

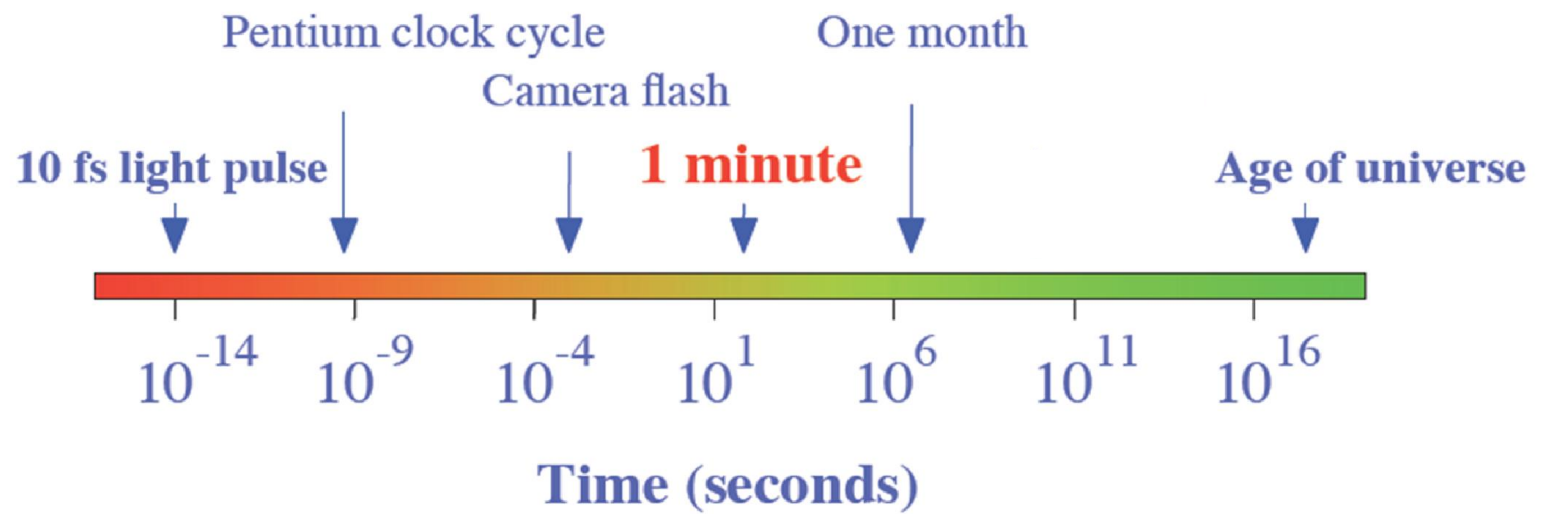
# Femtosecond laser pulses: nonlinear spectroscopy and microfabrication

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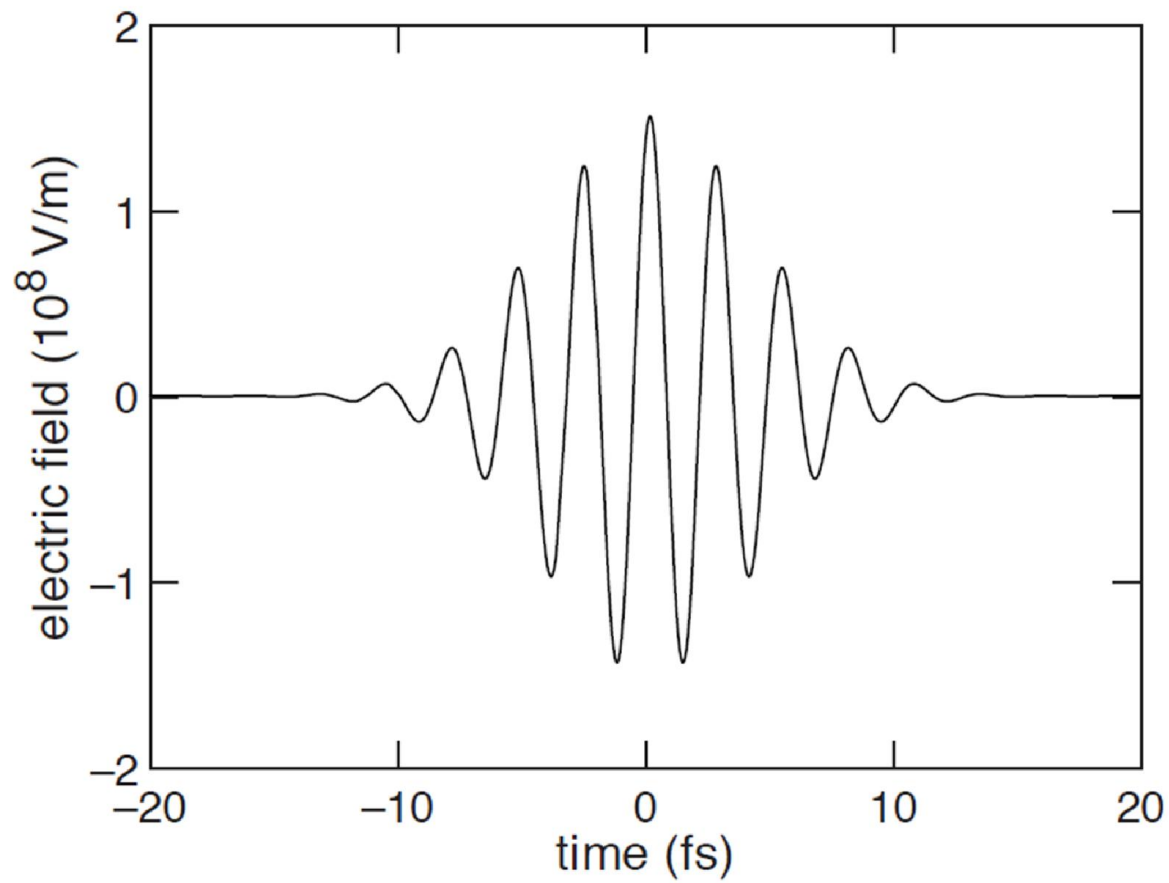
# Microfabrication

$$1 \text{ fs} = 10^{-15} \text{ s}$$



# introduction

how short is a femtosecond pulse ?



# Microfabrication

Ti:Sapphire lasers



100 fs



50 fs



20 fs

Very intense light

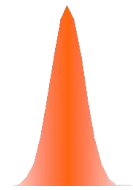
*Laser intensities*  $\sim 100 \text{ GW/cm}^2$   
 $1 \times 10^{11} \text{ W/cm}^2$

Laser pointer:  $1 \text{ mW/cm}^2$  ( $1 \times 10^{-3} \text{ W/cm}^2$ )



# fs-laser micromachining

Ti:Sapphire lasers



100 fs



50 fs

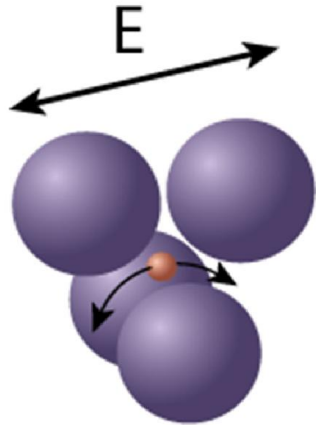


20 fs

Very intense light

***Nonlinear Optical Phenomena***

# Nonlinear Optics



anharmonic oscillator

high light intensity

$$E_{\text{rad.}} \sim E_{\text{inter.}}$$

nonlinear polarization response

$$P = \varepsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \right)$$

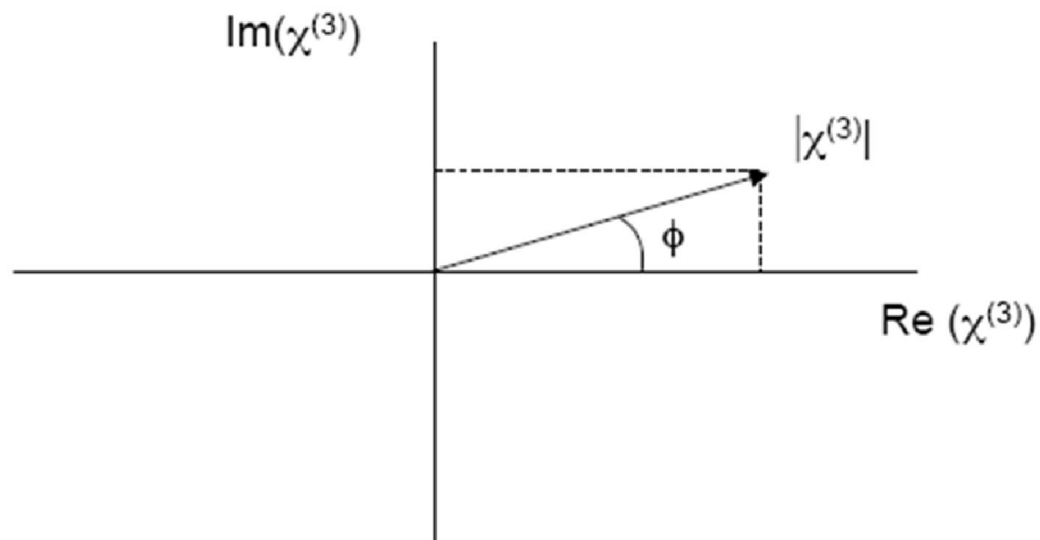
# Nonlinear Optics

$\chi^{(3)}$  is a complex quantity

$$\chi^{(3)} = \text{Re}(\chi^{(3)}) + i \text{Im}(\chi^{(3)})$$

Related to intensity  
dependent refractive index

Related to two-photon  
absorption

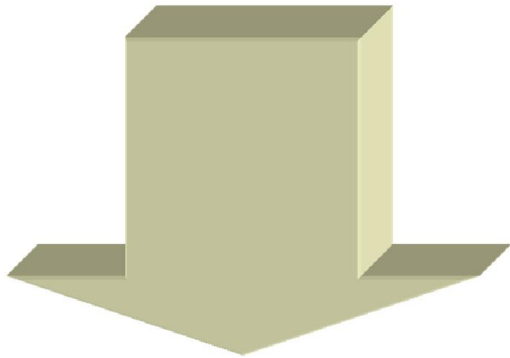


# Nonlinear Optics

Third order processes:  $\chi^{(3)}$

Refractive process:

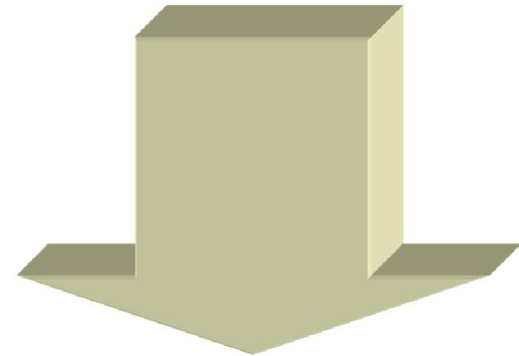
$$n = n_0 + n_2 I$$



- self-phase modulation
- lens-like effect

Absorptive process:

