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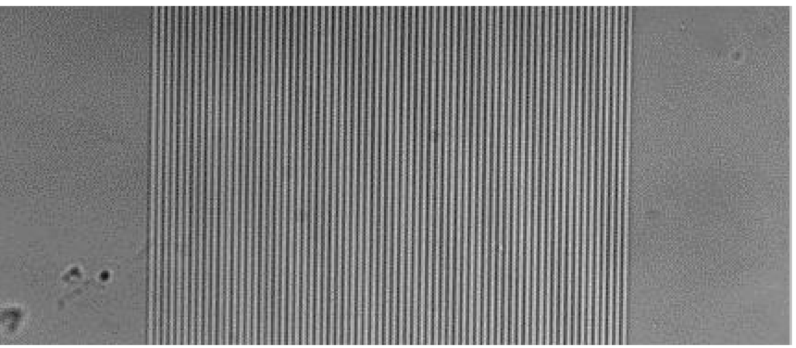

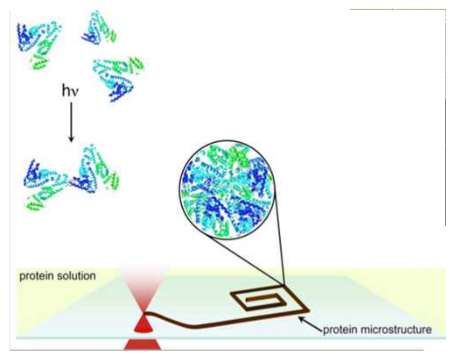

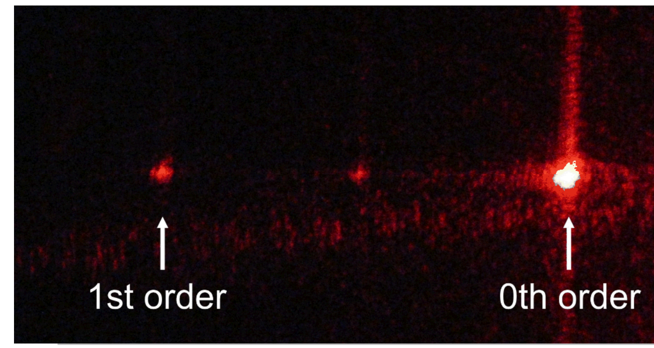

Direct-Write Graded Index Materials Realized In Protein Hydrogels

David Scrymgeour & Bryan Kaehr

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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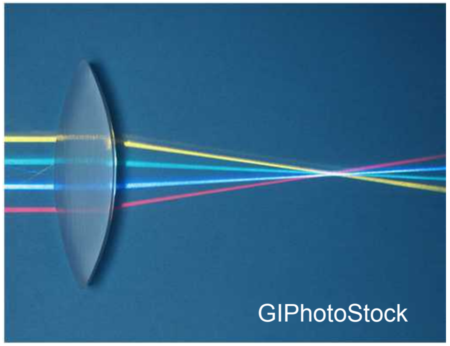
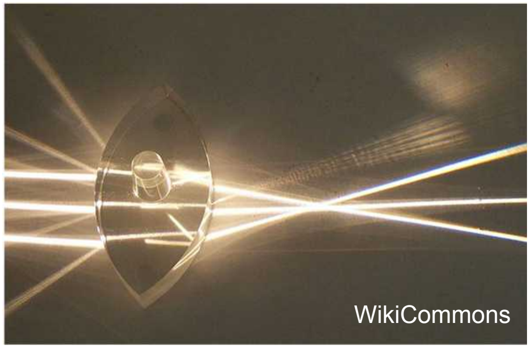
GRaded INdex materials give additional freedom for optical design

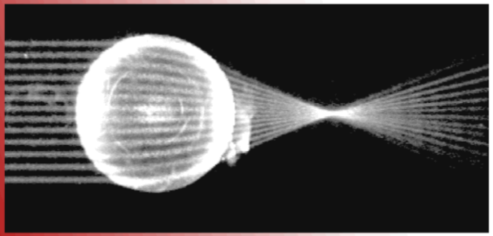
Traditional optical designs: uniform index of material + surfaces





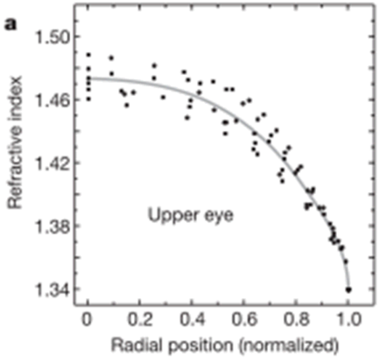
GRIN optical designs: non-uniform spatial variation of refractive index *n* with position

Crystalline Fish Eye Lens



Acosta et al, JOSA-A, 22, 424, (2005)

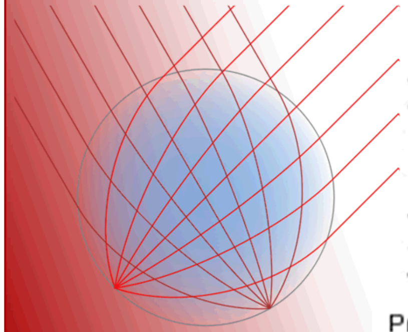
Jellyfish eye



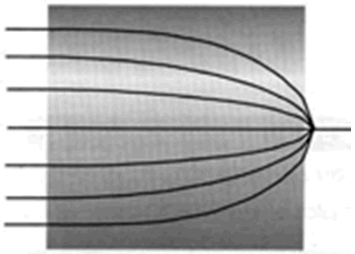
Nature 435 pg 201-205 (2005)

