circled in (b) shows photon anti-bunching with \( g^{(2)}(0) \sim 0.08 \), without any background subtraction, due to the presence of a single embedded NV center.

The sample was then characterized with a home-built confocal microscope system as described elsewhere \[3\]. An image of the fluorescence emitted under 532 nm continuous-wave (CW) excitation is presented in figure 2(b). It shows a 10 \( \times \) 10 square array of bright spots that correspond to the nanopillar devices shown in figure 2(a), and the observed variation in the overall intensities results from the random embedding process that couples an NV center into each device. Measurements of their photoluminescence spectra show the characteristic zero-phonon line (ZPL) as well as broad phonon sideband of an embedded NV center (figure 2(c)). In most cases, however, significant deviation was observed in the position of the ZPL from its characteristic value of 637 nm in a bulk diamond sample. This appears to be consistent with reported ZPL shifts for diamond nanocrystals \[34\].

We then quantified the number of NV centers embedded inside individual nanopillar devices in this same array. In general, the number of quantum emitters may be obtained from measurements of the fluorescence intensity autocorrelation function \( g^{(2)}(\tau) = \langle I(t)^*I(t + \tau) \rangle/\langle I(t) \rangle^2 \) using a beam-splitter, two single-photon counting avalanche photodiodes (Perkin Elmer) and a time-to-amplitude converter (PicoHarp) in the Hanbury Brown and Twiss configuration \[1\]. This \( g^{(2)}(\tau) \) function is obtained from the number of self-coincidences \( C.C.(\tau) \) as a function of delay time \( \tau \) according to \( g^{(2)}(\tau) = C.C.(\tau)/(R_1R_2wT) \), where
Figure 3. Approach to implant individual NV centers in large arrays of diamond nanowire antennas made from high-purity single-crystal diamond: (a) start with clean type-IIa diamond, (b) deposit electron beam lithography resist on the diamond surface, (c) electron beam lithography defines an etch mask, (d) HF wet etch of the diamond reveals the structures, (e) high-energy ion implantation of nitrogen and finally (f) annealing activates NV centers.

$R_1$ and $R_2$ are the photon count rates on channels 1 and 2, respectively, $w$ is the bin width and $T$ is the integration time. No background subtraction was performed. A single NV center cannot emit two photons at the same time, and the number of self-coincidence counts at zero delay, $g^{(2)}(0)$, is therefore expected to be zero in the absence of any sources of background fluorescence (e.g. surface contamination, impurities). The observed contrast decreases according to the formula $g^{(2)}(0) = 1 - 1/N$ for additional emitters $N$. Ten of the 17 devices that we tested showed strong photon anti-bunching $g^{(2)}(0) < 0.5$ (figure 2(d)), which indicates that the nanopillar contains a single NV center. The other seven devices were characterized by $0.5 < g^{(2)}(0) < 0.7$, which is consistent with the presence of two or three NV centers in the device.

There are several conclusions that we may draw from these results. Firstly, the anti-bunching data make it clear that background fluorescence generated by our processing technique is not prohibitively high for room-temperature studies of single-color centers. Secondly, since at least ten of the 100 total devices in this particular array contained a single NV center, this combined implantation and fabrication routine may be implemented with a high yield (>10%) operating in the single-photon regime. Finally, our high-throughput fabrication technique can generate many more devices than can be tested in serial with the standard confocal microscope system. This suggests the future need to develop automated characterization tools or wide-field microscope approaches that optically address many devices in parallel.

3. Fabrication and characterization of diamond nanowires

In this section, we modify the approach slightly and implant single NV centers in diamond nanowire antennas (figure 3). This geometry has recently been shown to offer significant enhancement in the excitation and extraction of single photons from an NV center compared...
Figure 4. (a) SEM image of an array of nanowires of height $\sim2\mu$m and diameter $\sim200$ nm. Thousands of devices can be realized in parallel due to high-throughput nanofabrication techniques that were used. (b) and (c) Higher magnification images of nanowire arrays.

to bulk crystals due to the presence of an HE$_{11}$ waveguide mode that efficiently collects input pump power and facilitates single-photon collection via vertical emission from the top facet [3, 32]. An SEM image of the sample shows large arrays with thousands of nanowire antennas of diameter $\sim200$ nm and of height $\sim2\mu$m fabricated in a single diamond chip (figure 4). The diamond nanowires were then implanted with $^{15}$N at 1.7 MeV and $1 \times 10^9 \text{cm}^{-2}$ dosage and annealed at 750 $^\circ$C in high vacuum ($<10^{-6}$ Torr) for 2 h. SRIM calculations indicate that this produces a layer of NV centers $\sim1.0\mu$m below the diamond surface. The reduced dosage, used to potentially minimize implantation-related damage (important for future low-temperature studies), resulted in a relatively low yield of nanowires containing a single NV center.

In order to identify working devices, we scanned over large ($\sim30 \times 30 \mu$m) sections of the array at high powers ($\sim3$ mW) with a 532 nm CW laser. This allowed us to quickly bleach residual background fluorescence from the nanowire devices and observe sustained brightness in implanted devices due to the photostability of the NV center. Photoluminescence spectra did not exhibit the broad dispersion in the ZPL position that was observed in the nanopillar case, although some variation was observed from 637 to 639 nm. Figure 5 shows intensity auto-correlation measurements taken from one representative device at a series of increasing pump powers. Photon anti-bunching in the nanowire fluorescence $g^{(2)}(0) \sim 0.06$ was possible without background subtraction (figure 5(b)), which represents a fivefold reduction compared to nanowire devices demonstrated in type-Ib material [3]. In addition, photon anti-bunching $g^{(2)}(0) < 0.5$ is sustained at pump powers where the single-photon signal is saturated.