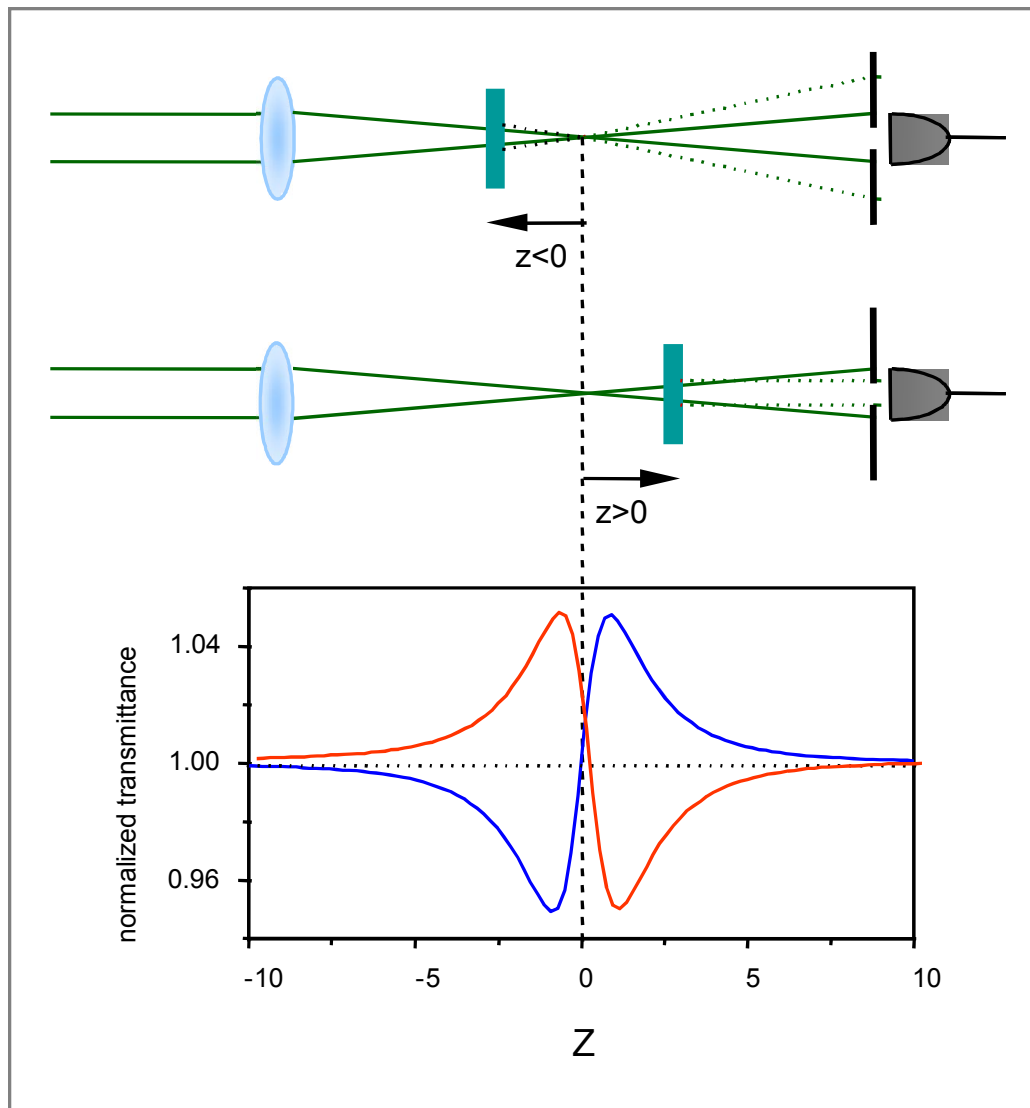
$$\alpha = \alpha_0 + \beta I$$



- nonlinear absorption
- two-photon absorption

# Measuring nonlinear refraction

## Z-scan: close aperture



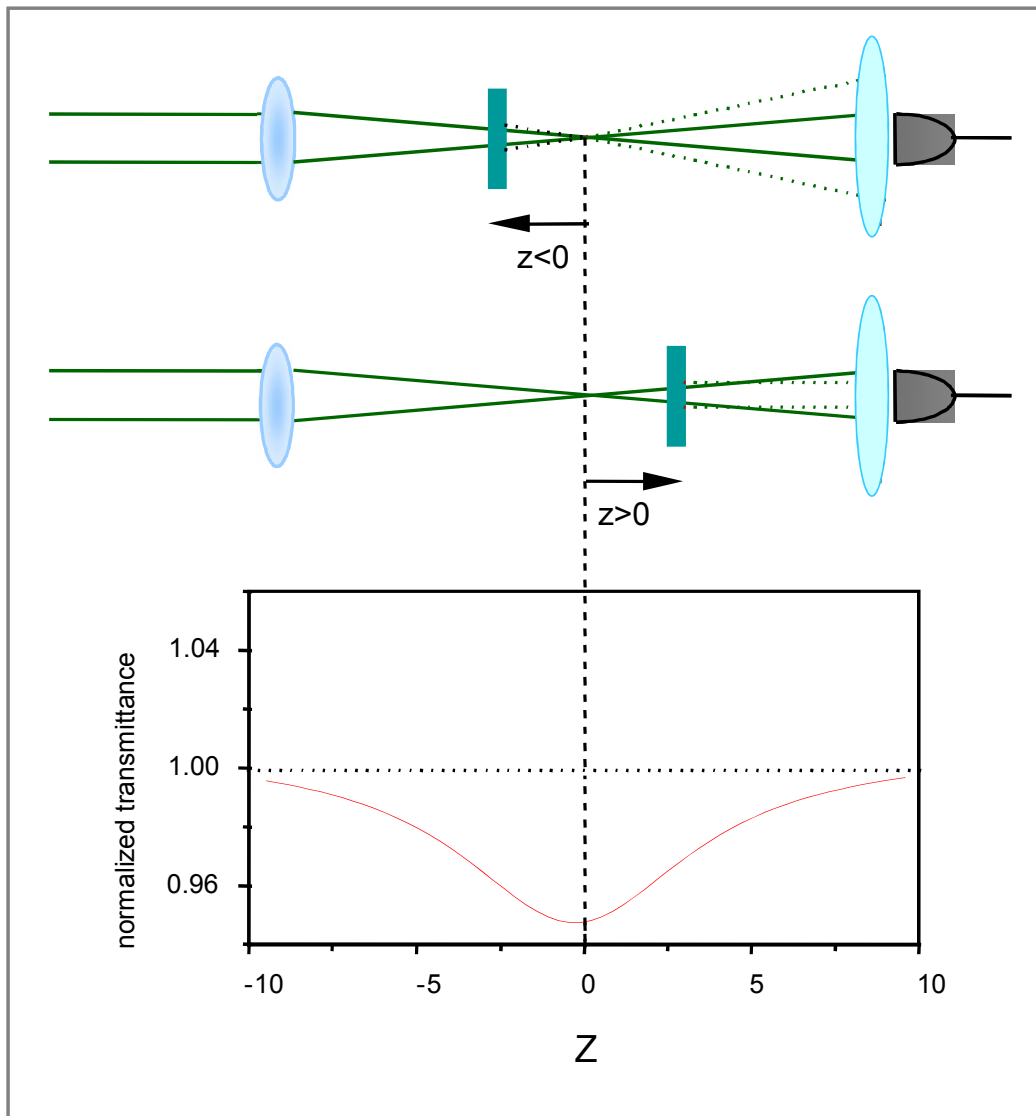
$$n = n_0 + n_2 I$$

$$|\Delta Z_{pv}| \approx 1.7 Z_0$$

$$\Delta T_{pv} \cong 0.406(1 - S)^{0.27} |\Delta \Phi_0|$$

$$\Delta \Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff}$$

# Measuring nonlinear absorption



$$\alpha(I) = \alpha_0 + \beta I$$

$$\Delta T \propto \beta I$$

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

$$q_0(z,t) = \beta I_0 L / (1 + z^2 / z_0^2)$$

# Nonlinear spectroscopy

nonlinear spectrum



Laser amplifier (Ti:Sapphire)

$\tau = 150 \text{ fs}$   
 $\lambda = 775 \text{ nm}$   
 $E = 800 \text{ } \mu\text{J}$



Optical parametric amplifier

$\tau = 120 \text{ fs}$   
 $\lambda = 460 - 2600 \text{ nm}$   
 $E = 20\text{-}60 \text{ } \mu\text{J}$

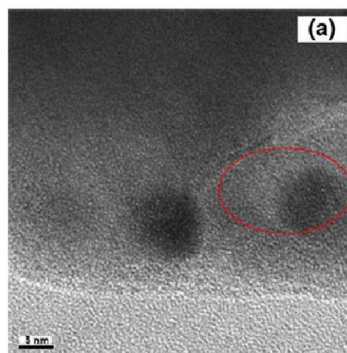
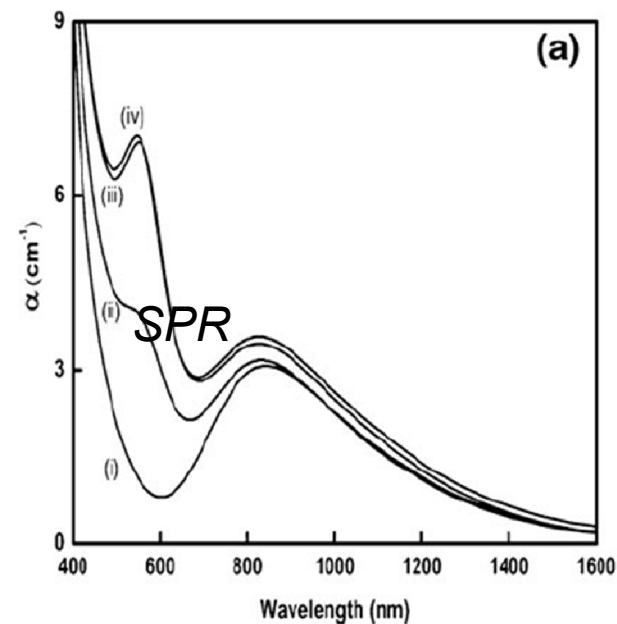
# Tungsten Lead-Pyrophosphate + Cu

$70\text{Pb}_2\text{P}_2\text{O}_7\text{-}30\text{WO}_3$  (in wt. %) for glass host

+  
 $\text{CuO}$  (0.5 wt. %)

Table 1 Sample labels, synthesis conditions, and characteristic temperatures of PW glasses doped with CuO

Sample labels	Annealing conditions		Characteristic temperatures	
	$T_{\text{ht}}$ (°C)	$t_{\text{ht}}$ (min)	$T_g$ (°C)	$T_x$ (°C)
(i) PW-0	410	0	410	575
(ii) PW-5		5		
(iii) PW-20		20		
PW-60		60		
(iv) PW-120		120		

