



Volumetric integration of nanodiamonds in optical fiber cores

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Agenda

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I. Optical fibers with with NV nanodiamonds: magnetometry



1. Step-index multimode fiber



2. Step-index suspended core microstructured fiber



3. Hollow-core anti-resonant fiber

II. Optical fibers with nanodiamonds: reduction of nonlinearity



2. Step index fiber based on F2 glass with NDs



2. Vitrified silica glass with NDs







Magnetic field sensing with NV nanodiamonds









- Efficient fluorescence collection requires integration of NDs with specific platforms
- Optical pumping: population transfer from $|\pm 1\rangle$ to $|0\rangle$
- Optical readout: Optically Detected Magnetic Resonance (ODMR)
- OPTICAL probing and readout of ND state can benefit from the integration with optical fibers





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Nanodiamond integration with optical fibers – the state of the art

Optical fiber tapers

(evanescent field operation)

Xiaodi Liu et al. Appl. Phys. Lett. 103, 143105 (2013)



Fiber tip functionalization

T. Schröder et al. Optics Express 20, 10490 (2012) D. Duan et al. Optics Express 27, 6734 (2019)







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Both approaches: ultra-precise, but highly localized interaction with monitored object / field







Diamond particle-doped glass & optical fiber

Doping of diamond particles into glass and drawing into fibers: magnetically sensitive optical fibers - 2014 & on: prof. H. Ebendorff-Heidepriem & group, The University of Adelaide

What for? + advantages

- Magnetically sensitive endoscopes for remote Bfield sensing
- Immobilization and protection of diamonds
- Improvement of NV fluorescence collection efficiency





Magnetically sensitive nanodiamond-doped tellurite glass fibers

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Limitations

- Survivability of diamonds at fiber-drawing temperatures
- Scattering loss at diamond particles

Fluorescent diamond microparticle doped glass fiber for magnetic field sensing

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Solutions

2020

- Soft glasses drawable into fibers at 400-700 deg.C
- Mixing diamonds into raw materials and melting glass tellurite fibers (i)
- Dip-coating preforms and drawing into fibers lead-silicate glass fibers (ii
- Structure modifications i.e. ring-shaped area of core doped with diamonds ٠



Nanodiamond in tellurite glass Part II: practical nanodiamond-doped fibers

Yinlan Ruan,¹ Hong Ji,¹ Brett C. Johnson,² Takeshi Ohshima,³ Andrew D. Greentree,⁴ Brant C. Gibson,⁴ Tanya M. Monro¹ and Heike Ebendorff-Heidepriem¹

2014

Results

- Guiding of NV fluorescence over fiber sections ~50 cm long
- $< 1 \mu T V Hz$ magnetic field ٠ sensitivity in ODMR measurements



Our approach

What do we do?

volumetric incorporation of NV diamonds in the fiber core

Why is it important?

- Enables scaling of concentration
- Enables distributed sensing
- Does not sacrifice magnetic response?
- Different fiber geometries enable addressing coupling effciency of NV⁻ to guided modes

















Our approach

How do we do it?

1. dip coating of glass preform components in ND liquid suspensions







D. Bai, ^{1,a} ¹ M. H. Huynh,² D. A. Simpson,³ P. Reineck,⁴ ¹ S. A. Vahid,⁵ A. D. Creentree,⁶ S. Foster,⁶ H. Ebendorff-Heidepriem,² ⁰ and B. C. Gibson⁴

2. infiltration of hollow core fibers with ND liquid suspensions





Q U N N A

The ND deposited by infiltrating the core with IPA suspension followed by drying and flushing with pristine IPA.



