

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 25-02-2021		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 15-May-2017 - 14-May-2019	
4. TITLE AND SUBTITLE Final Report: Ultrapure Reactive Ion Etching for Scalable Nanofabrication of Carbon-Based Semiconductor Quantum Devices			5a. CONTRACT NUMBER W911NF-17-1-0268		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611103		
6. AUTHORS			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Massachusetts Institute of Technology (MIT) 77 Massachusetts Avenue NE18-901 Cambridge, MA 02139 -4307			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 70016-PH-RIP.5		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dirk Englund
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 617-324-7014

RPPR Final Report

as of 29-Oct-2021

Agency Code: 21XD

Proposal Number: 70016PHRIP

Agreement Number: W911NF-17-1-0268

INVESTIGATOR(S):

Name: Dirk Robert Englund
Email: englund@MIT.EDU
Phone Number: 6173247014
Principal: Y

Organization: **Massachusetts Institute of Technology (MIT)**

Address: 77 Massachusetts Avenue, Cambridge, MA 021394307

Country: USA

DUNS Number: 001425594

EIN: 042103594

Report Date: 14-Aug-2019

Date Received: 25-Feb-2021

Final Report for Period Beginning 15-May-2017 and Ending 14-May-2019

Title: Ultrapure Reactive Ion Etching for Scalable Nanofabrication of Carbon-Based Semiconductor Quantum Devices

Begin Performance Period: 15-May-2017

End Performance Period: 14-May-2019

Report Term: 0-Other

Submitted By: Dirk Englund

Email: englund@MIT.EDU

Phone: (617) 324-7014

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 3

STEM Participants: 2

Major Goals: Quantum information science requires networks of entangled quantum bits (qubits) on which single and multi-qubit logic operations can be performed. Thanks to rapid progress over recent years, color centers in diamond have emerged as one of the leading contenders for scalable and reliable qubits. The diamond nitrogen vacancy (NV) center has spin coherence times in excess of one second, and the spin state can be optically initialized, manipulated, and measured. Quantum network protocols based on these unique qualities have been proposed, two-node quantum networks have been implemented over more than 1 km (by far the longest distance for all matter qubits), and full quantum error correction has been demonstrated including non-destructive measurements and real-time feedback.

The goal of this program was to develop diamond fabrication processes to achieve high-performance nanophotonic spin-photon interfaces to these color centers.

Accomplishments: Due to the limitations of bulk optical diamonds, entanglement rates are typically a factor of 100 times less than the electron spin coherence time. We have identified two key improvements that must be made in order to increase the entanglement rate and enable large scale quantum information processors: (T1) High quality factor (Q) cavities in diamond for enhanced emission to a single frequency and spatial mode. The Englund group has expanded their 1D cavity fabrication to more novel cavity designs as well as introduced techniques to fabricate 2D structures. and (T2) Defect-free nanofabrication in order to reduce spectral diffusion and dephasing through a stable electronic environment. To this end, we have investigated the effect of the implantation process and are looking into the further effect of different fabrication techniques on the NV properties.

Training Opportunities: Three PhD students were trained through this DURIP to develop high-performance diamond nanophotonic devices: Sara Mouradian, Noel Wan, and Kevin Chen.