Nature

Luneburg Lens



Selfloc Lenses®



Profile of SELFOC GRIN Lens

Manmade

New fabrication techniques needed to create arbitrary GRIN distributions

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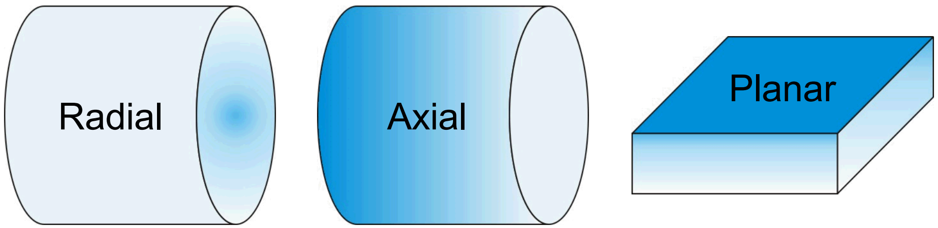
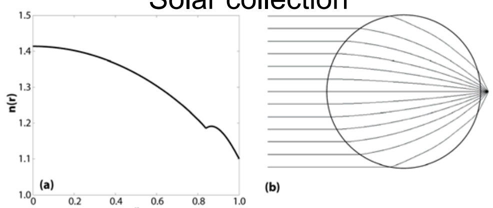
Current GRIN Geometries – limited by fabrication techniques



- Diffusion
- Ion exchange
- Polymerization
- Melt/drawing glasses/polymers

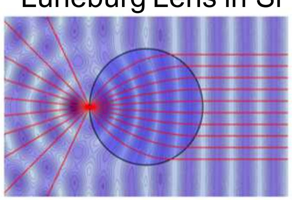
Arbitrary distributions allow many new applications ➔ need new fabrication routes

Solar collection



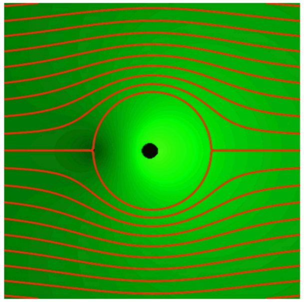
Optics Express, 19, 15584 (2011)

Luneburg Lens in Si



Optics Express, 19, 5156 (2011)

Optical cloaking



arXiv:physics/0602092v1

- Reduced weight, size, and complexity
- Next generation optical designs
- Combine optical functions (imaging – spectroscopy)
- Transformational/cloaking optics

Multiphoton Lithography can create arbitrary shapes in 3D

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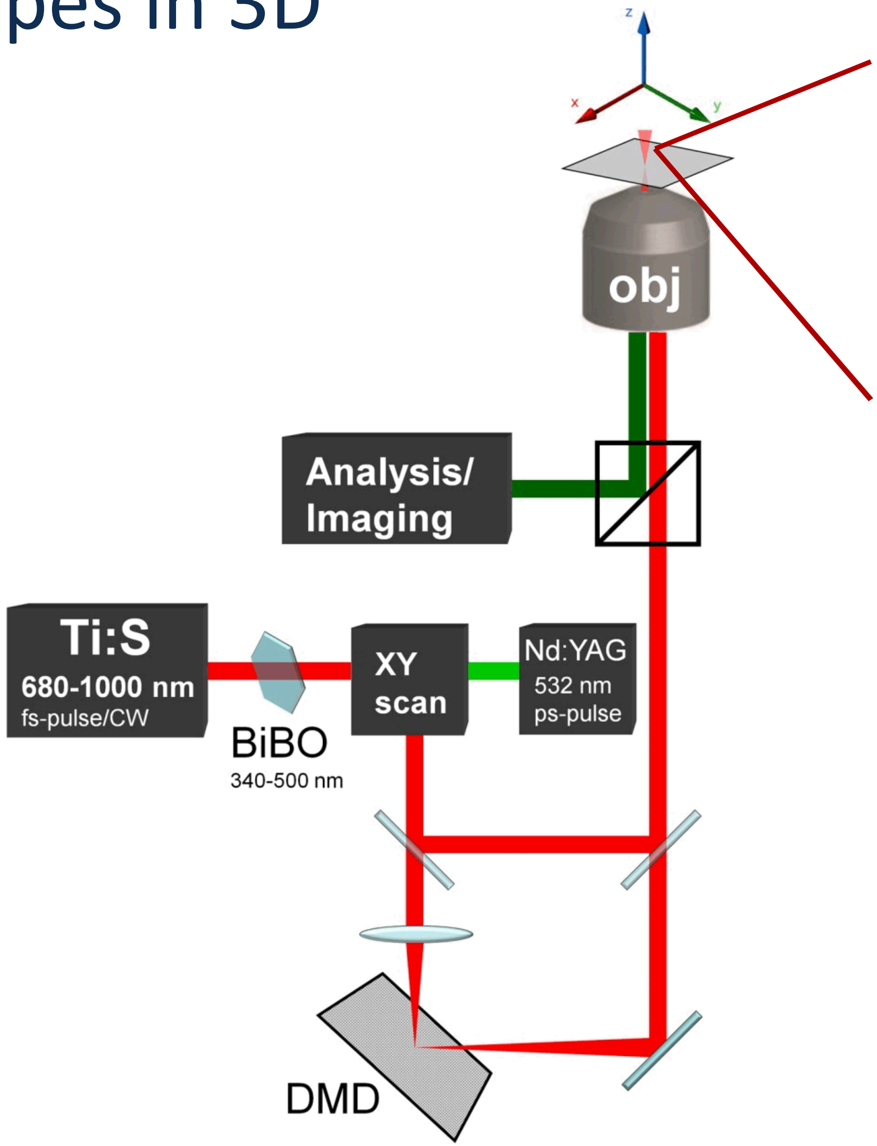