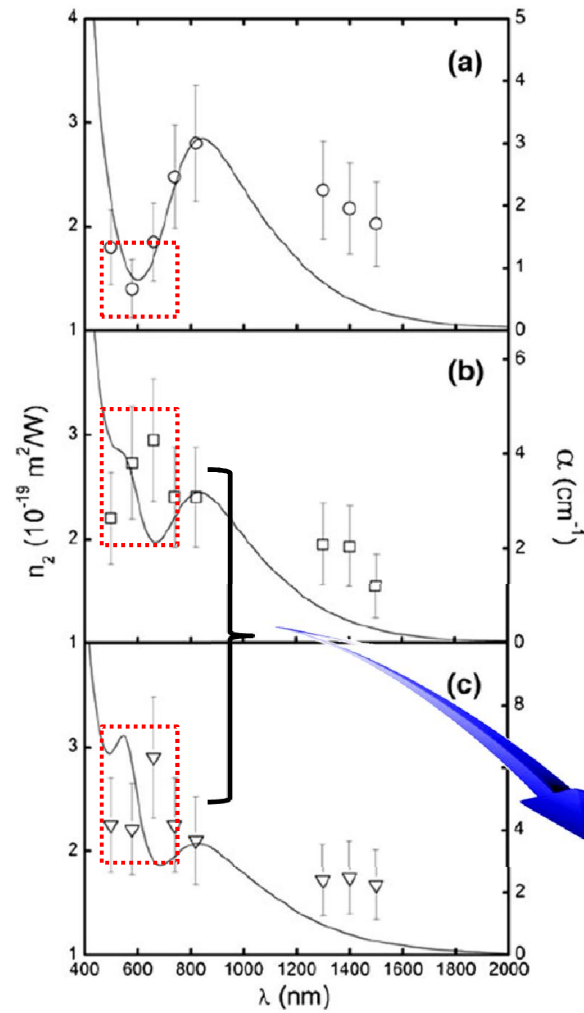




# Nonlinear refraction



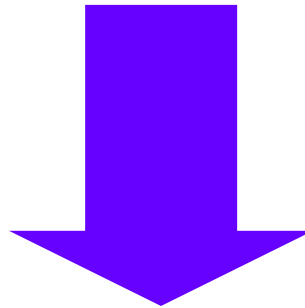
$$\Delta\phi_0 = kn_2I_0L.$$



Enhancement effect

# fs-laser microfabrication

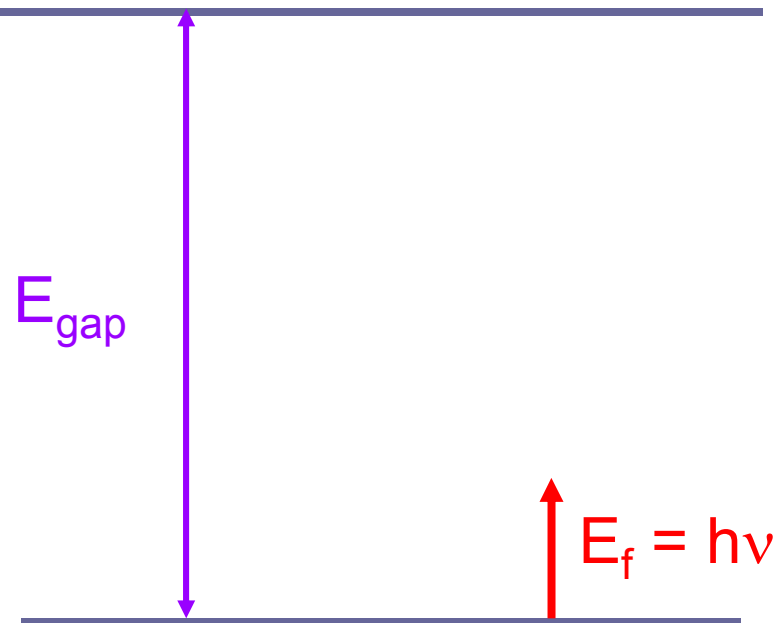
photon energy  $<$  bandgap



nonlinear interaction

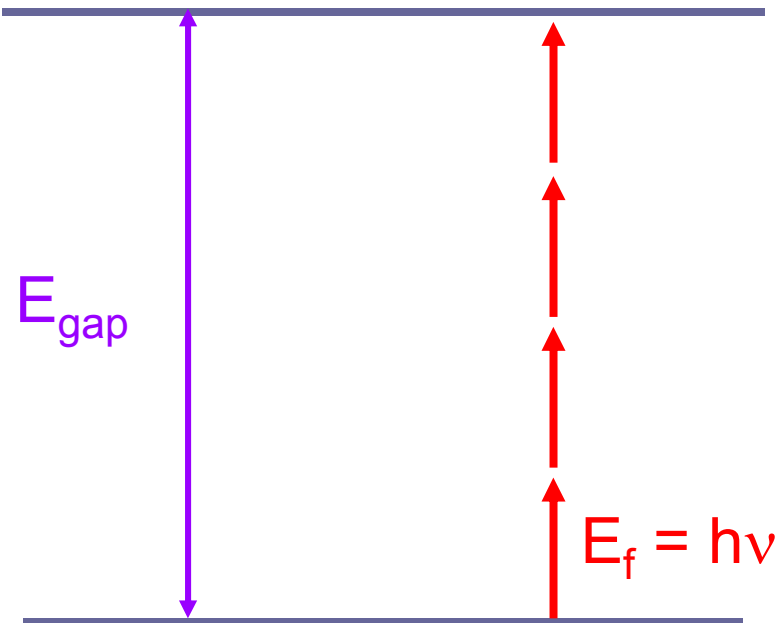
# fs-laser microfabrication

nonlinear interaction



# fs-laser microfabrication

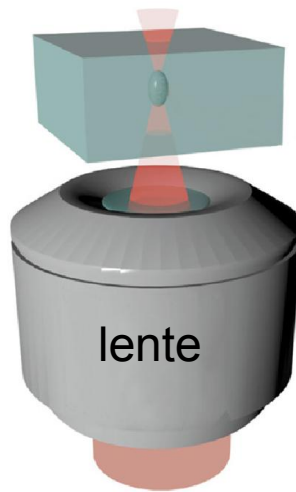
nonlinear interaction



multiphoton absorption

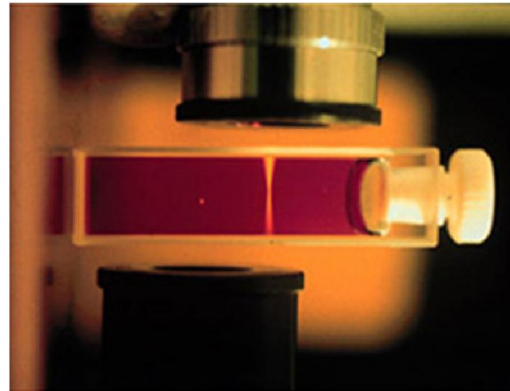
# multiphoton absorption

nonlinear interaction



spatial confinement of excitation

two-photon absorption

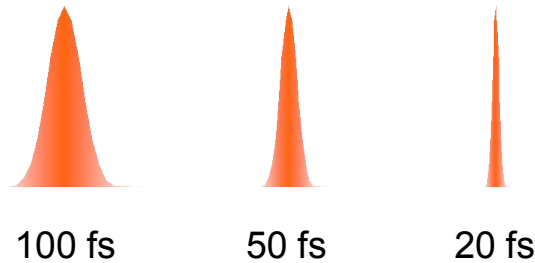


$$\alpha = \alpha_0 + \beta I$$
$$R \propto I^2$$

feature exploited for microfabrication

# femtosecond pulses

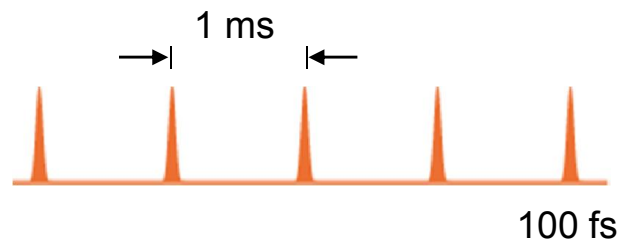
Ti:Sapphire lasers



$$1 \text{ fs} = 10^{-15} \text{ s}$$

Repetition rate

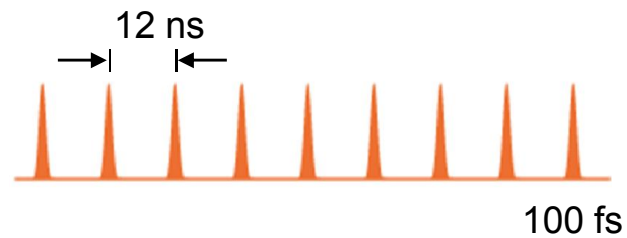
1 KHz



Energy

mJ

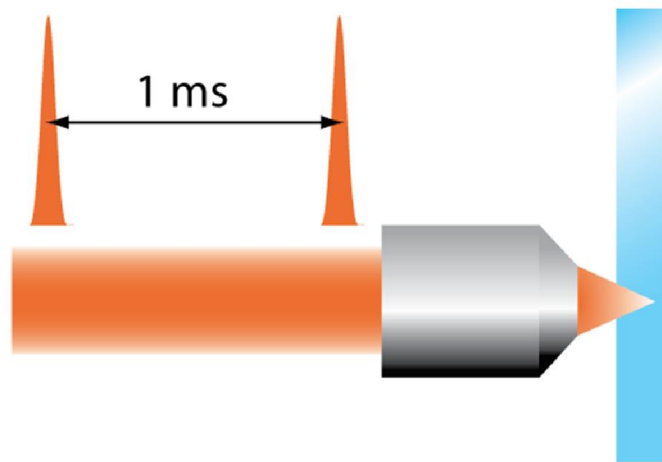
86 MHz



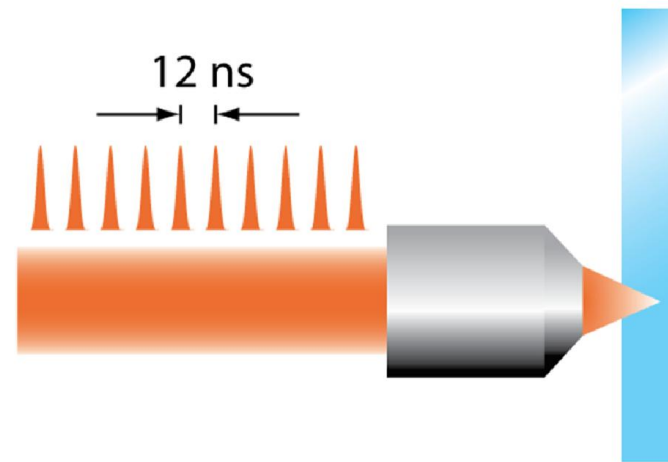
nJ

# fs-micromachining

amplified laser



oscillator



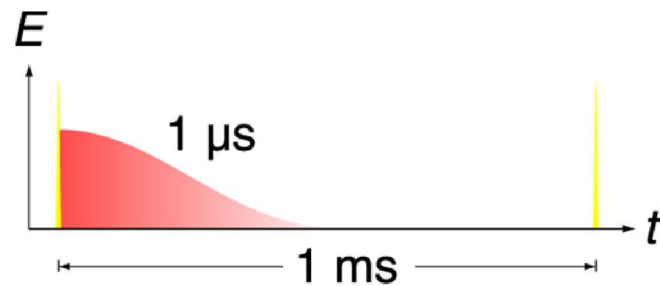
heat diffusion time:  $t_{\text{diff}} \sim 1 \mu\text{s}$

# fs-micromachining

amplified laser

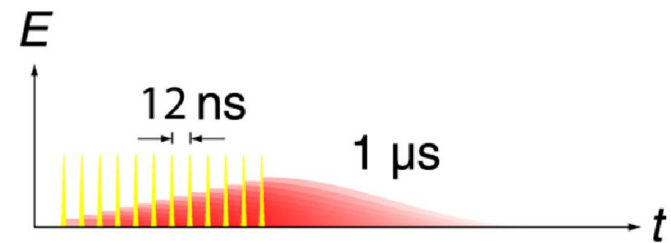
oscillator

low repetition laser



repetitive

high repetition laser

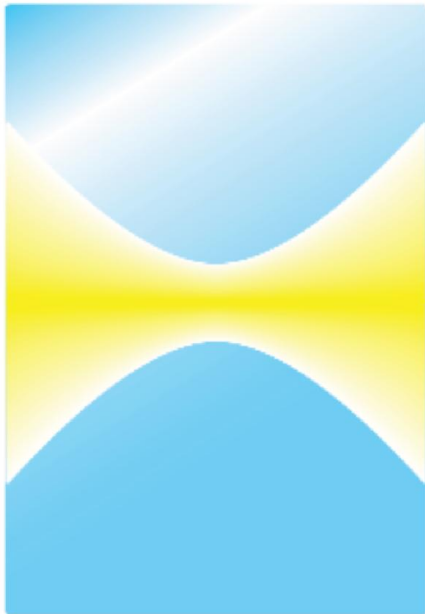


cumulative

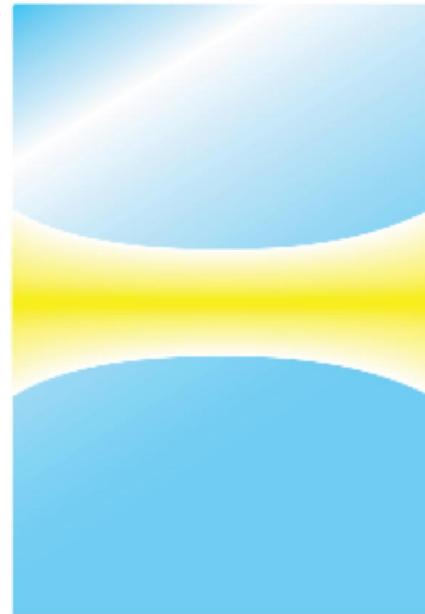


what is the difference ?

high NA



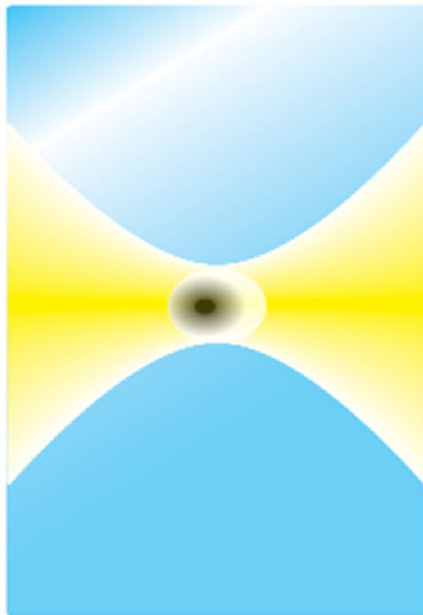
low NA



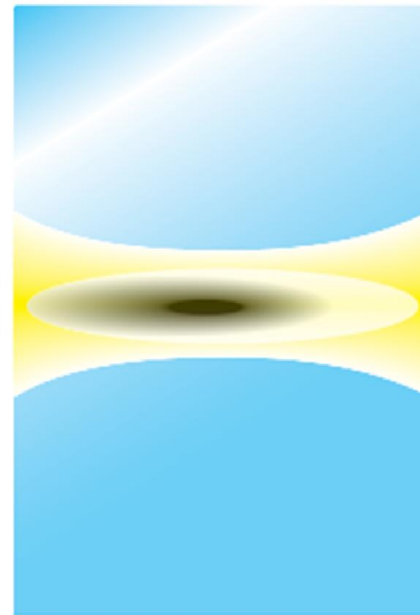
$$w_0 = \frac{\lambda}{\pi NA} \sqrt{1 - NA^2}$$

*very different confocal length/interaction length*

high NA



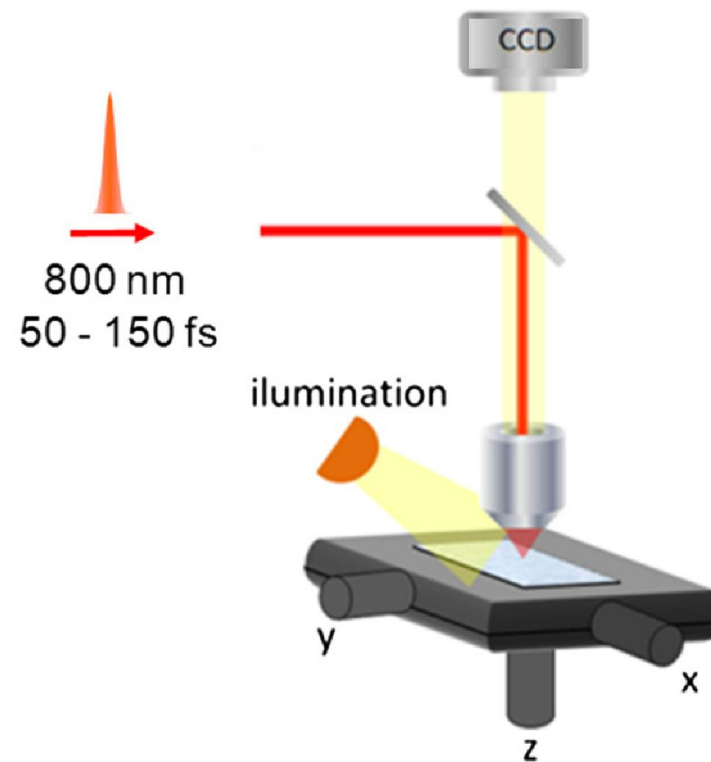
low NA



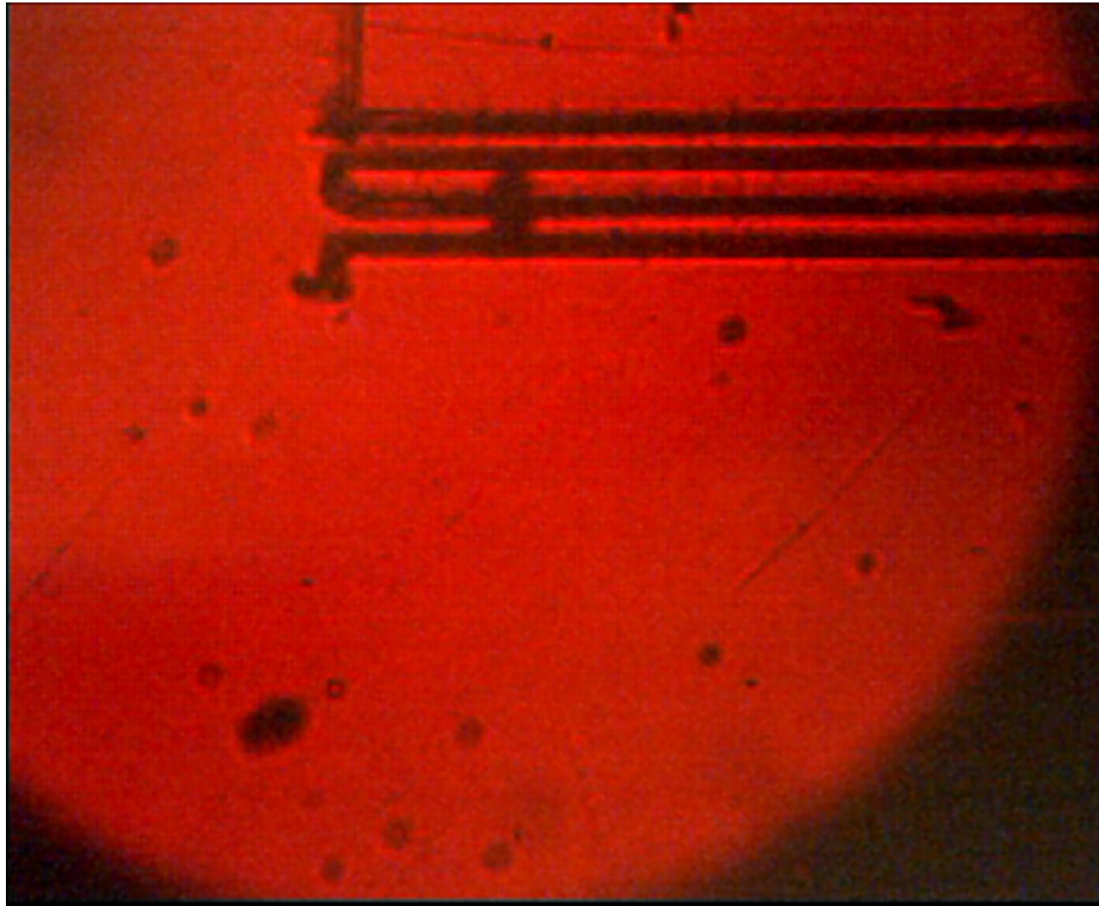
## two main techniques

- fs-laser micromachining/microstructuring
- microfabrication via two-photon polymerization

# fs-laser microstructuring experimental setup

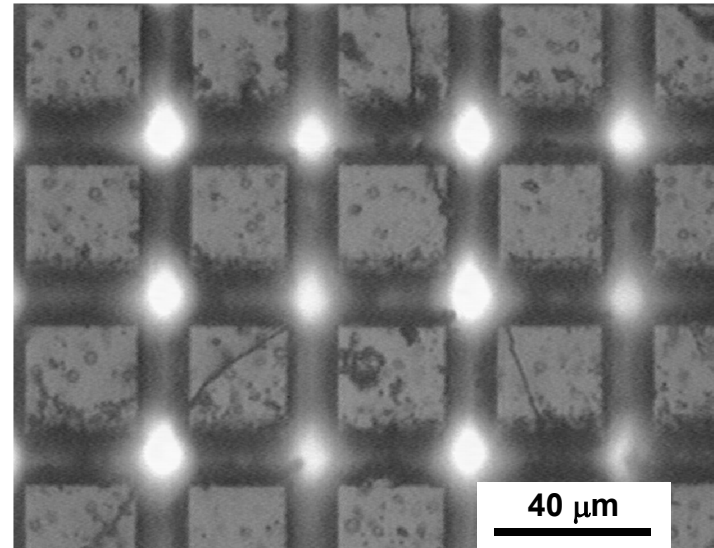
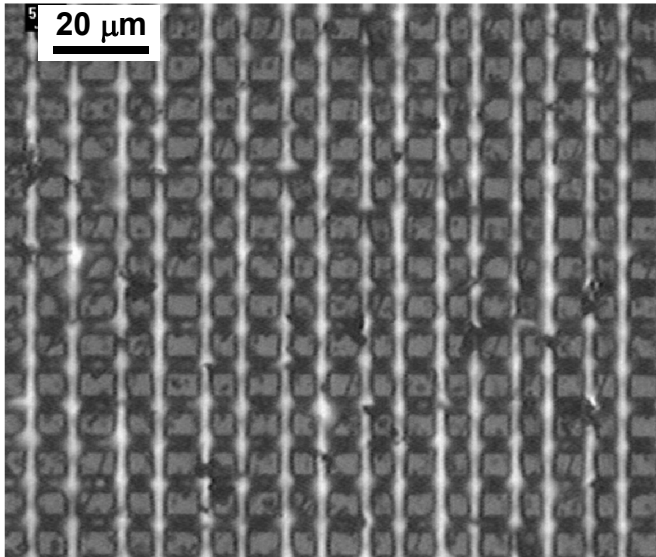


microstructuring polymer: super hydrophobic surface



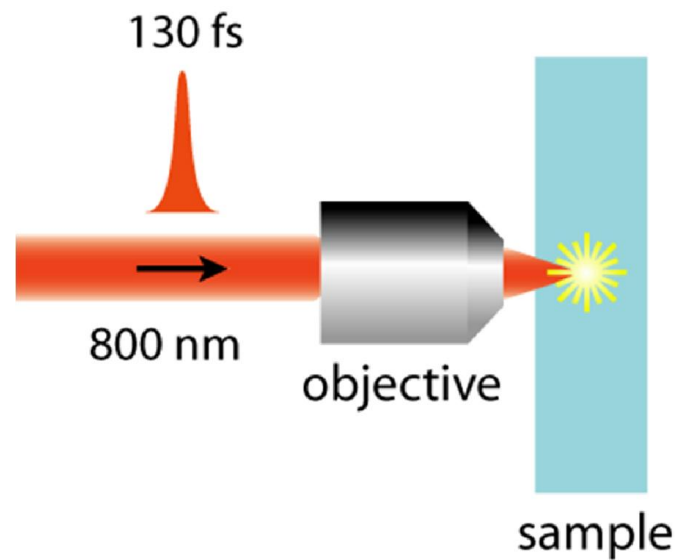
# laser microfabrication: super hydrophobic surface