RPPR Final Report

as of 29-Oct-2021

- Results Dissemination:** N. H. Wan, S. Mouradian, and D. Englund, Appl. Phys. Lett. 112, 141102 (2018).
[2] S. B. van Dam, M. Walsh, M. J. Degen, E. Bersin, S. L. Mouradian, A. Galiullin, M. Ruf, M. IJspeert, T. H. Taminiau, R. Hanson, and D. R. Englund, Phys. Rev. B Condens. Matter 99, 161203 (2019).
[3] E. Bersin, M. Walsh, S. L. Mouradian, M. E. Trusheim, T. Schröder, and D. Englund, Npj Quantum Information 5, (2019).
[4] M. E. Trusheim, N. H. Wan, K. C. Chen, C. J. Ciccarino, J. Flick, R. Sundararaman, G. Malladi, E. Bersin, M. Walsh, B. Lienhard, H. Bakhru, P. Narang, and D. Englund, Phys. Rev. B Condens. Matter 99, 075430 (2019).
[5] M. E. Trusheim, B. Pingault, N. H. Wan, M. Gundogan, L. De Santis, K. C. Chen, M. Walsh, J. J. Rose, J. N. Becker, B. Lienhard, E. Bersin, G. Malladi, H. Bakhru, I. Walmsley, M. Atature, and D. Englund, arXiv [quant-Ph] (2018).
[6] B. Hensen, H. Bernien, A. E. Dréau, A. Reiserer, N. Kalb, M. S. Blok, J. Ruitenbergh, R. F. L. Vermeulen, R. N. Schouten, C. Abellán, W. Amaya, V. Pruneri, M. W. Mitchell, M. Markham, D. J. Twitchen, D. Elkouss, S. Wehner, T. H. Taminiau, and R. Hanson, Nature 526, 682 (2015).
[7] J. Cramer, N. Kalb, M. A. Rol, B. Hensen, M. S. Blok, M. Markham, D. J. Twitchen, R. Hanson, and T. H. Taminiau, Nat. Commun. 7, 11526 (2016).
[8] Y. Chu, N. P. de Leon, B. J. Shields, B. Hausmann, R. Evans, E. Togan, M. J. Burek, M. Markham, A. Stacey, A. S. Zibrov, A. Yacoby, D. J. Twitchen, M. Loncar, H. Park, P. Maletinsky, and M. D. Lukin, Nano Lett. 14, 1982 (2014).
[9] J. P. Hadden, J. P. Harrison, A. C. Stanley-Clarke, L. Marseglia, Y.-L. Ho, B. R. Patton, J. L. O'Brien, and J. G. Rarity, Appl. Phys. Lett. 97, 241901 (2010).
[10] N. Mendelson, Z.-Q. Xu, T. T. Tran, M. Kianinia, C. Bradac, J. Scott, M. Nguyen, J. Bishop, J. Froch, B. Regan, I. Aharonovich, and M. Toth, arXiv [physics.app-Ph] (2018).

Honors and Awards: Englund was selected for Bose Research Fellowship

Protocol Activity Status:

Technology Transfer: The devices and methods are being transferred into quantum network deployments, including with MIT Lincoln Laboratory and through the NSF Center for Quantum Networks.

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Physical Review B

Publication Identifier Type: DOI

Publication Identifier: 10.1103/PhysRevB.99.075430

Volume: 99

Issue: 7

First Page #:

Date Submitted: 8/31/19 12:00AM

Date Published: 2/1/19 5:00AM

Publication Location:

Article Title: Lead-related quantum emitters in diamond

Authors: Matthew E. Trusheim, Noel H. Wan, Kevin C. Chen, Christopher J. Ciccarino, Johannes Flick, Ravishan

Keywords: quantum emitters

Abstract: M.T. acknowledges support by an appointment to the Intelligence Community Postdoctoral Research Fellowship Program at Massachusetts Institute of Technology, administered by Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy (DOE) and the Office of the Director of National Intelligence. N.H.W is supported in part by the Army Research Laboratory Center for Distributed Quantum Information. K.C.C. acknowledges funding support by the NSF Graduate Research Fellowships Program. J.F. acknowledges financial support from the Deutsche Forschungsgemeinschaft under Contract No. FL 997/1-1. E.B. was supported by a NASA Space Technology Research Fellowship and the NSF Center for Ultracold Atoms (CUA). D.E. and experiments were supported in part by the NSF Science-Technology center for integrated quantum materials (CIQM), NSF Grant No. DMR-1231319. This research used resources of the National Energy Research Scientific Computing Center, a

Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: Y

RPPR Final Report
as of 29-Oct-2021

Partners

,

I certify that the information in the report is complete and accurate:

Signature:

Signature Date:

ARO Grant No: W911NF1710268

Title: Ultrapure Reactive Ion Etching for Scalable Nanofabrication of Carbon-Based Semiconductor Quantum Devices

Principal Investigator: Dirk Englund

Lead Institution: Massachusetts Institute of Technology (MIT)

ARO Program Manager:

Dr. Sara Gamble: 800 Park Office Drive, Suite 4229; Research Triangle Park, NC 27709
919-549-4211

Program Objective: This program is focused on the development of high-performance nanofabrication of diamond nanophotonic structures, by a combination optimized diamond fabrication evaluated by automated cryogenic spectroscopy.