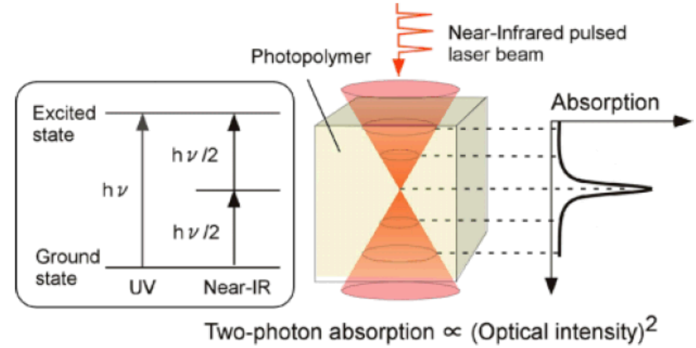

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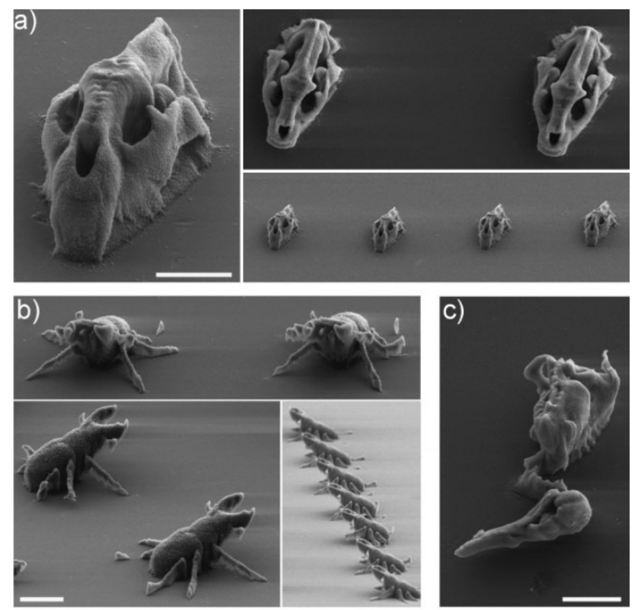
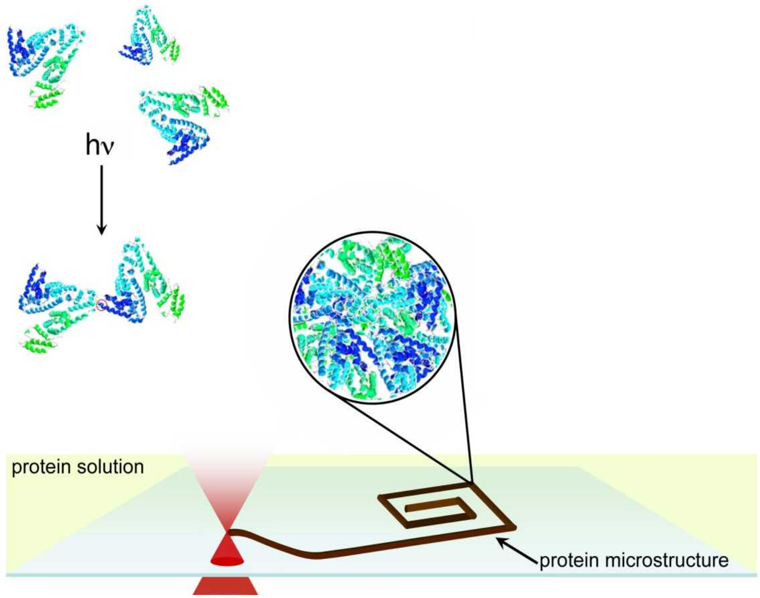
Laser & Photonics Reviews, 2, 1-2, pg 100–111 (2008)



Kaehr and Shear, *JACS* 2007 129 (7),1904-1905.
Nielson, Kaehr and Shear, *Small*, 2009, 5, 120-125

Structures were created in protein hydrogels because they have non-binary responses

1. Hydrogels from photocrosslinked proteins have variable densities
   - exposure time/ reactant concentrations
2. Compatible with conversion/functionalization chemistries



Hydrogel preparation:

- Dissolved bovine serum albumin (BSA) in buffered phosphate saline
- Sensitizer - ammonia persulfate
- Photosensitizer - $[Ru(bpy)^{3}]^{2+}$
- Flood illuminate broad band source 1 min
- Hydrogel is ready for MPL

