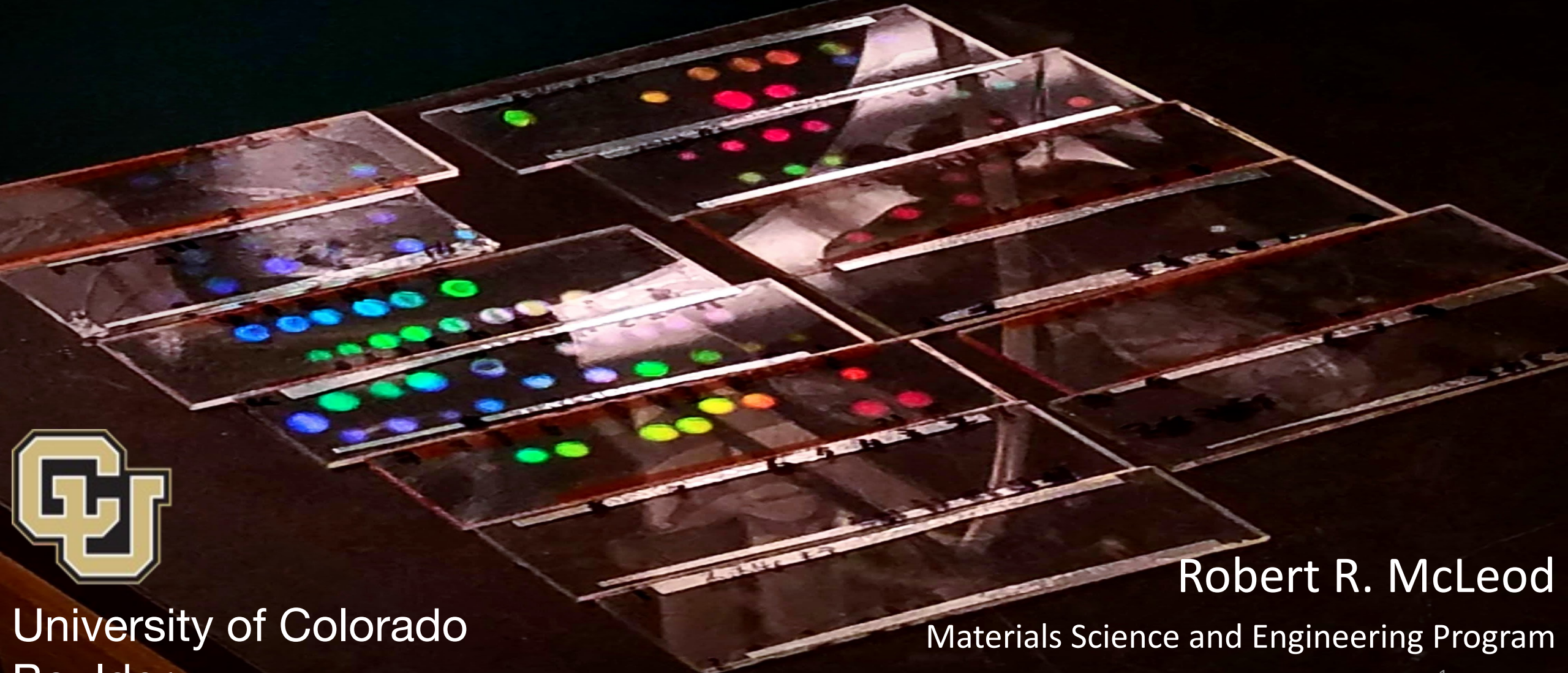


Materials and methods for creating 3D GRIN diffractive optics in photopolymers

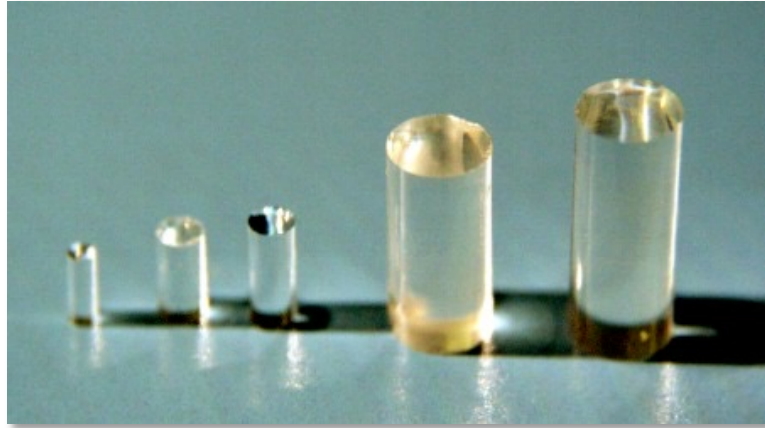


University of Colorado
Boulder

Robert R. McLeod

Materials Science and Engineering Program
Electrical, Computer and Energy Engineering Department

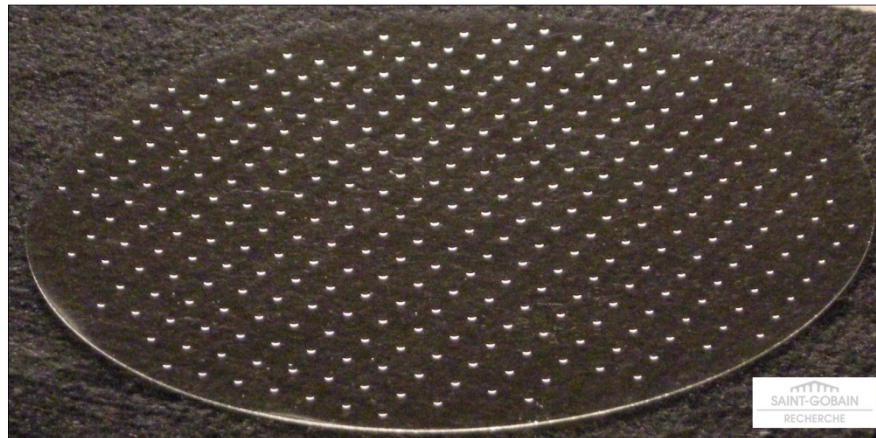
Traditional glass GRIN optics



http://www.acphotonics.com/products/product_files/GRIN%20Lens.htm

Disadvantages

- Limited profile control
- Expensive/heavy material
- Slow to fab at large scale
- Limited form-factors



<http://www.i-micronews.com/news/Saint-Gobain-Wafer-Level-planar-optics-Glass-substrate,3757.html>



<http://www.edmundoptics.com/optics/optical-lenses/aspheric-lenses/lightpath-gradium-lenses/2539>



Photopolymer diffractive optics

How to

- formulate
- understand
- expose



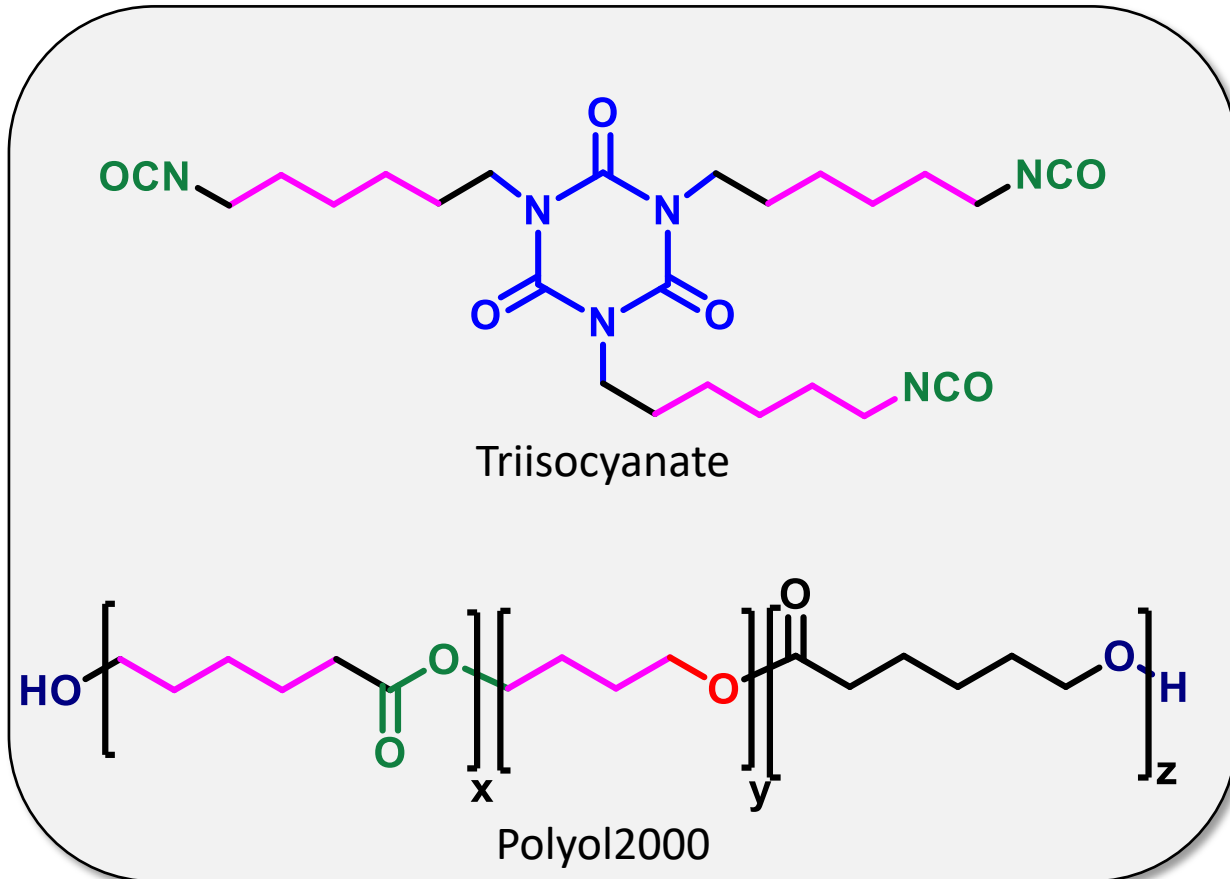
Photopolymer diffractive optics

How to

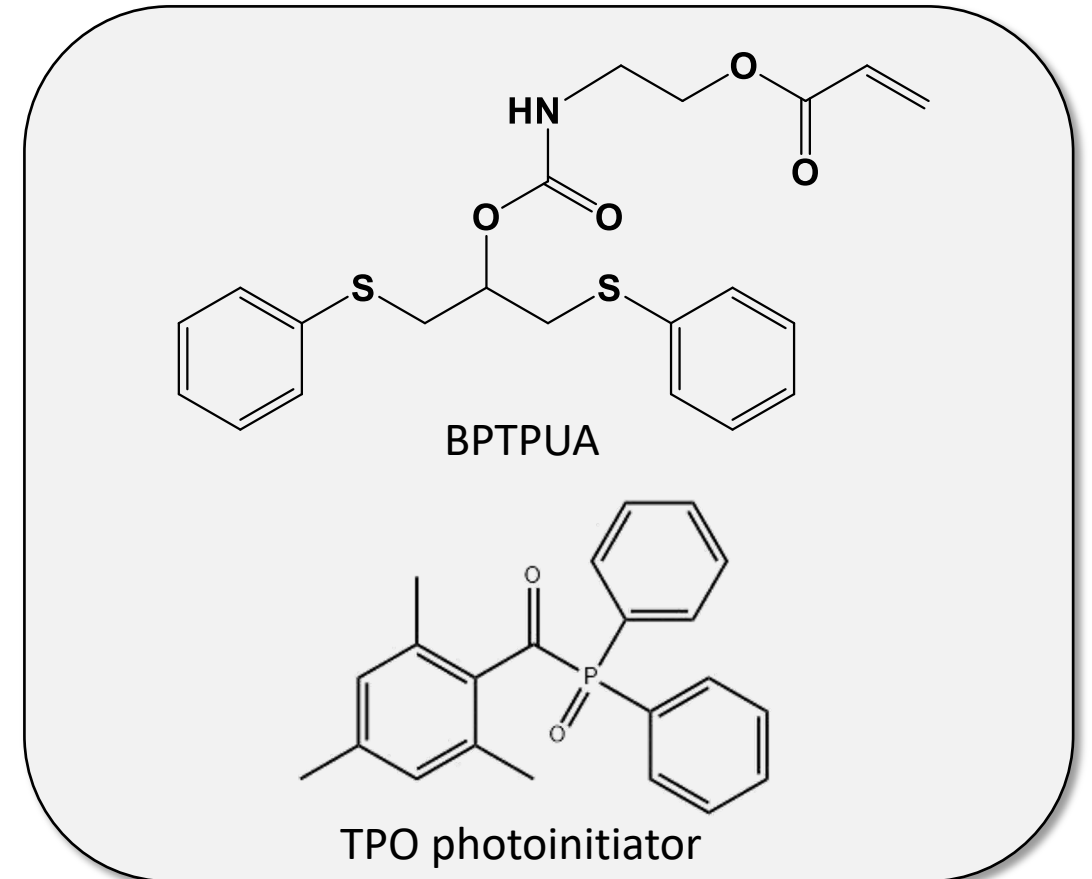
- formulate
- understand
- expose

Model material

Urethane Matrix



Acrylate Photopolymer



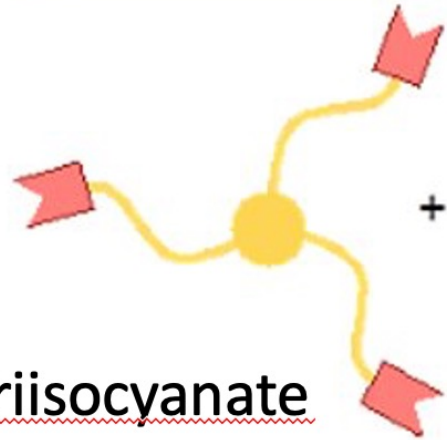
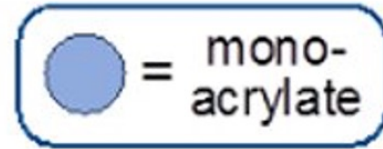
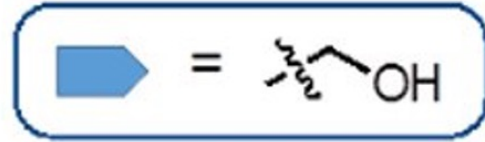
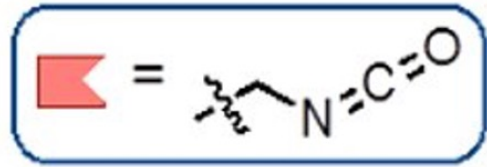
Materials scheme

First stage polymerization of the network

Urethane Matrix

+ Acrylate photopolymer

= Two-stage organogel

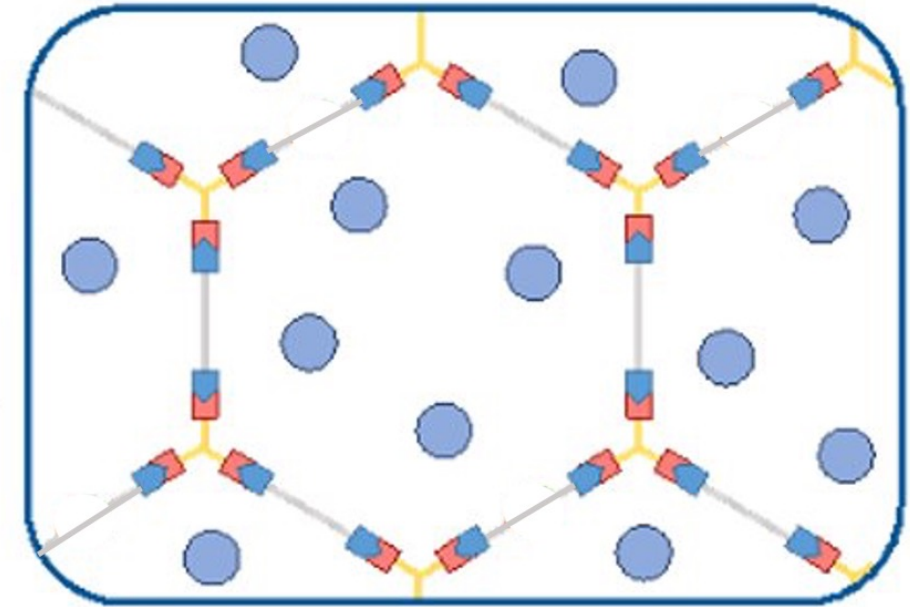


+



Polyol

TPO



1st stage: x-linked network swollen in acrylate

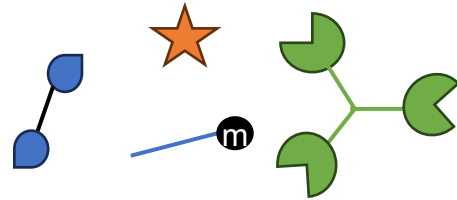
How to formulate

Key

- Monomer
- Photoinitiator
- Polyol
- Isocyanate

Step 1

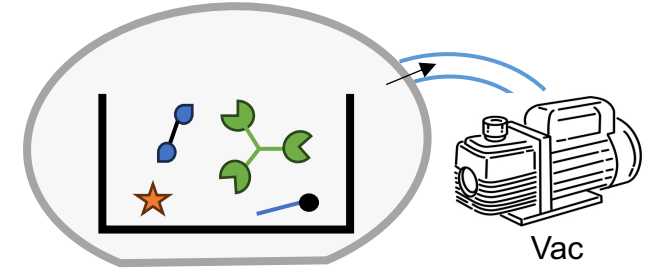
Mix Components:



Stir



Degas



How to formulate

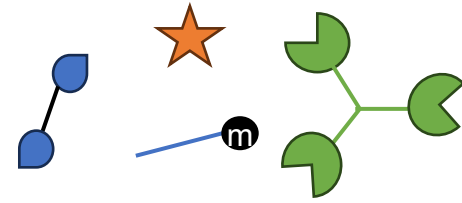
Key

- Monomer
- Photoinitiator
- Polyol
- Isocyanate

Step 1

Step 2

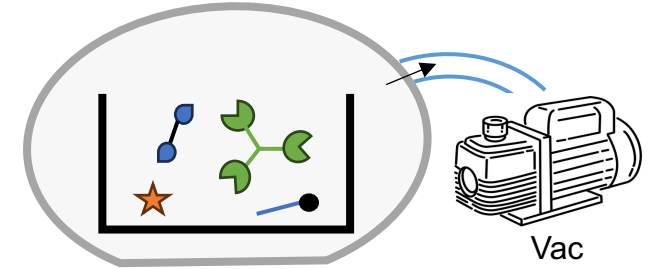
Mix Components:



Stir



Degas

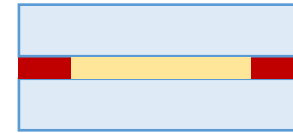


Cast Media:

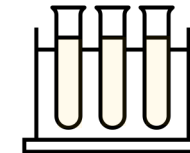
Planar Package



- Spacer
- Glass Slide



Cylindrical Package



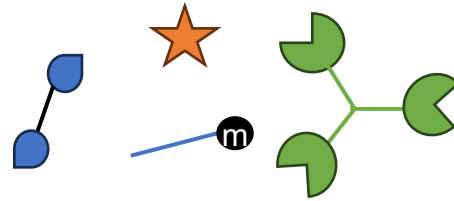
How to formulate

Key

- Monomer
- Photoinitiator
- Polyol
- Isocyanate

Step 1

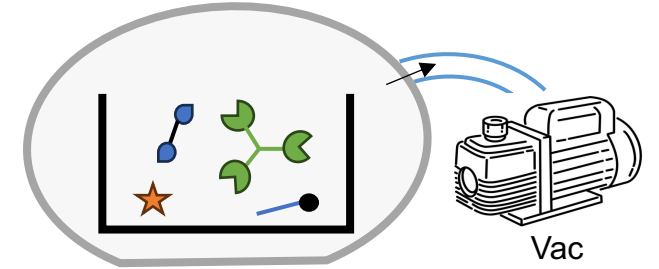
Mix Components:



Stir



Degas



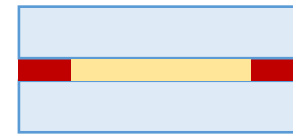
Step 2

Cast Media:

Planar Package



- Spacer
- Glass Slide



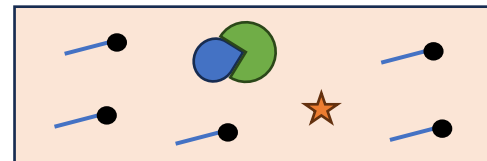
Cylindrical Package



Step 3

Stage 1 Cure:

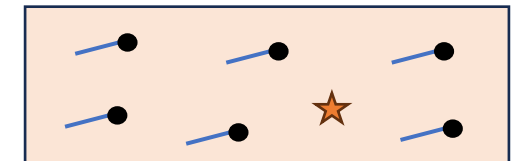
Polyol---Isocyanate



Thermal Cure
Or Tin Catalyst



Live Media





Photopolymer diffractive optics

How to

- formulate
- understand
- expose



Materials scheme

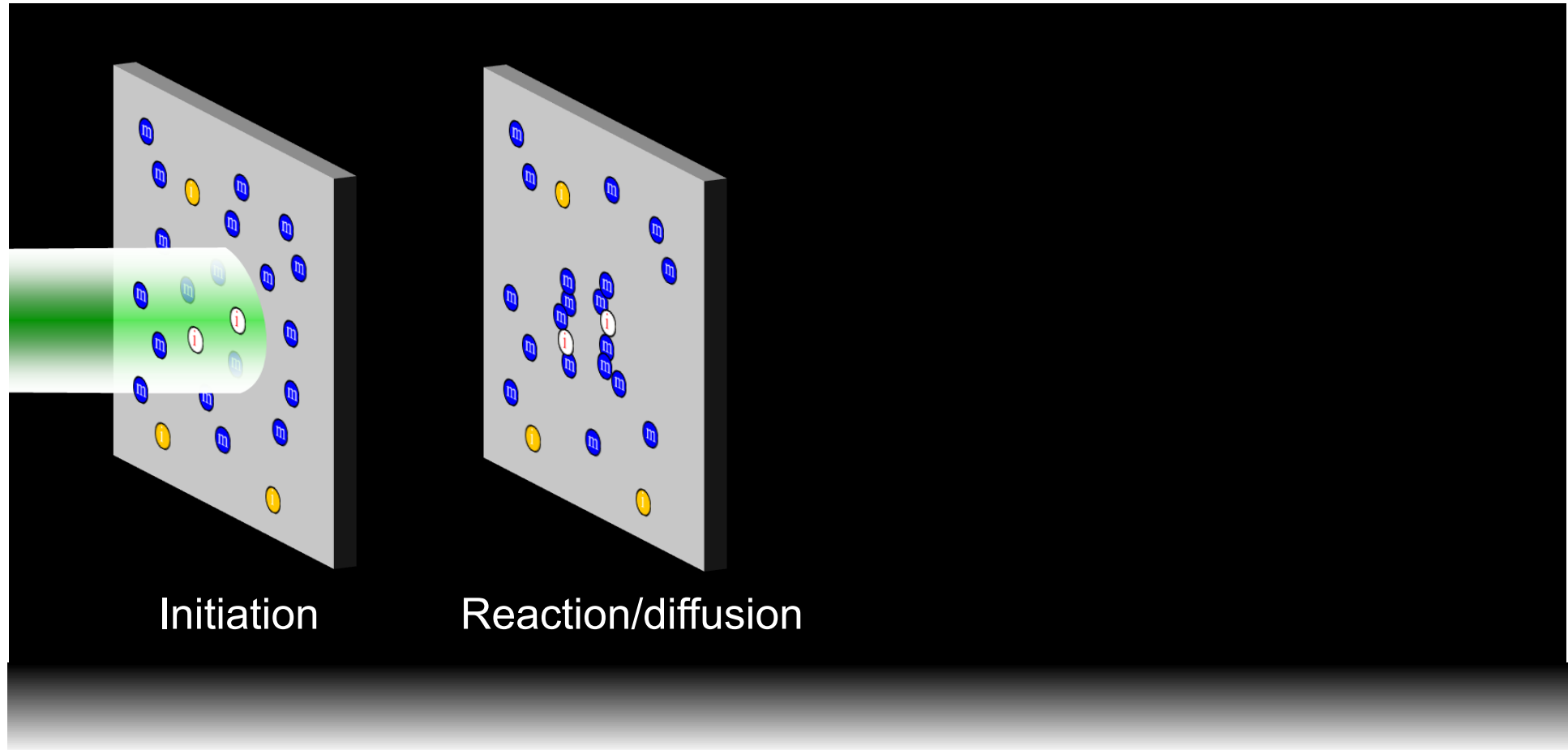
Second stage patterning of refractive index



Photons cleave initiator molecules, creating initiating radicals

Materials scheme

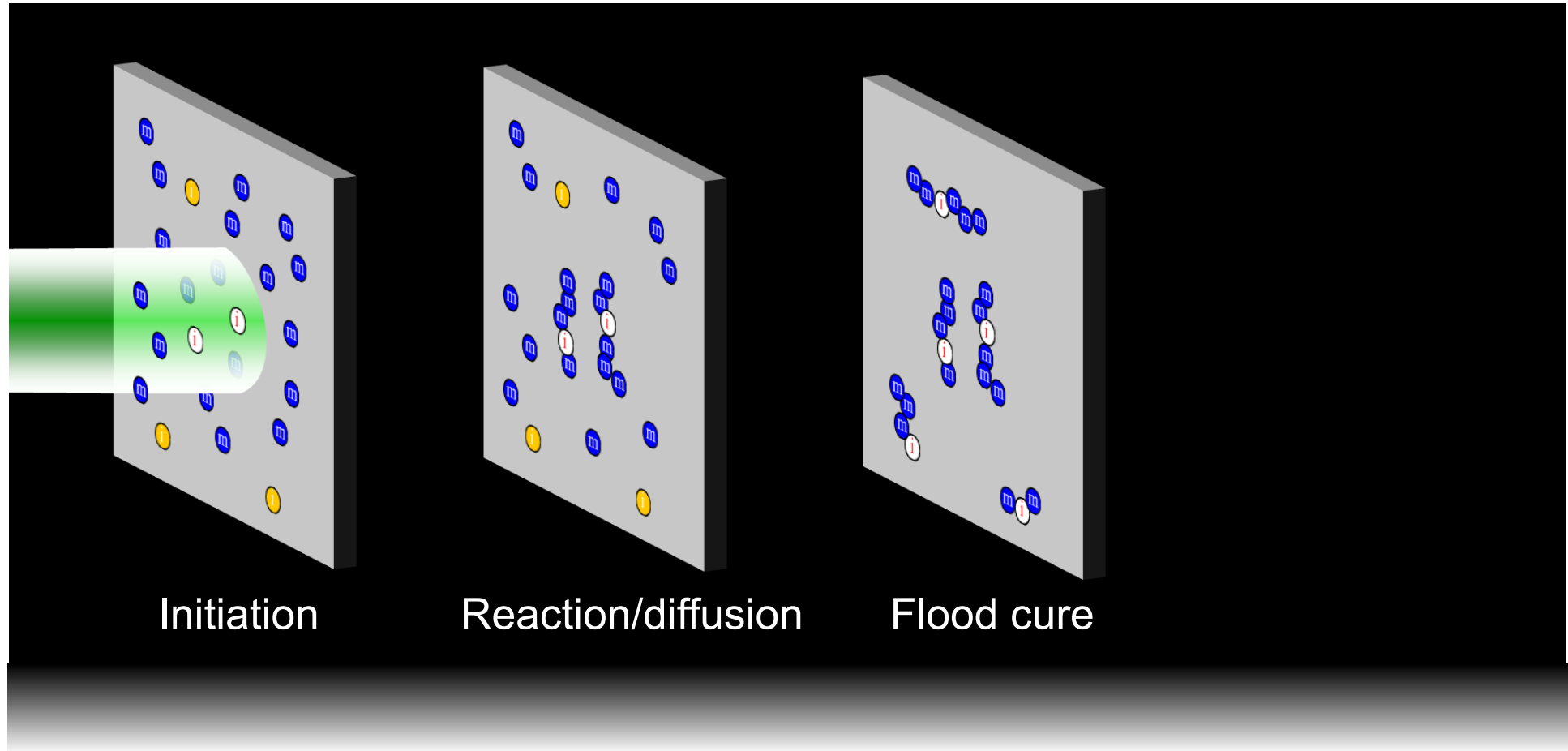
Second stage patterning of refractive index



Monomers undergo chain reaction, forming polymer.
Monomer diffuses into reaction region.