Scientific Approach: The program developed advanced reactive ion etching as well as a cryogenic microscope to characterize quantum emitters within the diamond. The DURIP program was highly successful in enabling several experimental advances, including reliable fabrication of diamond nanophotonic devices[1] and emitter studies[2–5].

Abstract

Quantum computation and communication systems leverage the advantages of quantum information to surpass their classical counterparts in certain applications. Impurities in diamond, such as the nitrogen vacancy (NV) color center, have emerged as a leading platform for solid-state spin qubits. High-fidelity logic gates, error correction, and long-range entanglement have already been demonstrated, but improved experimental techniques are required to enable scalable systems. In these solid-state systems, the quality of the substrate patterning is of utmost importance - contamination leads to decoherence of quantum properties, lowering entanglement rates and decreasing fidelity. Here, we report on a systematic architecture to study how different etching techniques impact the properties of carbon-based semiconductor quantum devices.

Project Narrative

Quantum information science requires networks of entangled quantum bits (qubits) on which single and multi-qubit logic operations can be performed. Thanks to rapid progress over recent years, color centers in diamond have emerged as one of the leading contenders for scalable and reliable qubits. The diamond nitrogen vacancy (NV) center has spin coherence times in excess of one second, and the spin state can be optically initialized, manipulated, and measured. Quantum network protocols based on these unique qualities have been proposed, two-node quantum networks have been implemented over more than 1 km (by far the longest distance for all matter qubits)[6], and full quantum error correction has been demonstrated including non-destructive measurements and real-time feedback[7].

Due to the limitations of bulk optical diamonds, entanglement rates are typically a factor of 100 times less than the electron spin coherence time. We have identified two key improvements that must be made in order to increase the entanglement rate and enable large scale quantum information processors: **(T1)** High quality factor (Q) cavities in diamond for enhanced emission to a single frequency and spatial mode. The Englund group has expanded their 1D cavity fabrication to more novel cavity designs as well as introduced techniques to fabricate 2D structures. and **(T2)** Defect-free nanofabrication in order to reduce spectral diffusion and dephasing through a stable electronic environment. To this end, we have investigated the effect of the implantation process and are looking into the further effect of different fabrication techniques on the NV properties.

T1: High Quality Fabrication of Diamond Nanophotonic Structures

The entanglement rate between two NVs is proportional to the product of the collection efficiencies into the same spatial and frequency mode for two NV centers. Thus, the emission enhancement into a single spatial and frequency mode through the Purcell effect is essential to achieve multiple successful entanglement gates during the spin coherence time. For example, a $> 10x$ increase into a single frequency and spatial mode is needed to improve the current entanglement success rate (1 per 250s) to below the longest reported electron spin coherence time (1s). Moreover, network protocols which rely on high cooperativity NV-cavity systems ($C > 20$) can generate topological cluster states, which is a promising platform for quantum information processing. Their low mode volume and high quality factor (Q) makes photonic crystal (PhC) cavities the current leader in Purcell enhancement. Decades of advances in silicon fabrication have enabled PhC cavities with $Q > 10^6$. However, the fabrication of high Q cavities in diamond lags behind due to the difficulties of fabricating suspended PhC cavities.

While trying to improve the physical process of the etching technique, we also intend to broaden the types of tools accessible. While one dimensional photonic crystals are generally easier to etch with current diamond etching techniques, two dimensional designs provide better simulated quality factors and mode volumes due to the additional dimension of confinement. Figure 1 shows our recent success at expanding the 1 dimensional photonic crystal etching technique to a 2 dimensions.