D. Fancy et al. PNAS, 96, (1999) pp. 6020–6024

Variable density + 3D writing MPL = arbitrary GRIN structures

Gratings and line structures were written by rastering beam focus

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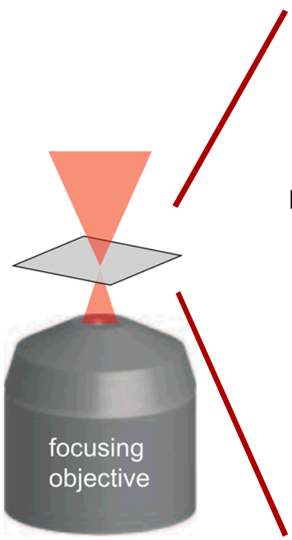
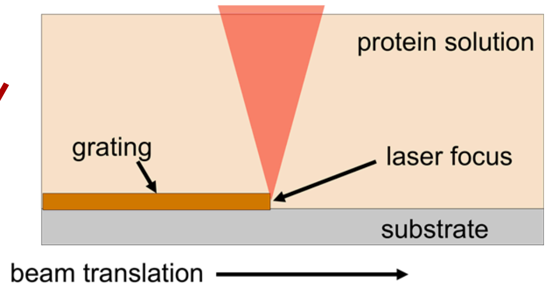
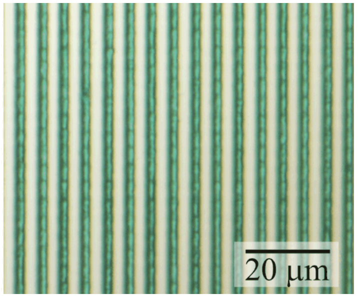
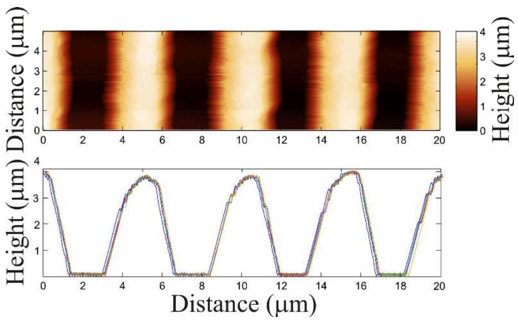