examples of fabricated surfaces

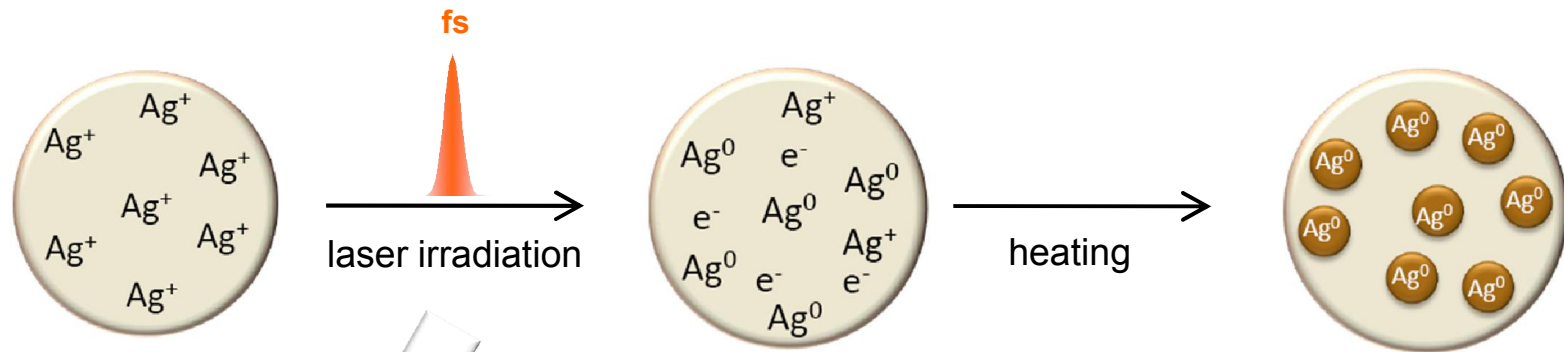


# fs-laser micromachining

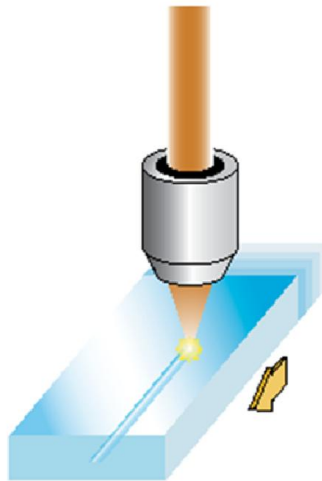
Volume



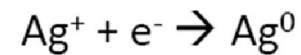
# Generation of Ag nanoparticles



Ag nanoparticles are generated only in the irradiated area due to the **fs-laser induced photoreduction**

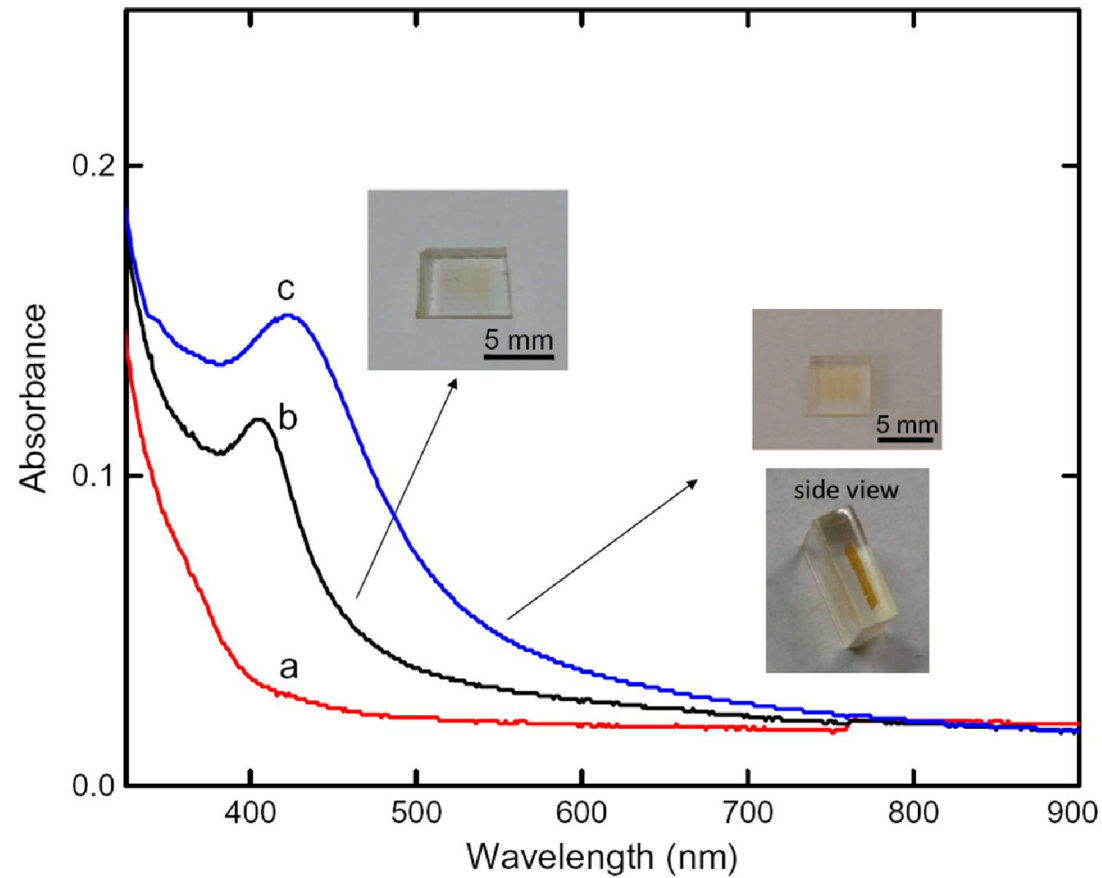


Free electron generation  
Photoreduction reaction



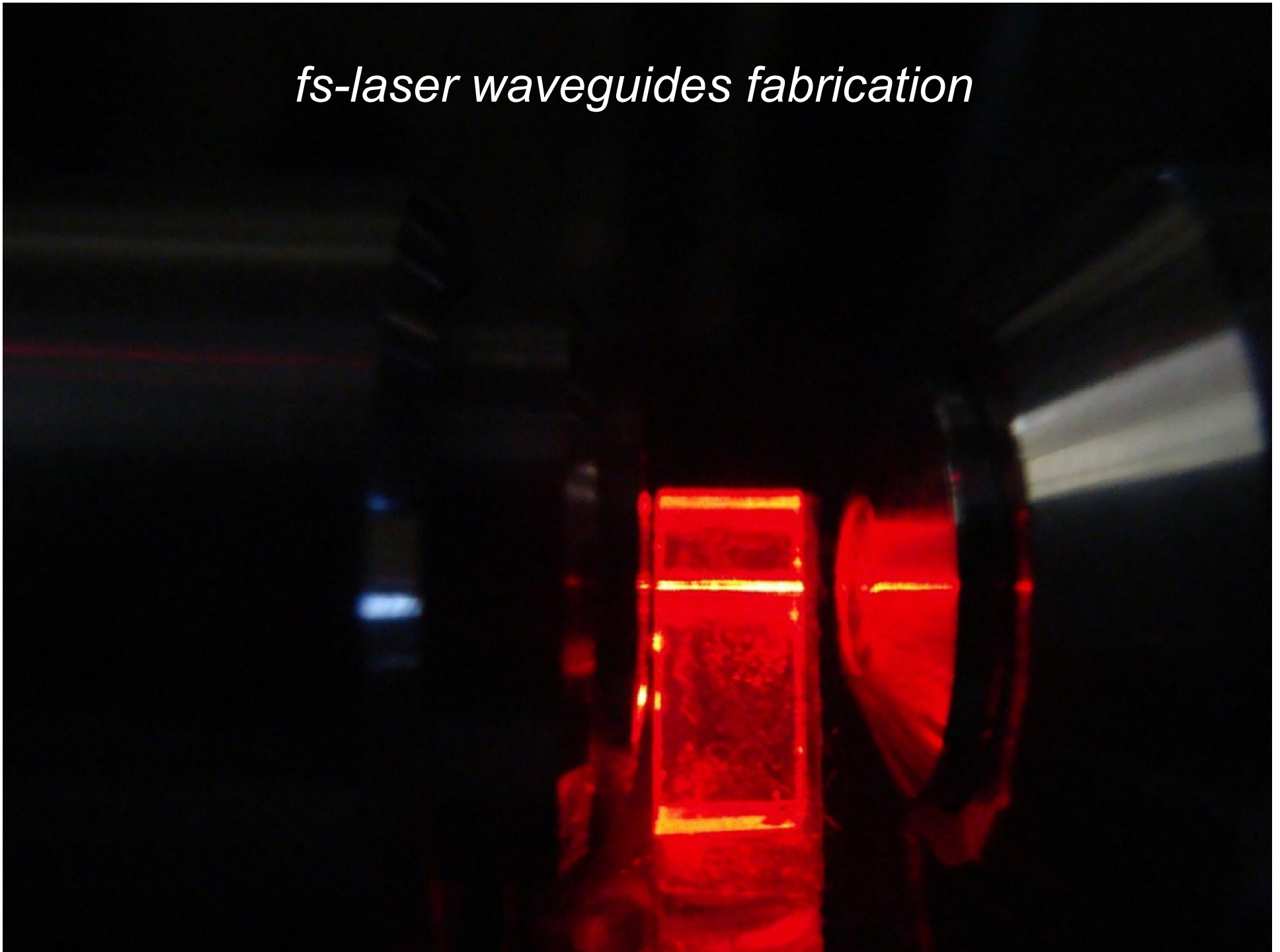


# *Generation of Ag nanoparticles*



Absorption spectrum of the Ag:BBO sample as prepared (a), after irradiation with the 5 MHz fs-laser (b) and after irradiation with the amplified fs-laser (1 kHz) and subsequent thermal treatment.

# *fs-laser waveguides fabrication*



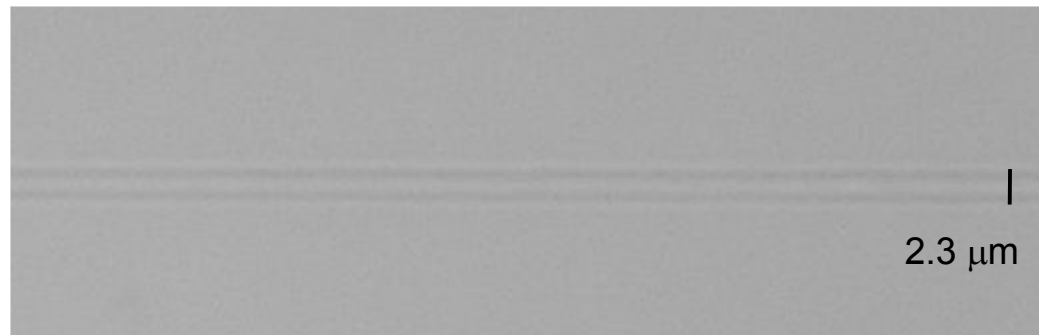
# Waveguides fabrication

Sample:

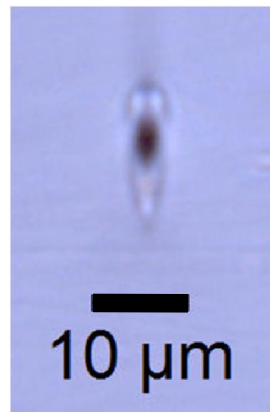
**Ag:P7W3**

*Tungsten lead pyrophosphate glass -  $(70\text{Pb}_2\text{P}_2\text{O}_7\text{-}30\text{WO}_3):1\text{AgCl}$  (%mol)*

Waveguides fabricated using the 5-MHz laser system (50 fs) with 37 nJ/pulse and  $v = 10 \mu\text{m/s}$



Top view



Cross-section  
view

# Waveguides fabrication

Coupling light into the waveguides

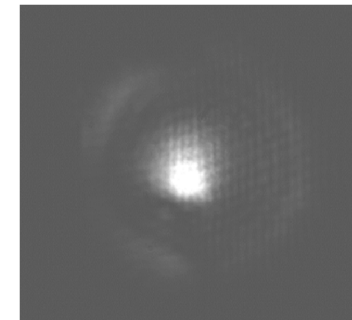
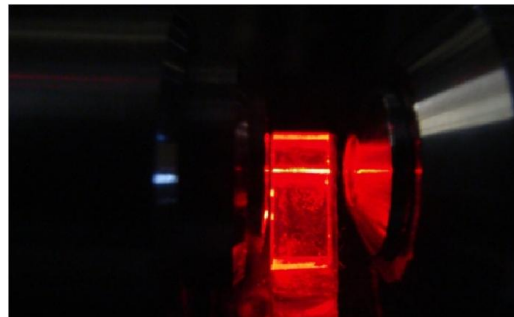
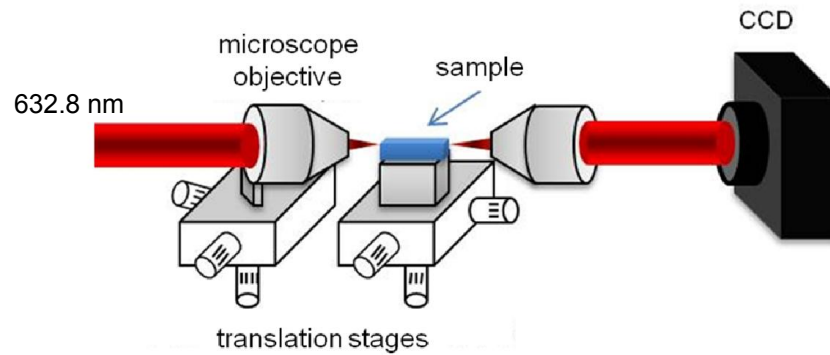
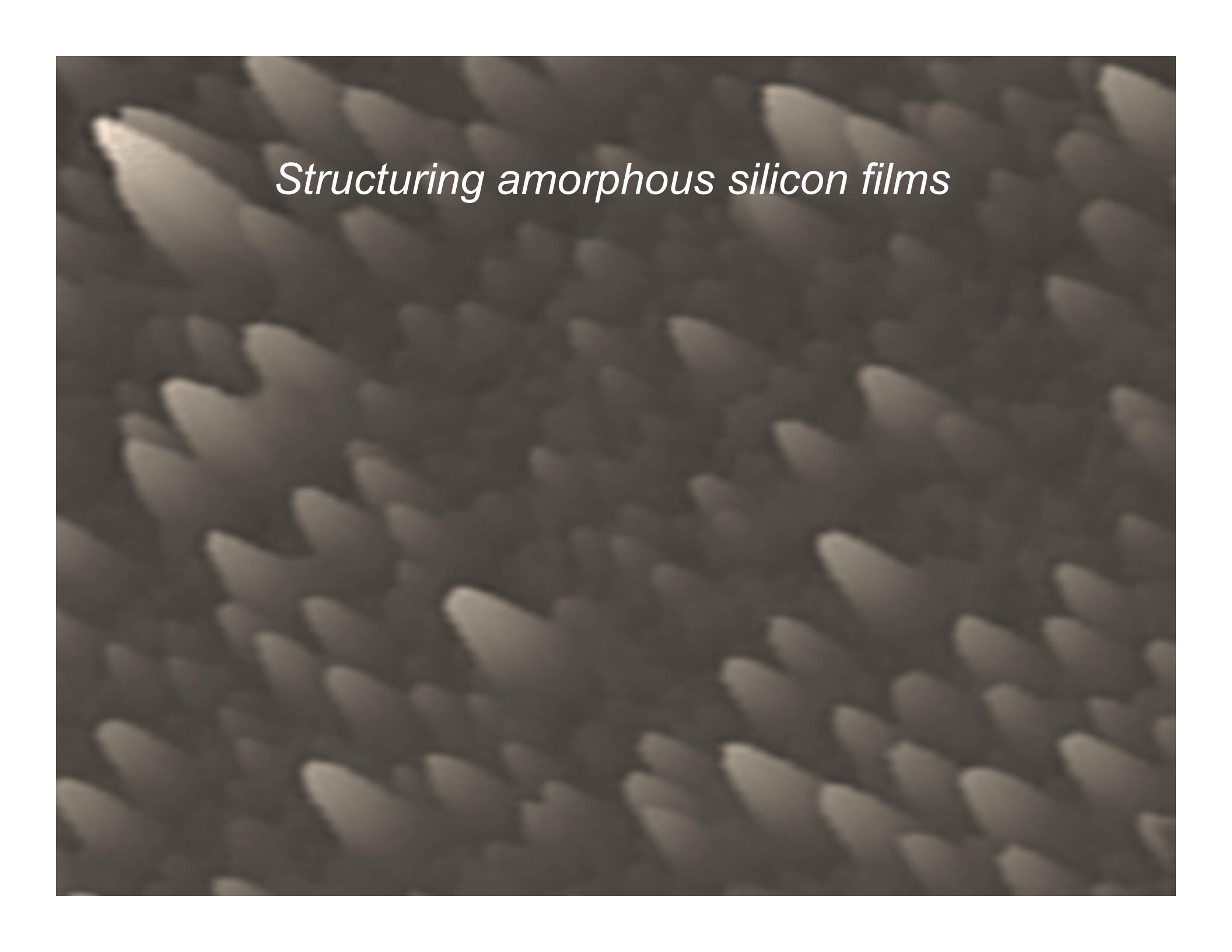