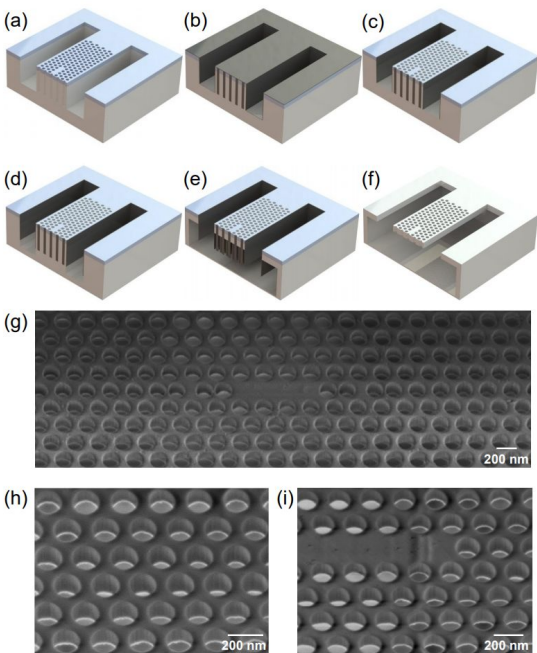
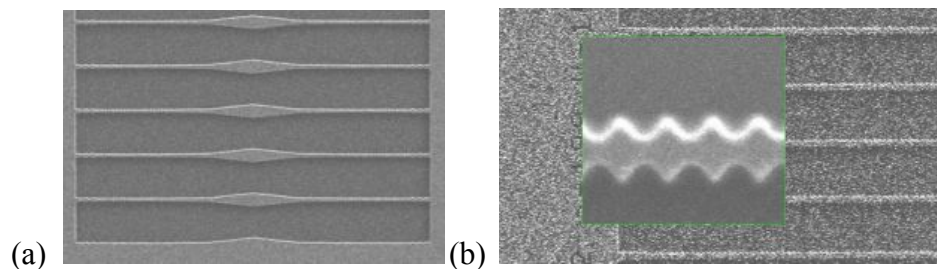


Figure 1. (a) Electron-beam lithography and oxygen plasma reactive-ion etching (RIE) of diamond (grey) using a SiN hard mask (blue). (b) Atomic layer deposition (ALD) of alumina (black) for conformal protection. (c) Break-through etch of alumina using tetrafluoromethane. (d) RIE of diamond. (e) Quasi-isotropic undercut of diamond using oxygen plasma (f) Mask removal using hydrofluoric acid. (g-i) Scanning electron micrograph (SEM) of a 2D photonic crystals suspended in air. [1]

Taking into account observations and insights gleaned from T2, we have also begun considering novel cavity designs. While still under investigation, we believe the quantum emitter's proximity to an etched surface introduces more noise due to surface states that arise from dangling bonds on a non-uniform facet of the diamond. Figure 2 shows some examples of two new designs that maintain a high Q in simulation but move the closest etched surface further from the center of the cavity mode where the defect resides.



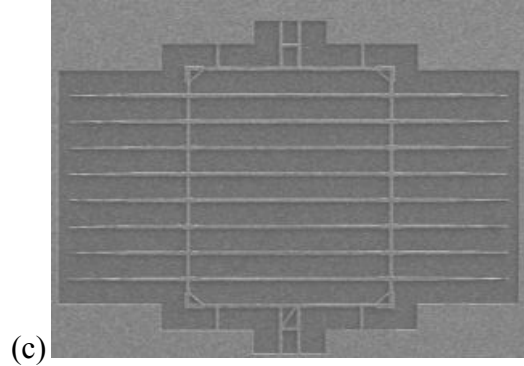


Figure 2: Examples of fabricated designs modified to move the closest etched surface further from the cavity center. (A) shows a defect constructed from creating a tapered bulge near the cavity center. (B) shows a modification of the DBR region of the cavity using a modulation in the width of the beam rather than the introduction of holes in the center. (C) shows the framing structure used to align the cavity-emitter devices to a parent chip.

T2: Preservation of Fourier-limited Emitters in Nanostructures

Maintaining Fourier-limited spectral linewidths is critical for achieving high entanglement rates between distant NV centers. Lifetime-limited emission allows for maximal wavefunction overlap between photons from separate NVs and facilitates the entanglement protocol. The narrowest reported linewidths are observed on naturally occurring emitters buried deep in the diamond lattice[2,8], far away from any potential defects or inhomogeneities caused during fabrication. Figure 3 shows a resonant photoluminescence excitation (PLE) scan of an NV 7 μm from the diamond surface, under a solid immersion lens (SIL) [9] milled by Focused Ion Beam (FIB) milling.