Materials scheme

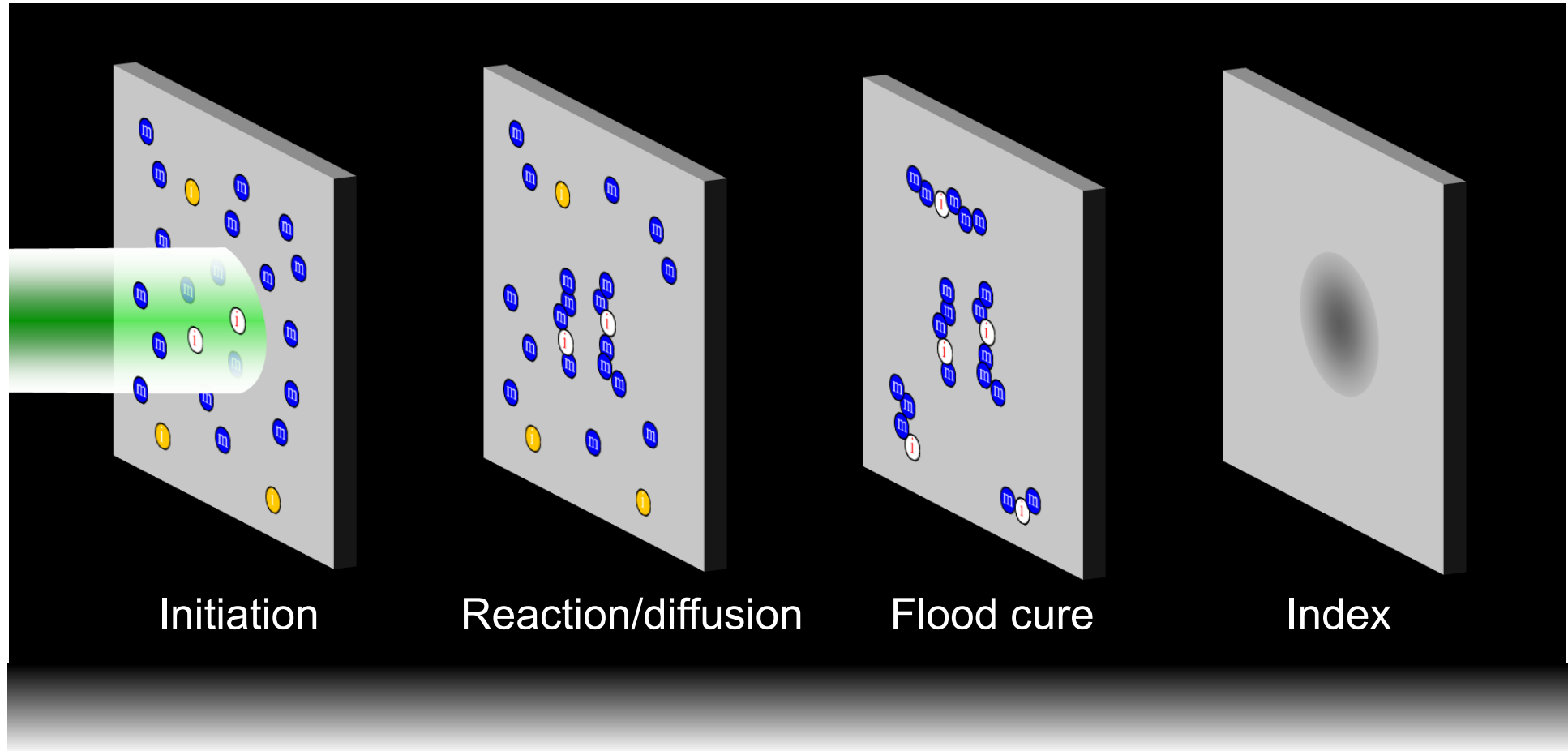
Second stage patterning of refractive index



An optical flood exposure consumes all initiator and monomer.

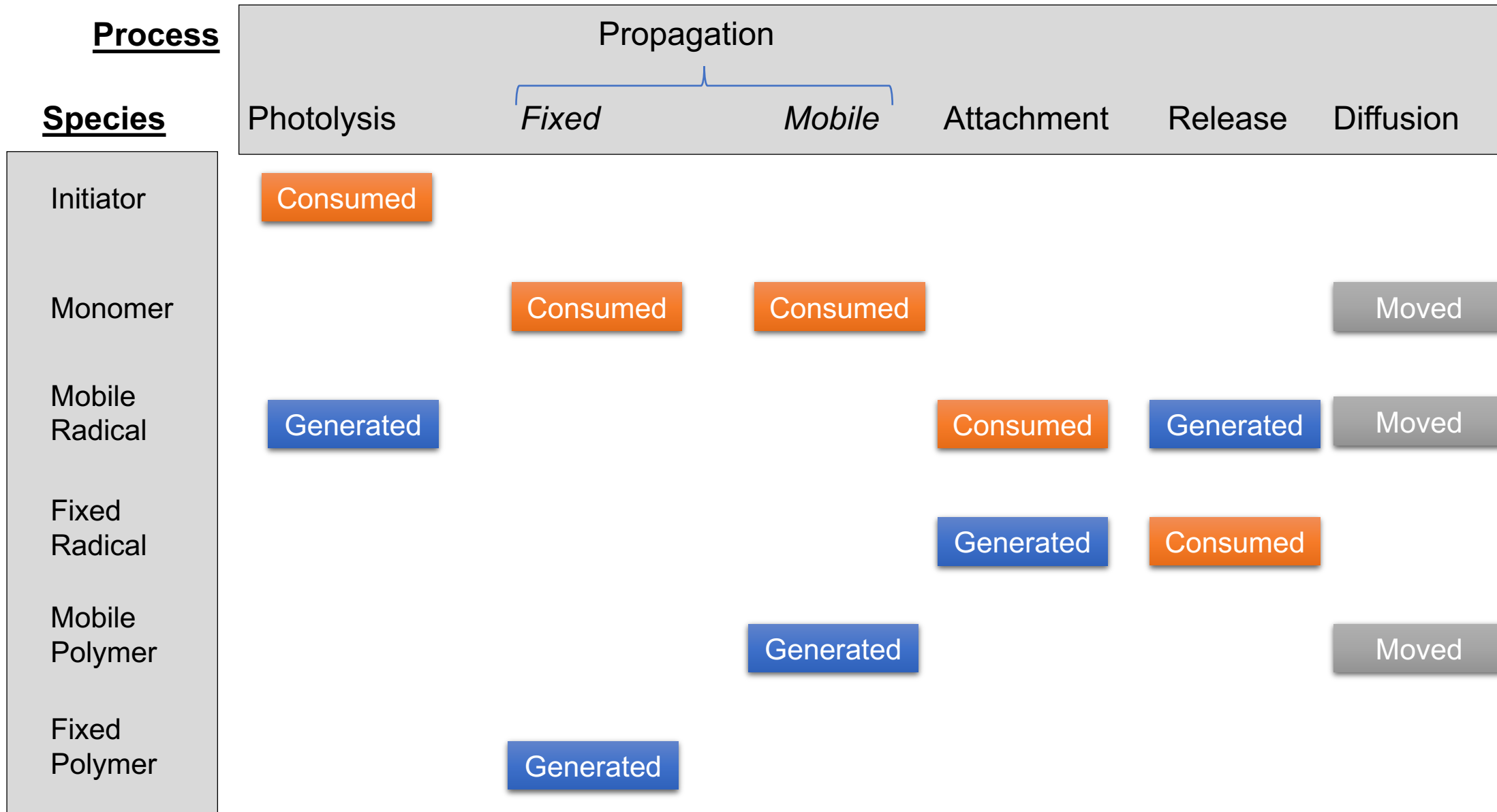
Materials scheme

Second stage patterning of refractive index



Refractive index change, δn , is roughly proportional to optical dose.

First order reaction/diffusion model



First order reaction/diffusion model



<u>Species</u>	<u>Process</u>					
	Photolysis	Propagation		Attachment	Release	Diffusion
		<i>Fixed</i>	<i>Mobile</i>			
$\frac{\partial}{\partial t} [PI]$	$= -K_d I(\vec{r}) [PI]$					
$\frac{\partial}{\partial t} [M]$		$-K_p [R_{fix}] [M]$	$-K_p [R_{mob}] [M]$			$+D\nabla^2 [M]$
$\frac{\partial}{\partial t} [R_{mob}]$	$= 2\epsilon K_d I(\vec{r}) [PI]$			$-K_a [R_{mob}]$	$+K_{ct} [R_{fix}]$	$+D\nabla^2 [R_{mob}]$
$\frac{\partial}{\partial t} [R_{fix}]$				$+K_a [R_{mob}]$	$-K_{ct} [R_{fix}]$	
$\frac{\partial}{\partial t} [P_{mob}]$			$+K_p [M] [R_{mob}]$			$+D\nabla^2 [P_{mob}]$
$\frac{\partial}{\partial t} [P_{fix}]$		$+K_p [M] [R_{fix}]$				

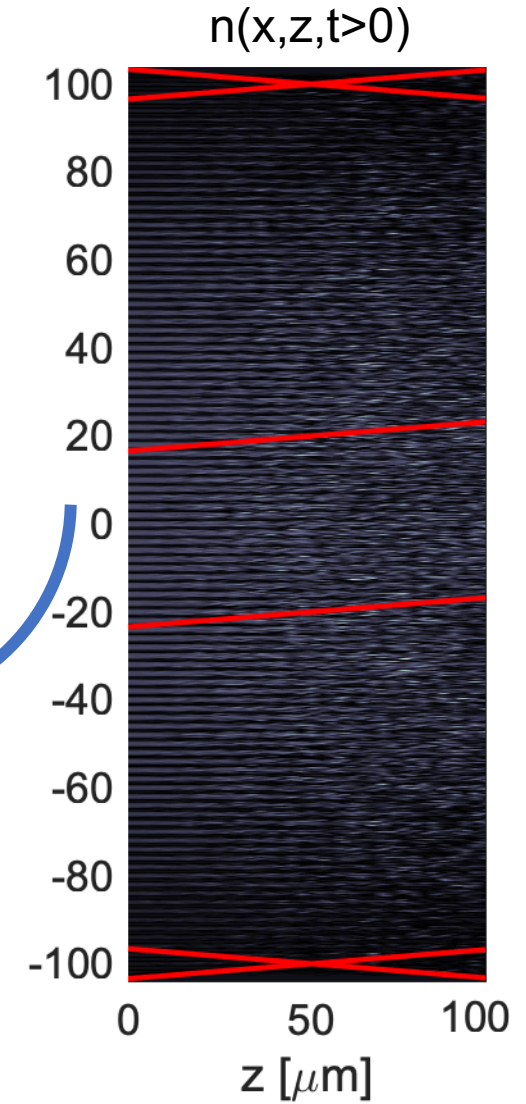
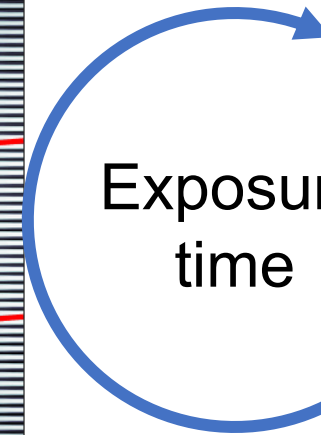
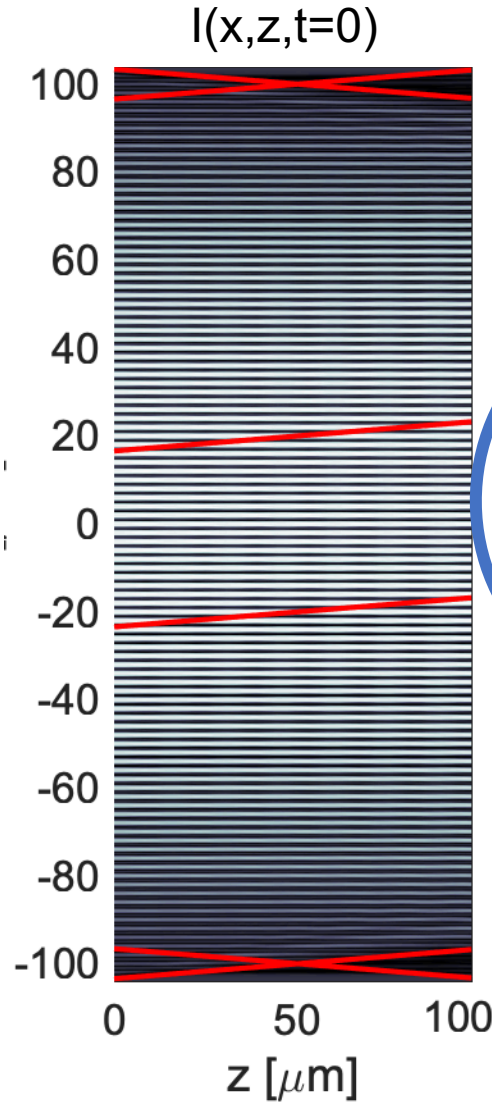
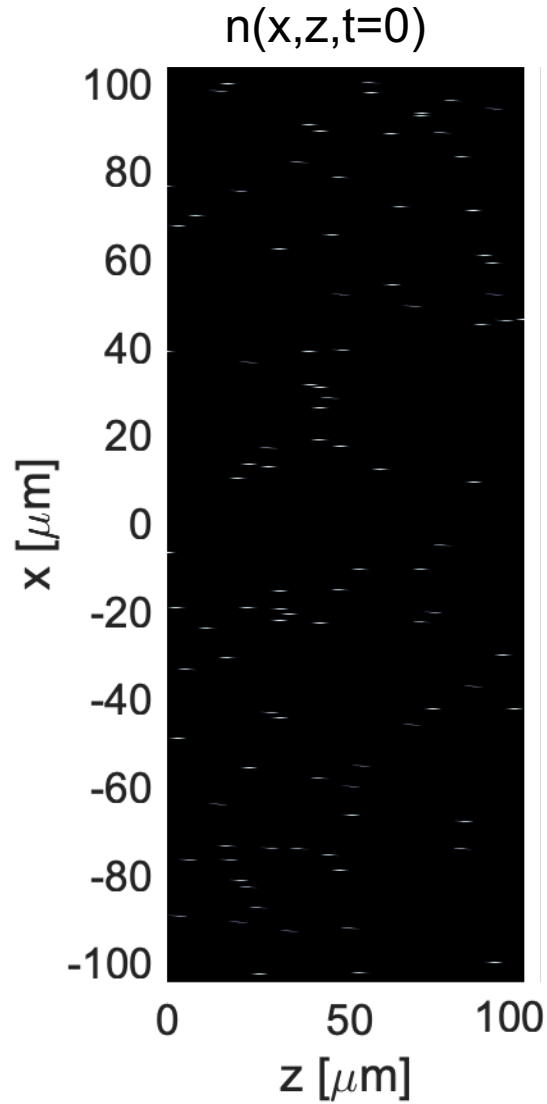
How to solve these equations numerically



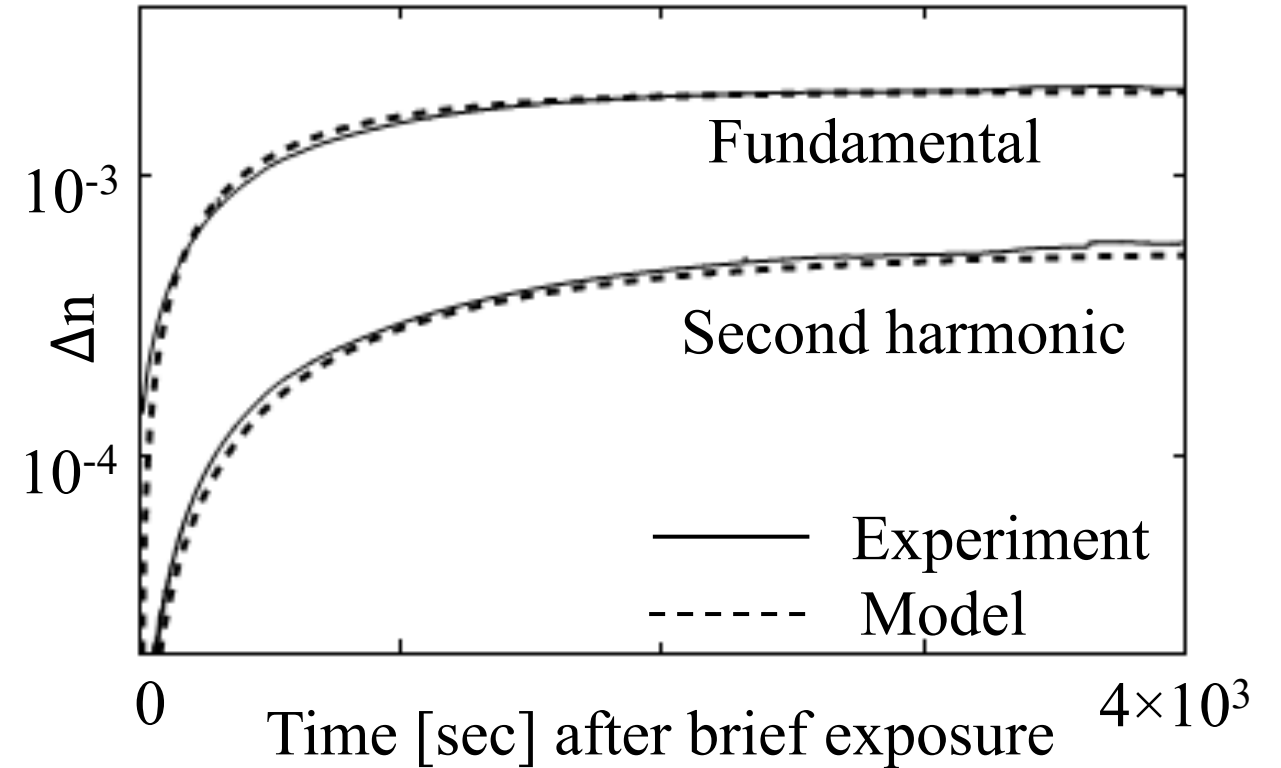
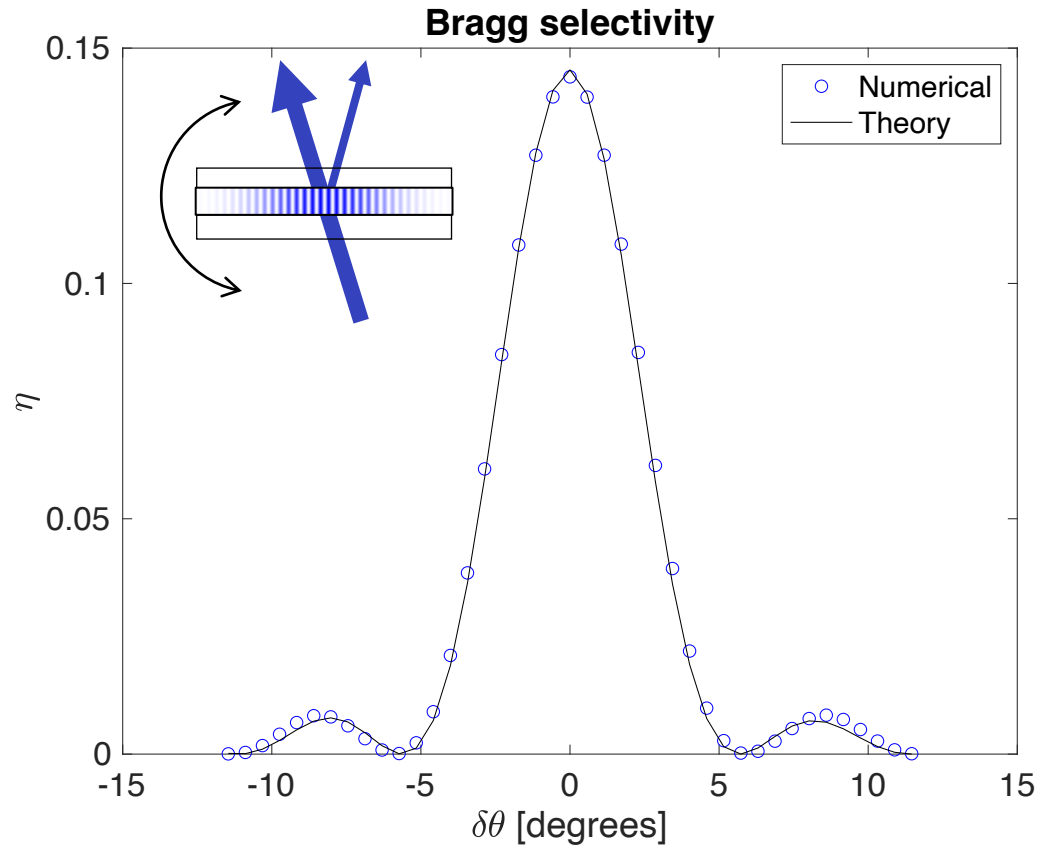
Initial scatter

Diffract

React, diffuse, develop n



Results: Comparison to theory and experiment

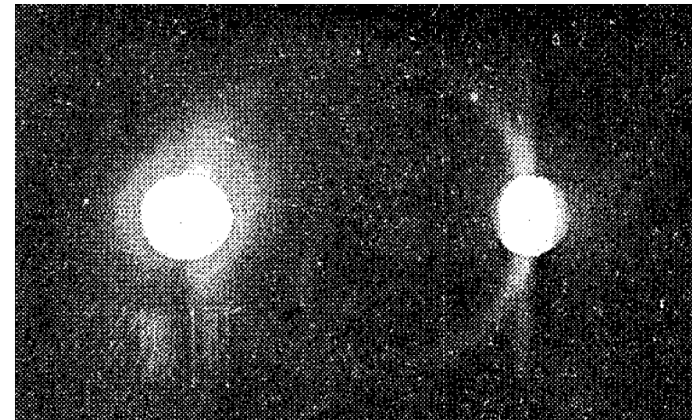
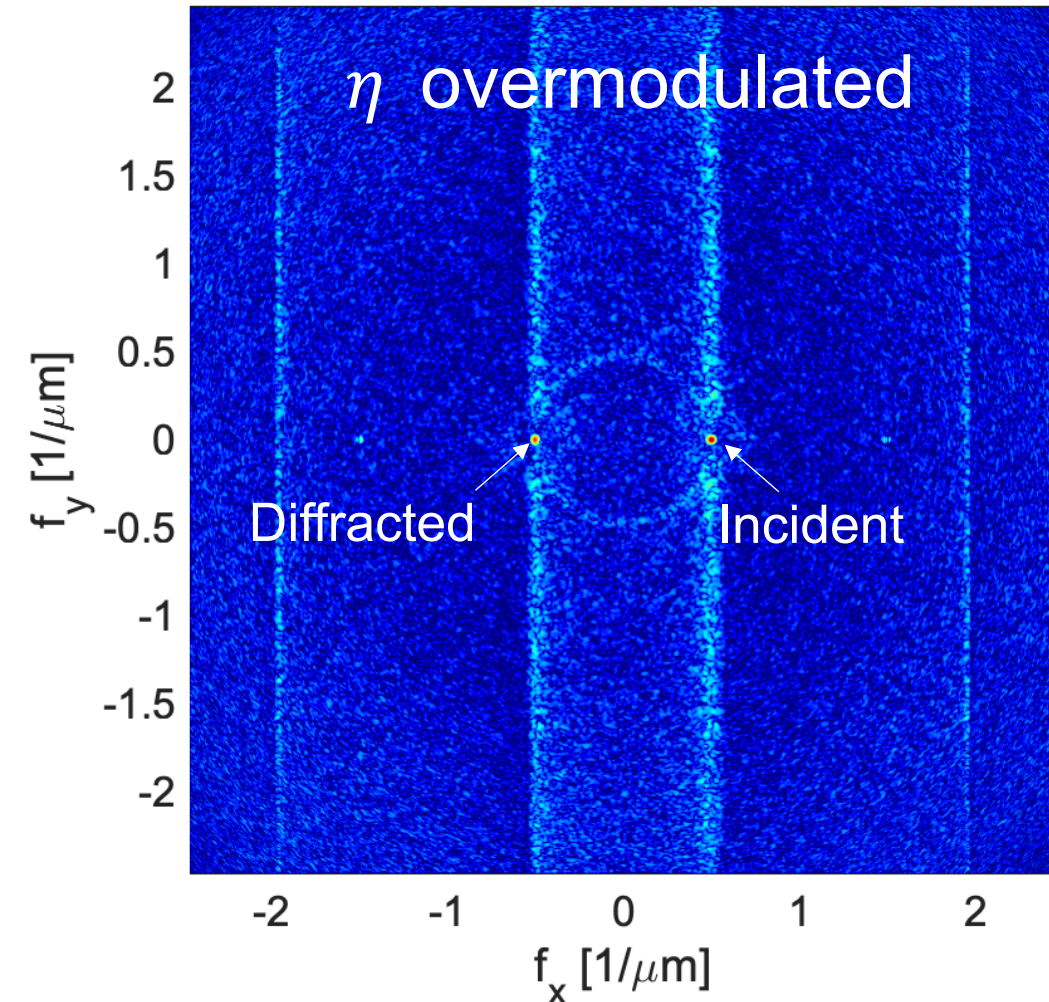


- B. A. Kowalski, A. C. Urness, M-E. Baylor, M. C. Cole, W. L. Wilson, R. R. McLeod, "Quantitative modeling of the reaction/diffusion kinetics of two-component diffusive photopolymers," *Optics Materials Express* 4, pp. 1668-1682, 2014.
- McLeod, R.R., "Numerical Technique for Study of Noise Grating Dynamics in Holographic Photopolymers," *Polymers* 2020, 2744, 2020.