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Diamond particles for integration with glass

MDNV1um, Adámas Nanotechnologies (developed using HPHT by vendor) Mean particle size 750 nm

measured with the dynamic light scattering method







1. The step-index fiber









- Nanodiamonds used: - MDNV1um, Adámas Nanotechnologies ,
- NV concentration 3.5 ppm

Fibre core:

- stacked using 790 glass rods
- coated with MD-NV-1um-Hi nanodiamonds 750 nm in size
- Schott F2 glass
- Low-index F2 modification for cladding tube



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Without high pass filter

With the filter

1. The step-index fiber

Cross-section of the fabriacted fibre



Light intensity distribution for NV red fluorescence



Fibre core:

- Core diameter 50 um
- Schott F2 glass
- Low-index F2 modification for cladding tube
- Measured NA = 0.16

NV⁻ Zero phonon line at 637 nm visible Assymetry of spectra Scattering observed



Fluorescence spectrum for: Light propagation in fibre (a) excitation and detection from the same fibre end (a) (b) from different ends of the fiber (b)

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distribution of diamond particles at the glass surface

Surface of F2 silicate glass preform elements dip-coated with the nanodiamonds No significant agglomeration Typical particle-to-particle distance is between 2 μm and 5 μm

SEM images of fiber cross-section:

 homogenous glass structure with sectionally incorporated diamond particles

- no agglomerates
- no gass bubbles





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imaging of diamond particles distributionin the fiber core

Confocal microscopy imaging of ND distribution

• Observable fluorescence of individual NDs



- The method validates a reasonable degree of control over spatial ND distribution
- possible control of ND distribution by layout design







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imaging of diamond particles distributionin the fiber core

metodology

- recording of diamond fluorescence from either the face or the side of a fiber sample under a confocal microscope
- projecting the images from the 3 fiber samples (signal intensity) onto one axis,
- obtaining an intensity curve for either longitudinal or transverse axis of the fiber
- the distance between adjacent peaks is measured and obtained values are stacked in a histogram

Example of fiber image with fluorescing diamonds under a confocal microscope



Intensity curve from image projected onto fiber' longitudinal axis





imaging of diamond particles distributionin the fiber core

results

Longitudinal separation histogram: major nanodiamond fractions separated either by 15 µm or 25 µm This corresponds to roughly 2.5 µm diamond-diamond distance at recorded at the dip-coated glass surface, when fiber drawing dynamics and drawing thin-down ratio are taken into account.



Transverse separation histogram: major fraction of NDs separated 1-3 μ m which corresponds with mean cane diameter in the final fiber core (1.5 μ m).







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The read-out contrast between 0.5% to 1.3% - in both cases most of the fiber was not covered by the antenna (related to small fraction of fiber interacting with microwave)





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Magnetic field sensing performance

II. Direct magnetic field measurement - no microwaves

- Typical fluoresecence decay curve observed
- 35 mT dynamics range, but low sensitivity
- (-) No microwaves requires calibration for readout of magnetic field value
- (++) No microwaves attractive for biosensing
- Only for high magnetic fields







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2. The suspended core fiber

State of the art, comparable performance:

fiber tip/taper magnetic field probes: tens of μT/sqrt(Hz) magnetic sensitivity & NV fluorescence collection efficiency usually <1%



What we do and why is it imporatant:

- suspended core geometry: ND particles localized inside the volume and along the length of a 1.5µm diam. core
- tight confinement of the guided mode and spatial overlap of NDs with the guided mode



- The ND suspension introduced inside the glass tube and allowed to dry.
- The process repeated 10 times,
- avoiding wetting of the tube outside, to ensure even coating of nanodiamonds only at the inside surface of the glass tube
- Tube collapsed on fiber drawing tower





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Magnetic field sensing performance

Side-mode operation verification

- Attempt to collect NV fluorescence from the fiber
- Hardly any fluorescence visible under the confocal microscope
- Error-bar level sensitivity :-(
- ✓ Supports strong confinement and guidance of NV fluorescence







Magnetic field sensing performance







RESULTS:

- Magnetic sensitivity 500 nT/sqrt(Hz)
- ✓ suspended core fiber 7% optical readout contrast in end-to-end ODMR
- ✓ ("Transmission mode opertation")
- ✓ Strong confinement of NV fluorescence strong coupling









3. Hollow-core anti-resonant fiber

Why hollow core fiber?