image of the waveguide output

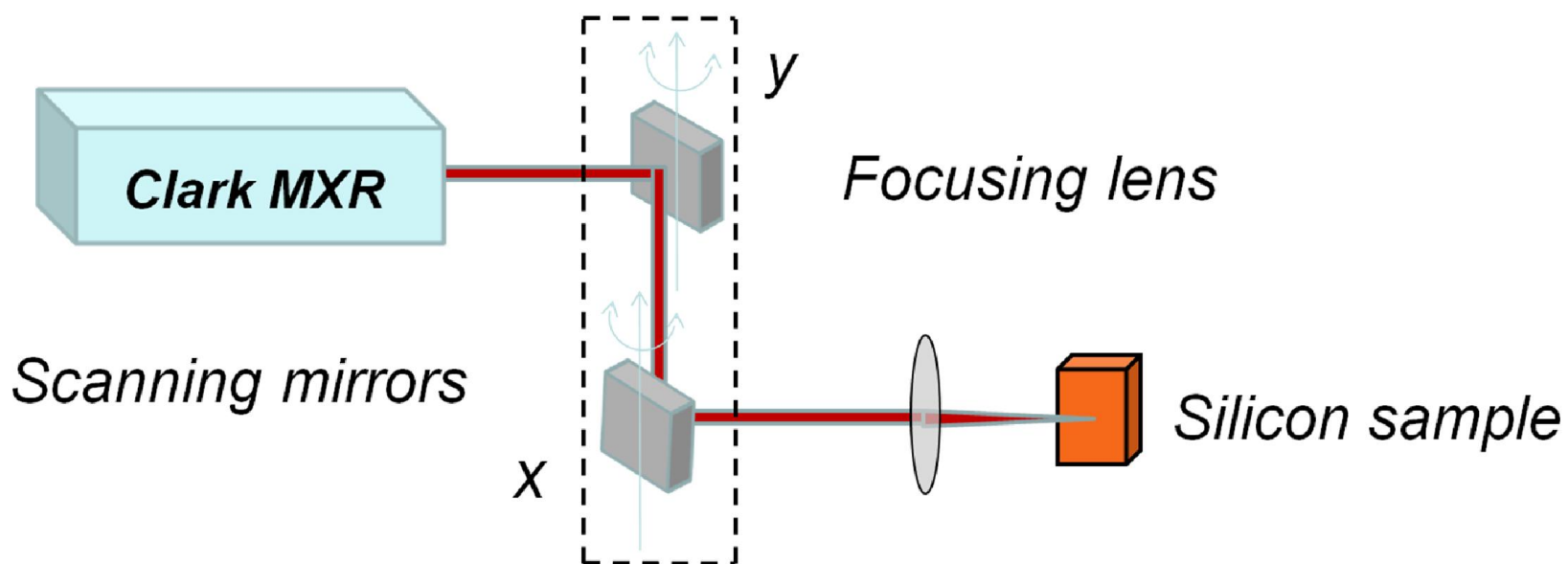
measured waveguide loss  $L = 1.3 \text{ dB/mm}$

The background of the slide is a grayscale micrograph showing a dense, repeating pattern of small, light-colored, elongated, and somewhat pointed structures. These structures are arranged in a regular, grid-like fashion, suggesting a highly ordered surface texture or a specific material morphology. The lighting creates a slight gradient, with the structures appearing brighter towards the top left.

## *Structuring amorphous silicon films*

## *structuring amorphous Si surface*

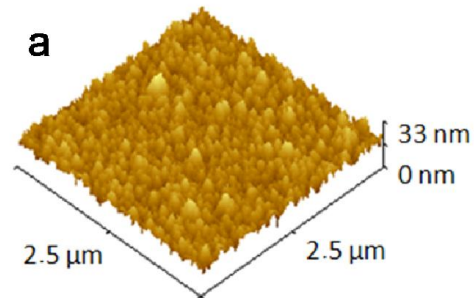
Experimental setup uses a pair of scanning mirrors



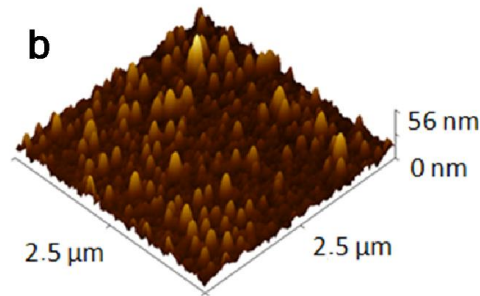
150 fs, 775 nm, 1 KHz,  $v = 5$  mm/s,  $f = 20$  cm

# structuring amorphous Si surface

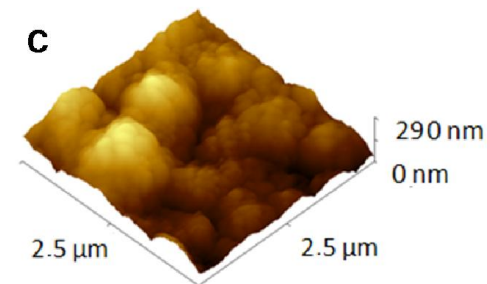
AFM micrographs of aSi microstructures at different laser intensities



before irradiation



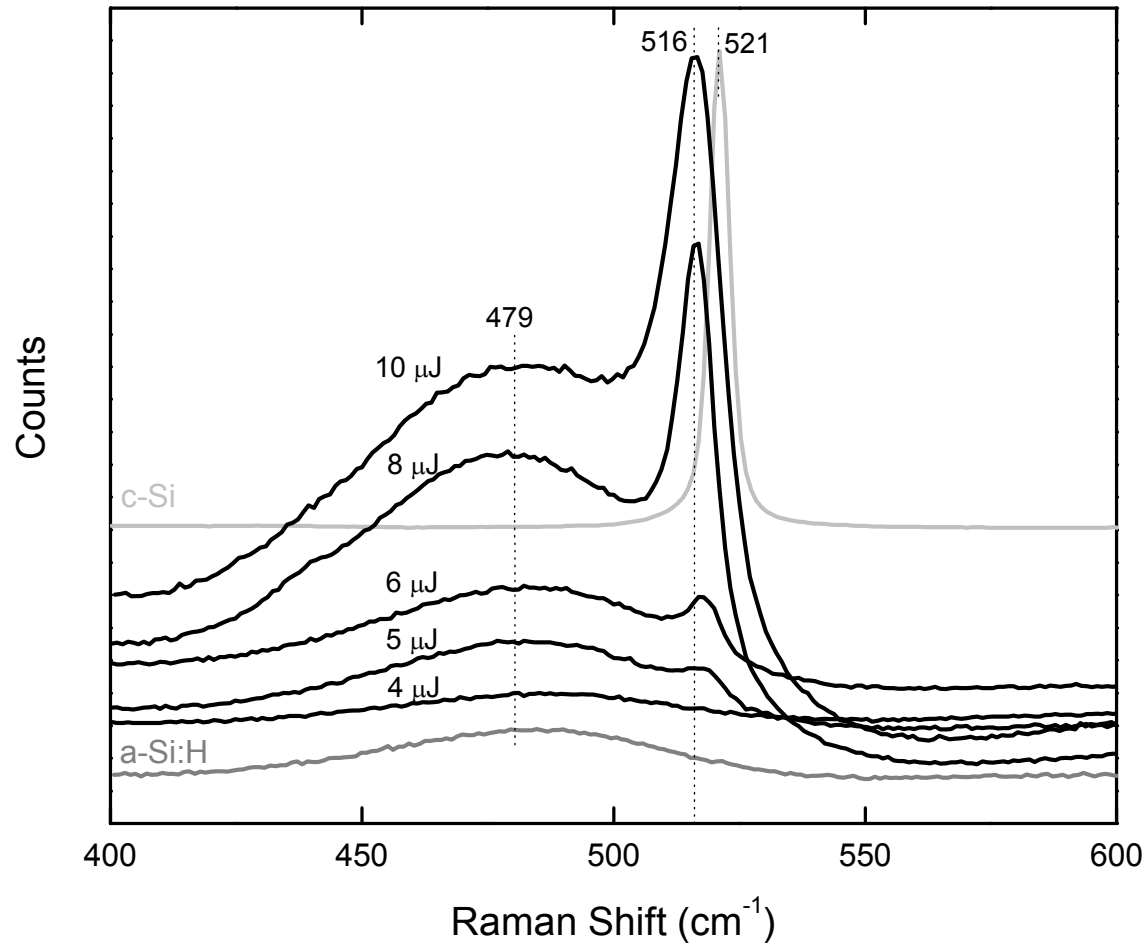
$E = 5 \mu\text{J/pulse}$



$E = 8 \mu\text{J/pulse}$



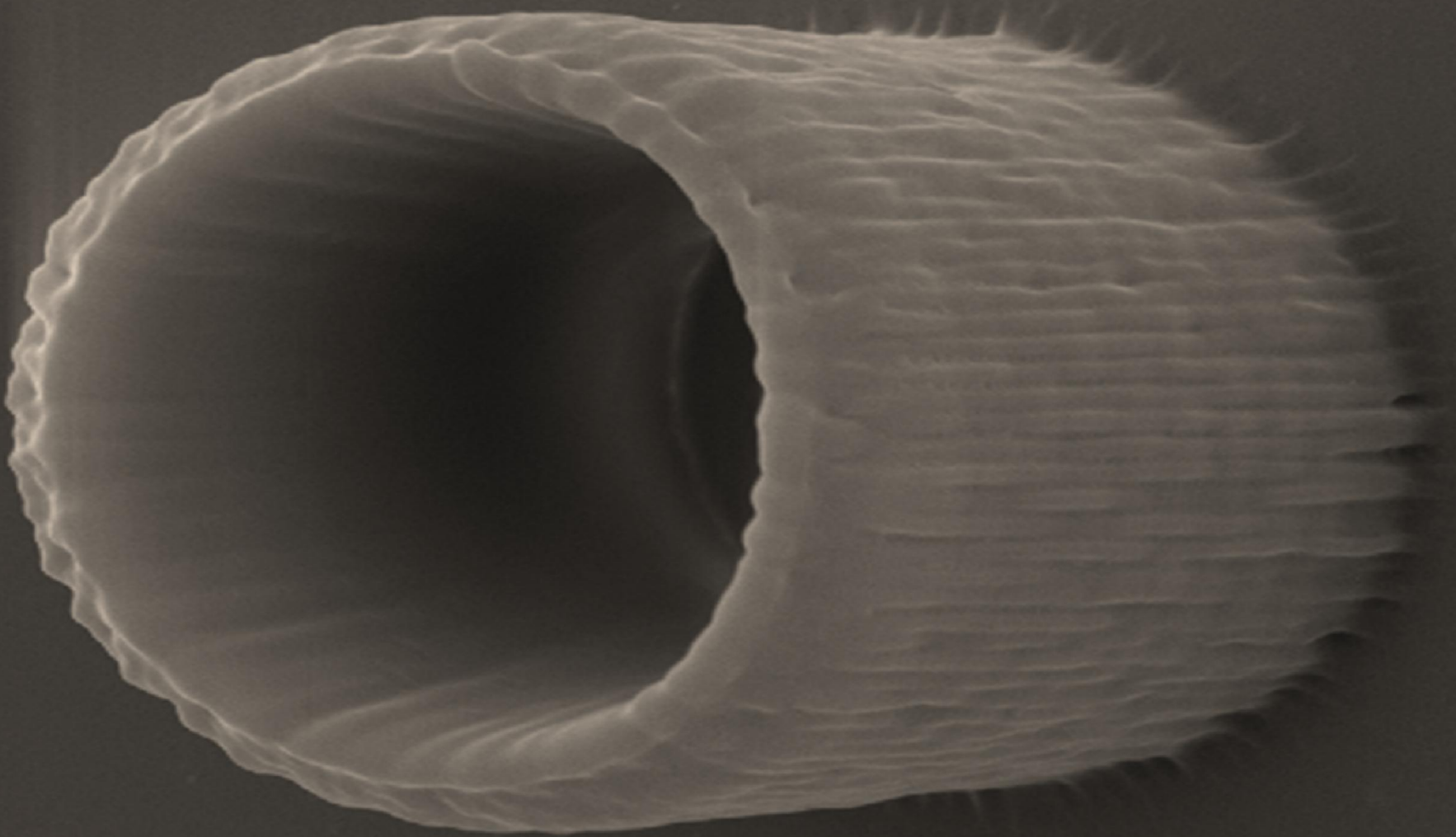
## structuring amorphous Si surface



Micro-Raman analysis reveals the crystallization of the aSi upon fs-laser irradiation