Results: Haze prediction

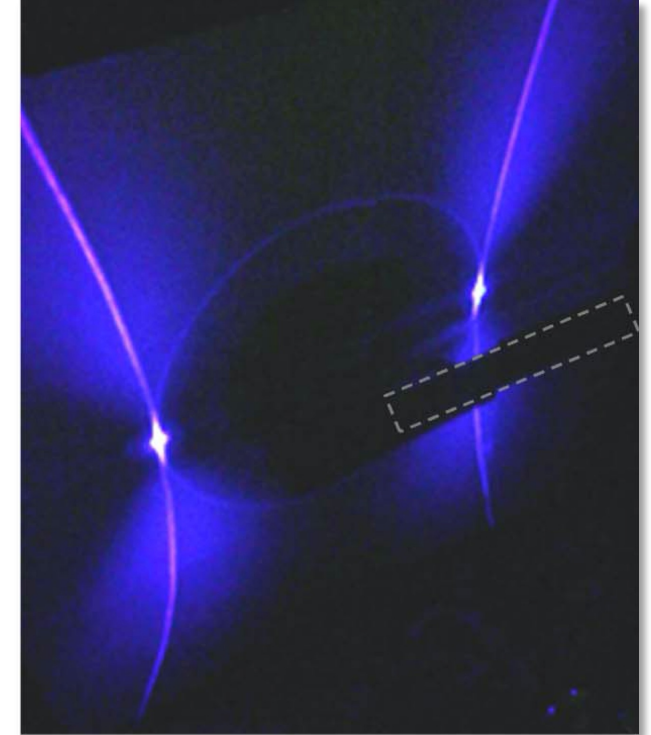
Numerical model

Observations in the literature



Scattering phenomena in volume holograms with strong coupling

Sven Ingmar Ragnarsson



Research Article Vol. 57, No. 3 / January 20 2018 / Applied Optics 827

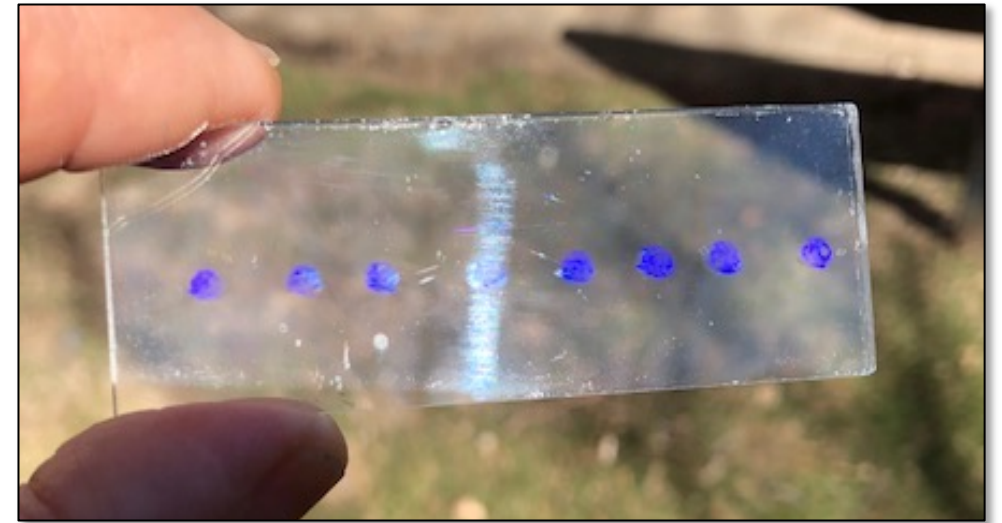
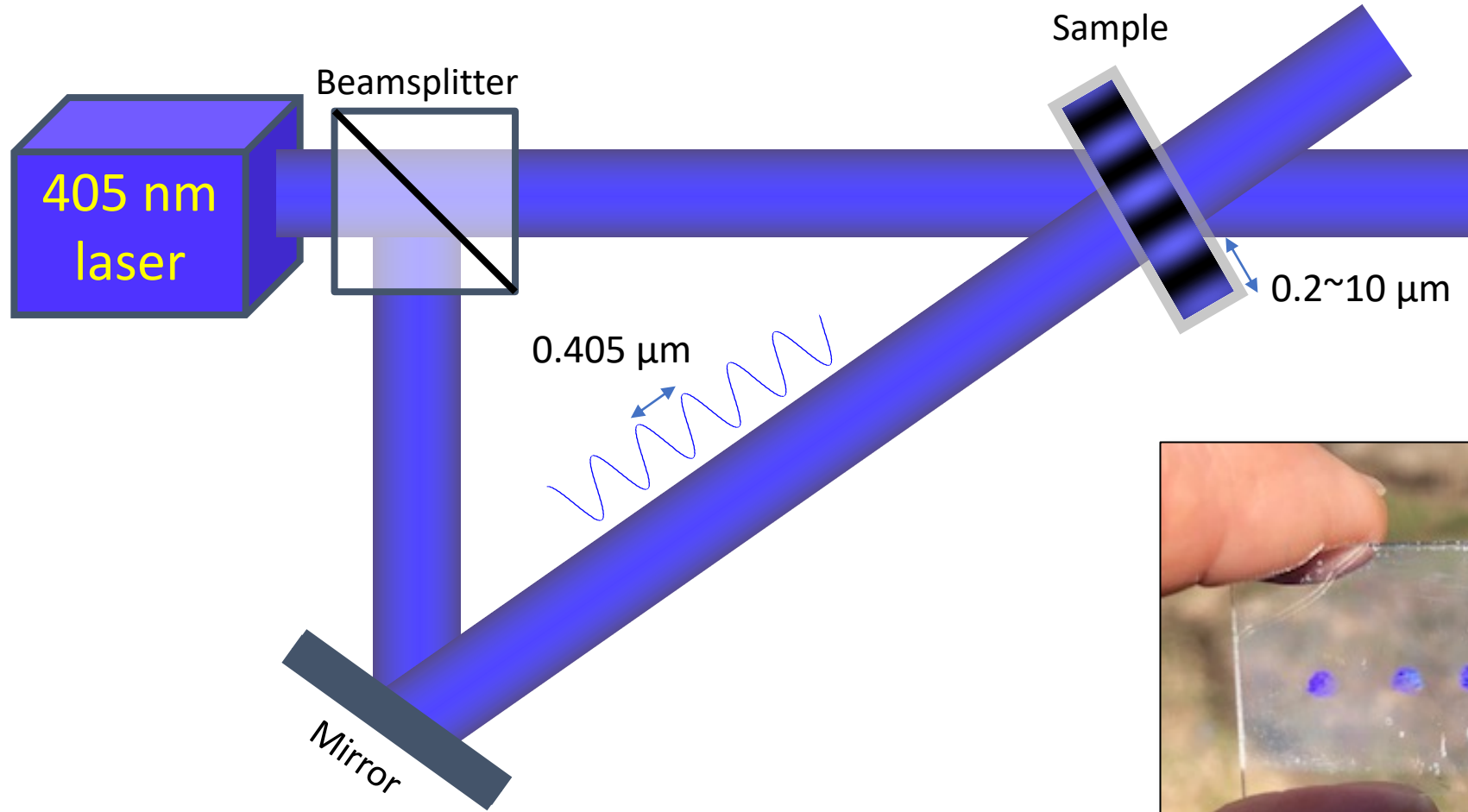
applied optics

Holographic scattering in an angular-multiplexed hologram on a photopolymer

TAKERU UTSUGI
Hitachi-LG Data Storage, Inc., 292, Yoshida-cho, Totsuka-ku, Tokohama-shi, Kanagawa-ken 244-0817, Japan (takeru.utsugi.qb@hitachi.com)

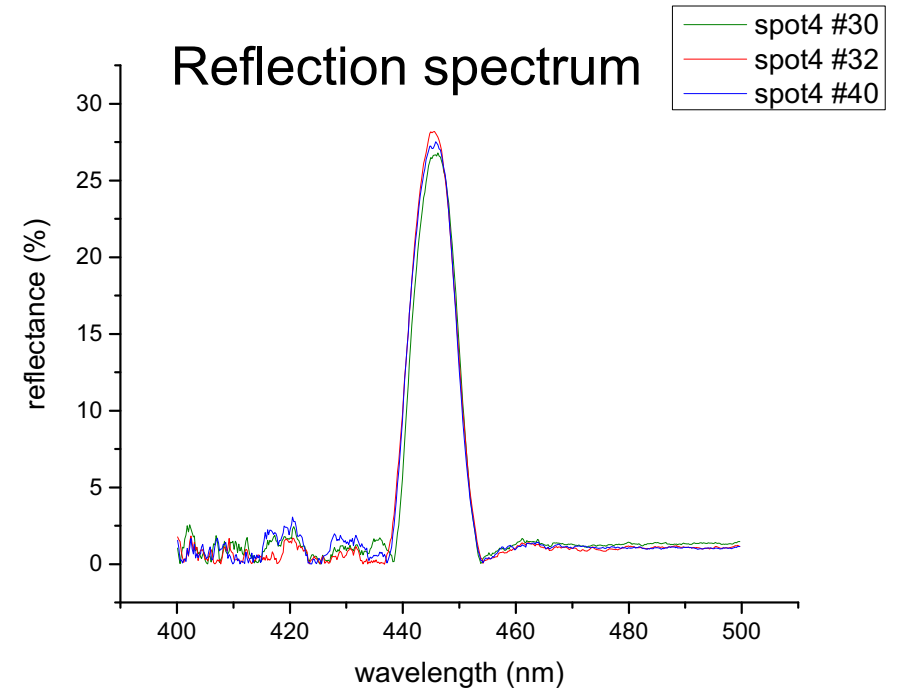
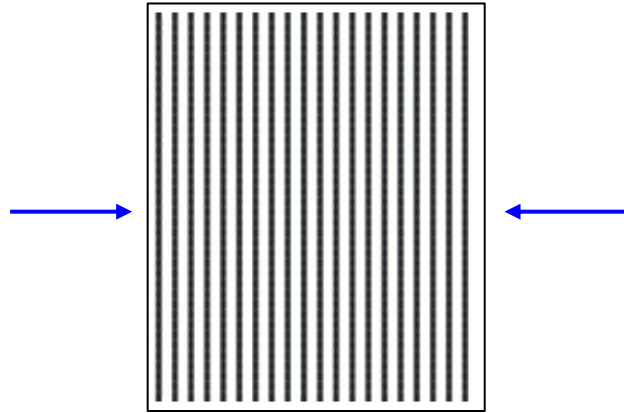
How to write a diffractive optical element

Two beam interference aka holography



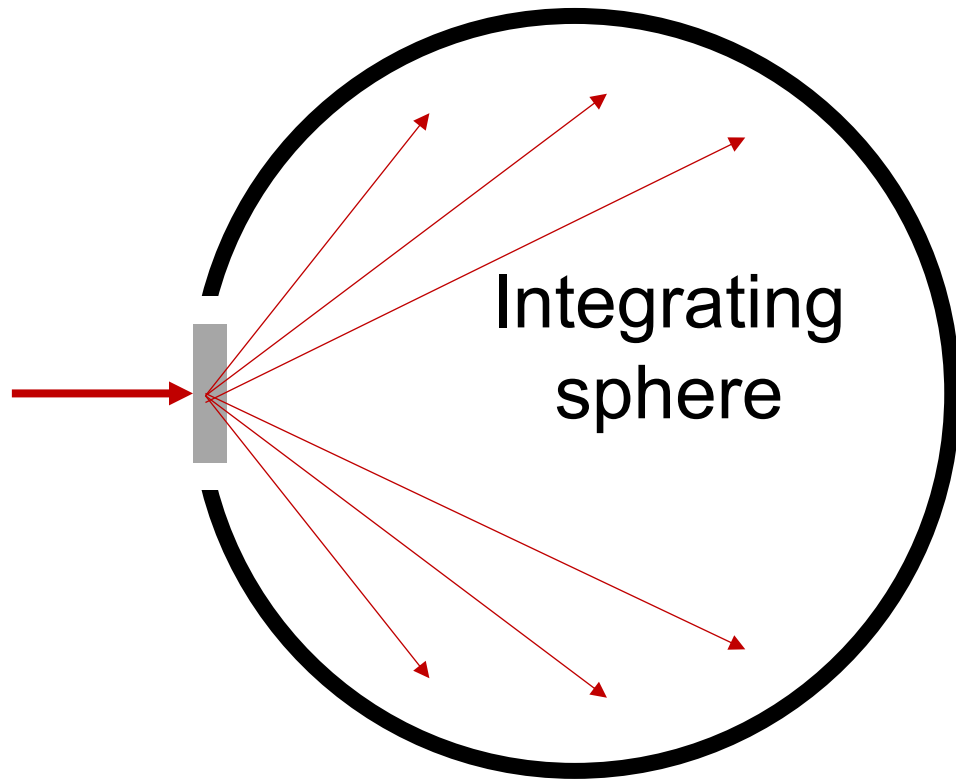
Typical results

100-300 nm pitch standing wave

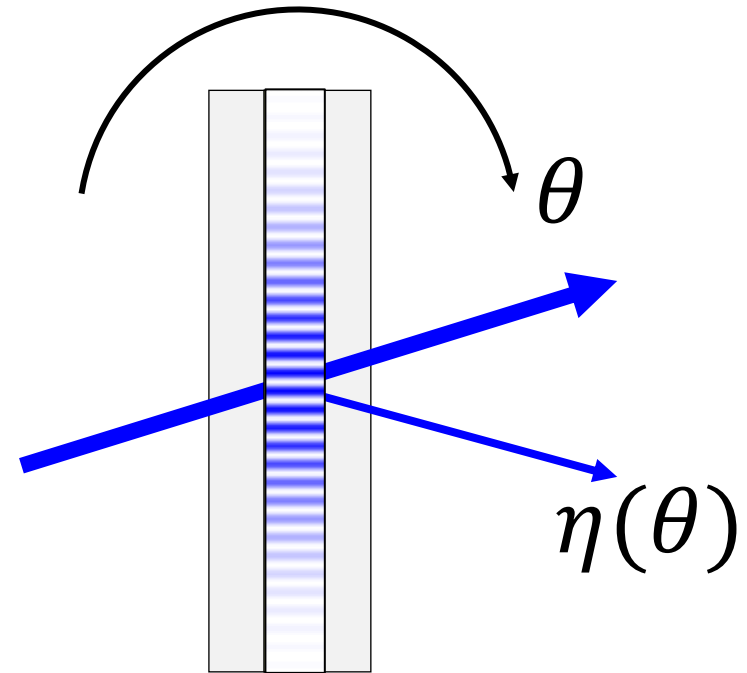


How to characterize a DOE

Haze



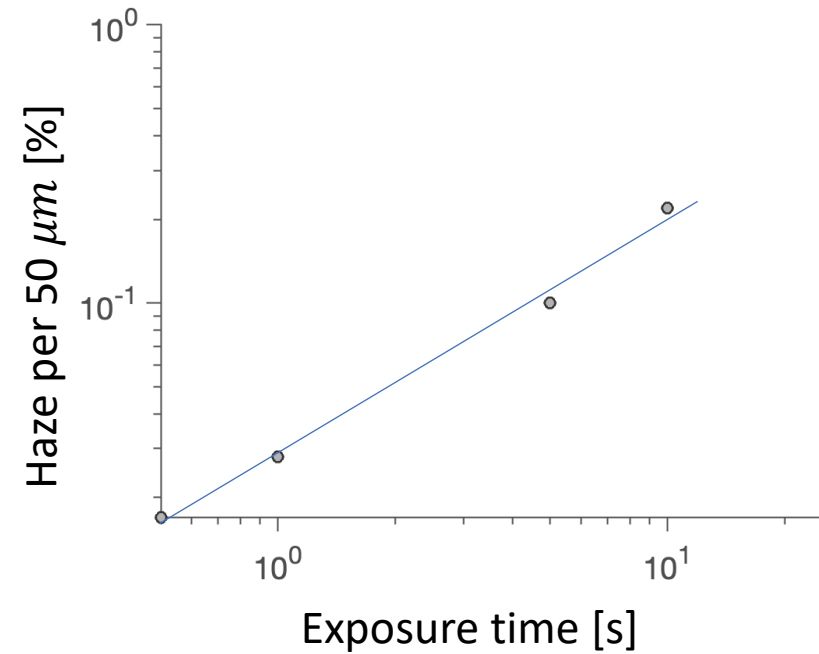
Bragg selectivity



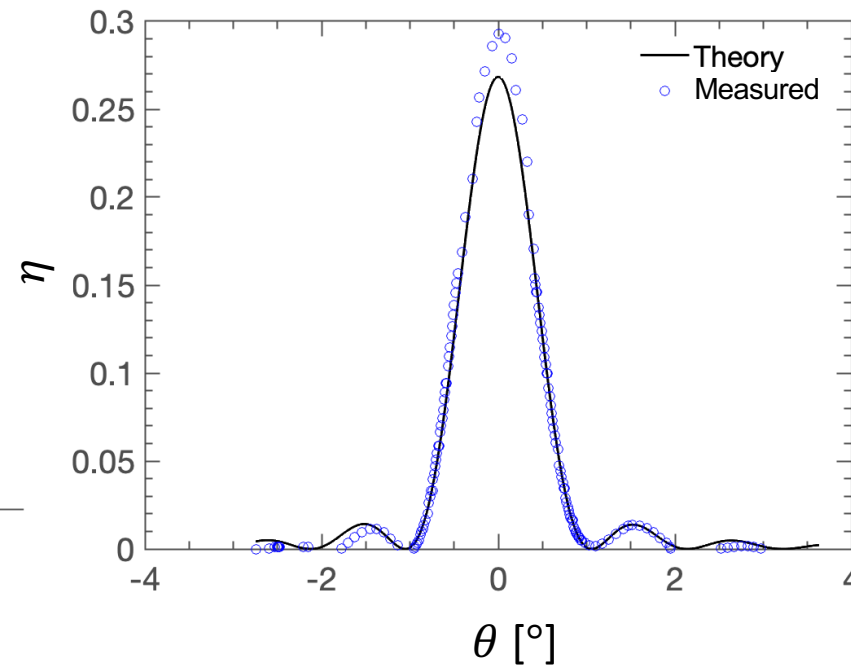


Typical results

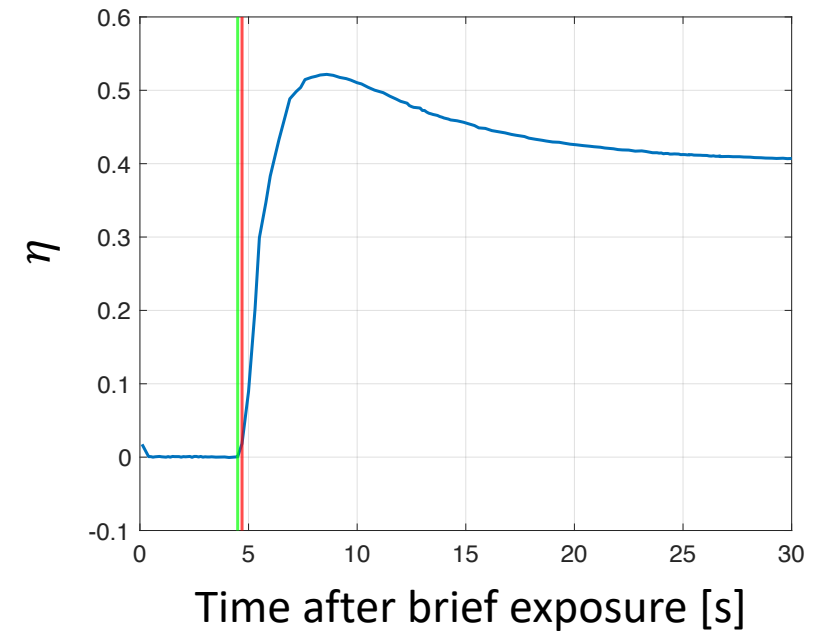
Haze



Bragg selectivity

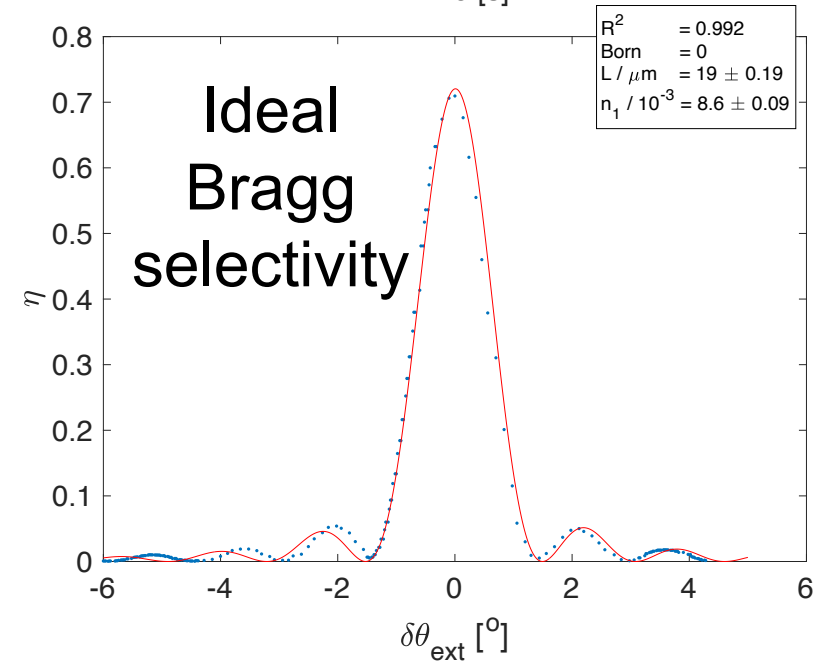
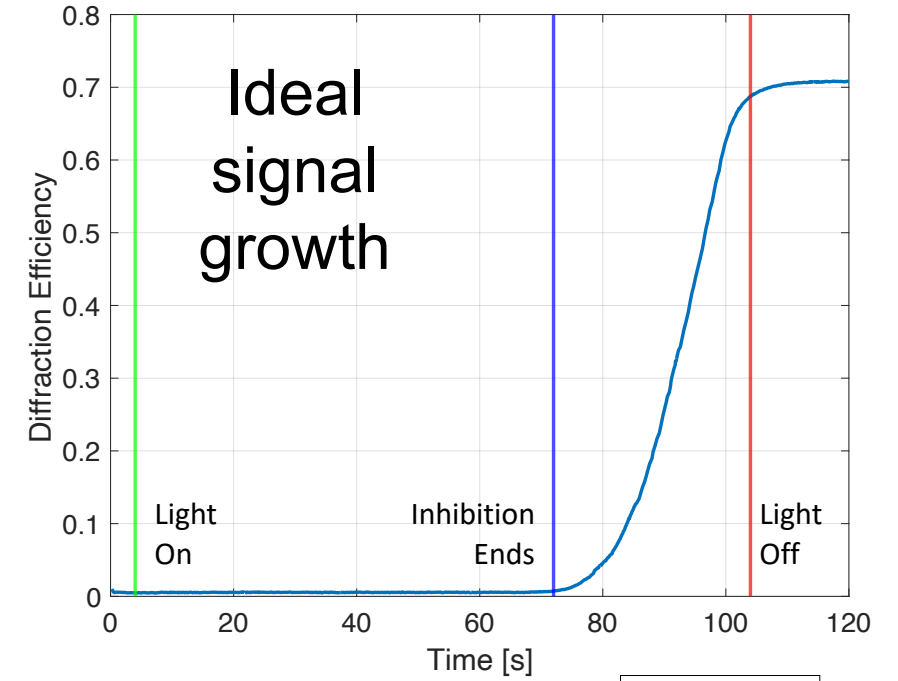
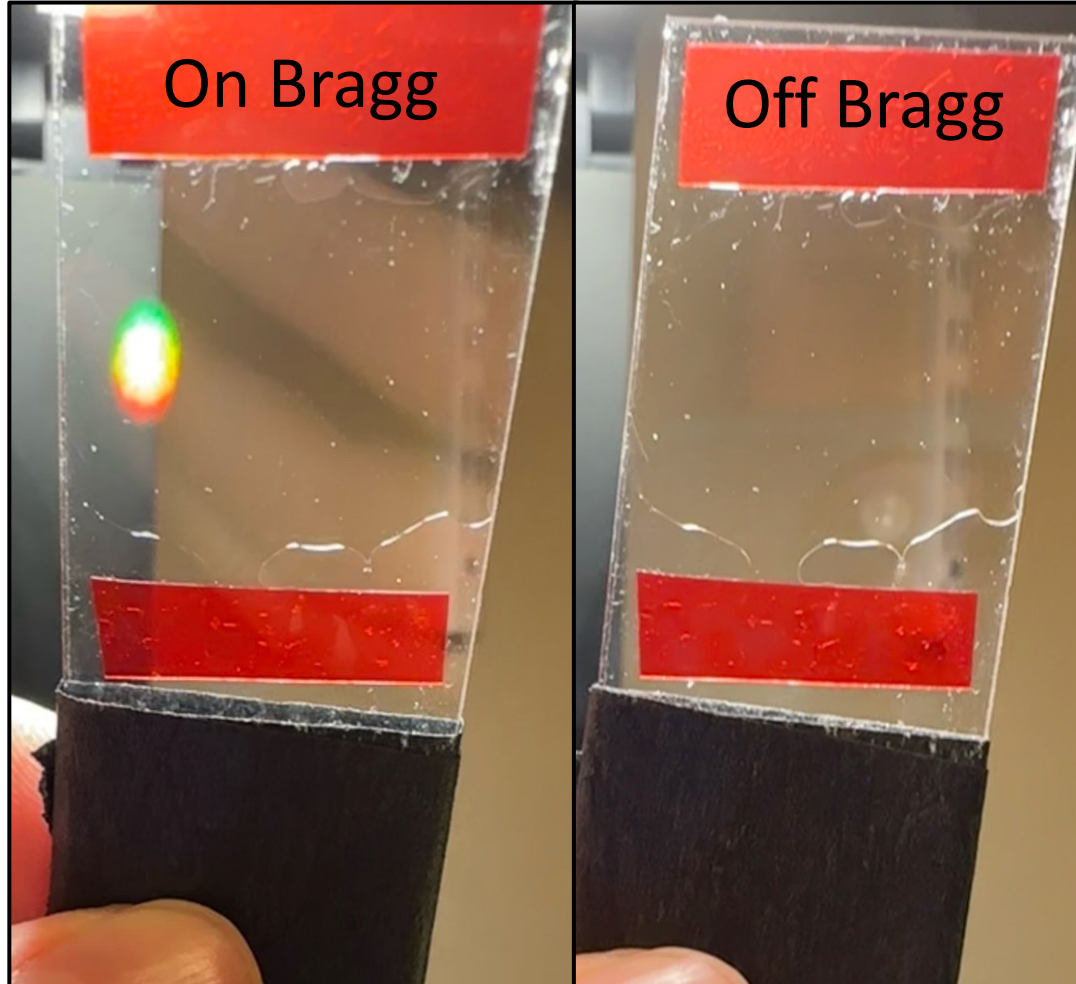