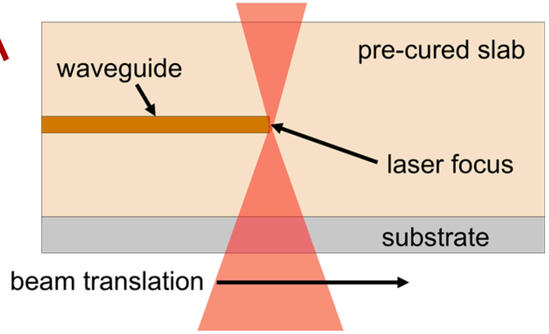
Surface gratings

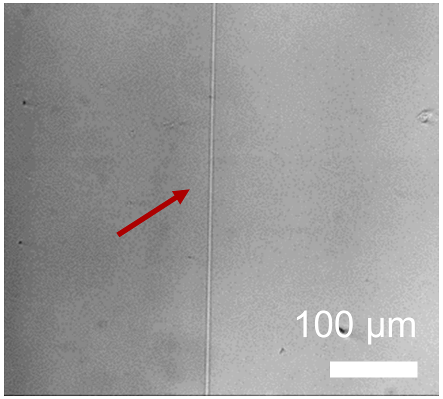


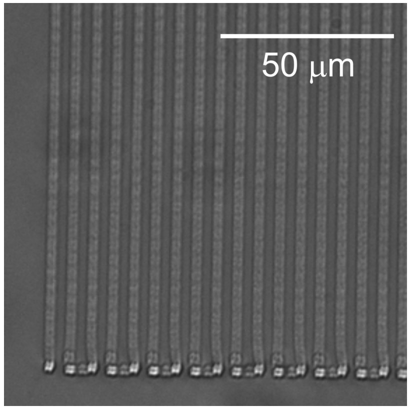




Embedded waveguides and gratings

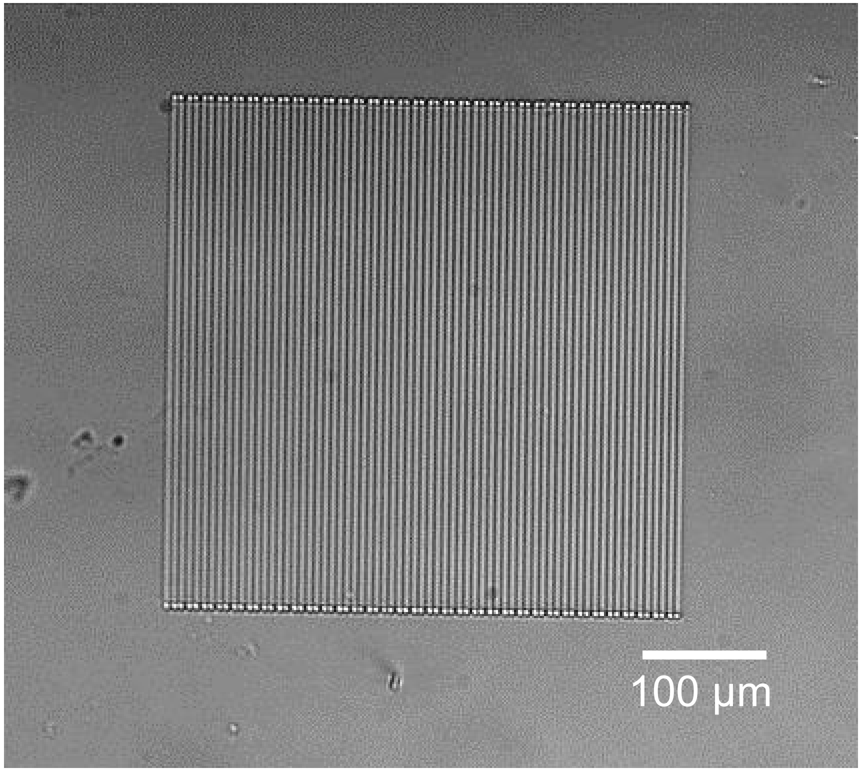


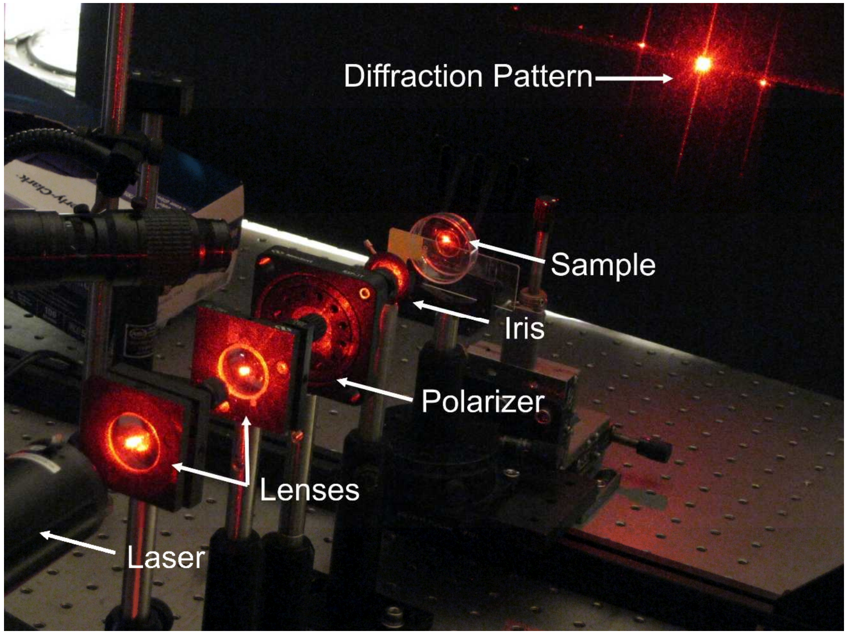


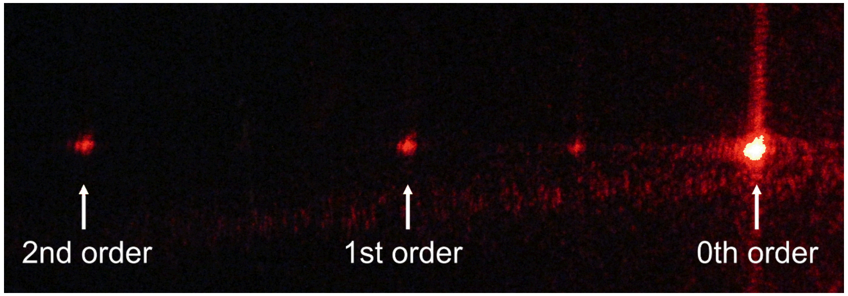


Optical properties were estimated from diffraction efficiency of the gratings

Quantify Δn and Δn/Δx







Optical properties were estimated from the diffraction efficiency of the gratings

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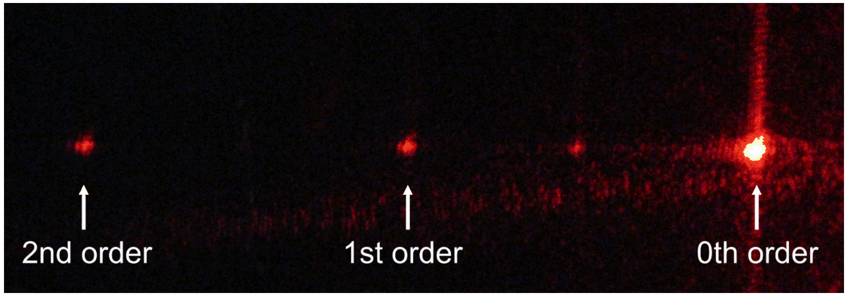

Index of refraction of given order:

$$\eta_l = (\pi \Delta n_l T / \lambda_o cos\theta_B)$$

Δn_l = index change of l order
η_l = efficiency of l order
T = grating thickness
θ_B = diffraction angle
λ = illuminating wavelength

Change of index distribution:

$$n(x) = \frac{1}{2}\sum_{l=1}^{m} \Delta n_l cos\left(\frac{2l\pi x}{\Lambda}\right)$$

Δn_l = index change of l order
l = order
x = spatial extent || grating
Λ = grating period
λ = illuminating wavelength

Kogelnik, H., Bell System Technical Journal, 1969. **48**(9): p. 2909
Toma, T., Y. et al., Optical Review, 2000. **7**(1): p. 14-17.