## fs-laser microfabrication



fabrication of microstructure using fs-laser  
and nonlinear optical processes

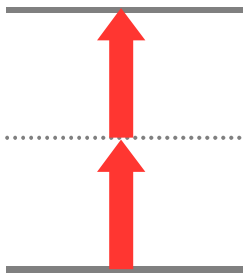
# Two-photon polymerization



laser pulse

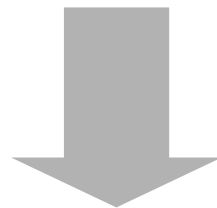
100 fs

Photoinitiator is excited by ***two-photon absorption***

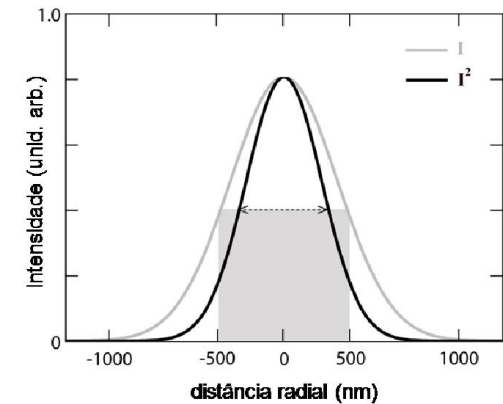
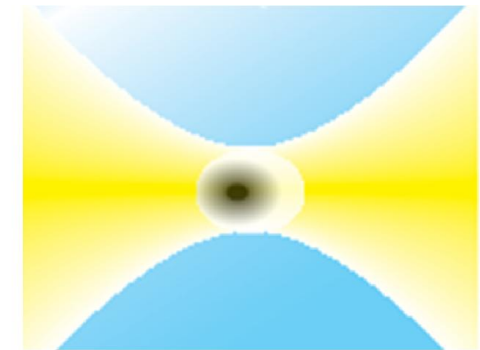


$$R \propto I^2$$

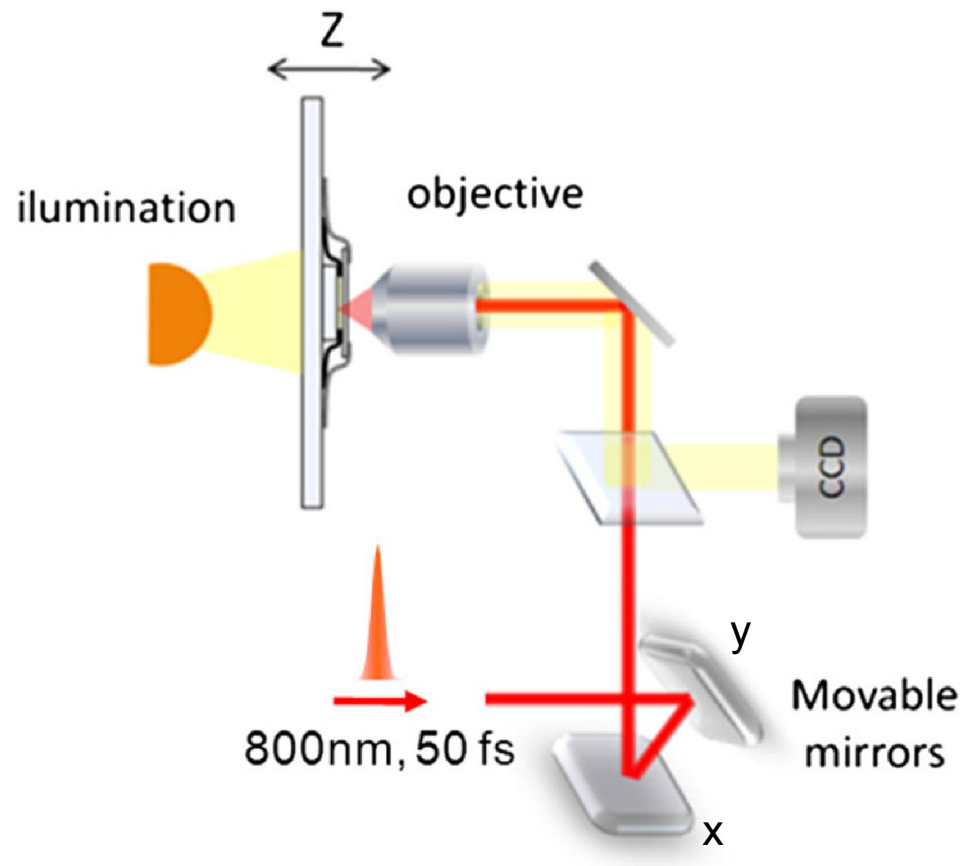
The polymerization is confined to the focal volume.



High spatial resolution



# Two-photon polymerization setup



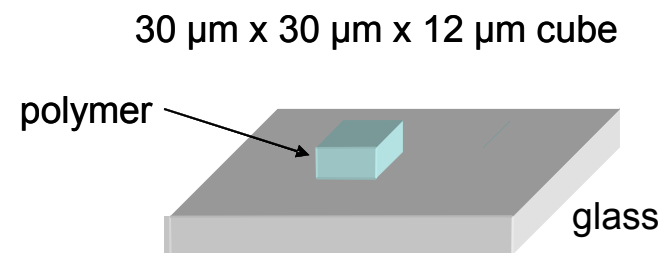
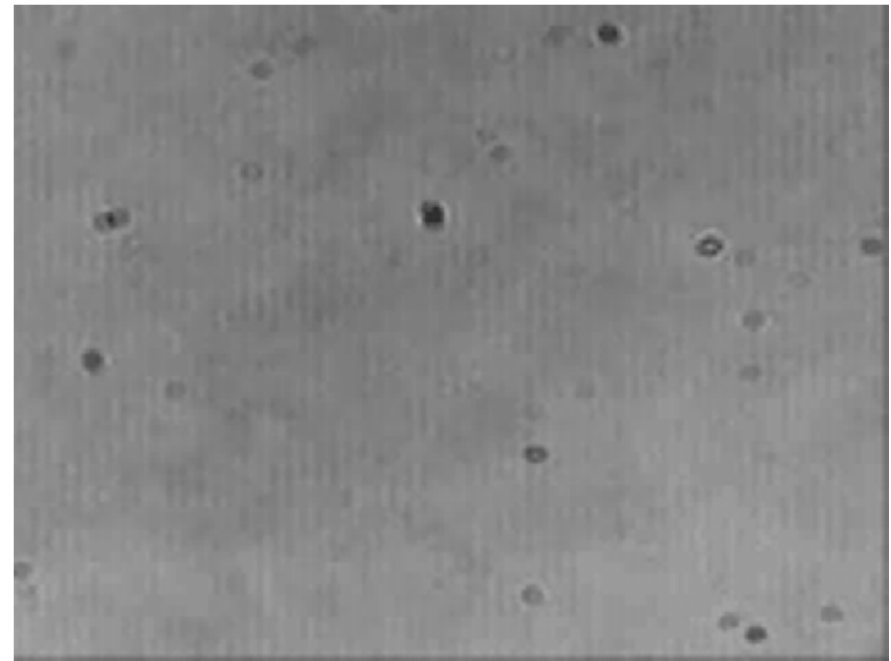
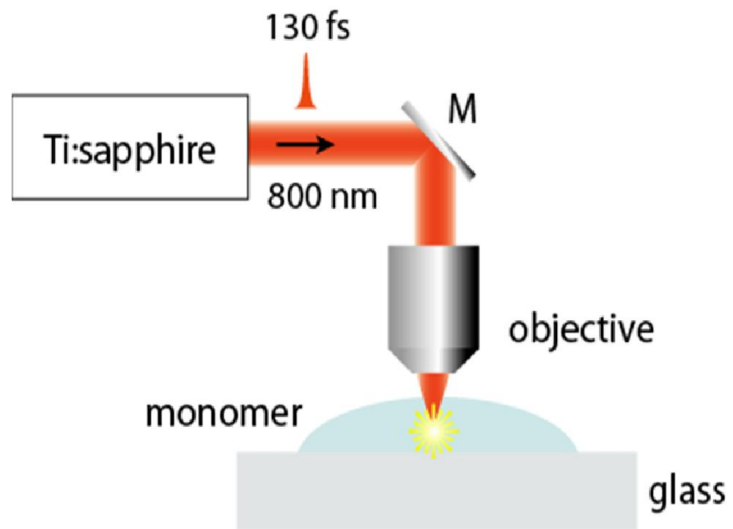
Ti:sapphire laser oscillator

- 50 fs
- 800 nm
- 80 MHz
- 20 mW

Objective

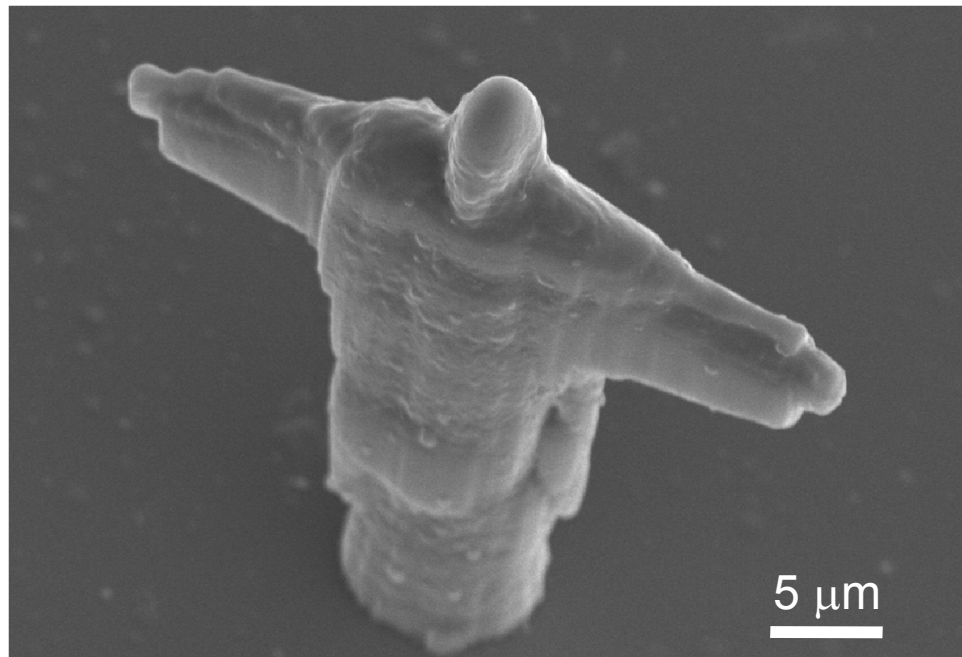
40 x  
0.65 NA

# Two-photon polymerization



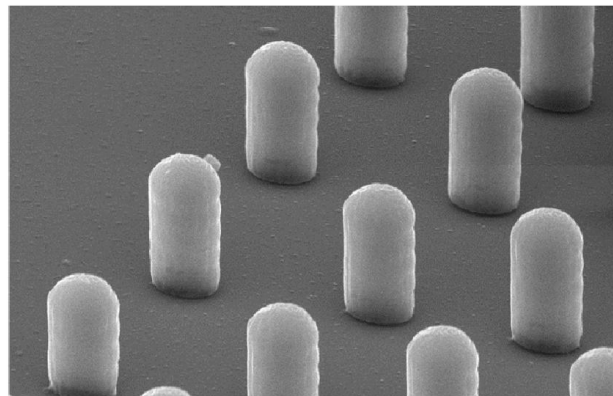
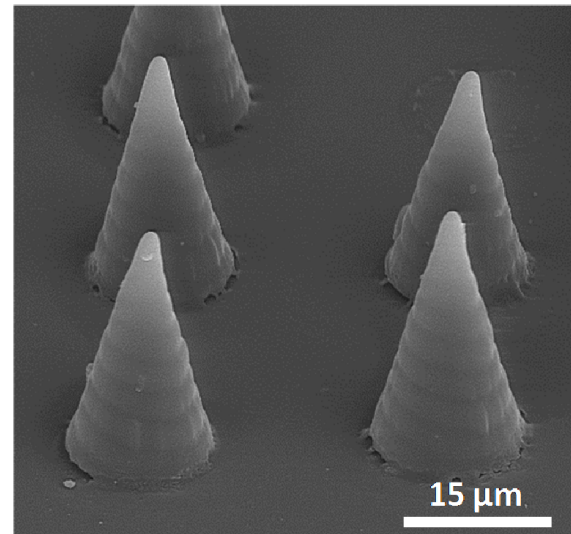
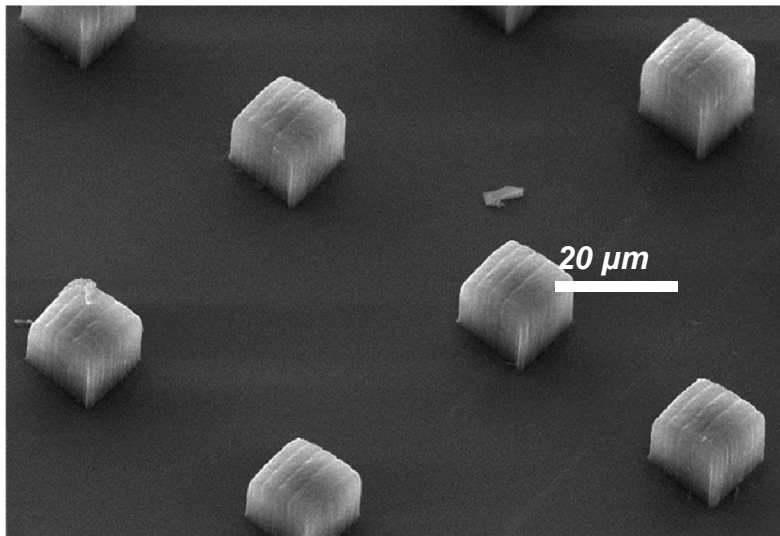
# two-photon polymerization

Microstructure fabricated by two-photon polymerization



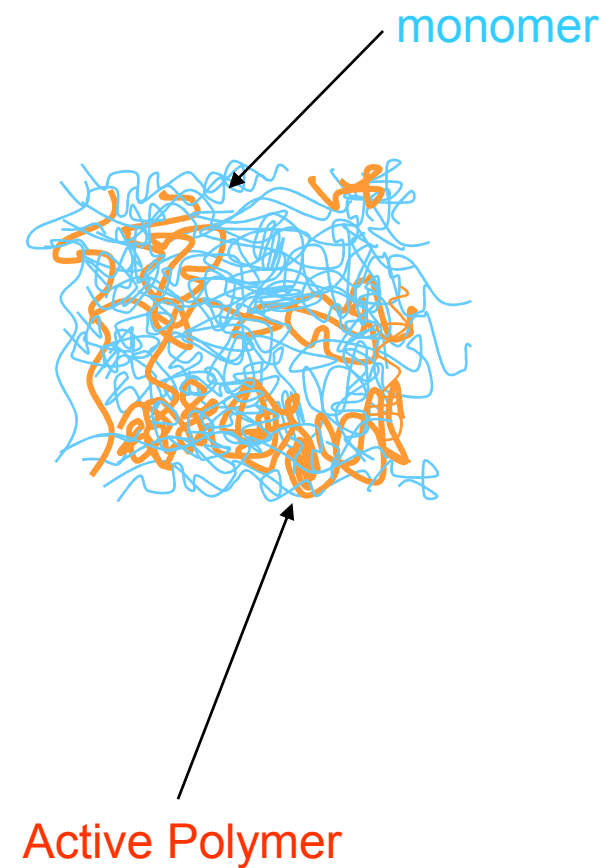
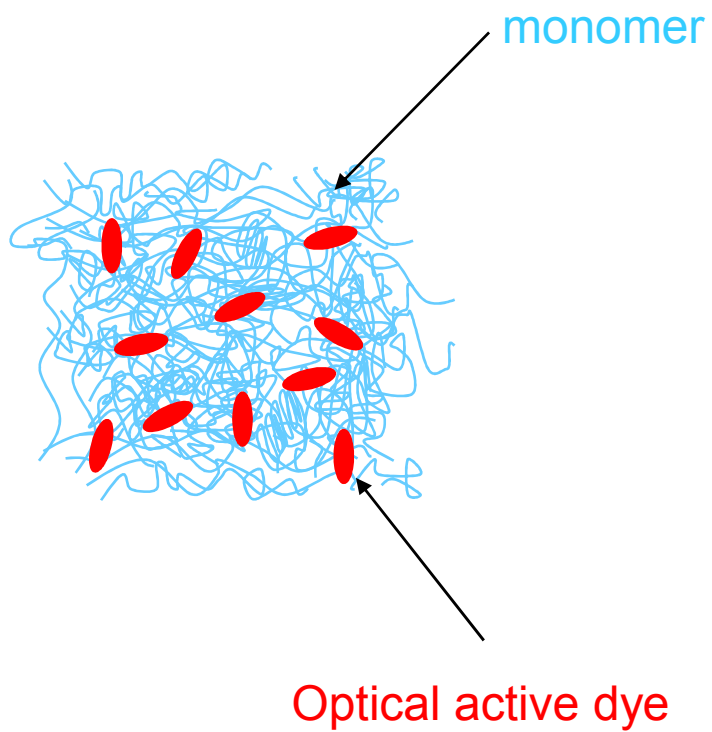
# Two-photon polymerization