Signal growth



The results you want to see

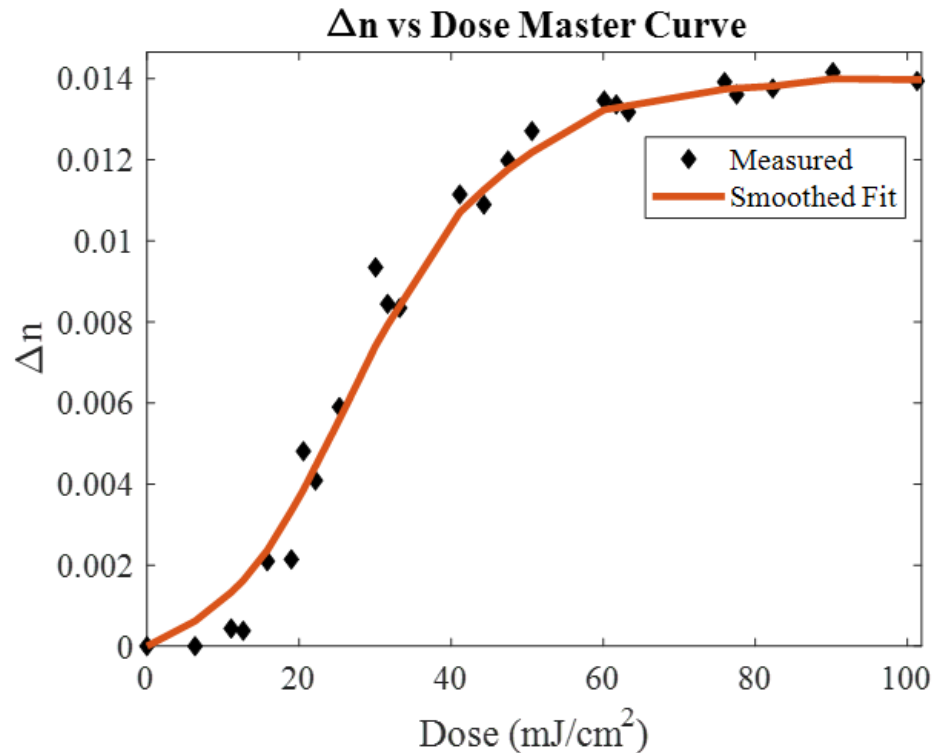
No haze



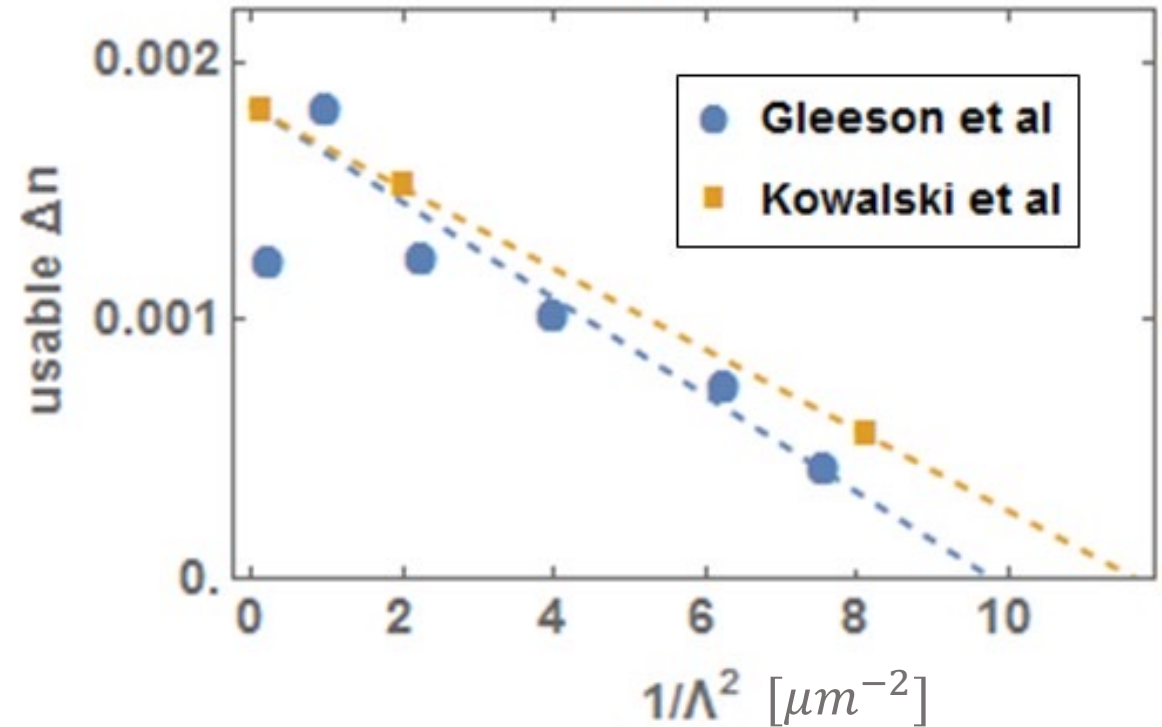


What you need to know to use a material

Index response to light



How this depends on scale





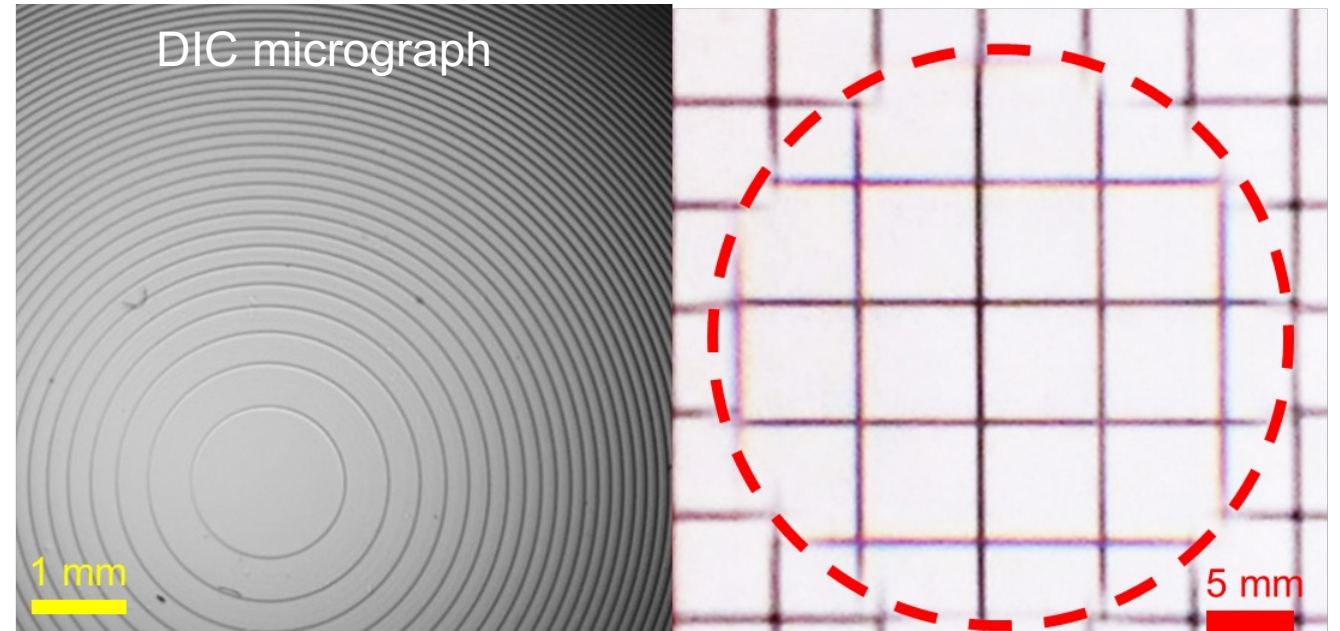
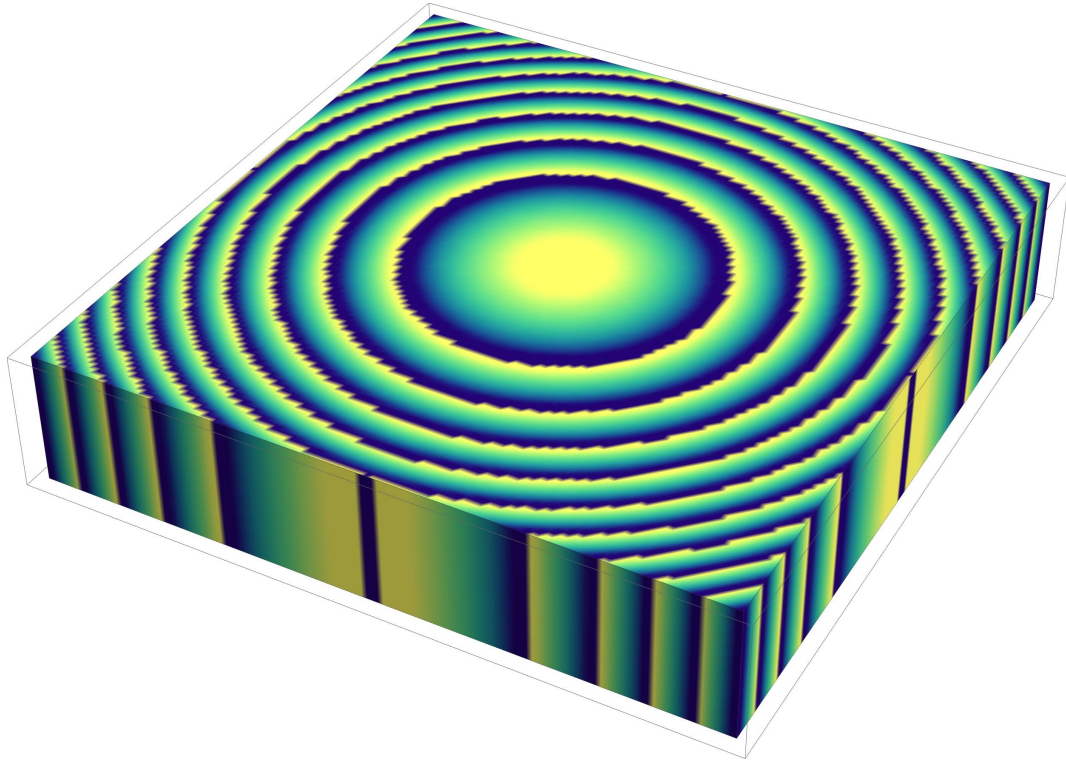
Photopolymer diffractive optics

How to

- formulate
- understand
- **expose**

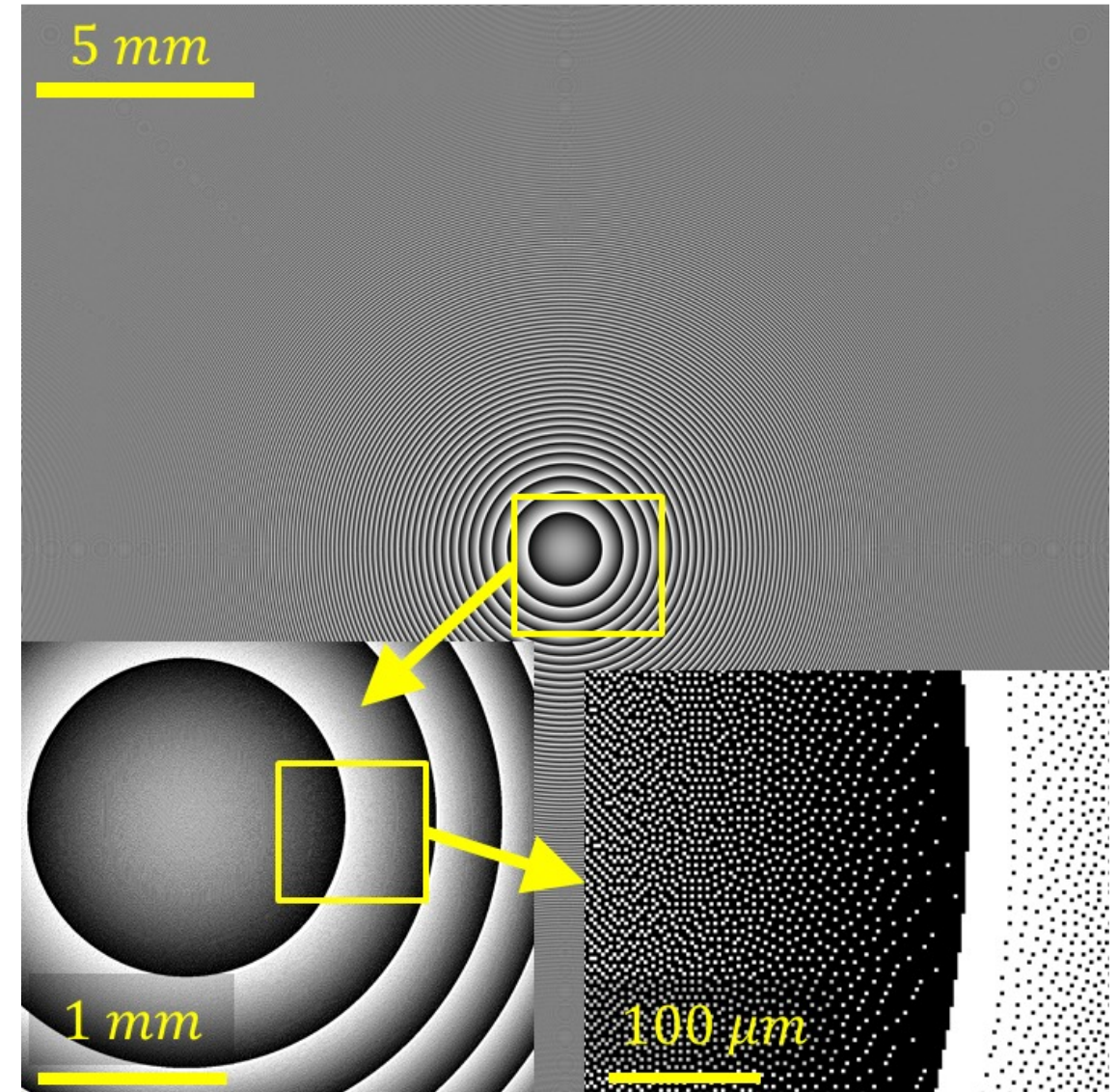
How to create custom diffractive optics

Mask projection lithography

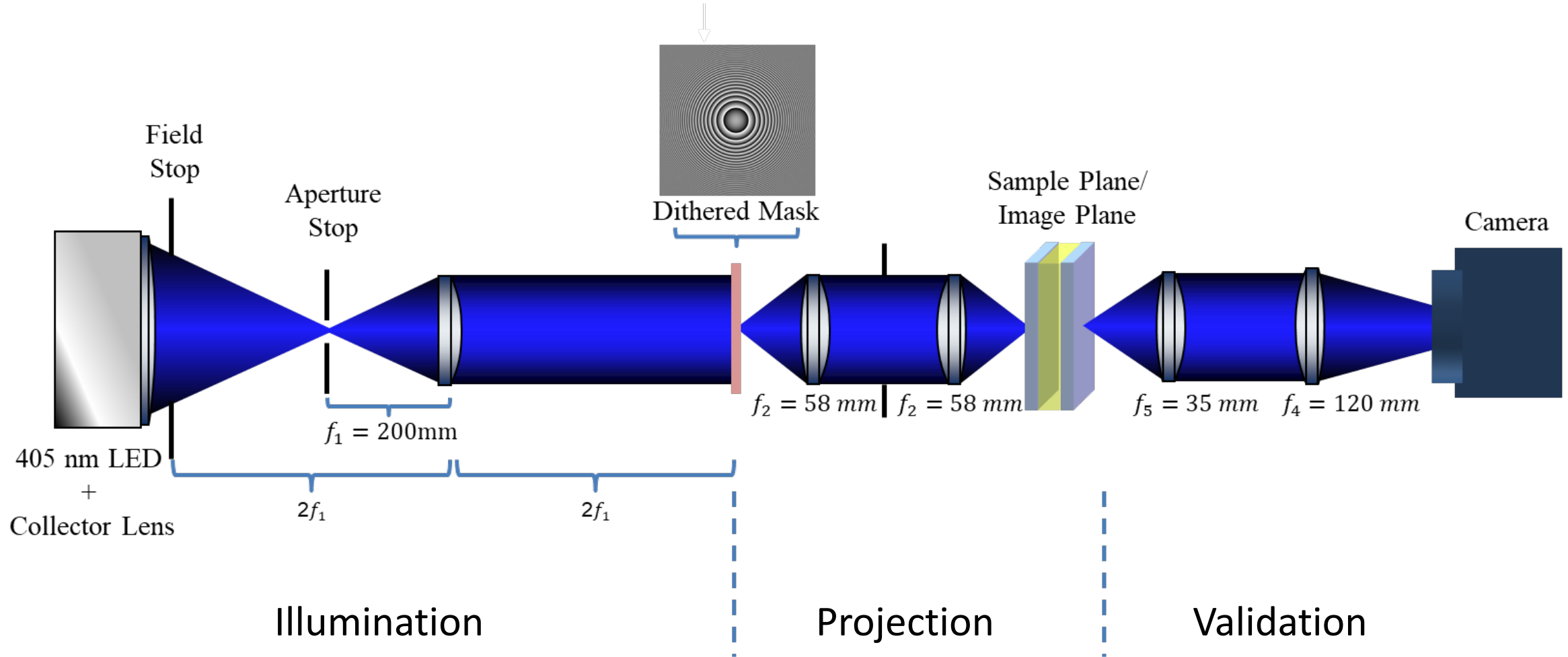


How to create the mask

- Spatial light modulator
 - Liquid crystal
 - DMD
- Photomask
 - Gray scale
 - Binary dithered



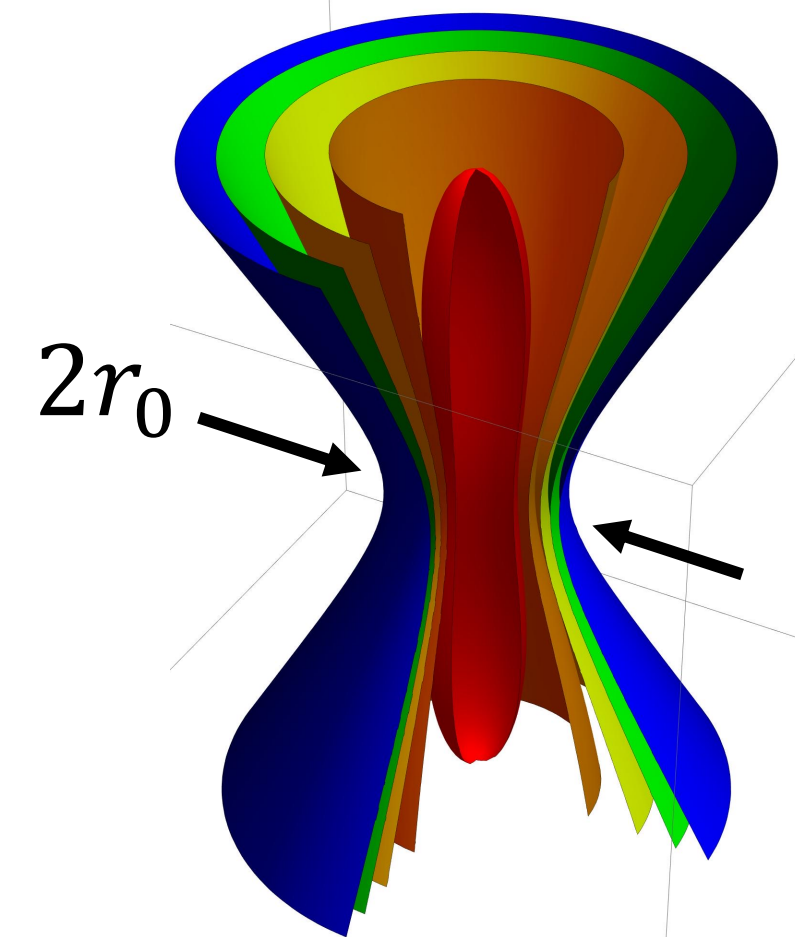
How to project the mask





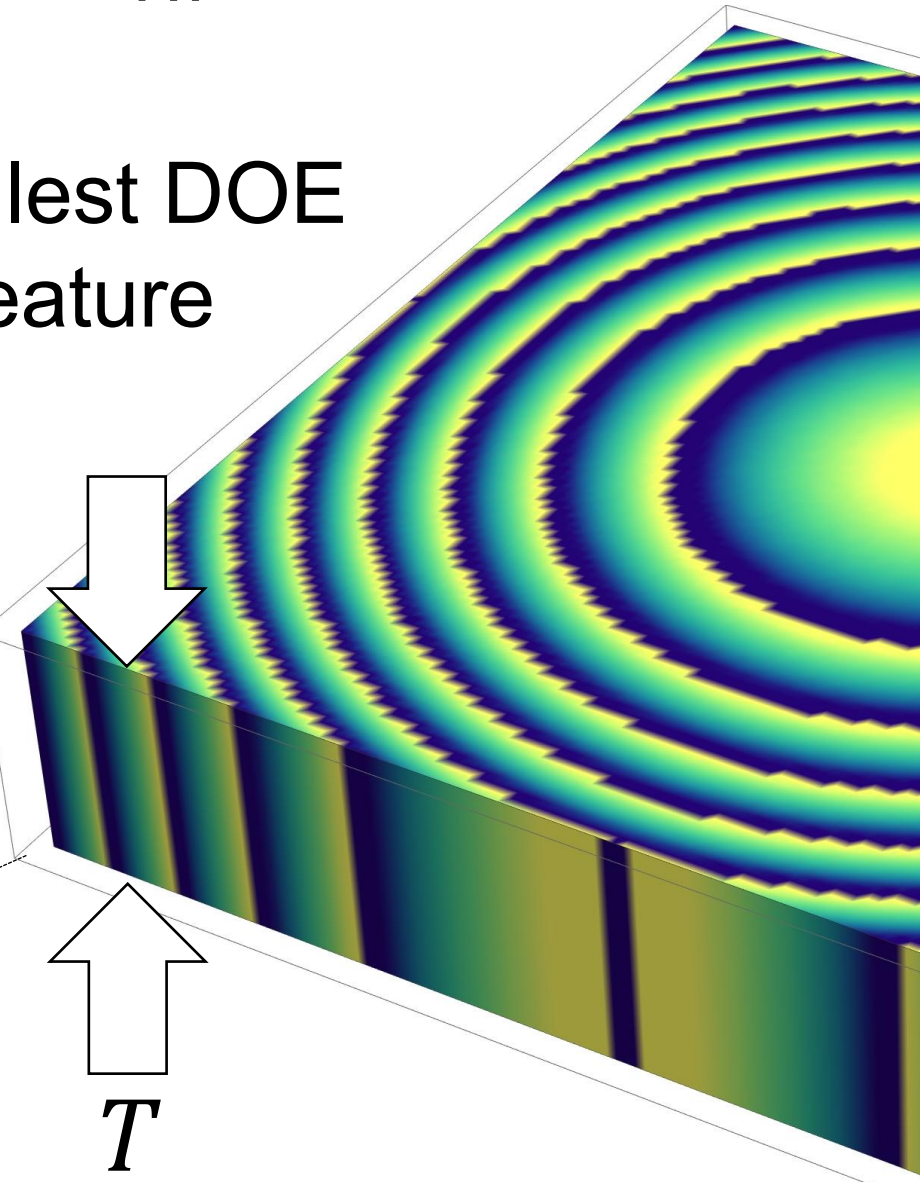
Limit 1: Material Δn sets minimum DOE F/#

Optical PSF



Smallest DOE feature

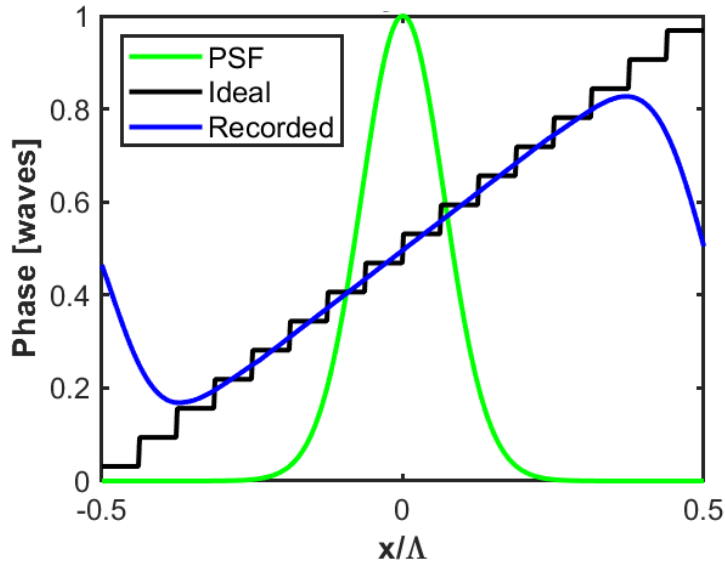
$2z_0$



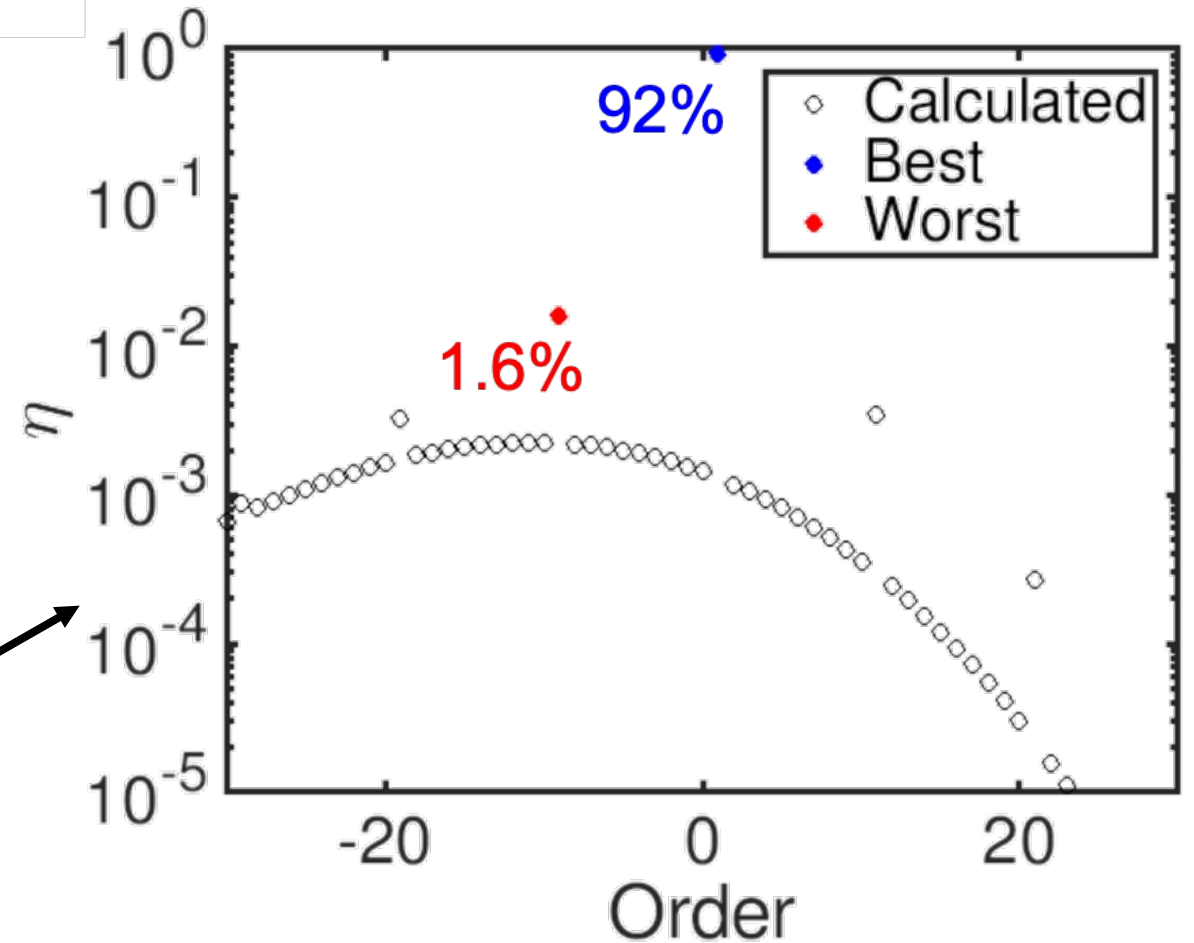
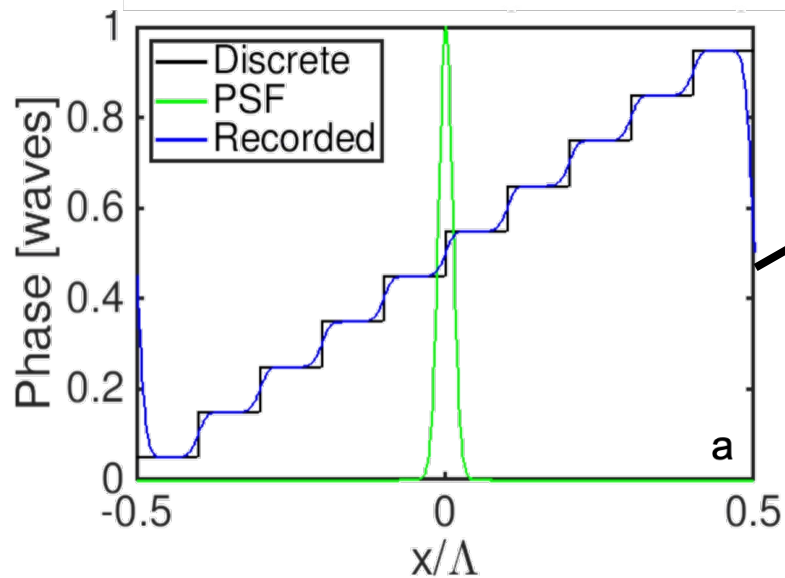