Extracted Δn of BSA gratings equivalent to laser densified glass

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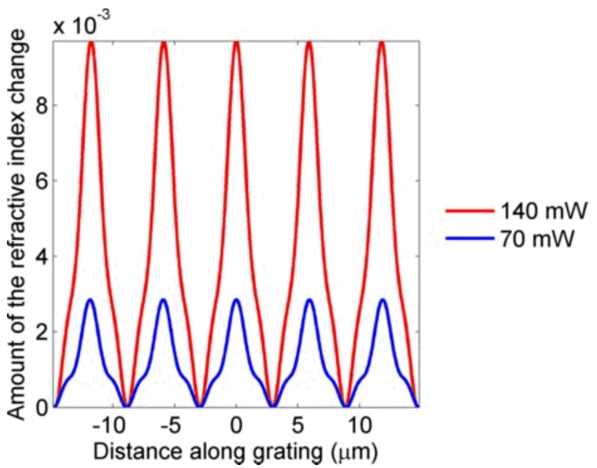
	Order	Diffraction efficiency	Refractive index change (x 10^{-3})
70 mW grating Λ = 5.93 μm	1	1.2 x 10^{-3}	2.34
	2	7.7 x 10^{-3}	0.58
	3	6.1 x 10^{-3}	0.50
140 mW grating Λ = 5.89 μm	1	1.6 x 10^{-3}	8.34
	2	6.6 x 10^{-3}	1.36
	3	4.6 x 10^{-3}	1.11



BSA system:

Δn @ 70 mW ~ 2.5 x 10^{-3}
Δn @ 140 mW ~ 1 x 10^{-2}

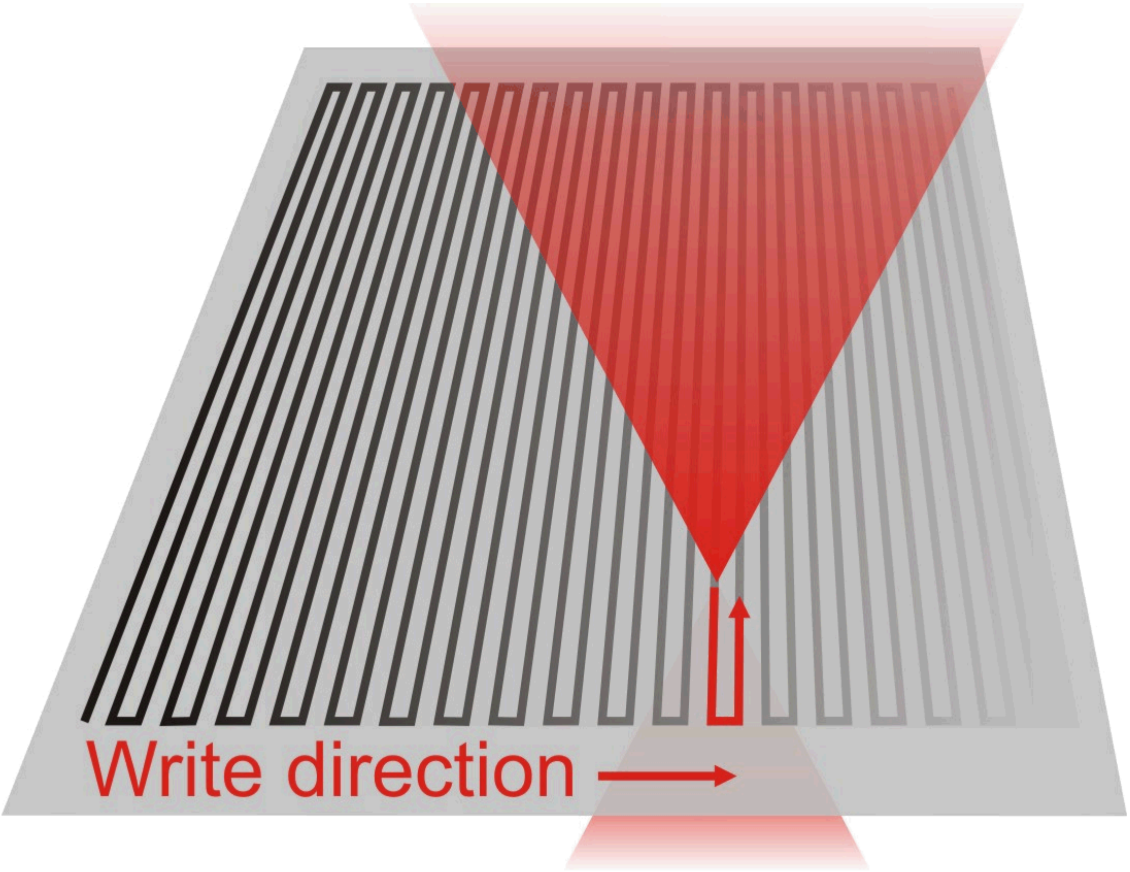
$\Delta n/\Delta x$ ~1.5 x 10^{-3}/μm

Other systems:

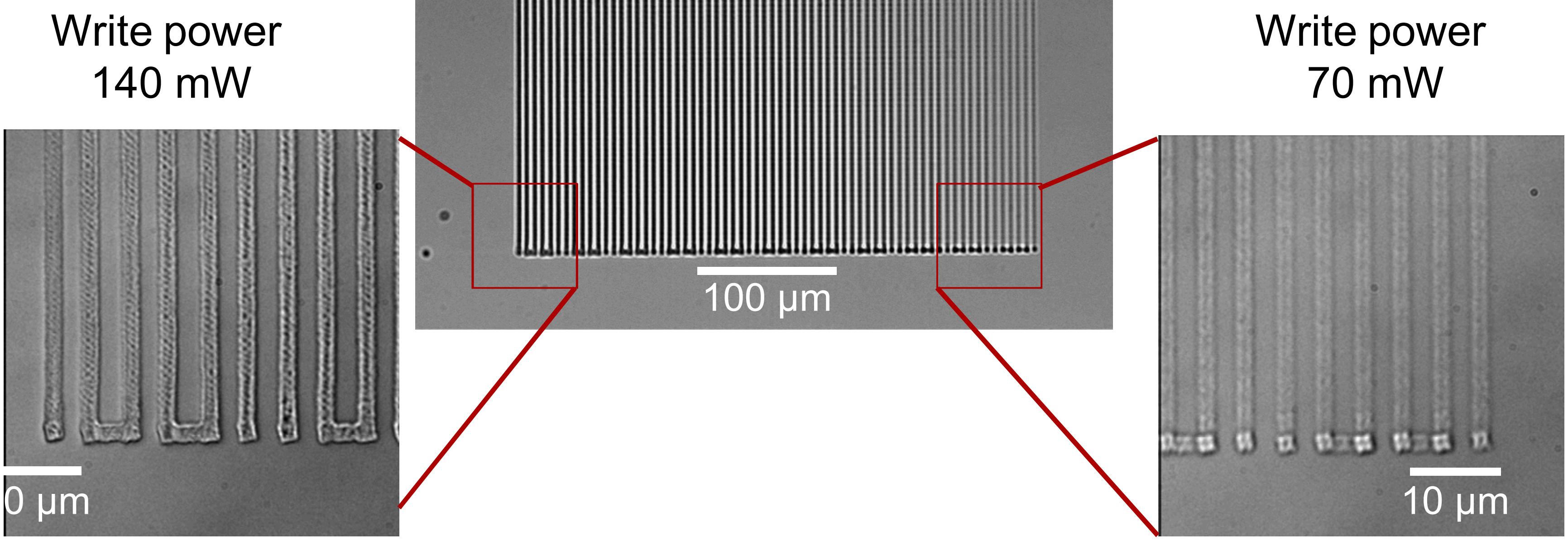
Laser densified glass ~1.5-10 x 10^{-3}
Other polymer systems ~ 1 x 10^{-2}

Varying the write power while writing structures yields graded materials

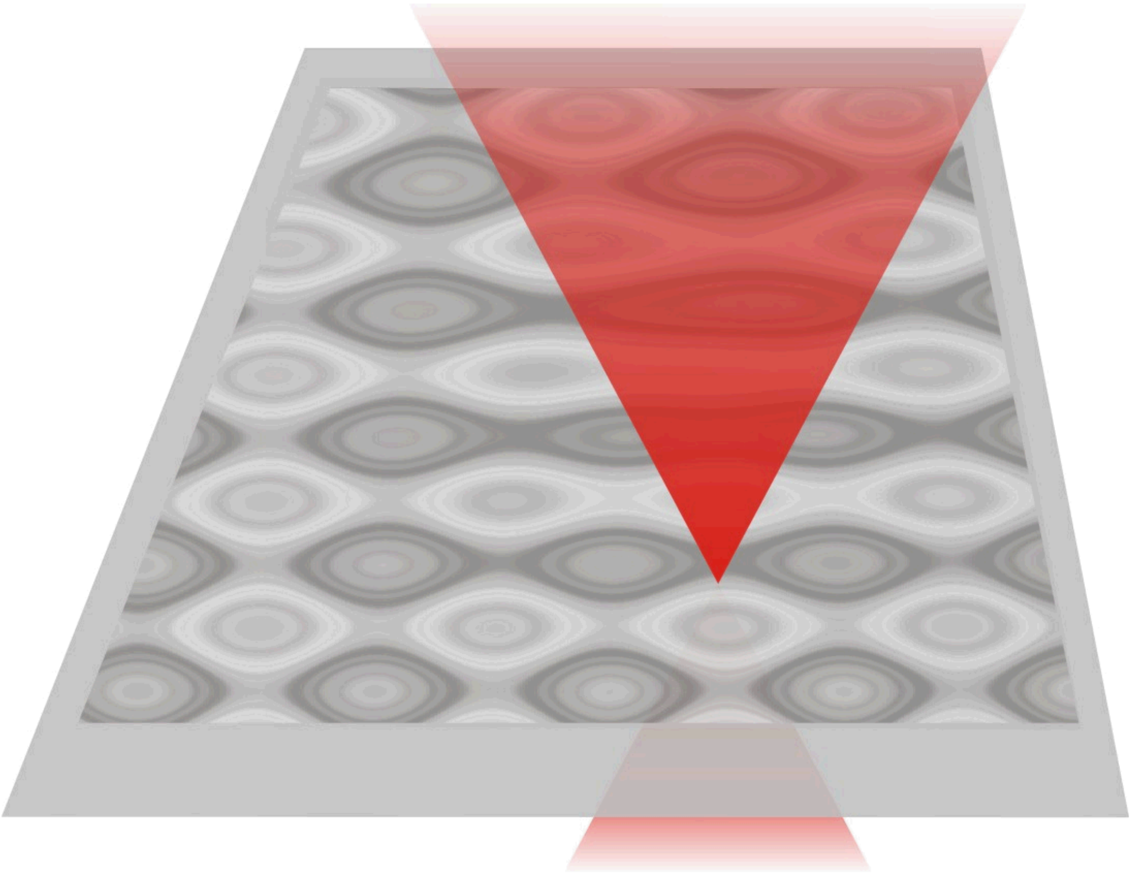
Beam power is continually varied from start of line creation to end