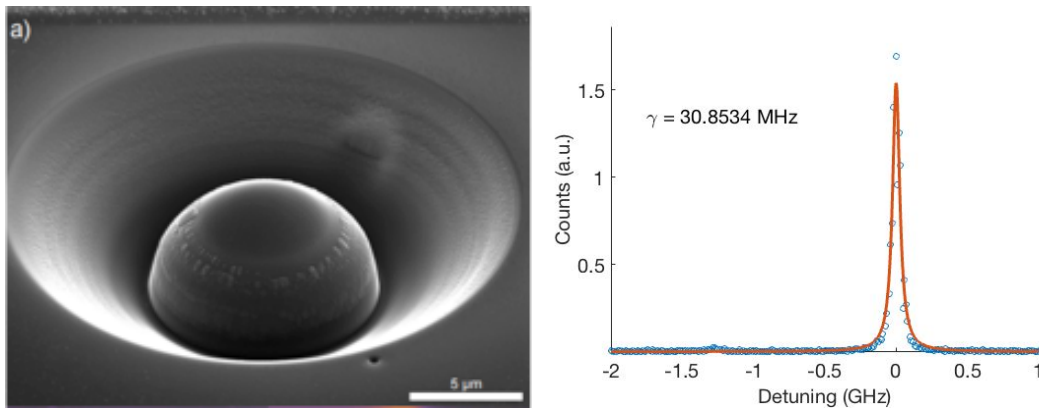


Figure 3. A. Scanning electron micrograph (SEM) of a SIL containing a single NV 7 μm below the surface. B. Single line PLE scan showing nearly Fourier-limited linewidth due to crystal purity and distance from the surface.

We investigated engineered NVs that would be used in our fabrication technique, which requires them to be 100 nm below the surface. Figure 4 shows that the implantation and annealing technique used to form these NV centers produces linewidths much broader than naturally occurring centers. This result will require us to further investigate novel approaches to annealing and/or using different techniques to incorporate the nitrogen in the lattice (both are being pursued). An automated infrastructure that uses etched position markers in the diamond along with machine vision has enabled collection of larger datasets, similar to the one shown in figure 4. This system will also allow the tracking of individual NVs as they go through the various etching procedures.

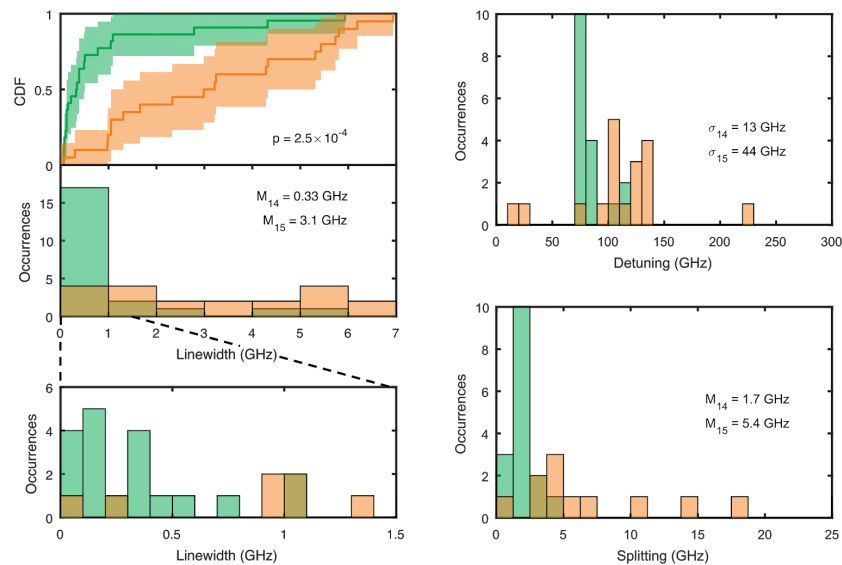


Figure 4: Green shows NV centers that were formed with naturally occurring nitrogen. Orange shows NV centers that were formed from implanted nitrogen. Both reside 100 nm below the surface. The left column shows the cumulative distribution (and associated histogram) of linewidths observed from both implanted and natural NVs. The right column shows the observed axial (top) and transverse (bottom) strain manifesting itself in shifts and splitting of the optical transition. [2]