Limit 2: Optical resolution limits efficiency

PSF width
>
mask step



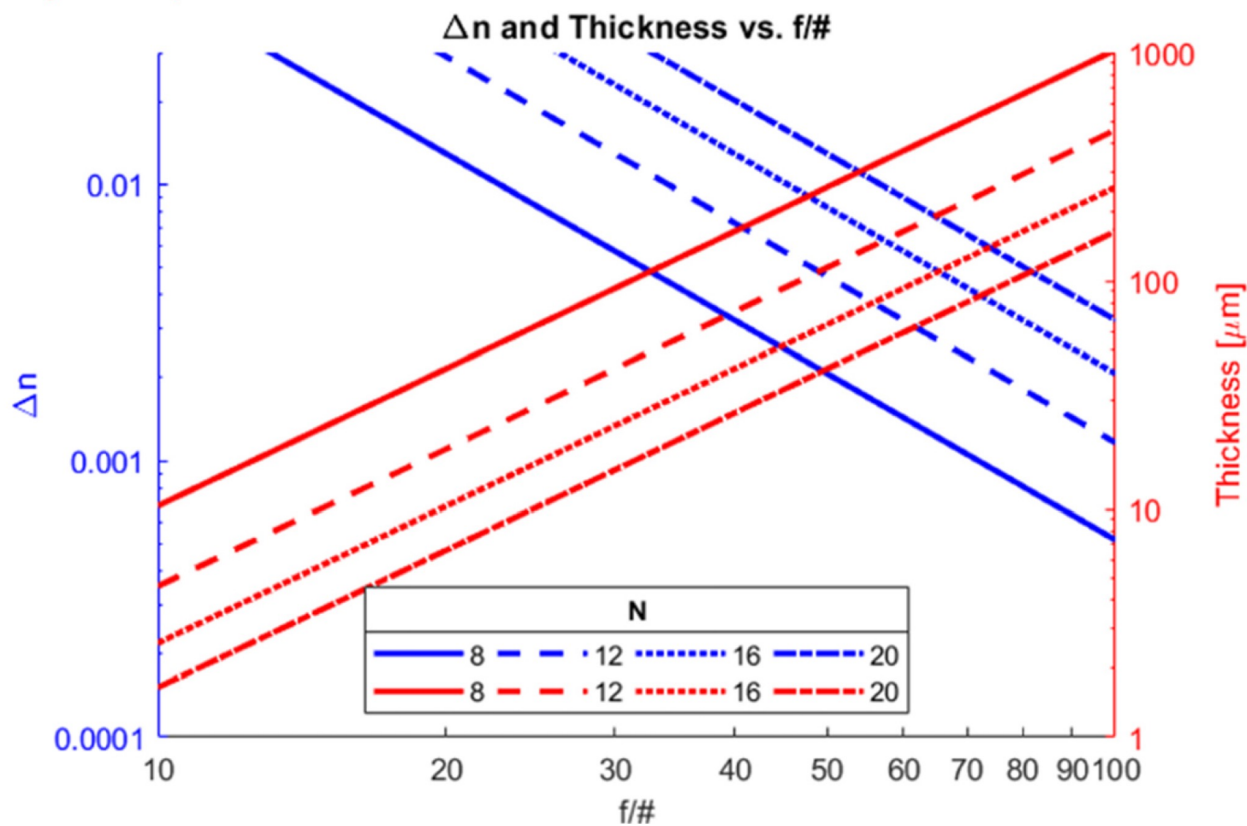
PSF width
<
mask step



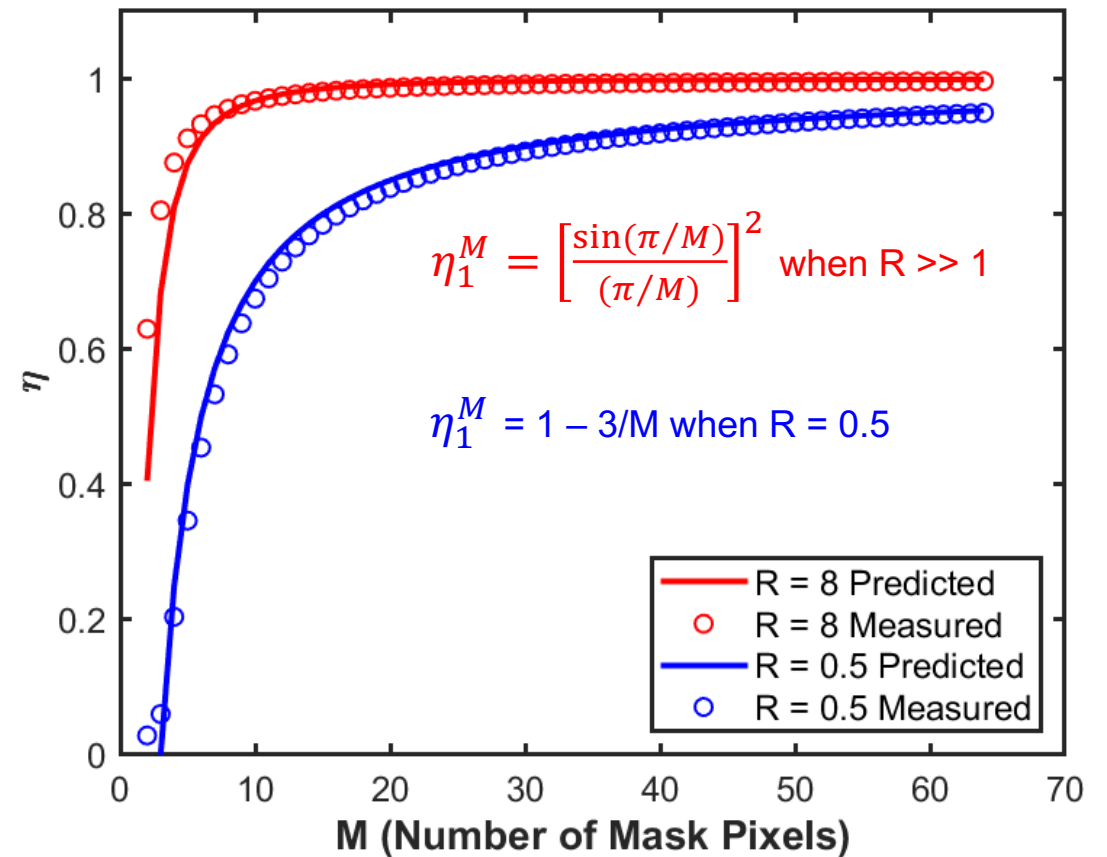


Summary of both limits

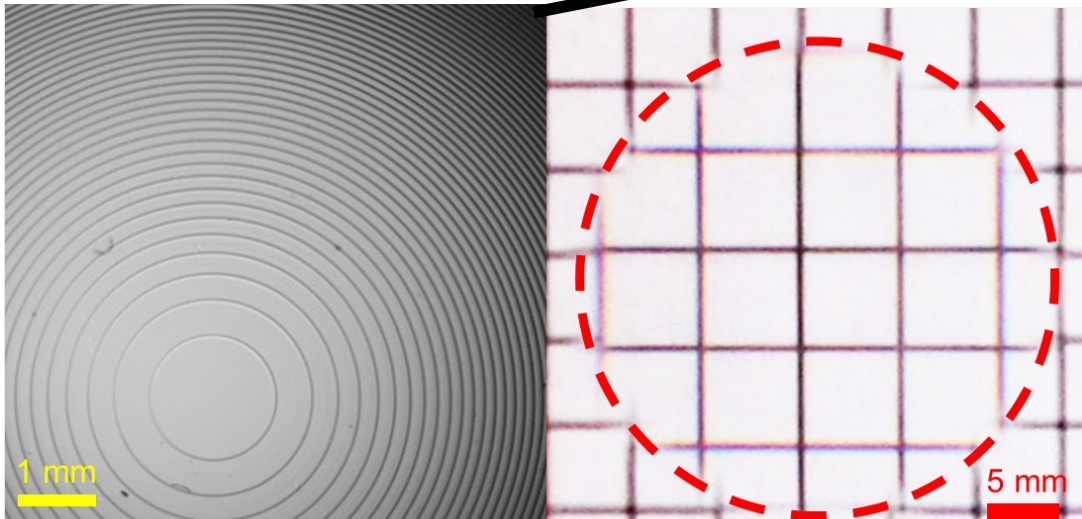
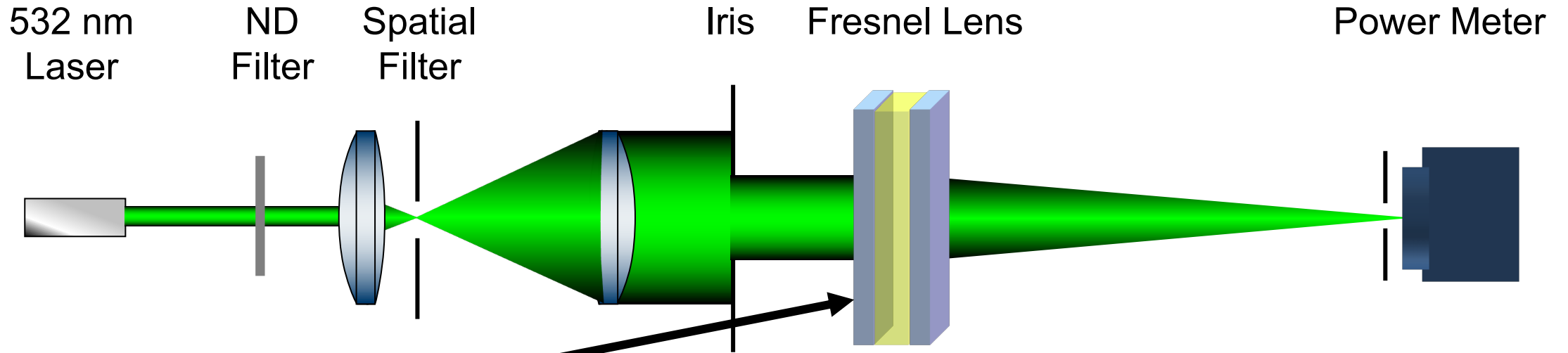
Index contrast limit on F/#



Number and resolvability of pixels limit on η



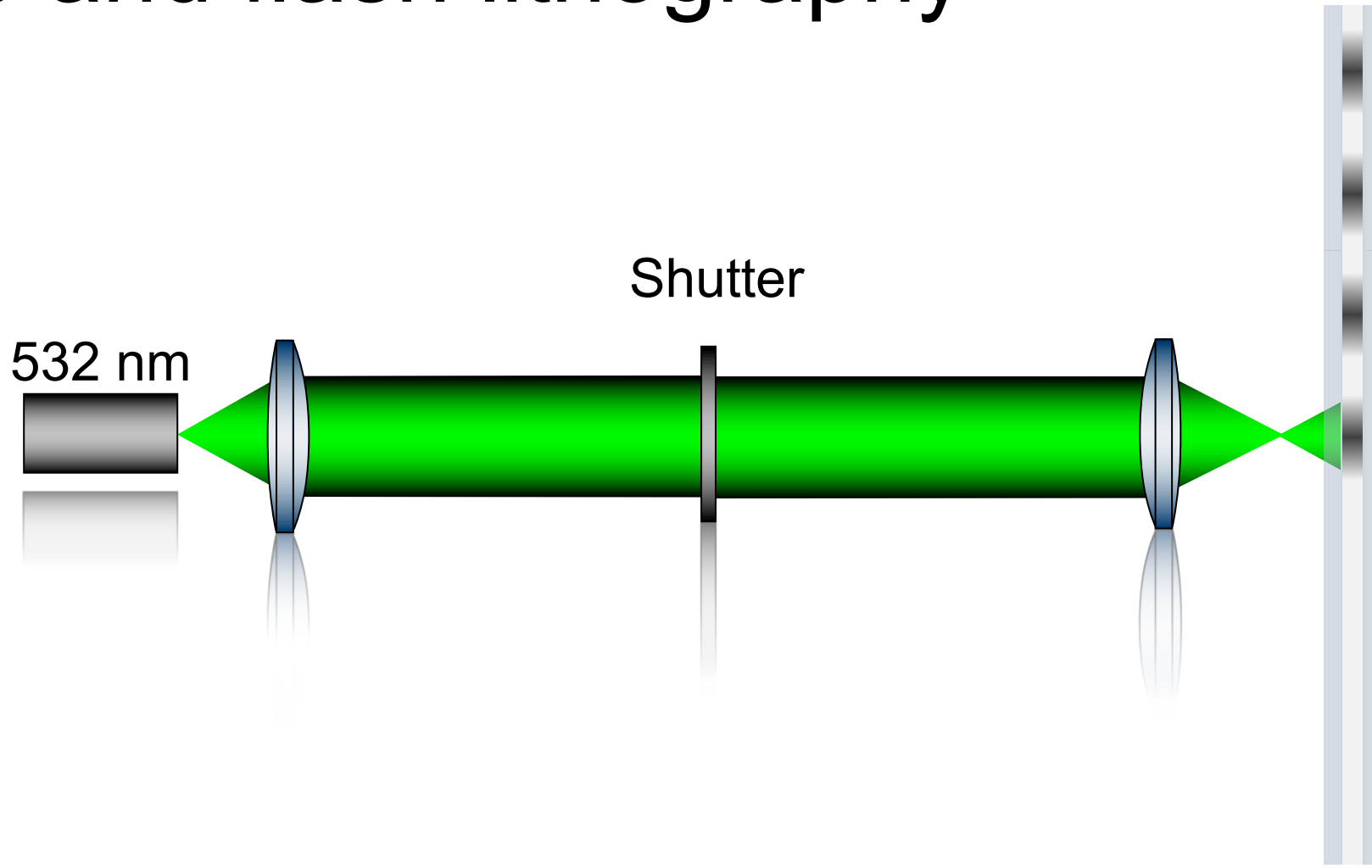
How to test DOEs



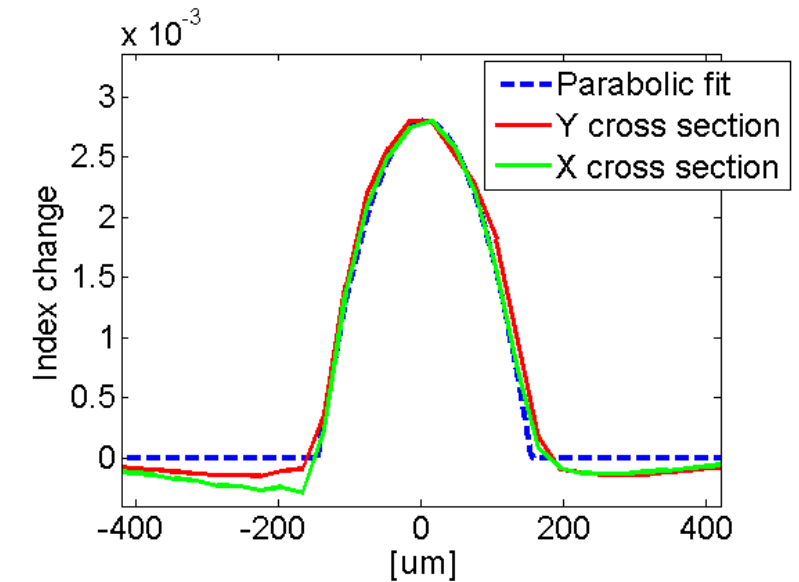
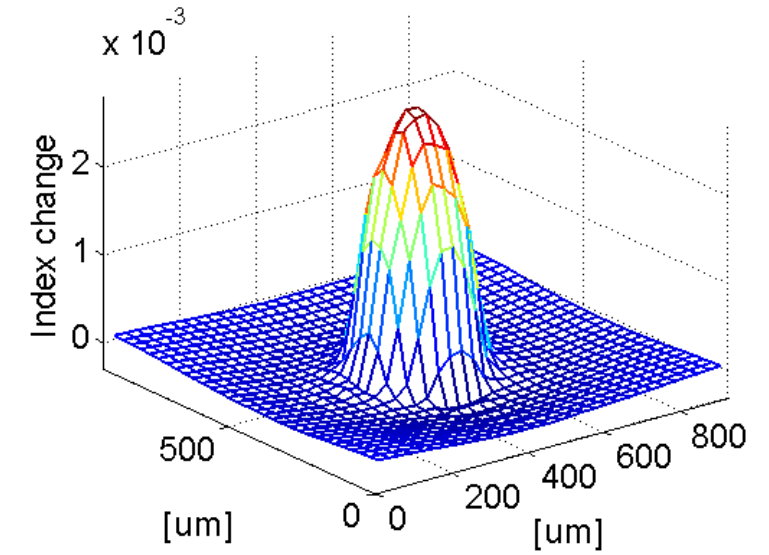
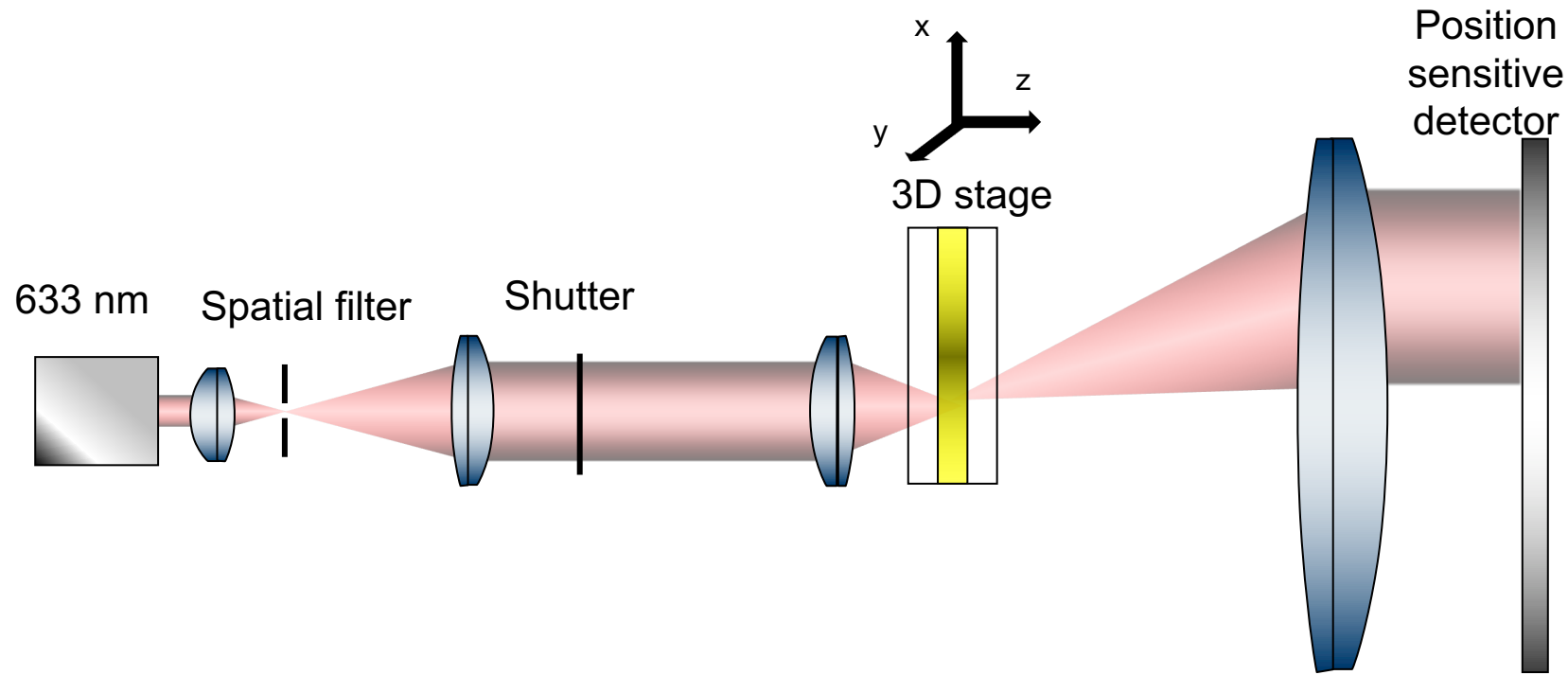
Lens Diameter (mm)	<i>f</i> /#	Diffraction Efficiency
12.6	79	83%
16.6	60	78%
22.7	44	76%