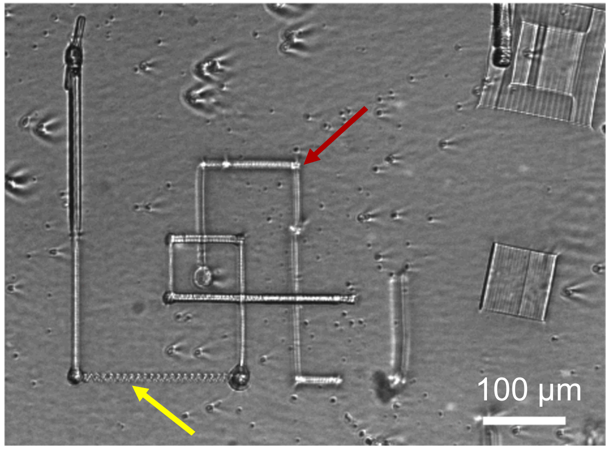
Varying the write power while creating structures yields graded materials



Arbitrary GRIN created by 3D raster and beam power control

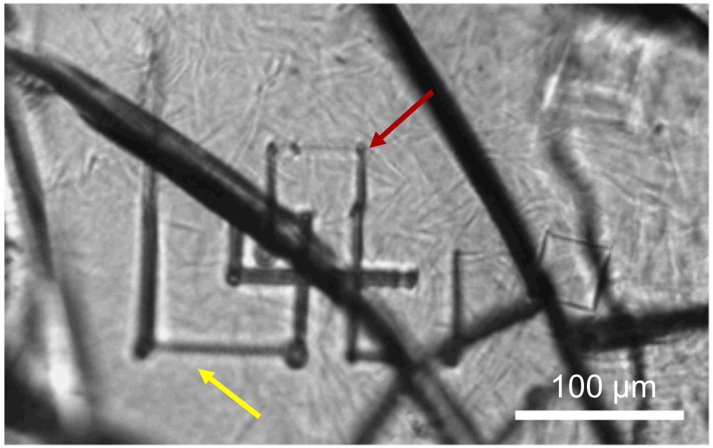


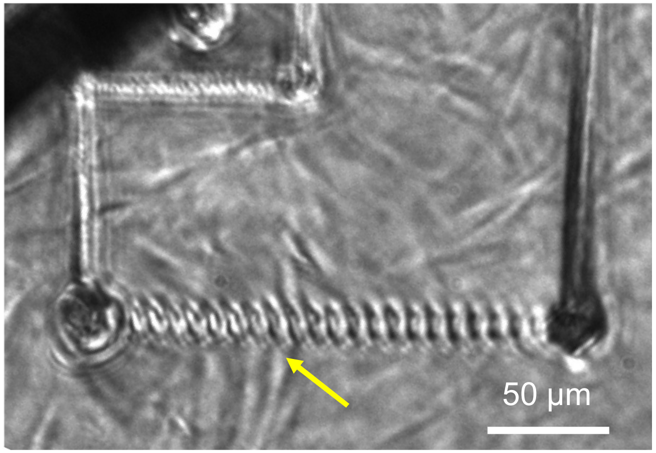
BSA structures were successfully converted to silica preserving write features



Silicification
Calcination

0.1 M silicic acid pH 3 (48 hours)
450°C (4 hours)

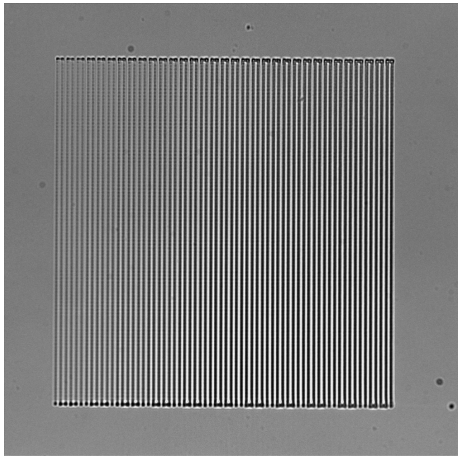




Process needs refinement, cracking a problem in converted structure

Bryan Kaehr et. Al. ACS Nano, 2011, 5 (2), pp 1401–1409

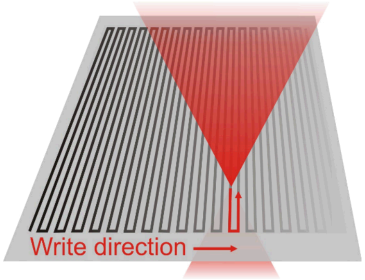
Conclusions/Future Work

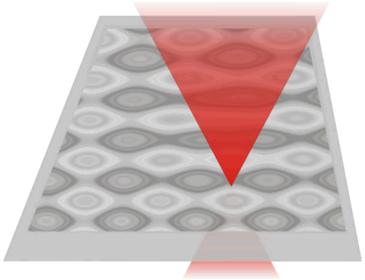


- Demonstrated GRIN materials in protein hydrogels
- Achieved a maximum index change of 1 x 10^{-2}
- Demonstrated chemical route to preserve structures in silica
- Path forward for arbitrary GRIN material fabrication

Future work:

- Residual stress/strain in structures
- Alternative MPL write materials
- Preserving written structures via conversion/replacement chemistries





The End