Microstructures fabricated by two-photon polymerization



# Doping microstructures

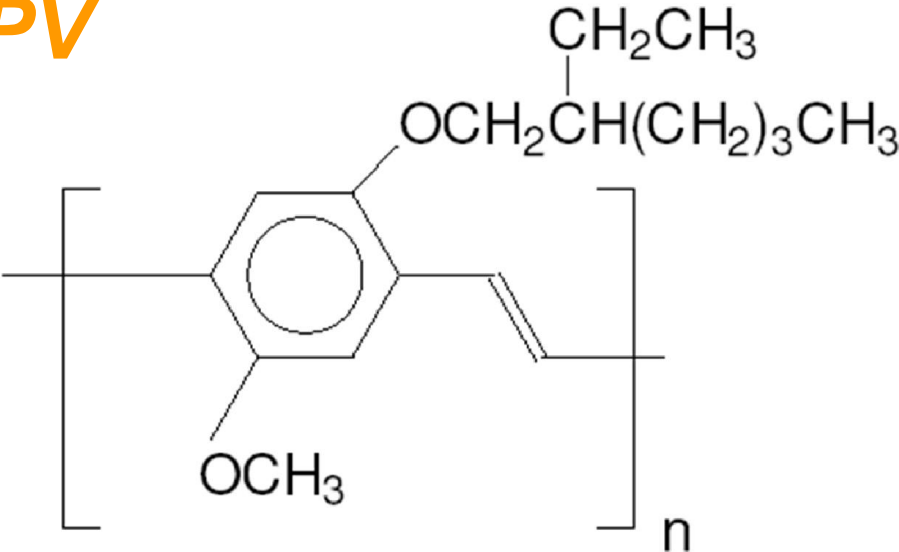
Microstructures containing active compounds





Microstructure containing MEH-PPV

# MEH-PPV

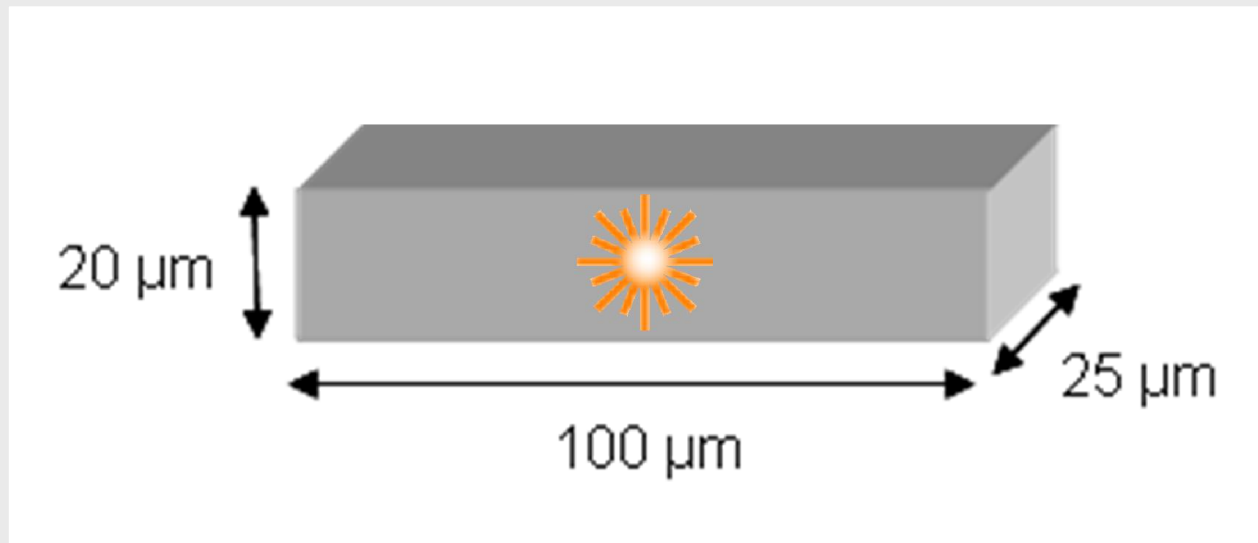


- Fluorescence
- Electro Luminescent
- Conductive

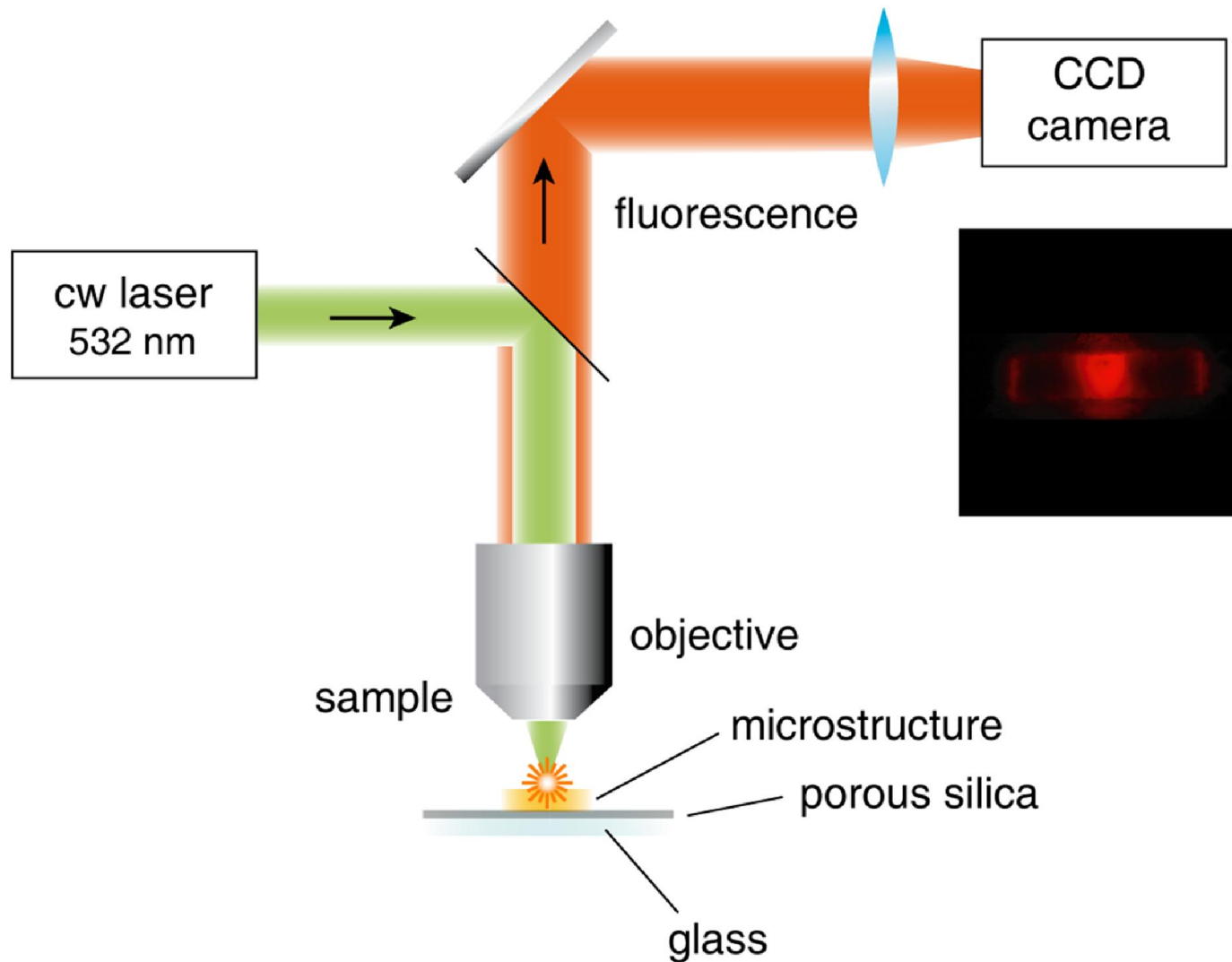


## Microstructure containing MEH-PPV

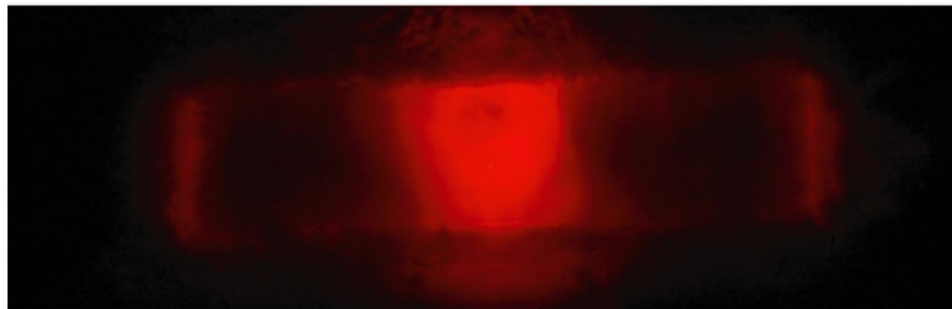
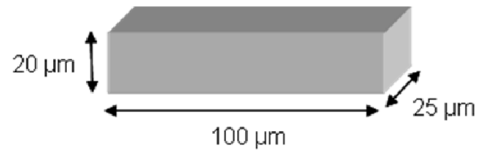
Do we have waveguiding in the microstructure ?



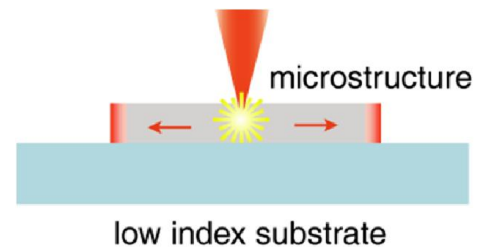
# Microstructure containing MEH-PPV



# Microstructure containing MEH-PPV



$20\ \mu\text{m}$  



waveguiding of the microstructure fabricated  
on porous silica substrate ( $n = 1.185$ )

*Applications:* micro-laser; fluorescent microstructures; conductive microstructures

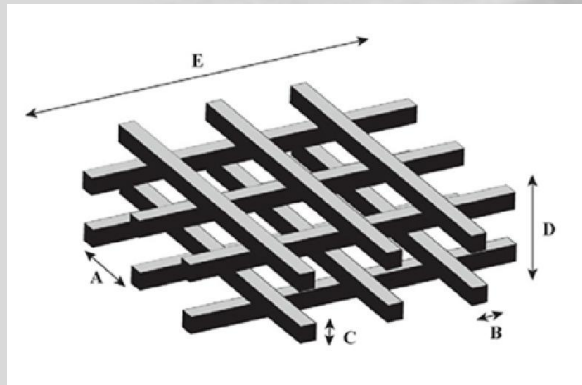
micro-environment to study cells and bacteria

microfabrication of special  
microstructures to biology



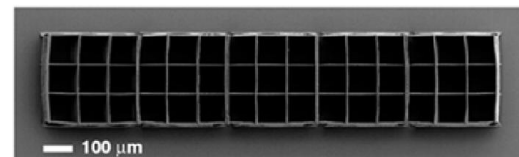
# 3D cell migration

- 3D cell migration studies in micro-scaffolds



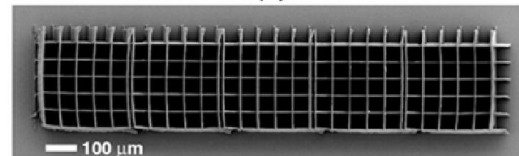
*SEM of the scaffolds*

*110  $\mu\text{m}$  pore size*



(c)

*52  $\mu\text{m}$  pore size*



(d)

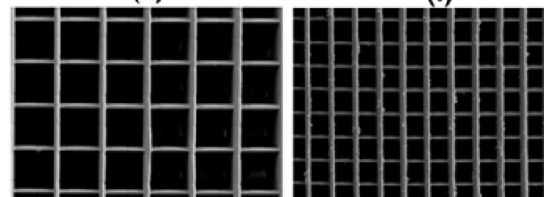
*Top view*



(e)

(f)

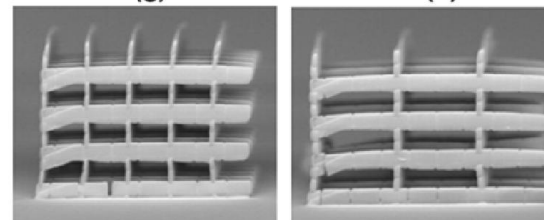
*110, 52, 25, 12  $\mu\text{m}$  pore size*



(g)

(h)

*Side view*



(i)

(j)