How to create GRIN lenslet arrays

Step and flash lithography

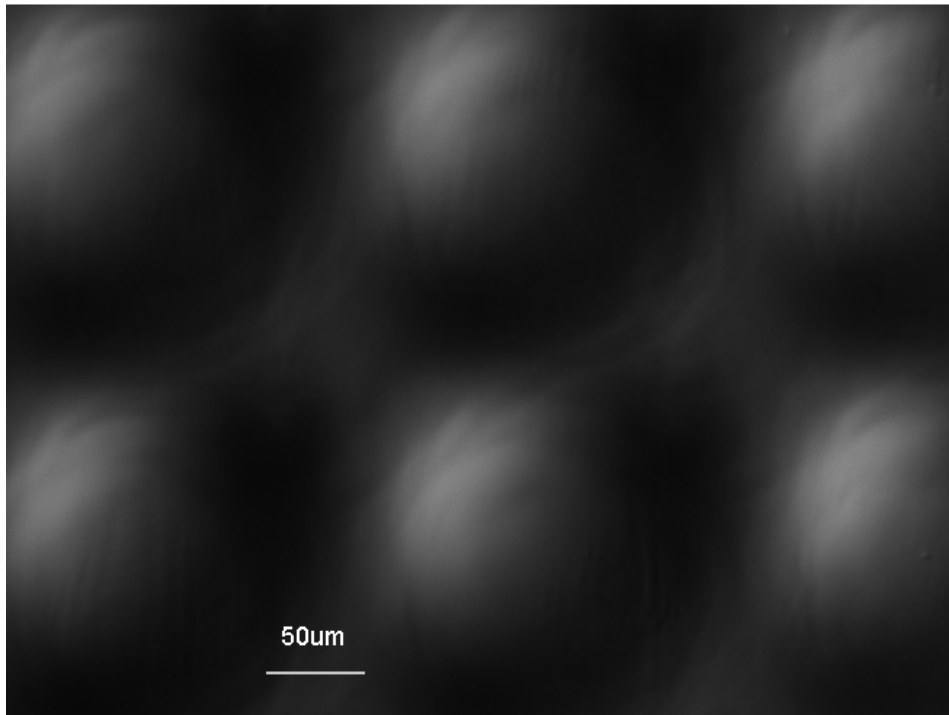


How to test lenslets

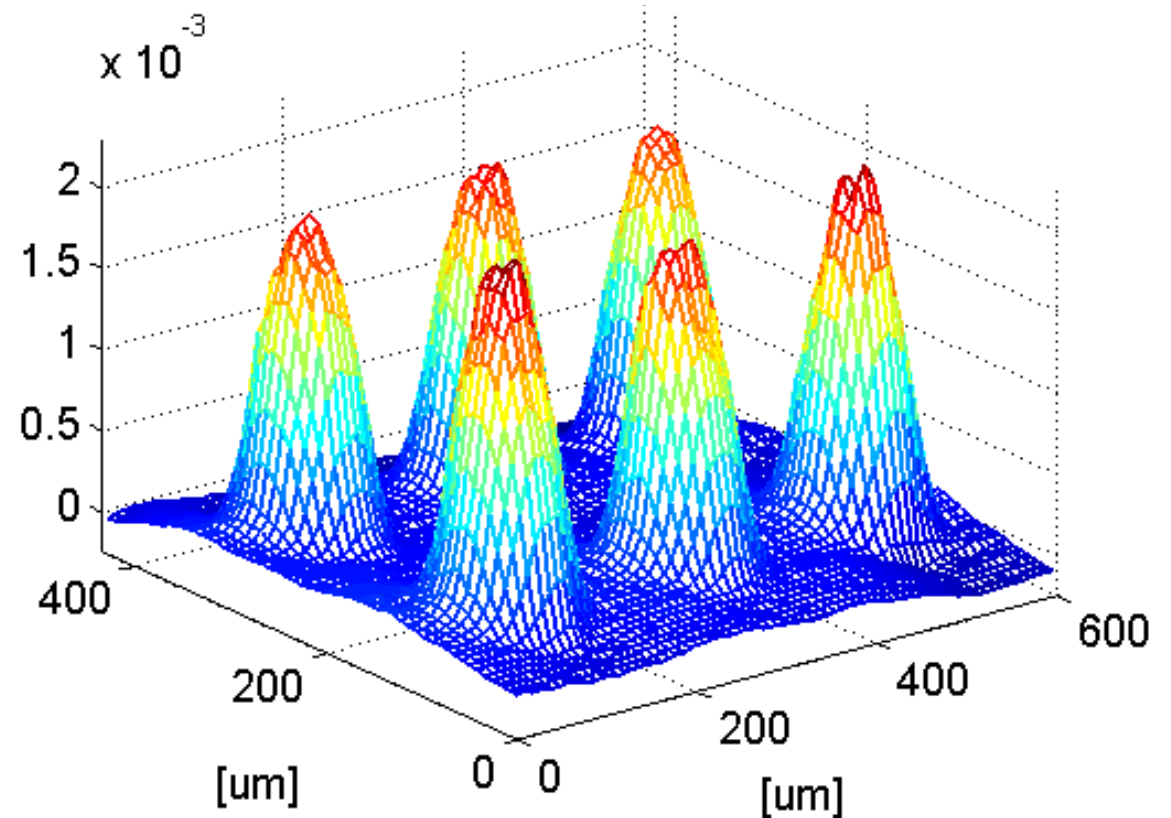


Results: characterizing arrays

DIC phase micrograph

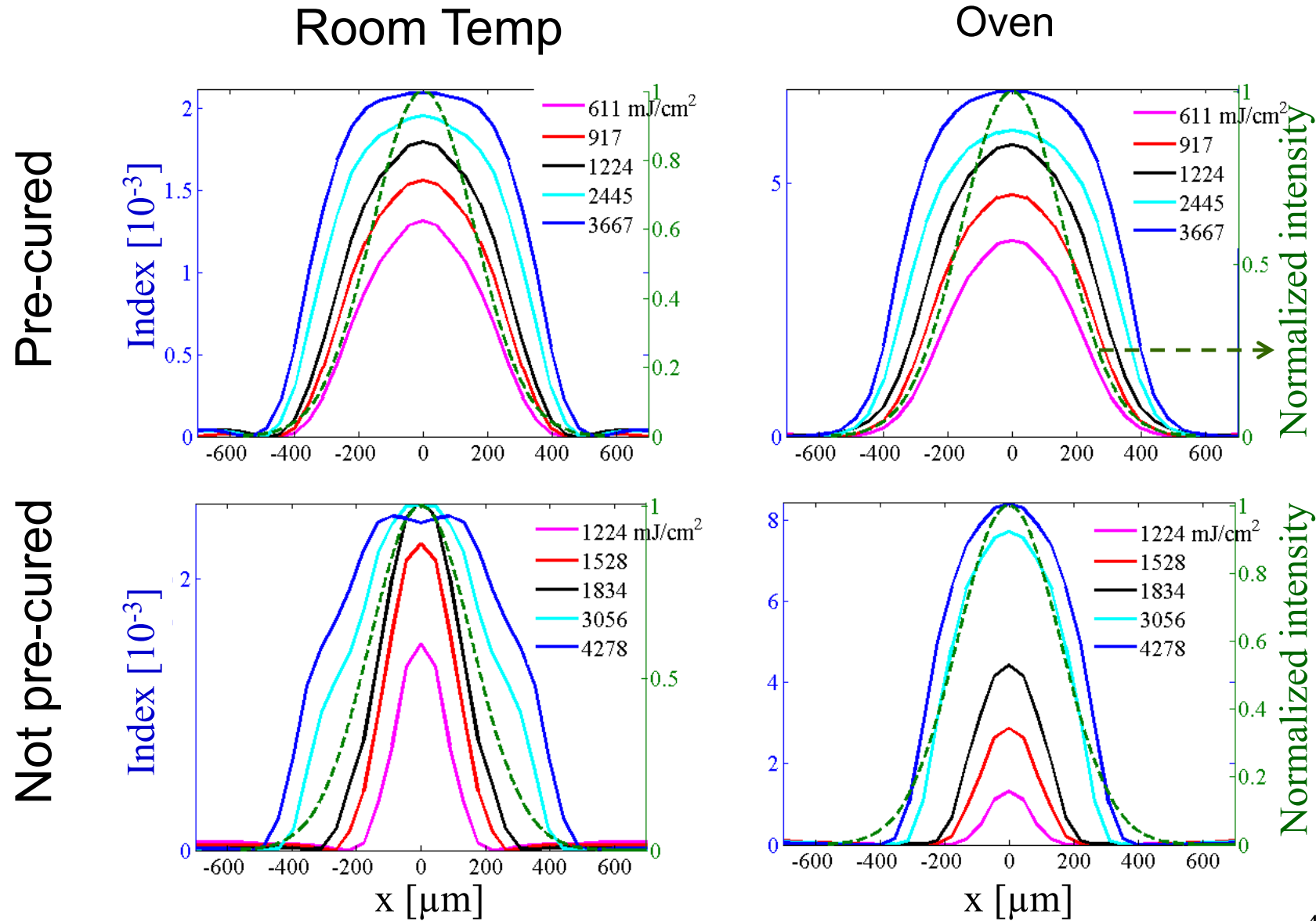


Measured index profile



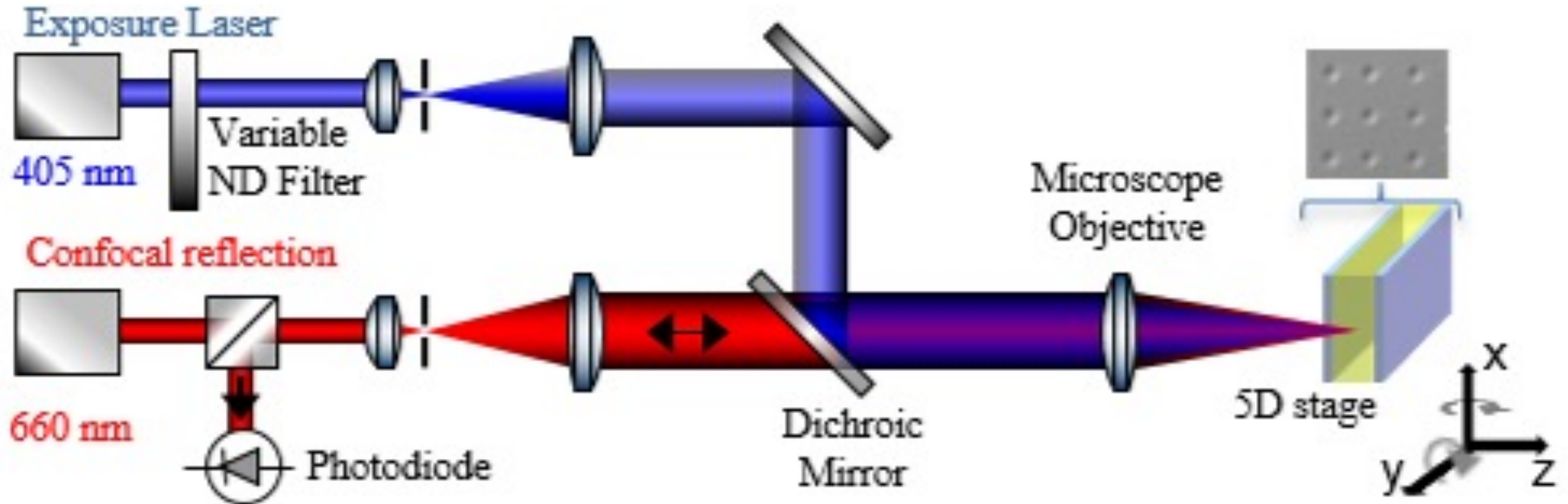
Lens diameter $129.3 \pm 3.2 \mu m$
Peak index $(2.1 \pm 0.13) \times 10^{-3}$

Results: control of GRIN profile



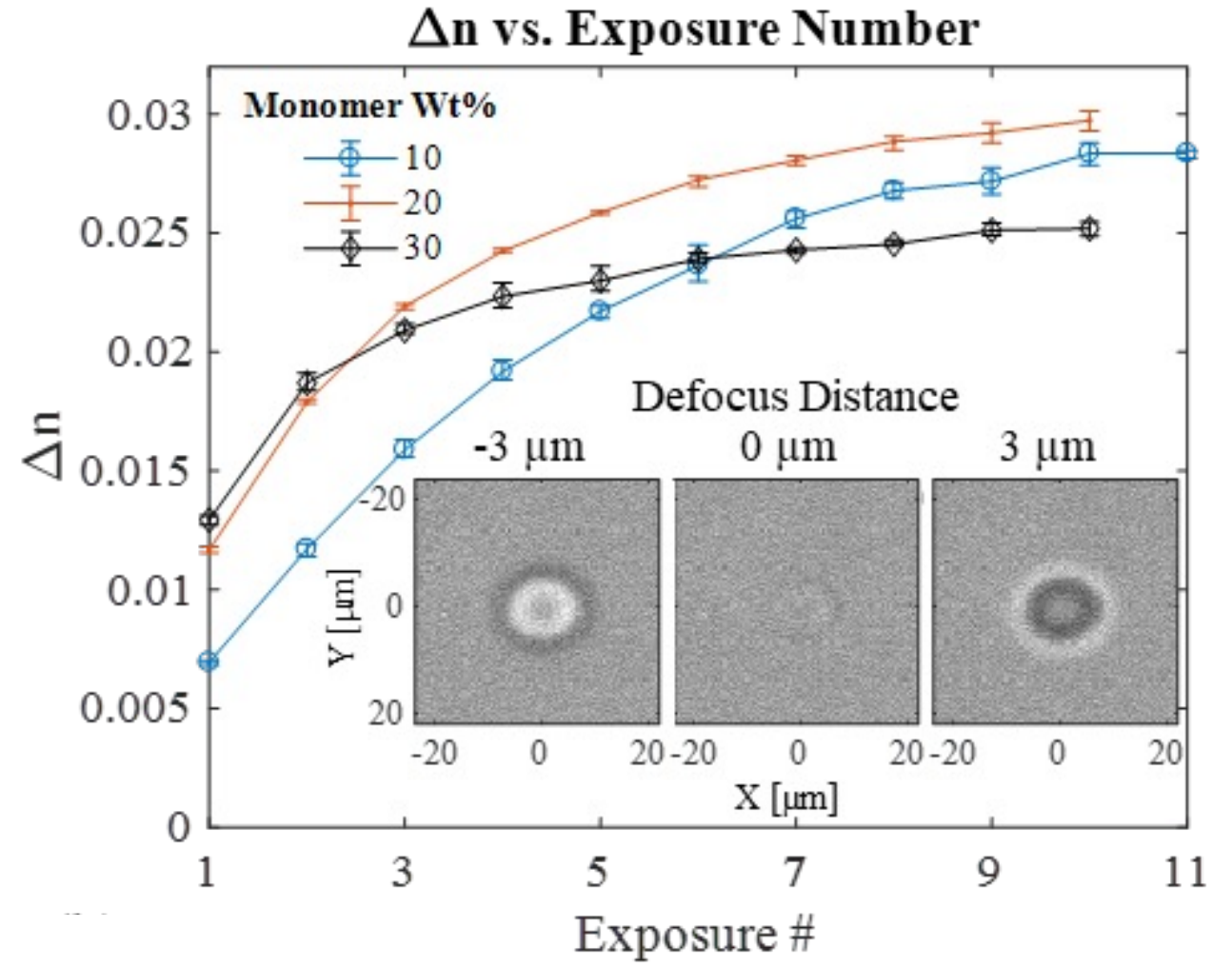
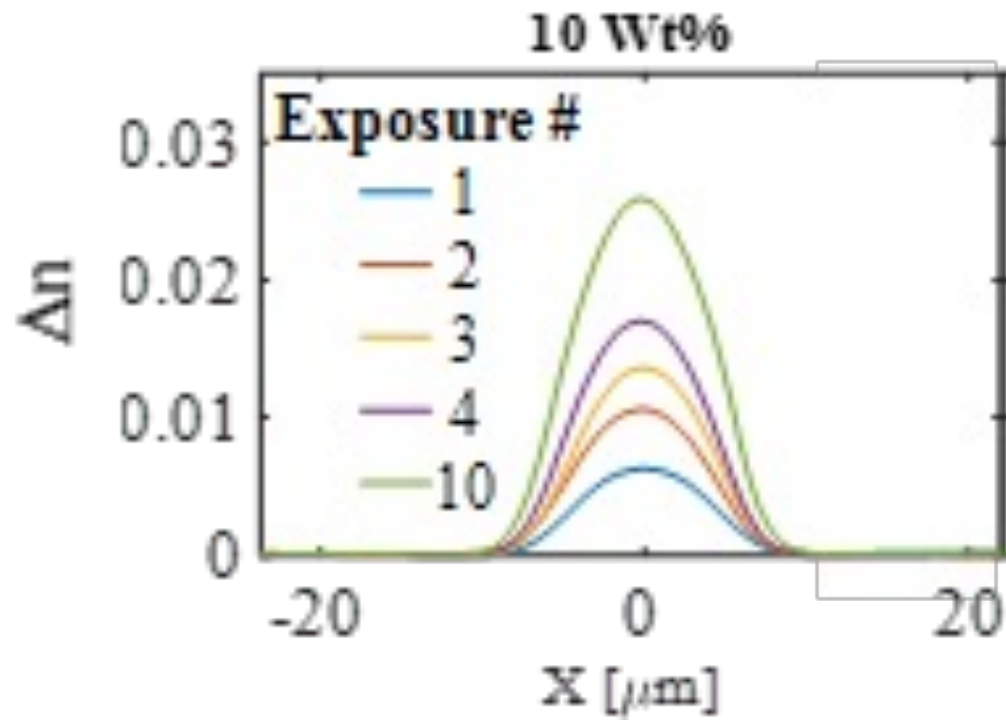
How to: increase δn

Multiple exposure direct write



How to: increase δn

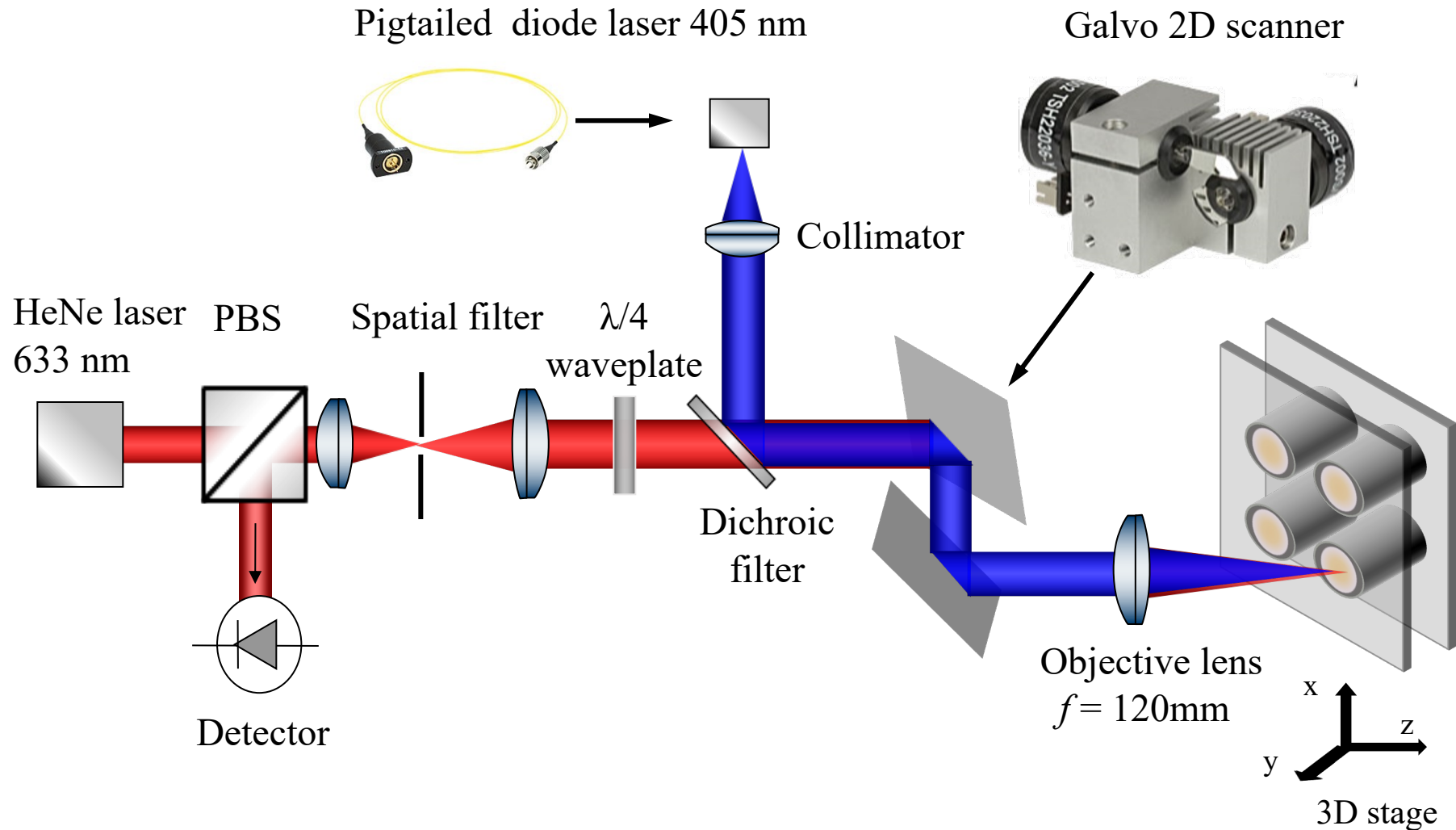
Multiple exposure direct write





How to write arrays of arbitrary GRIN lenses

Fast raster scanning point lithography

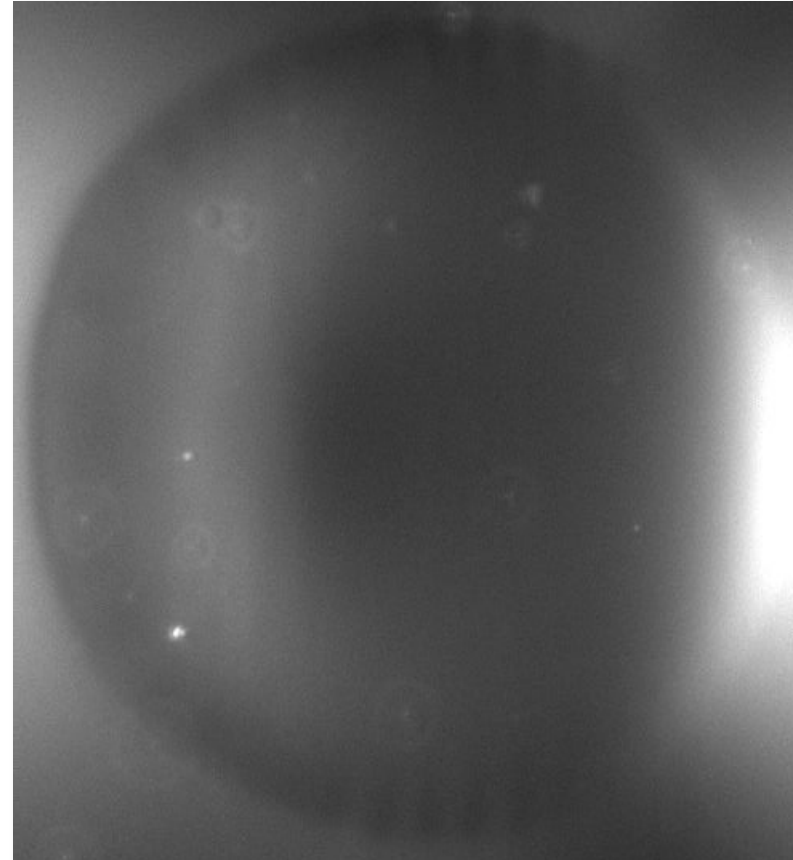


Results: Zernike polynomials

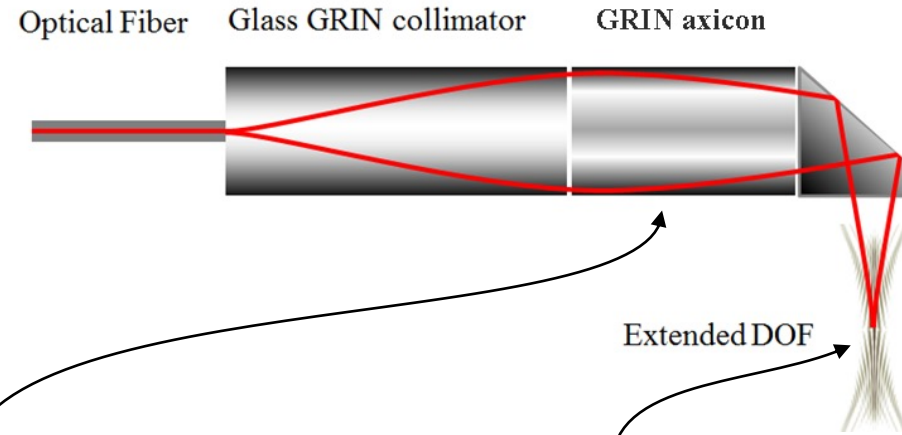
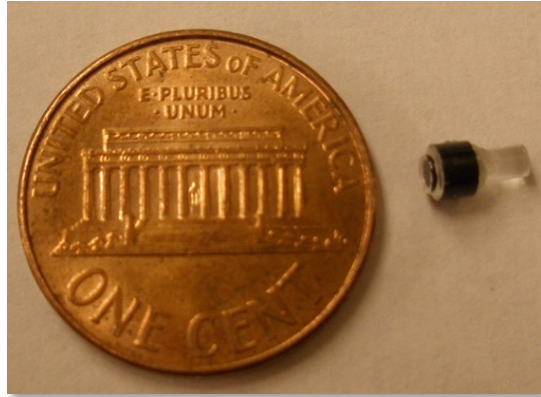
Design



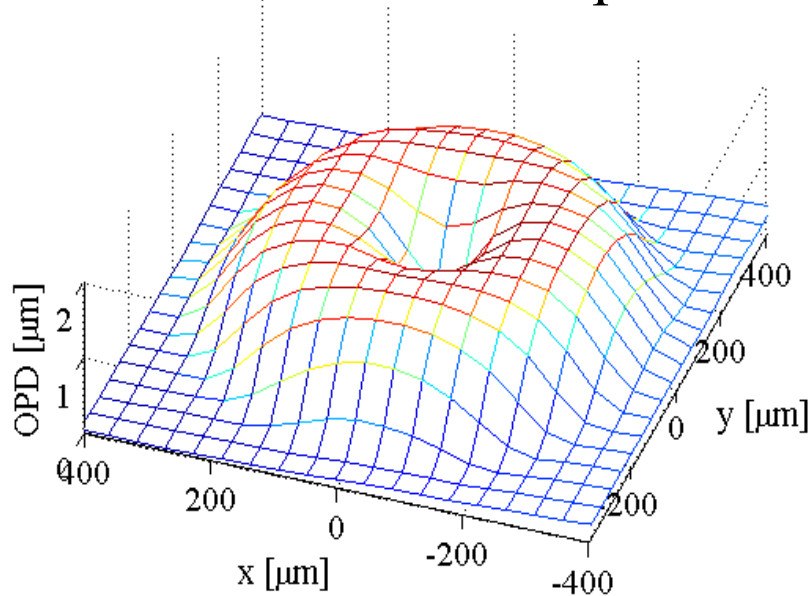
DIC microscope image of lens



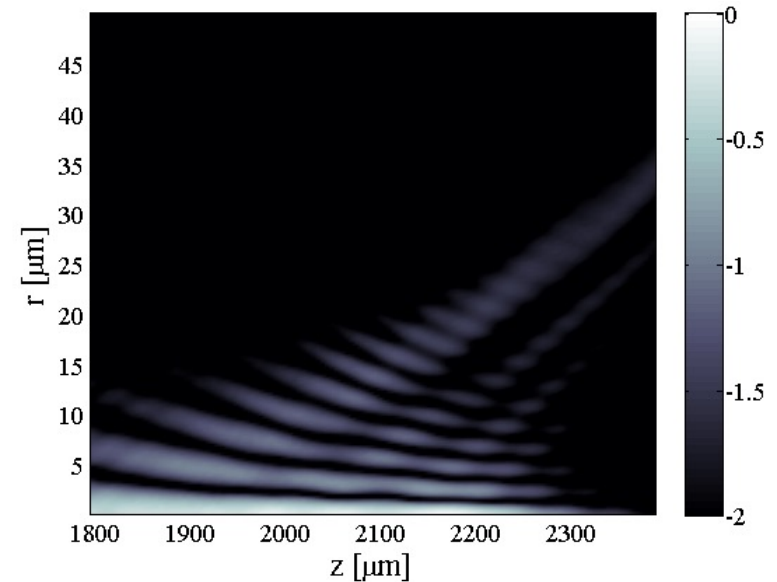
Results: Impossible (traditional) lens functions



Measured index profile

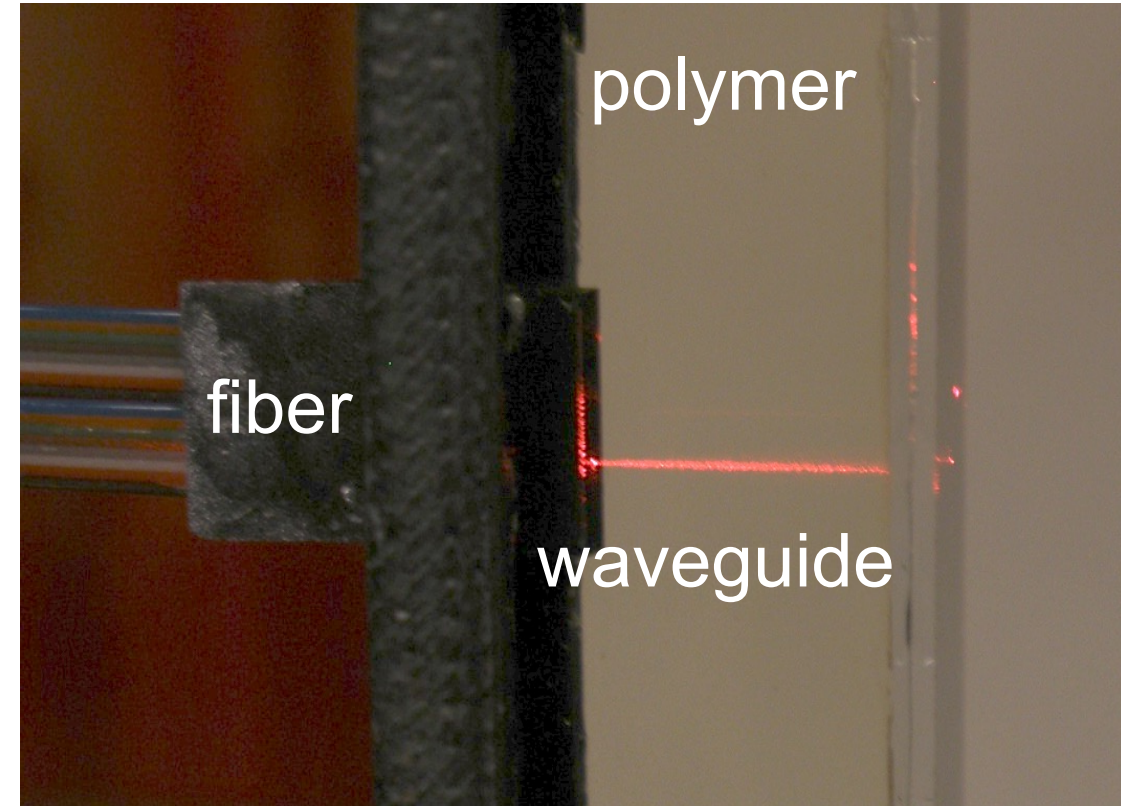
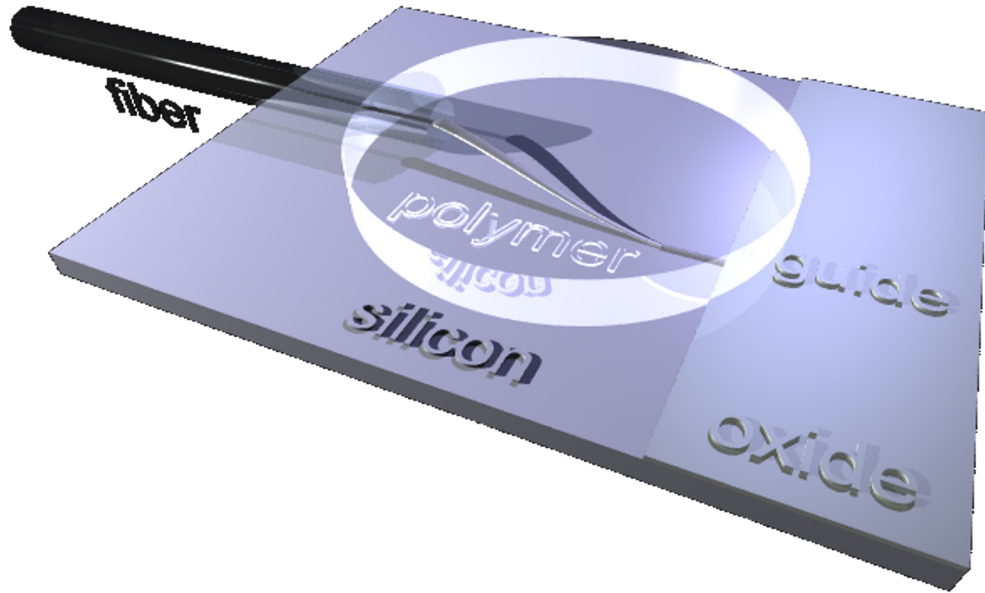