- \checkmark Largely unexplored in this application
- ✓ Coupling to guided mode difficult to anticipate
- ✓ Possible exposure of NDs to agents introduced into the hollow core
- ✓ Potentially low scattering loss







Hollow core fiber selection

- Silica, six non-touching capillaries in cladding
- 30 µm core diam.
- , 500 nm membrane thickness
- Broad VIS transmission covering both 532 nm excitation line and 637 nm NV⁻ Zero phonon line
- Effectively single mode at 637 nm







3. Hollow-core anti-resonant fiber

Fiber functionalization and characterization

- 40 cm long fiber samples
- Infiltrated with nanodiamond isopropanol (IPA) suspension by a syringe pump
- Flushed with pristine IPA and dried
- Even longitudinal distribution of particles at caldding capillaries



Confocal microscope imaging





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- 30 G

3. Hollow-core anti-resonant fiber

Verification of ODMR magnetic field sensing performance







frontiers

Diamond

Parabolic

Fiber

Fiber

Collimator

1 cm

Condenser

in Photonics

MW Wire



Magnetic field gradiometry

State of the art in NV nanodiamond vector measurements

Any random oriented nanodiamond fixation precludes a vector measurement

Alternatives already demonstrated:

- Single crystal vector gradiomete
 have been on fiber tips
- Dual-core fiber gradiometer with random-oriented ND tip

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APPLIED PHYSICS LETTERS 113, 011112 (2018)



Quantum stereomagnetometry with a dual-core photonic-crystal fiber

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S. M. Blakley et al., Appl. Phys. Lett. 113, 011112 (2018)



Fiberized Diamond-Based Vector Magnetometers

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G. Chatzidrosos et al., Frontiers in Photonics 2, 732748 (2021)

Magnetic field gradiometry - present alternatives employing diamond sensors

Single-crystal diamond-based microscope Complex but ultra-senstive



J. M. Taylor et al., Nature Physics 4, 810 (2008)

S-C diamond on fiber taper Robust and sensitive Requires -preorientation



Guo-Bin Chen et al. IEEE J. Quantum Electron. 56(3), 7500106 (2020)



Differential gradient measurement Addressing 1 or 2 diamonds over two separate fibers or 1 diamond over a dual core fiber

- Required pre-oriented diamonds



S. M. Blakley et al. Appl. Phys. Lett. 113, 011112 (2018)



Magnetic field gradiometry - present alternatives

All realizations relied on pre-oriented diamond sensors

Single-crystal dia microscope Complex but ult

employin



J. M. Taylor et a Nature Physics



over a dual core fiber - Required pre-oriented diamonds



S. M. Blakley et al. Appl. Phys. Lett. 113, 011112 (2018)

Device simplification



NV[–] nanodiamond hollow core fiber proof-of-concept gradiometer



Experimental setup

- Two 40 cm long hollow core fibers with NV⁻ nanodiamonds
- Fiber outputs positions one under-the-other under a magnet
- Removable microwave antenna in place



No microwaves variant

- Two experiments
- No-MW variant intresting for bid but requires calibration
- ODMR variant with 5% relative readout contrast (out of 15% achievable single fiber ODMR contrast)

ODMR variant

Magnetic field gradient obtained despite entirely random diamond orientation









Performance comparison



Step-index multimode fiber

Suspended core fiber



Hollow-core fiber

Material	soft glass (F2)	soft glass (F2)	fused silica				
MDNV1um, Adámas Nanotechnologies, in all fibers							
ODMR readout contrast	3%	7%	15%				
Direct B-field meas.	yes	no	yes				
Sensitivity	5 μT/√ <i>Hz</i>	500 nT/√ <i>Hz</i>	1 μT/√ <i>Hz</i>				
Usefull fiber length	25 cm	20 cm	40-50 cm				
and limitating factor	scattering	scattering	infiltration uniformity				
Main advantages	Transverse nanostructure	Strong confinement and guiding	controlled exposure of nanodiamonds				
	shaping		strong NV ⁻ signal, low propagation loss				

A. Filipkowski et al. Carbon (2022)

A. Filipkowski et al. Opt. Express (2022)

Optical sytems not optimised – still room for improvment



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II. Optical fibers with nanodiamonds: reduction of nonlinearity



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Nonlinear refractive index



• nonlinear index of refraction n_2 in the range of 10^{-20} (fused silica, ZBLAN) up to 10^{-17} m²/W (chalcogenide glass)

Negative index of n_2 :