For an NV with a typical excited state lifetime of 12 ns, the Fourier-limited linewidth is ~ 13 MHz. Due to the distance to the surface, as well as the crystal quality, this NV emits with a linewidth of 31 MHz, close to the lifetime limit. Moreover, the line remains stable in frequency over many scans. However, while this type of SIL structure allows NVs to remain far from the surface, it provides no emission enhancement, severely limiting the theoretical maximum entanglement rate. As elaborated on in T1, cavity structures that enhance the emission require the NV to be in much greater proximity to the fabricated diamond surface. Here, the often harsh environment of fabrication can cause inhomogeneities in the diamond's surface chemistry, impurities in the

crystal structure, and crystal strain, all of which can cause spectral diffusion and dephasing. As a result, PLE taken on NVs in these cavities is often quite broad, as shown by the 11 GHz line in Figure 5b.

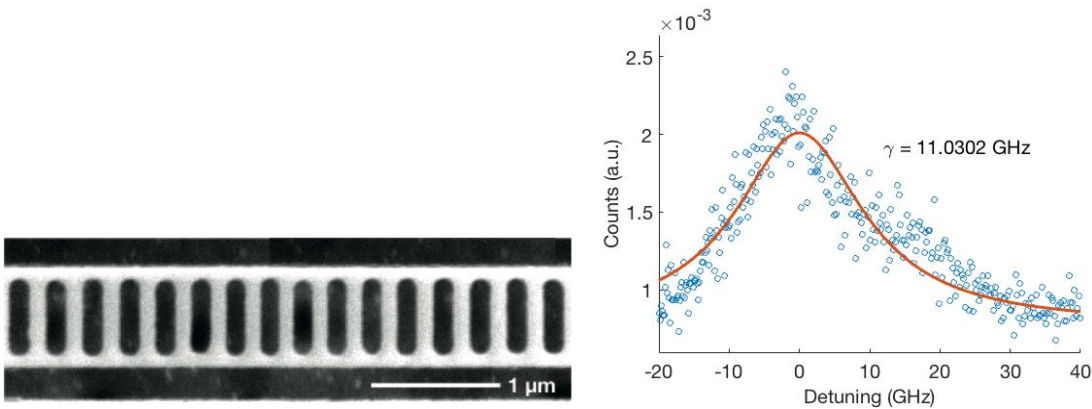


Figure 5. A. SEM of a PhC cavity with a $Q > 5000$ containing a single NV. B. Single-line PLE scan showing significant linewidth broadening (1000x) due to surface proximity.

The current understanding of spectral diffusion suggests that the main source is the creation of charge traps and other impurities on the surface after fabrication. As surface electrons hop around between these traps, the local electric field environment at the site of the NV changes, Stark tuning the resonance of the NV and shifting the spectral local of the emission. This spectral diffusion causes inhomogeneous broadening of the emission which decreases the spectral overlap of photons from separate NVs, lowering the entanglement probability. There is evidence that this spectral diffusion can be mitigated by employing fabrication techniques that better preserve the homogeneity of the diamond surface. We have collaborated with the Loncar Group at Harvard to produce and characterize triangular nanobeams (Figure 6A) using an oxygen etching technique that is more isotropic and less aggressive than traditional oxygen plasma etching, allowing it to better preserve surface homogeneity. We are also in collaboration with Professor Aharonovich at the University of Technology in Sydney who uses an electron beam induced etching technique [10]. Samples are under preparation to perform a systematic study of these techniques, similar to how we performed the implantation study mentioned above.