Calculated extended focus



How to: create 3D GRIN waveguides

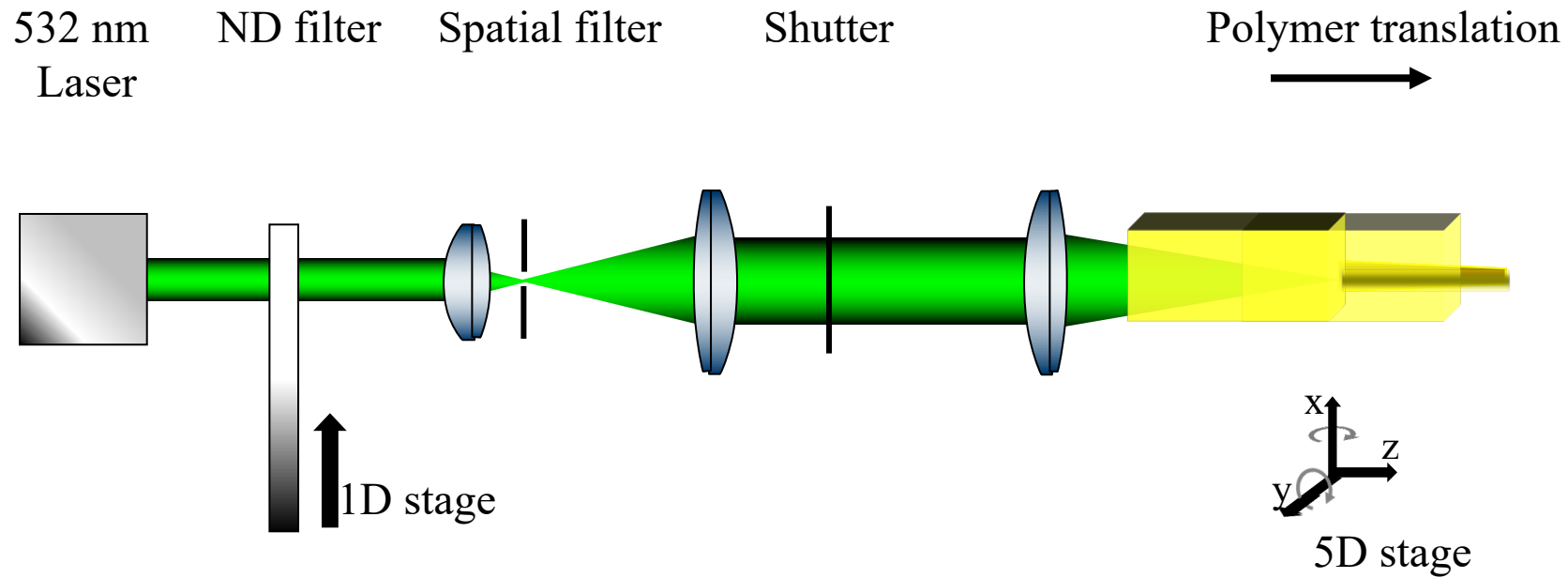
3D direct write lithography



- A. C. Sullivan, M. W. Grabowski, R. R. McLeod, "Three-dimensional direct-write lithography into photopolymer," *Applied Optics* 46, 295-301, 2007.
- C. Ye, K. T. Kamysiak, A. C. Sullivan, R. R. McLeod, "Mode profile imaging and loss measurement for uniform and tapered single-mode 3D waveguides in diffusion-based photopolymer," *Optics Express* 20, 6575-6583, 2012.