Contributions to the nanowire fluorescence come from single photons, $S$, that lead to non-classical correlations at zero time delay, as well as background fluorescence, $B$, emitted with Poisson statistics that reduces the observed contrast. For a given pump power, the relative contributions of $S$ and $B$ to the total fluorescence are encoded in the anti-bunching contrast according to [2] $g^{(2)}(0) = 1 - \rho^2$, where $\rho = S/(S+B)$. We therefore measured both the total number of photon counts per second from the nanowire as well as $g^{(2)}(0)$ for different pump
Figure 5. Intensity autocorrelation data for a single NV center implanted in a diamond nanowire shows sustained anti-bunching, without background subtraction, at increasing excitation powers due to high single-photon collection efficiency and low background. (a) 50 µW: \( g^{(2)}(0) \sim 0.08 \), (b) 100 µW: \( g^{(2)}(0) \sim 0.06 \), (c) 250 µW: \( g^{(2)}(0) \sim 0.16 \) and (d) 1000 µW: \( g^{(2)}(0) \sim 0.27 \). Pump power was measured before the microscope objective. Raw data (black) and theoretical fits (red) are shown.

Additional information on the optical properties of an NV center in a diamond nanowire may be obtained by triggering the emission of single photons. We have constructed a versatile-pulsed excitation system for this task [35]. Ultrafast (∼200 fs) pulses generated by a Ti:sapphire (Coherent Mira 800-F) laser were used to generate supercontinuum white light in a photonic crystal fiber (Newport, SCG-800). A pump wavelength of ∼800 nm maximized the overall spectral density at green wavelengths, which was then isolated using band-pass filters in the 510–540 nm wavelength range (Semrock), collected with an optical fiber and used as an excitation source for our confocal microscope. Since the radiative rate of an NV center in a diamond nanowire (∼60–80 MHz) [3] is comparable to the fundamental repetition rate of the Ti:sapphire pulse train (76 MHz), an electro-optic modulator (ConOptics, Model 350) was used to reduce the repetition rate to ∼10.8 MHz prior to launching in the photonic crystal fiber.
Figure 6. (a) $g^{(2)}(0)$ as a function of pump power. Data points correspond to the values of the normalized $g^{(2)}(0)$ data presented in figure 5. The dashed curve is the expected level of coincidence counts $1 - \rho^2$ based on the measured saturation data presented in (b), where $\rho = S/(S+B)$, $S$ is NV center single-photon count rate and $B$ is background fluorescence count rate. (b) Total nanowire fluorescence from the same device is presented in red, the background fluorescence obtained from contrast in photon anti-bunching data in (a) is shown in blue and the remainder of the net single-photon counts from an embedded NV center is shown in black. A fit of the NV center fluorescence to the saturation model is given by the dashed black line. Pump power was measured before the microscope objective.

We used this excitation scheme to observe the full temporal dynamics of the diamond nanowire fluorescence. Pulsed intensity auto-correlation measurements show a series of spikes in coincidence counts at times separated by an integer number of laser repetition cycles (figure 7(a)). Strong suppression of the central peak $g^{(2)}(0) \sim 0.16$ is observed at 65 $\mu$W average pump power, which is consistent with the extent of the photon anti-bunching observed using CW excitation. Additionally, we were able to make a direct measurement of the exponential decay of the nanowire fluorescence after pulsed excitation (figure 7(b)). A fit was obtained from a bi-exponential function using a fast time constant $\tau_{bg} \sim 1.4 \pm 0.1$ ns, which corresponds to the decay of the background fluorescence, and a slow time constant $\tau_{nv} \sim 13.7 \pm 0.2$ ns, which corresponds to the fluorescence decay of the NV center in the nanowire. This value of $\tau_{nv}$ is consistent with previously reported values inferred from the width of the anti-bunching dip in CW studies of type-Ib nanowires [3].

4. Conclusions and future directions

We have demonstrated two novel techniques to implant color centers in diamond nanostructures, and both could be an important part of future solid-state quantum photonic systems. For example, embedding the nanopillar arrays presented in section 2 in a metal layer could allow for plasmon-enhanced single-photon emission [36]. These deterministically positioned nanopillars also offer convenient, evanescent coupling to other photonic crystal cavities in semiconductor material systems that have been proposed for cavity quantum electrodynamics studies [37]–[39]. In either case, the observed scalability provided by this system is an attractive resource for the development of more complex and integrated device architectures.
There are also several natural extensions of the deep implantation of NV centers into the nanowires shown in section 3. Ion implantation of other intrinsically brighter defects [7] into the nanowire devices is an exciting prospect. Moreover, the outstanding combination of high directionality of emission from the nanowire antenna combined with low background fluorescence in the pure diamond crystal has allowed us to observe anti-bunching $g^{(2)}(0) \sim 0.16$ in a confocal microscope system with reduced numerical aperture $\text{NA} \sim 0.6$. We therefore anticipate that it will be possible to collect the NV center emission directly with a lensed optical fiber (NA $\sim 0.4$) positioned above a nanowire. Finally, it is well known that at low temperatures the NV center ZPL can become transform limited in bulk type-IIa diamond samples [40], but that significant inhomogeneous broadening and spectral diffusion are typical in diamond nanocrystals [34]. Further low-temperature studies are therefore needed to investigate the impact of reactive-ion etching on the stability of NV centers (both natural and implanted ones) embedded within fabricated nanowires. Moreover, understanding the impact of ion implantation damage will also be an important issue in the future. Detailed studies on the optical transitions of implanted NV centers in diamond nanowire antennas will therefore be useful for understanding the broader role that diamond nanophotonics can play in quantum optics and information processing with NV centers.

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