- semiconductors (e.g. GaAs, AlGaAs), strong wavelength dependence, high negative n₂ near to energy gap
- organic liquids
- nanoparticles (Au, Ag, diamond), environment-surface effects



X. Feng et. al., J. Lightwave Technol. 23, 2046, (2005).





Motivation

nonlinear index of refraction n_2

crystalline diamond $n_2 = +4 \div 16 \text{ x} 10^{-20} \text{ m}^2/\text{W}$ [1]

nanodiamonds:

- negative n₂
- size of particles and surface functionalization -> modification of n_2
- successful integration with soft glass (eg. Schott F2) [4]
- GOAL: fiber-drawable hybrid glass with reduced n_2
- NDs influence on the nonlinearity of hybrid material
- in perspective, fiber optics with zero nonlinearity





nanodiamonds

 $n_2 = -2 \times 10^{-17} \,\mathrm{m^2/W}$ [2]

 $n_2 = -6 \text{ x} 10^{-19} \text{ m}^2/\text{W}$ [3] (detonation nanodiamond, 5-10 nm)

(nanocrystalline membrane, $1 \mu m$)







- [1] J.M.P. Almeida et. al., "Nonlinear optical spectrum of diamond at femtosecond regime", Sci. Rep. 7, 2017
- [2] F. Trojánek et. al., "Nonlinear optical properties of nanocrystalline diamond", Opt. Express 18(2), 2010
- [3] O. Muller et. al., "Optical limiting properties of surface functionalized nanodiamonds probed by the Z-scan method", Sci. Rep. 9, 2019

[4] D. Bai et al., "Fluorescent diamond microparticle doped glass fiber for magnetic field sensing," APL Materials 8, 081102 (2020)



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Measuring method – Z-scan



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InGaAs

power meter





Z-scan, system parameters

laser pulse characterization (Frequency Resolved Optical Gating - FROG)









portable Z-scan setup



- plano-convex lens f = 200 mm
- beam parameters: $M^2 < 1.2$, $\omega_0 = 37 \mu m$, $z_0 = 4.2 mm$
- beam diameter at scanning boundaries: 230 μm
- low power measurement for liquids

 $(P_{avg} = 2.27 \text{ mW}, E_p = 2.2 \text{ }\mu\text{J}, I_0 = 240 \text{ }\text{GW/cm}^2)$

- travel range 24 mm
- InGaAs power meter (700 ÷ 1800 nm)





System check

reference fused silica sample (2 mm)



• distilled water in quartz cuvette (5 mm)



toluene in quartz cuvette (5 mm) 17 x 10⁻²⁰ m²/W

results for reference samples (thin and thick sample assumption)

sample	sample thickness	lens	n ₂	n ₂ [Ref]	
Fused silica	2 mm	50 mm (Z ₀ = 0.86 mm)	1.8 – thin sample2.1 – thick sample	2.24 (1.7 – 2.7)	
	2 mm	100 mm (Z ₀ = 3.44 mm)	2.1 – thin sample2.2 – thick sample		
	5 mm	100 mm (Z ₀ = 3.44 mm)	2.2 – thin sample2.1 – thick sample		
Schott F2	2 mm	50 mm (Z ₀ = 0.86 mm)	5.0 – thin sample 5.7 – thick sample	2.9 8.9	
	2 mm	100 mm (Z ₀ = 3.44 mm)	6.9 – thin sample 7.0 – thick sample		
YVO4	0.9 mm	50 mm (Z ₀ = 0.86 mm)	18.6 (pol1), 18.3 (pol2)	15 - 19	
$n_2 \ge 10^{-20} \text{ m}^2/\text{W}$					

[1] M. L. Miguez et. al., "Measurement of third-order nonlinearities in selected solvents as a function of the pulse width," *Opt. Express* **25**, 3553-3565 (2017)





Nanodiamond in water



low n_2 and dense enough to avoid settling down

isopropanol? Quick particles settling -> unrepeatable scans DMSO? Very stable suspension but high n_2 (NDs don't change n_2 of suspension)

samples:

- detonation nanodiamonds (DND; Adámas Nanotechnologies, dominant particles size 5-10 nm), concentration of 0.01 mg/ml
- 2. DND concentration of 0.1 mg/ml
- 3. monocrystalline synthetic nanodiamonds (MSY, Pureon, average size 250 nm), concentration of 0.01 mg/ml
- preparation:
 - 1. mechanical shaking + 1h in ultrasonic cleaner
 - measurement in quartz cuvette (1 mm wall thickness and 5 mm optical path)

absorption coefficient α
 reflection from 4 surfaces included









Nanodiamond in water

- requirements for the selective measurement of electronic response in liquids: short pulses (< ps) and low repetition rate (< 1 kHz)
- long pulses or high repetition rate -> thermal lensing -> (spatial self-phase modulation)





- α rises for higher concentration of NDs
 -> scattering
- small particles -> lower n₂
- high concentration -> lower n₂
- distilled water: $n_2 = 3.27 \times 10^{-20} \text{ m}^2/\text{W}$
- DND 0.1 mg/ml: $n_2 = 3.04 \times 10^{-20} \text{ m}^2/\text{W}$
- up to 7% of n₂ reduction for DND 0.1 mg/ml





Bulk F2 glass with NDs - fabrication

- materials:
 - lead-silicate glass rods (Schott F2), $n_d = 1.6199$
 - nanodiamonds (MDNV, Adamas Nanotechnologies, 750 nm) suspended in isopropanol
 - modified in-house developed F2 glass with lower RI, $n_{\rm d}$ = 1.6133
- dip-coating + stack-and-draw method:
 - Schott F2 rods immersed in ND + IPA (10 x)
 - drawing the canes
 - core stacking (790 rods covered with NDs) and drawing
 - preform fabrication: core inside the modified F2 tube



sample of the preform thickness 2 mm



A. Filipkowski, et al., "Volumetric incorporation of NV diamond emitters in nanostructured F2 glass magneto-optical fiber probes," *Carbon* 196, 10-19, (2022).





Bulk F2 glass with NDs - nonlinearity

- Z-scan measurement of:
 - 1. core -> Schott F2 + NDs
 - 2. cladding -> modified F2 glass
 - 3. reference Schott F2 glass sample, thickness 2 mm
- 4% 7% of ole, thickness 2 mm





- 10x higher α in the core (scattering)
- 4% 7% of n_2 reduction for F2 + NDs glass





Vitrified silica glass with NDs - fabrication

- materials:
 - detonation nanodiamonds (DND 180 nm) mixed with silica powder in ethanol (10 μg DND per 1 g of silica)
 - silica tube
- CO₂ laser vitrification process
 - DND + silica mixture drying
 - heating DND + silica powder in silica tube (600°C)
 - laser vitrification along the capillary with powder
 - not uniform preforms due to process modification

two-sided polished sample of the preform thickness 2 mm





JIVERSITÄT

Prof. Alex Heidt







Vitrified silica glass with NDs - nonlinearity

- Z-scan measurement of:
 - 1. vitrified pure silica glass
 - 2. vitrified silica glass with NDs (samples ND3T1-3)





- vitrified silica has the same n₂ as commercial fiber grade silica glass
- all samples with NDs have higher α and lower n_2 than pure silica
- possibly inhomogeneous ND dopant
- 13% 19% of n₂ reduction for ND3T2 sample



Conclusions 1/2

- Volumetric functionalization of optical fibers with nanodiamonds enables practical magnetic field sensors across differnt fiber geometries
- Modified stack-and-draw fiber development enables control of diamond partice distribution at the micro-scale
- Diamond's NV fluorescence can be effectively captured and guided in strongly confining fibers
- Magnetic field gradient information is obtainable using randomly oriented spins in nanodiamond - towards vector measurements?















Conclusions 2/2

- Nanodiamonds decrease nonlinear index of refraction in all examined host materials:
 - water **4.5%** ÷ **7.0%** (0.8 μJ)
 - Schott F2 glass **4.2 %** (1.7 μJ)
 - vitrified silica glass $1.0 \% \div 16\% (1.7 \mu J)$
- Fabricated hybrid glass with NDs are useful for optical fiber development
- Nonlinearity can be controlled by NDs particle size, surface functionalization and concentration
- Further reduction of n_2 may result high loss (a zero nonlinear fiber can be a challenge)









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