How to: create 3D GRIN waveguides

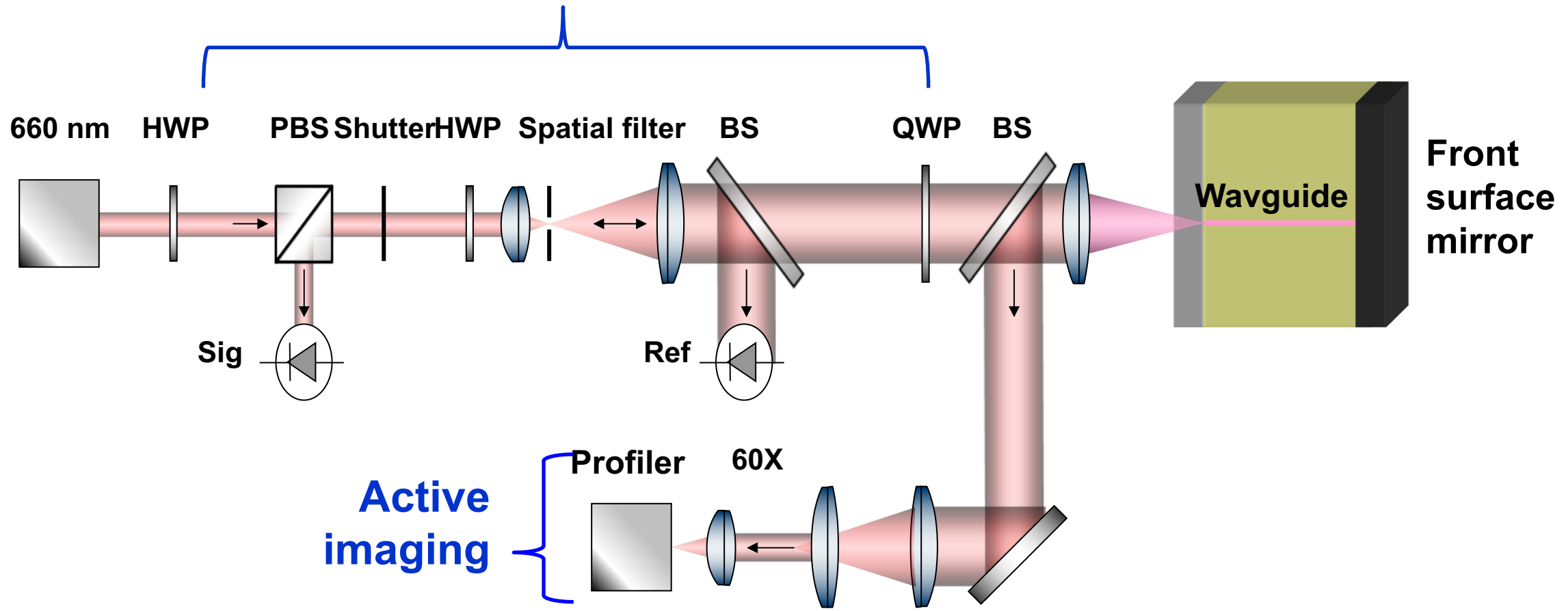
3D direct write lithography



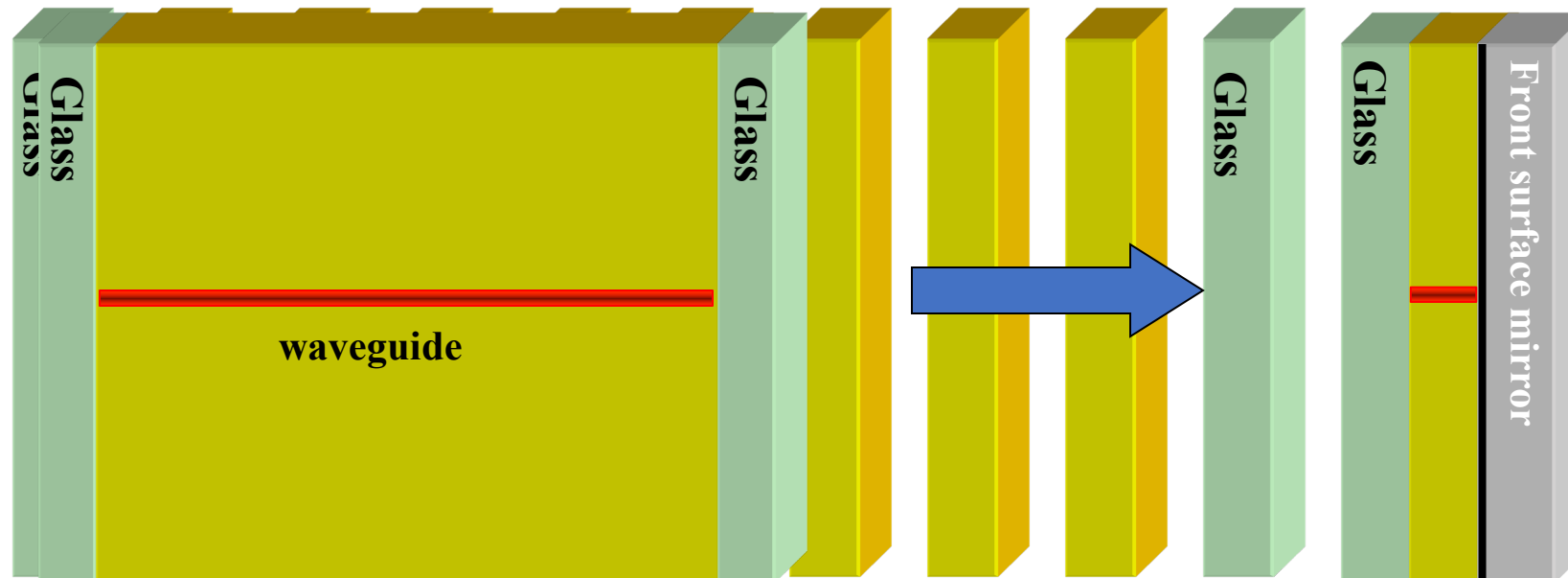


How to test waveguides in a soft polymer

Confocal microscope



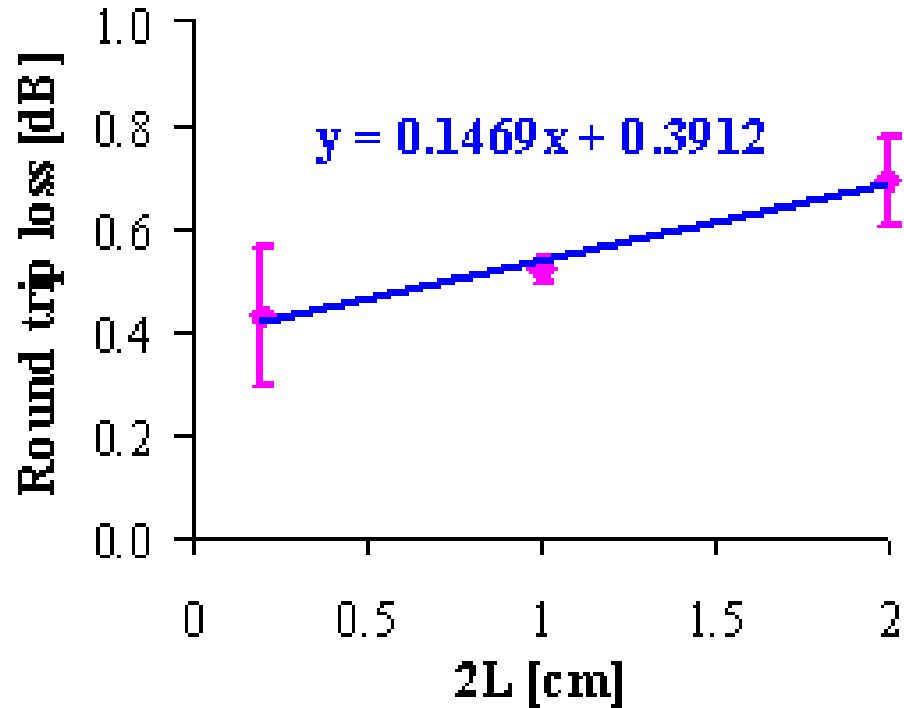
How to perform cutback measurement





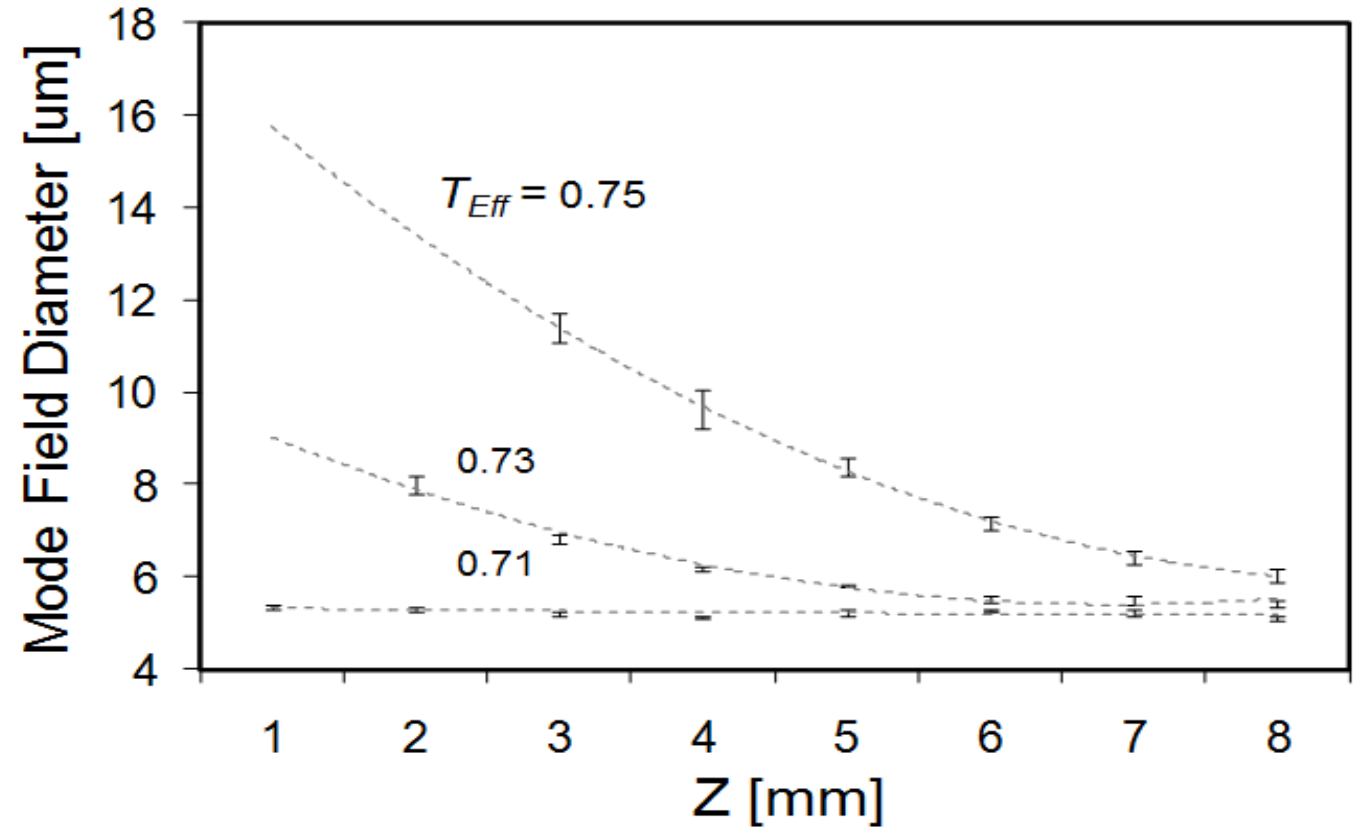
Results: Uniform and tapered waveguides

Single-mode uniform



Coupling loss 0.39 dB
Propagation loss 0.15 dB/cm

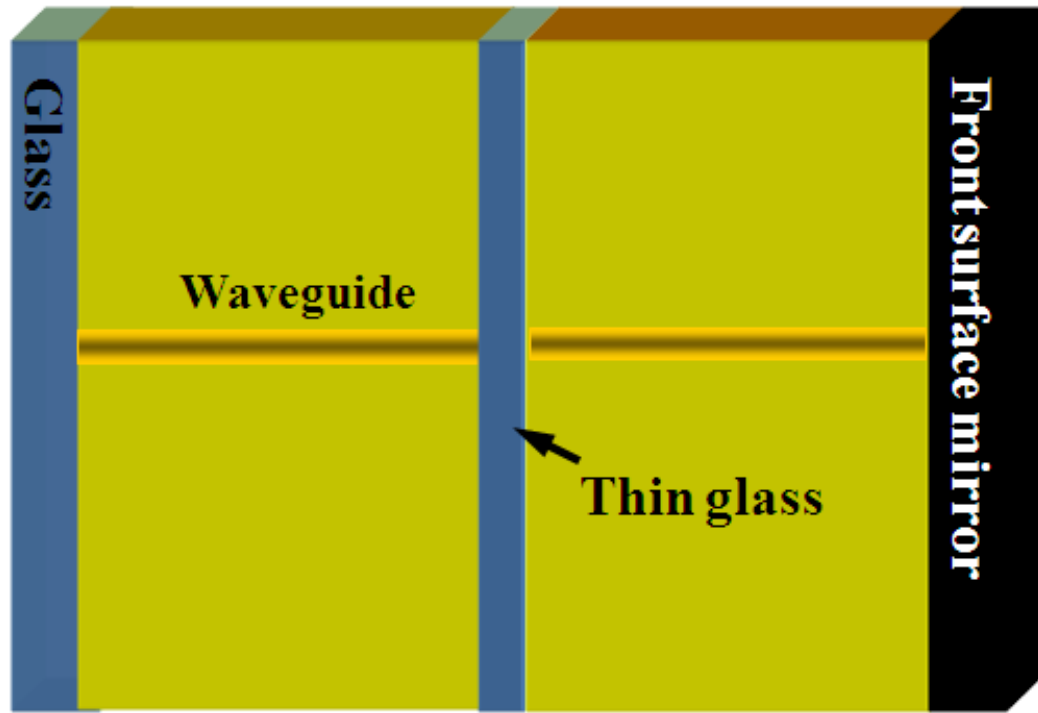
Single-model tapered



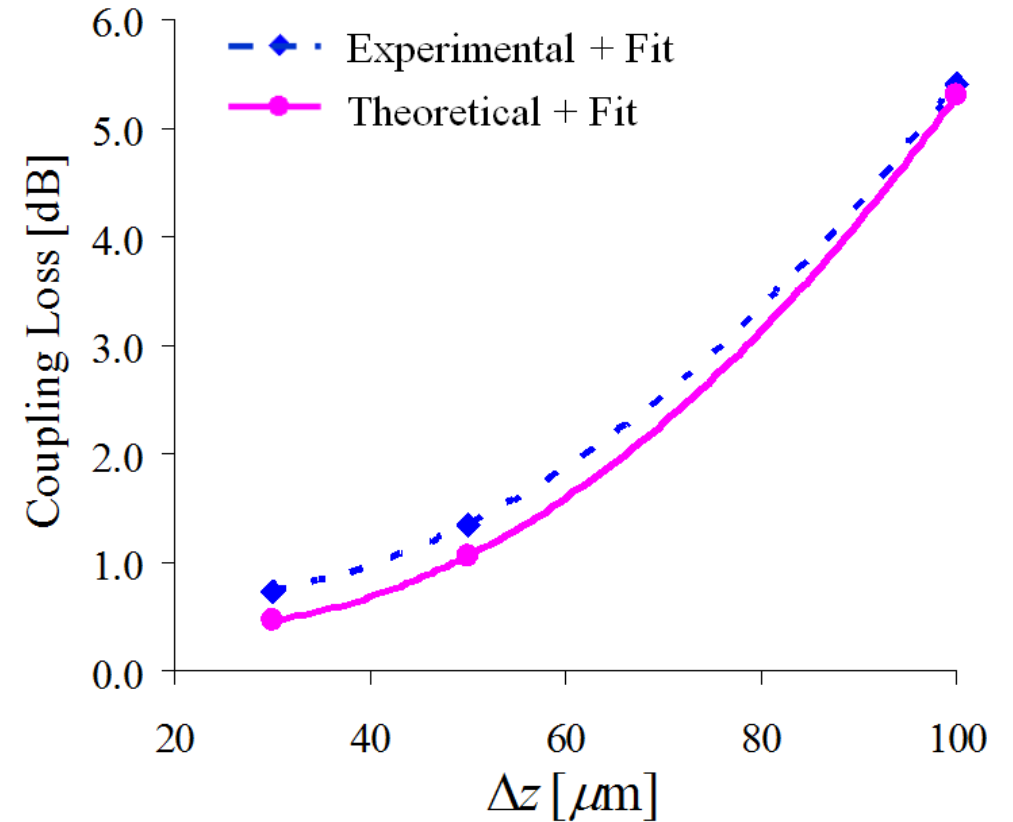
Largest transformation 2.5 to 1

Results: thin transmission optics

Sample Geometry

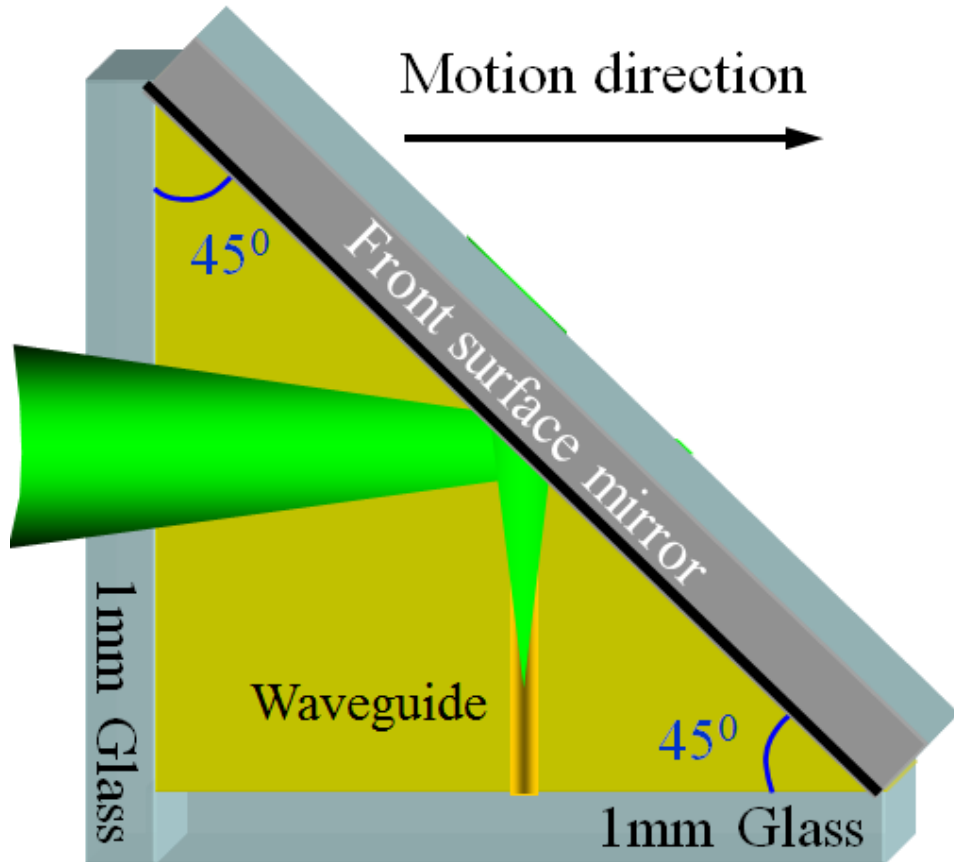


Coupling loss

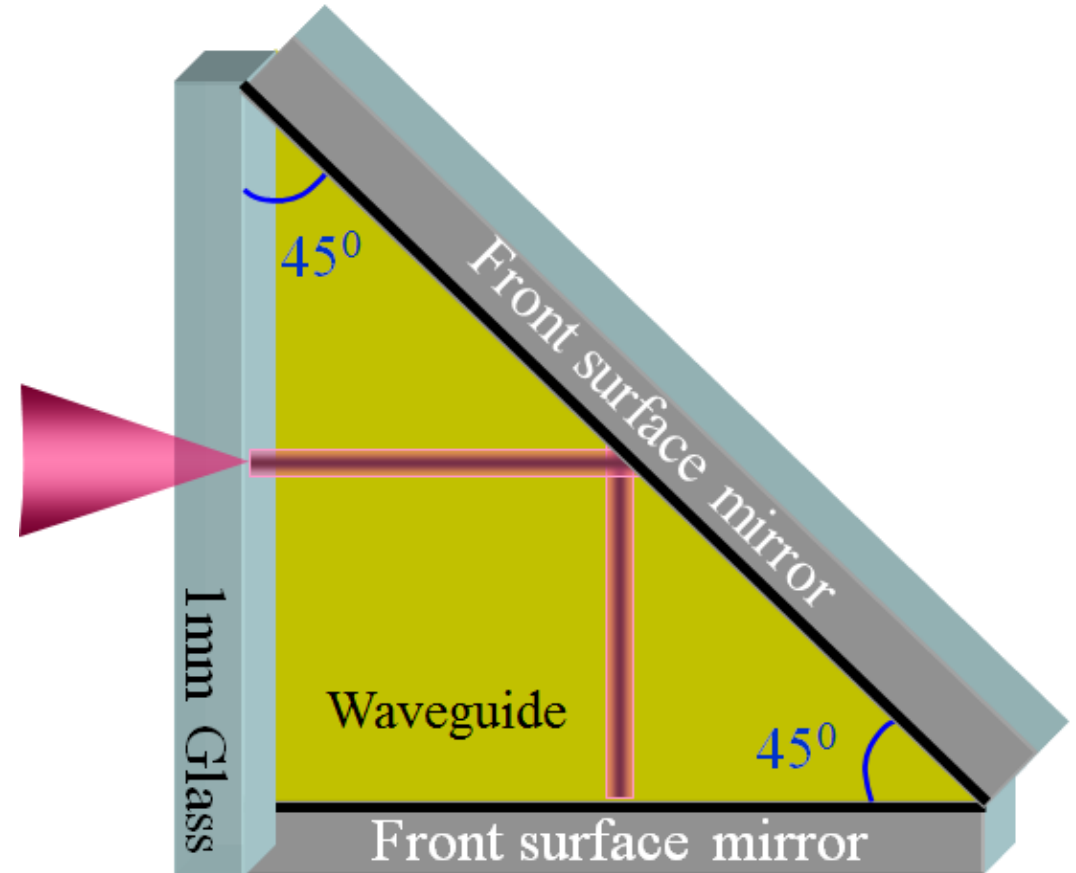


Results: reflective optics

Fabrication



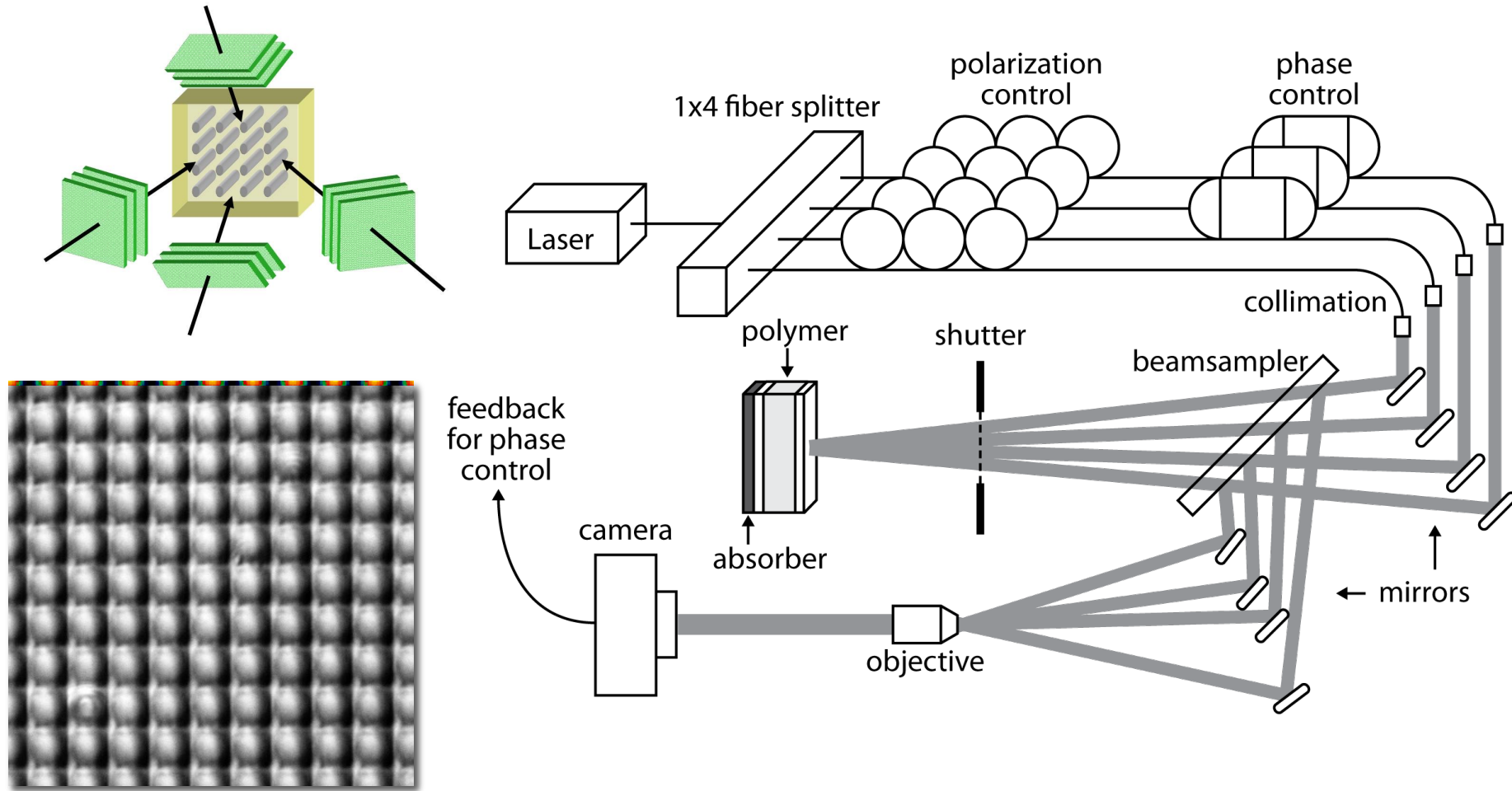
Measurement



Excess loss at the bend: 0.868dB

How to create imaging waveguide arrays

Four-beam interference lithography



Results: Imaging performance of array

1 mm array thickness

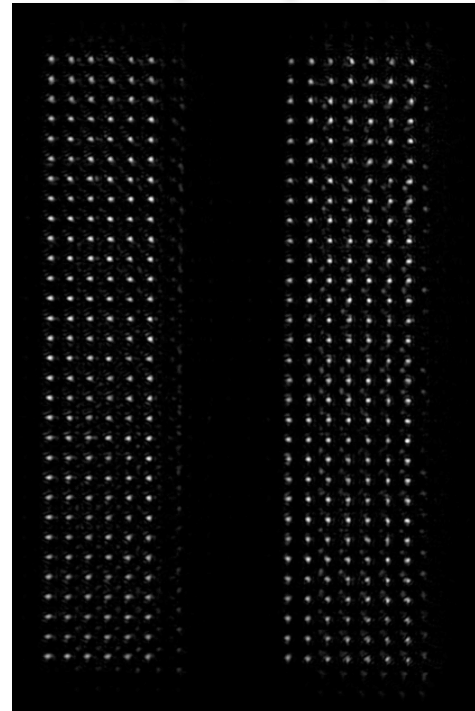
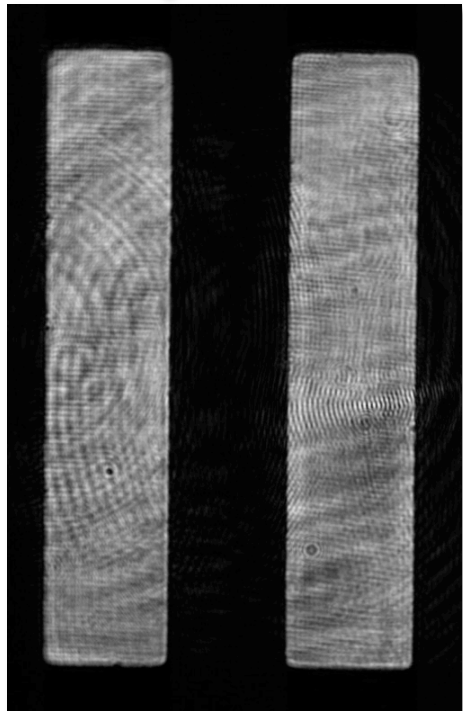
8 mm array thickness

Input

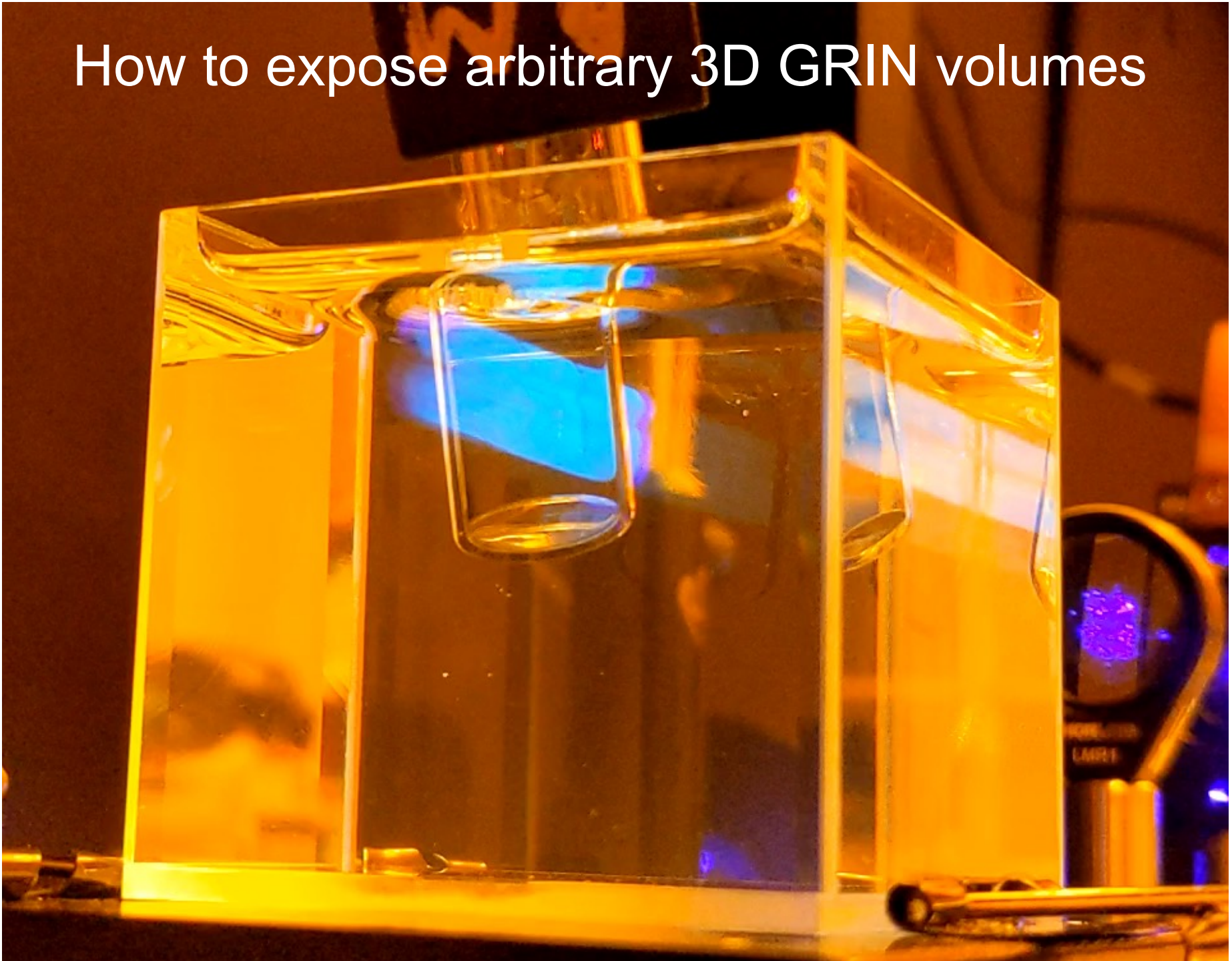
Output

Input

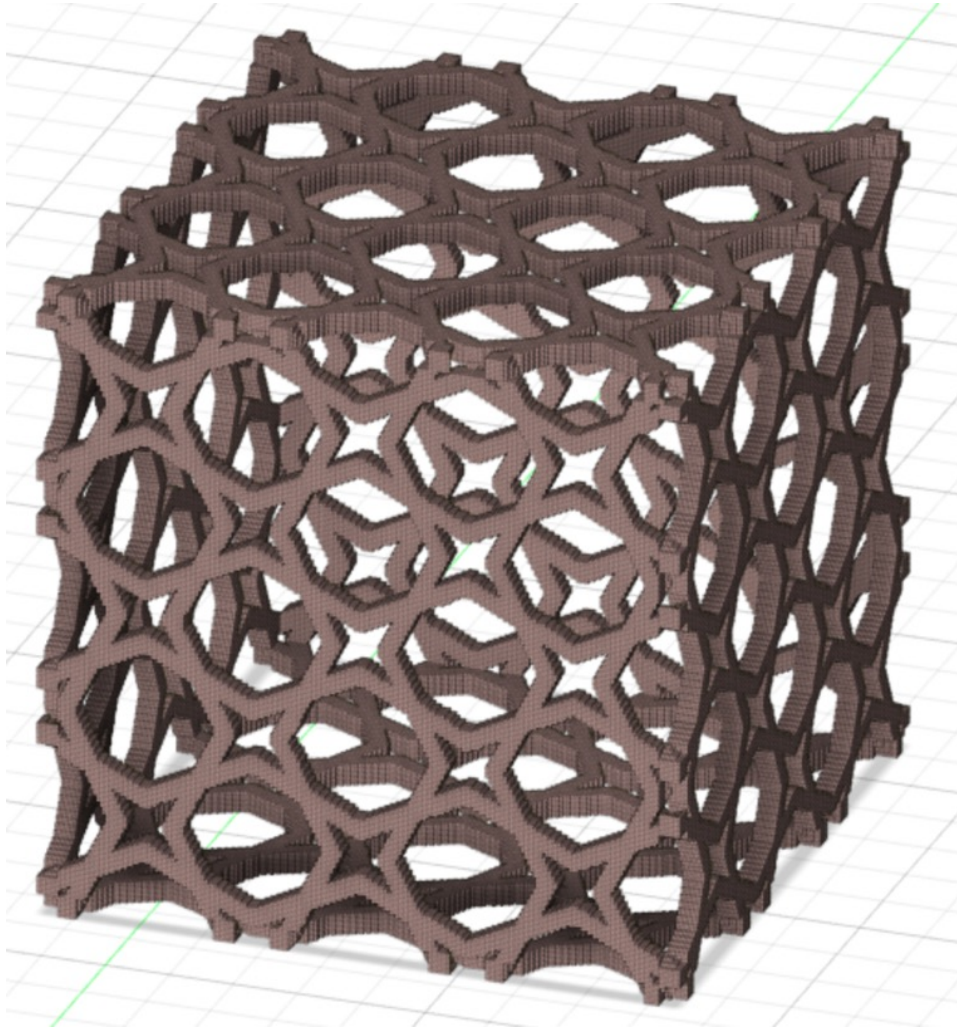
Output



How to expose arbitrary 3D GRIN volumes



Results: 3D GRIN control



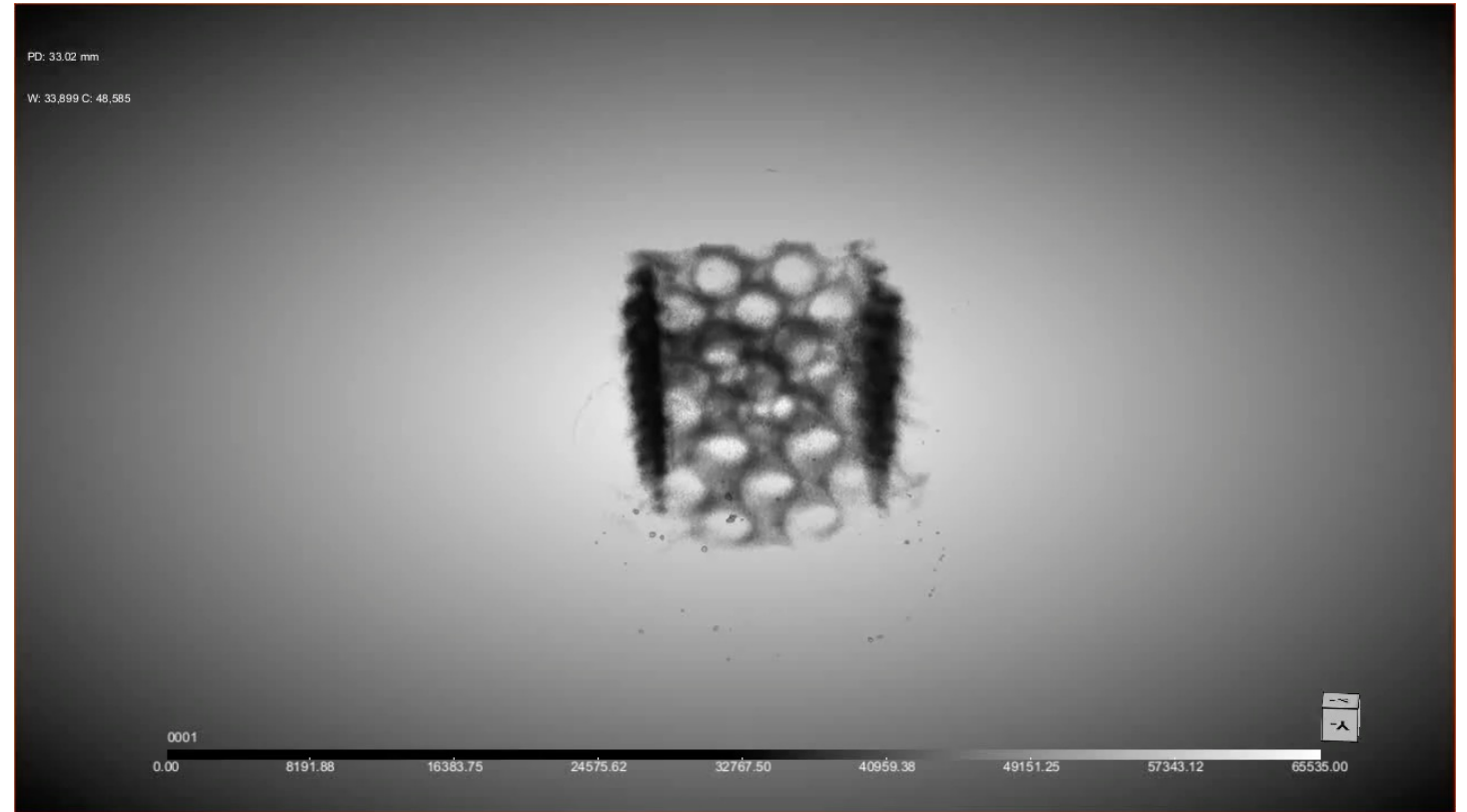


Label-free μ XCT imaging of 3D GRIN optics

TBPA in urethane



μ XCT image



Questions?



Holographic Photopolymer Formulation Instructions

McLeod Laboratory, University of Colorado Boulder
April 2023

Background

The basic “two stage” holographic photopolymer contains three principal components:

1. A permeable solid matrix such as urethane,
2. a mobile photopolymerizable monomer such as an acrylate, and
3. a photoinitiator such as one from the Irgacure series

These material systems are commonly referred to as ‘two-stage’ photopolymers because there are two orthogonal chemistries which react in two separate stages: the first reaction that creates the homogeneous solid matrix and the second photopolymerization reaction which creates the refractive index pattern. The first, matrix, reaction begins as soon as the reactive components are combined, so one typically casts the liquid formulation onto substrates such as glass as soon as the formulation is complete. The specific urethane matrix described below is created by the reaction between hydroxyl groups in the polyol and the isocyanate, possibly accelerated by a tin catalyst. A central requirement of this reaction is that it be “orthogonal” to the photopolymerization stage, meaning that the components needed for the photopolymerization reaction (2 and 3 from the list above) remain unreacted in the first stage and are thus available for later use in the second stage. A second reason for choosing the urethane as the matrix is that the hydroxyl/isocyanate reaction is step growth which results in less shrinkage stress.

Once the matrix reaction has completed, transforming the liquid formulation into a soft solid, the material is ready to be exposed to light to initiate the second stage reaction. This stage begins with the absorption of a photon by the photoinitiator within its absorption band, typically in the region of 365 to 450 nm. The Norrish type I-photoinitiators described below cleave into two radicals which begin the polymerization chain reaction of the monomer. This leads to a refractive index pattern in the material that is approximately proportional to the intensity of the exposing light, as described in the references at the end of this document. Typically, after one or more patterned photo-exposures, the material is exposed to uniform light to consume all remaining photoinitiator and monomer such that the part is no longer photosensitive.

Matrix chemistry

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This formulation uses a urethane matrix composed of a polyol and an isocyanate. The polyol is [polycaprolactone-block-polytetrahydrofuran-block-polycaprolactone](#) with a molecular weight of 2000 g/mol. This specific polyol was picked to tune the glass transition temperature, T_g , well below room temperature ($T_g \approx -70^\circ \text{C}$ in this case). The isocyanate is [Desmodur N 3900](#) from Covestro. Covestro sells this material by the drum, but in academia we have had good luck getting a *sample* bottle which is enough for a very large number of experiments. Request this sample early as you will have to fill out safety sheets and have multiple calls with people from Covestro about this material. That said, they are very friendly and easy to work with.

When using the isocyanate, we highly suggest storing the bottle in the fridge and creating a second, smaller bottle of filtered isocyanate for use. We prefer to do this using [1 \$\mu\text{m}\$ syringe filters](#). Additionally, the isocyanate + polyol reaction is very sensitive to humidity; we recommend covering the filtered isocyanate bottle with parafilm to reduce moisture in the bottle. Finally, if you are not familiar with chemical safety, we highly recommend having an expert recommend storage, safety and disposal protocols. While none of these materials are acutely toxic, exposure can cause severe allergic reactions.

Monomers

Many monomers can be used in this system. In our group, we use both off-the-shelf and synthesized monomers. Synthetic monomers are summarized in our publications which are summarized in the references section. We recommend you start with commercial off-the-shelf monomers. The two we recommend are [2,4,6-tribromophenyl acrylate \(TBPA\)](#) and [Bisphenol A ethoxylate diacrylate \(BPAEDA\)](#). The primary requirements of monomers are that they have large refractive index contrast with the matrix (typically larger) and are highly soluble in the matrix. TBPA has a solubility limit of ~ 40 wt% in the matrix mentioned above. The solubility limit of BPAEDA is approximately 53 wt%. Finally, TBPA monomer is a powder while BPAEDA is liquid, which can impact some experimental protocols. We observe haze more often with TBPA, possibly related to its powder form when pure. For the beginner, we recommend using BPAEDA over TBPA.

Note on TBPA: We have purchased our TBPA from TCI Chemicals and have had mixed results. Sometimes, the bottles we get are powdery, while other times they are crystalline. We have found that we can successfully make optically clear samples of two-stage photopolymer with TBPA only when the TBPA is crystalline. Unfortunately, it seems that we receive crystalline TBPA in only around 10% of the bottles of TBPA we purchase. The rest are powdery and make highly scattering photopolymer samples. We have reached out to TCI to understand why there is a

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difference in the samples but we have not received any useful information. Because of this, we have stopped using TBPA and now use BPAEDA for our off-the-shelf monomer.

Photoinitiators

Assuming your monomer is an acrylate or methacrylate, virtually any initiator that generates radicals should work. Norrish type I initiators are simpler to formulate and model, but type II initiators certainly work. Different initiators allow you to customize your material to respond to different wavelength ranges and to be packaged in different thicknesses. In general, the initiator concentration needs to be high enough to effectively polymerize all of the monomer but low enough to not limit light penetration due to Beer-Lambert absorption. Secondary considerations include photo-sensitivity, the absorption of the initiator after reaction and having sufficient initiator to not significantly deplete local initiator concentration during patterning. Note that it is typically the case that photoinitiator absorption is too large at the peak for the relatively thick samples used in diffractive optics, so design of a new formulation with a particular thickness often involves comparing potential lasers at different wavelengths to potential initiators via their absorption at those wavelengths.

We currently use two different photoinitiators – [2-Methyl-4'-\(methylthio\)-2-morpholinopropiophenone \(I907\)](#) and [TPO](#). Others that we have used include [LAP](#) (for hydrogels) and [I2959](#). For holography, we use TPO for nearly complete photo-bleaching and its appropriate absorptivity at 405 nm. Typical loading of TPO in photopolymers for holography is ~1 wt%.

Formulation procedure

This is the procedure we follow to create two-stage photopolymer samples with 40 wt% BPAEDA (molecular weight 512 g/mol, 40 wt% picked to be significantly below the solubility limit), 0.5 wt% I907 or 1 wt% TPO, and 59.5 wt% matrix. To have stoichiometric balance of polyol and isocyanate there must be a factor of 5.593 more polyol (by weight) than isocyanate. This value is set by the average number of functional groups per mol of each species as well as the molecular weight of each species.

For a 10 g batch of [40 wt% BPAEDA], [0.5 wt% I907], the formulation is as follows:

- 5.0475 g polyol.
- 0.05 g I907.
- 4 g BPAEDA.

- 0.9025 g isocyanate.

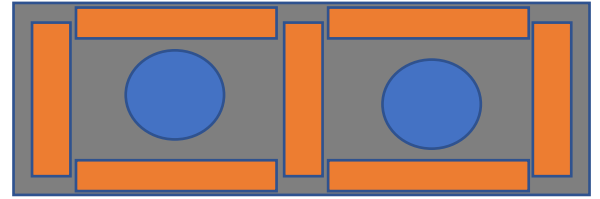
The procedure for mixing the materials and creating the samples is as follows:

1. Heat the polyol to 60 – 70° C to melt it. In its solid state, the polyol cannot be mixed. It is convenient to do this heating in a small glass rather than heating the entire bottle of material as received.
2. After the polyol melts, use a plastic pipette to weigh the desired amount into a glass beaker, jar, or vial.
3. Weigh out the photoinitiator. I personally just directly weigh the photoinitiator, but some prefer to create a mixture of polyol and photoinitiator to make measuring the PI easier. In that case, you must ensure that the pure polyol and polyol from the polyol + PI sums to the desired amount.
4. Weigh out the monomer. For BPAEDA, this is simply using a plastic pipette (a clean, new one) to weigh. For TBPA, a scoopula is useful.
5. Typically, I will add a solvent like acetone, ethanol, or dichloromethane (DCM). I typically add ~1 mL of DCM.
6. With a magnetic stir bar in the glass beaker/jar/vial, perform a heated stir between 60 and 80° C. I tend to stay closer to 60° C to prevent the chance that the monomer or photoinitiator may be thermally initiated at higher temps. I tend to stir at the highest speed capable of achieving a smooth stir. Stir for multiple hours (typically > 12 hours).
7. After stirring, de-gas the mixture. I tend to slowly pull vacuum to ensure my mixture doesn't bubble over the side of the glass vessel. I leave the mixture at the minimum pressure for ~30 minutes.
8. After de-gassing, add the filtered isocyanate to the mixture. At this point, the mixture of polyol + monomer + photoinitiator should have cooled down from the ~ 60° C it was held at, but it will still be warm. When the isocyanate is added the matrix starts to cure. *The following steps should be performed quickly.*
9. Perform a cold stir on the mixture. A vortex mixer (or even aggressively shaking the mixture by hand) seems to help. I typically mix aggressively for 5 to 10 minutes.
10. De-gas the material again. I try pulling vacuum rather quickly and then I leave the mixture at this pressure for ~10 minutes.
11. Remove the mixed, de-gassed material from vacuum and use a pipette to drop on microscope slides with shim spacers already in place. The shim spacers set the thickness of the material within the package. Cap with another slide on top and clip the ends with binder clips. More on slide geometries and method below
12. Place the clipped slide samples in the oven and allow to thermally cure for > 24 hours. Typically, I will drop a small amount of material in an open vial that is placed in the oven. Then, to check if the material is ready to remove, I will poke the material in the open vial with a scoopula. If the material seems solid, it is likely ready to be removed from the oven.

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More on Slide Sample Geometry

For creating samples between glass slides, I like to use the geometry shown on the right where gray represents the glass slide, orange represents [polyester shim stock](#) (Precision Brand shim stock has worked pretty well for us).



To ensure the slide samples are the thickness of the shim, we use small binder clips on the leftmost and rightmost spacers. We would like to explore using metal spacers instead, but this is untested thus far.