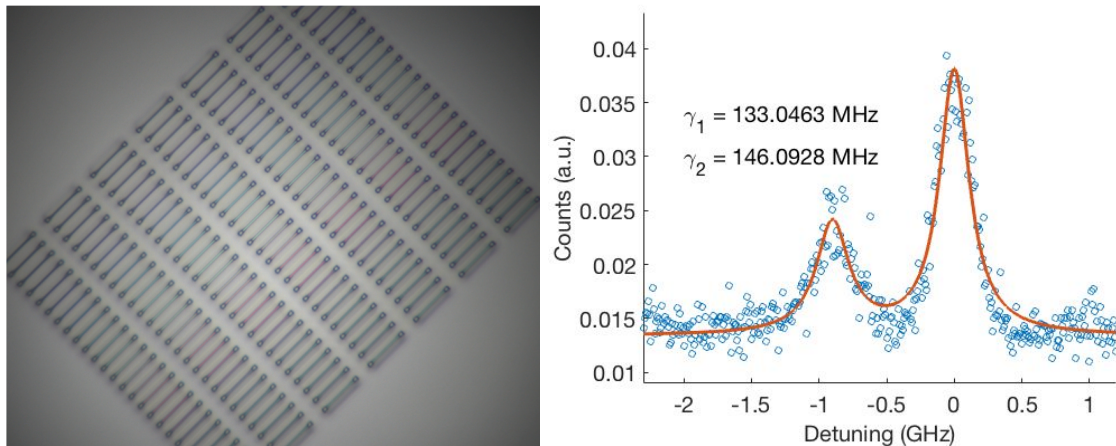


Figure 6. A. Optical Image of nanobeams. B. Single-line PLE scan showing two NV transitions, each only 10x broadened.

Early results in the structures etched at Harvard show linewidths as low as 133 MHz, much closer to the lifetime limit, as seen in Figure 6B. These results indicate that the choice of fabrication technique and fabrication environment are critical in determining the properties of NVs in nanostructures.

Bibliography

- [1] N. H. Wan, S. Mouradian, and D. Englund, *Appl. Phys. Lett.* **112**, 141102 (2018).
- [2] S. B. van Dam, M. Walsh, M. J. Degen, E. Bersin, S. L. Mouradian, A. Galiullin, M. Ruf, M. IJspeert, T. H. Taminiau, R. Hanson, and D. R. Englund, *Phys. Rev. B Condens. Matter* **99**, 161203 (2019).
- [3] E. Bersin, M. Walsh, S. L. Mouradian, M. E. Trusheim, T. Schröder, and D. Englund, *Npj Quantum Information* **5**, (2019).
- [4] M. E. Trusheim, N. H. Wan, K. C. Chen, C. J. Ciccarino, J. Flick, R. Sundararaman, G. Malladi, E. Bersin, M. Walsh, B. Lienhard, H. Bakhru, P. Narang, and D. Englund, *Phys. Rev. B Condens. Matter* **99**, 075430 (2019).
- [5] M. E. Trusheim, B. Pingault, N. H. Wan, M. Gundogan, L. De Santis, K. C. Chen, M. Walsh, J. J. Rose, J. N. Becker, B. Lienhard, E. Bersin, G. Malladi, H. Bakhru, I. Walmsley, M. Atature, and D. Englund, *arXiv [quant-Ph]* (2018).
- [6] B. Hensen, H. Bernien, A. E. Dréau, A. Reiserer, N. Kalb, M. S. Blok, J. Ruitenbergh, R. F. L. Vermeulen, R. N. Schouten, C. Abellán, W. Amaya, V. Pruneri, M. W. Mitchell, M. Markham, D. J. Twitchen, D. Elkouss, S. Wehner, T. H. Taminiau, and R. Hanson, *Nature* **526**, 682 (2015).
- [7] J. Cramer, N. Kalb, M. A. Rol, B. Hensen, M. S. Blok, M. Markham, D. J. Twitchen, R. Hanson, and T. H. Taminiau, *Nat. Commun.* **7**, 11526 (2016).
- [8] Y. Chu, N. P. de Leon, B. J. Shields, B. Hausmann, R. Evans, E. Togan, M. J. Burek, M. Markham, A. Stacey, A. S. Zibrov, A. Yacoby, D. J. Twitchen, M. Loncar, H. Park, P. Maletinsky, and M. D. Lukin, *Nano Lett.* **14**, 1982 (2014).
- [9] J. P. Hadden, J. P. Harrison, A. C. Stanley-Clarke, L. Marseglia, Y.-L. Ho, B. R. Patton, J. L. O'Brien, and J. G. Rarity, *Appl. Phys. Lett.* **97**, 241901 (2010).

- [10] N. Mendelson, Z.-Q. Xu, T. T. Tran, M. Kianinia, C. Bradac, J. Scott, M. Nguyen, J. Bishop, J. Froch, B. Regan, I. Aharonovich, and M. Toth, arXiv [physics.app-Ph] (2018).