*25, 52  $\mu\text{m}$  pore size*

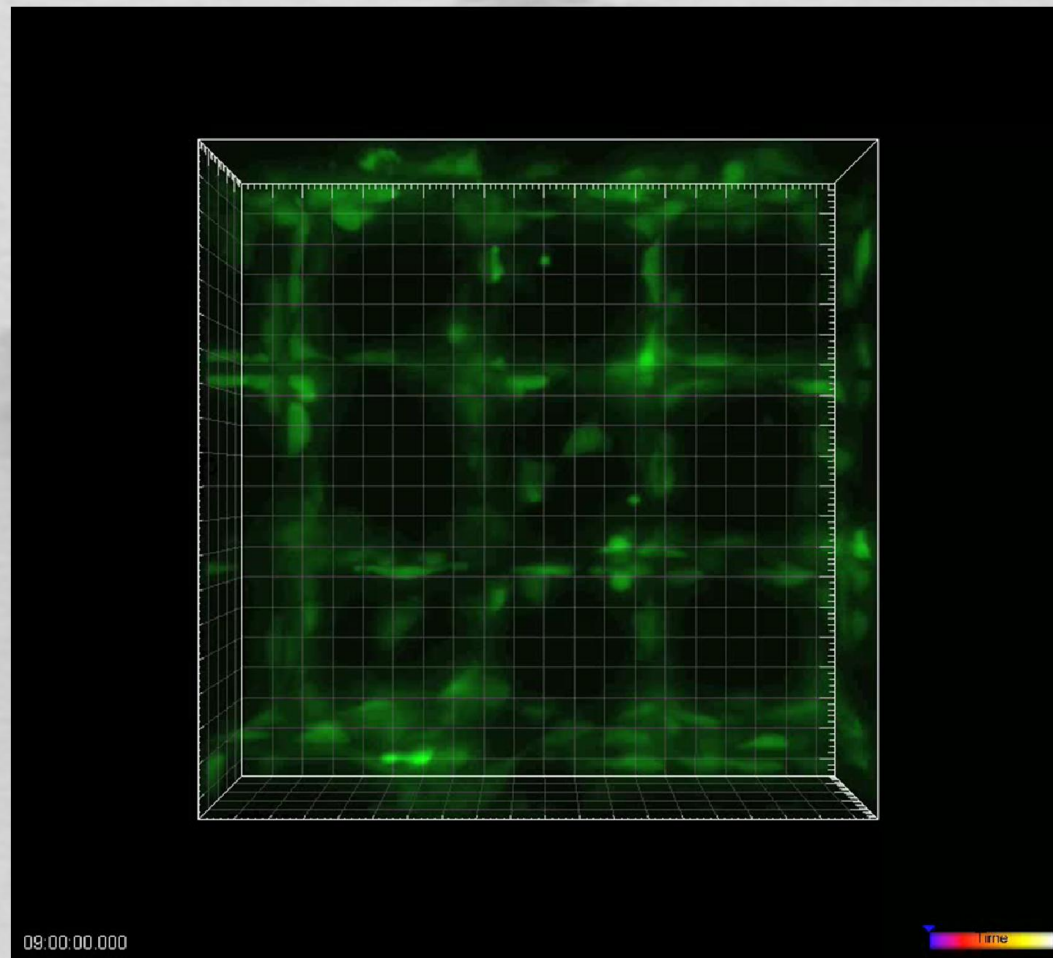
# 3D cell migration

50  $\mu\text{m}$  pore size



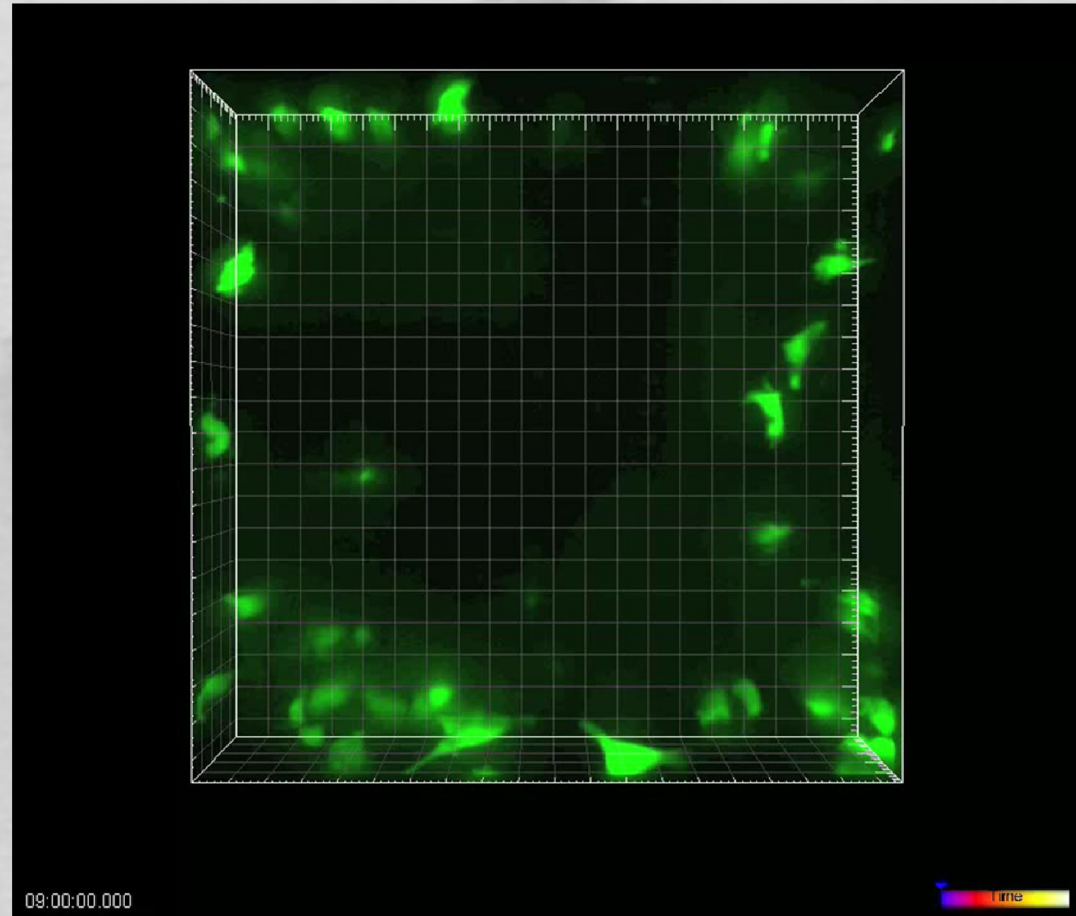


# 3D cell migration



110  $\mu\text{m}$  pore size

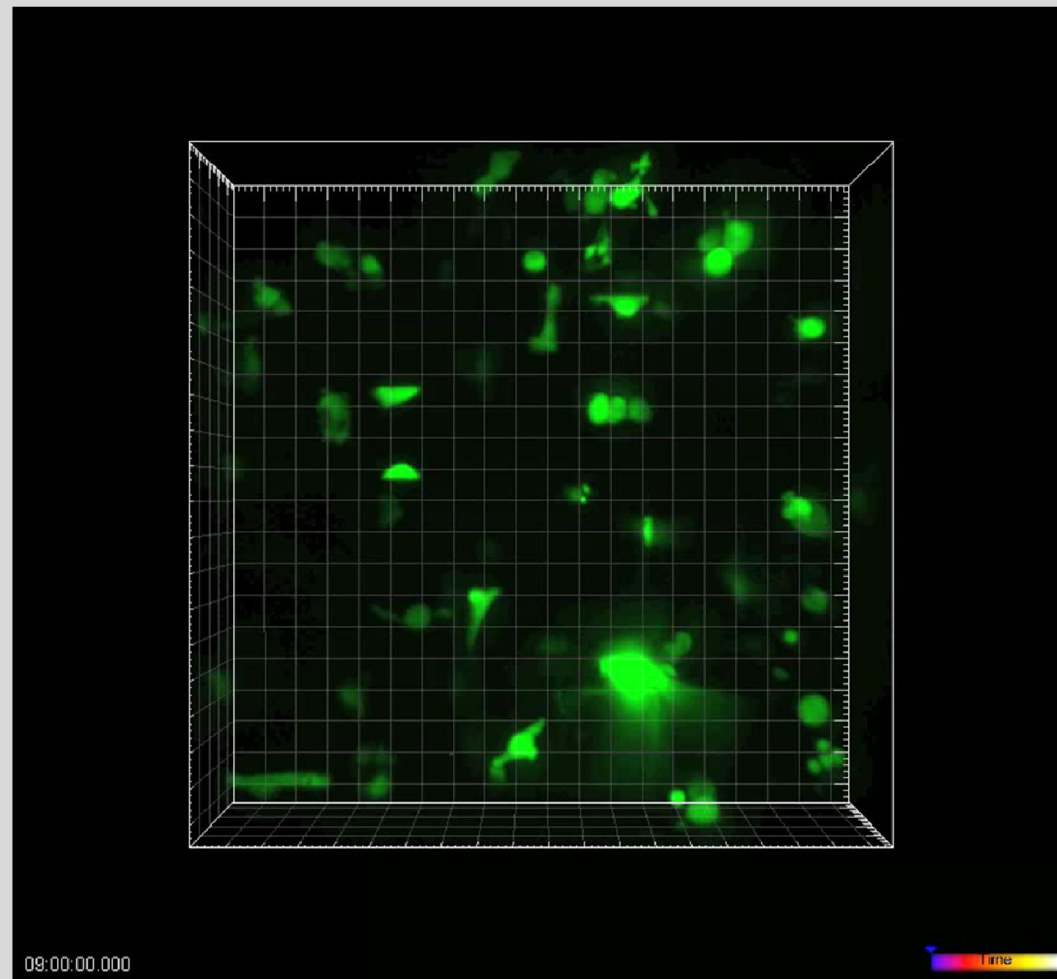
# 3D cell migration



12  $\mu\text{m}$  pore size



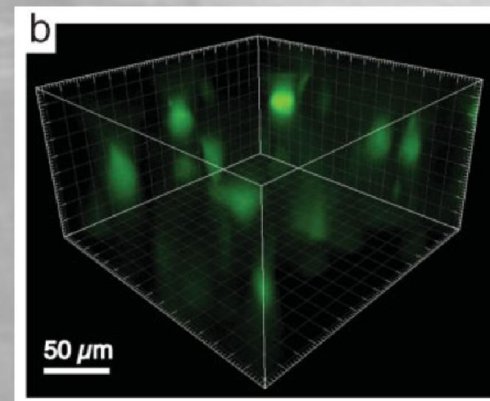
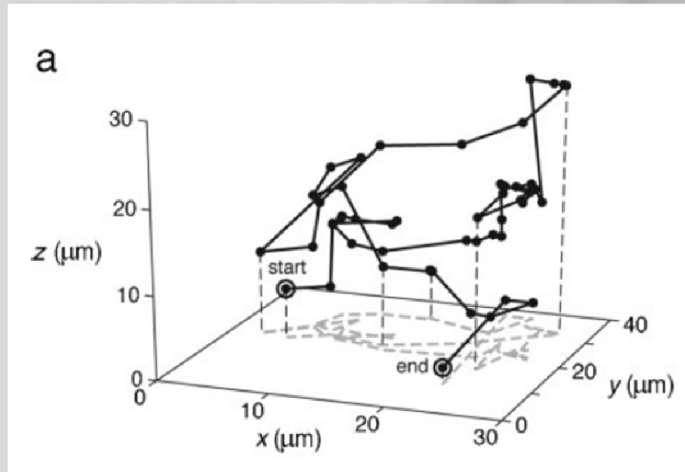
# 3D cell migration



52  $\mu\text{m}$  pore size

# 3D cell migration

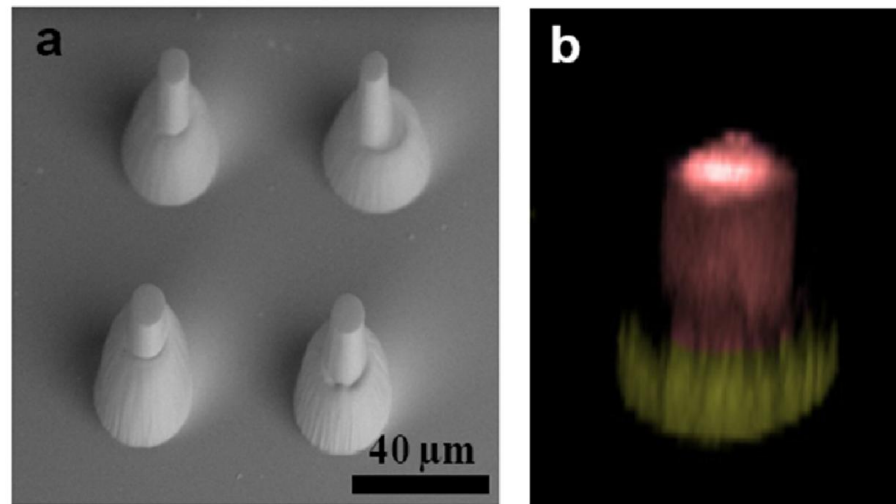
- 3D cell migration studies in micro-scaffolds



# Guiding bacterial growth in a micro-environment

to study bacterial growth it was needed to develop **double doped microstructures**

microstructure containing Fluorescein and Rhodamine

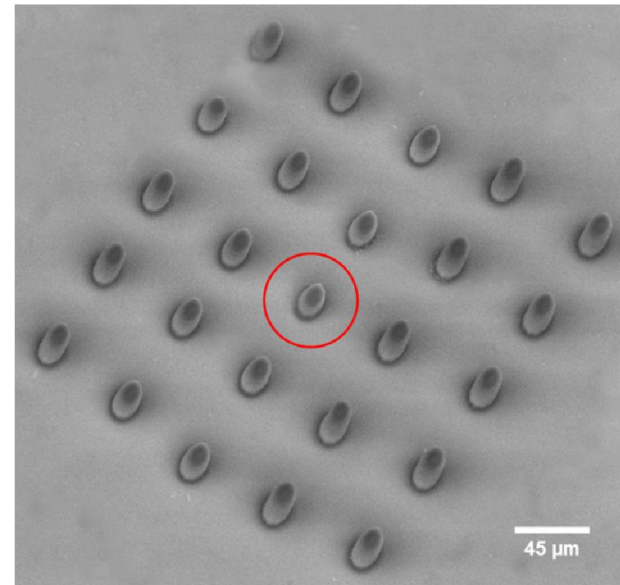
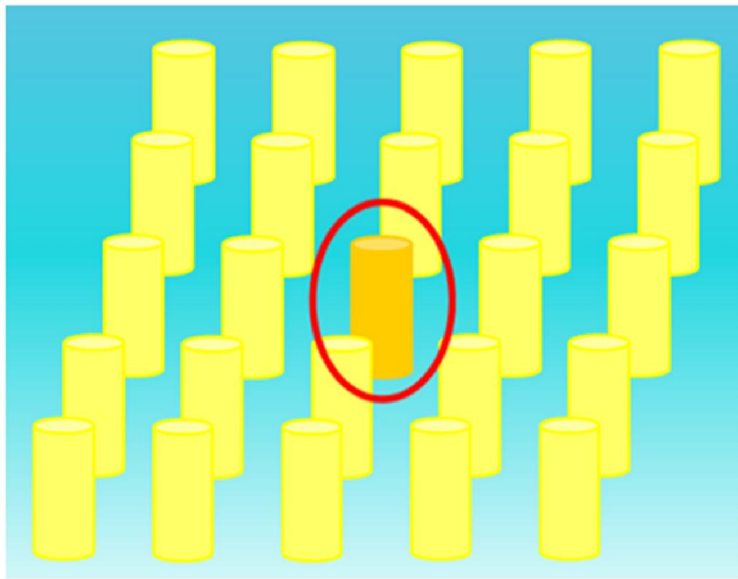


(a) SEM of a double-doped microstructure (top view).

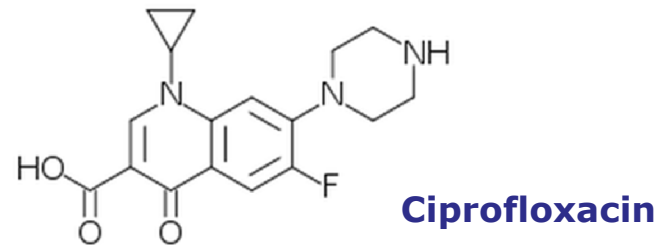
(b) Confocal fluorescent microscopy image of the same microstructure.

# Guiding bacterial growth in a micro-environment

Study the development of *E. coli* in micro-environments:

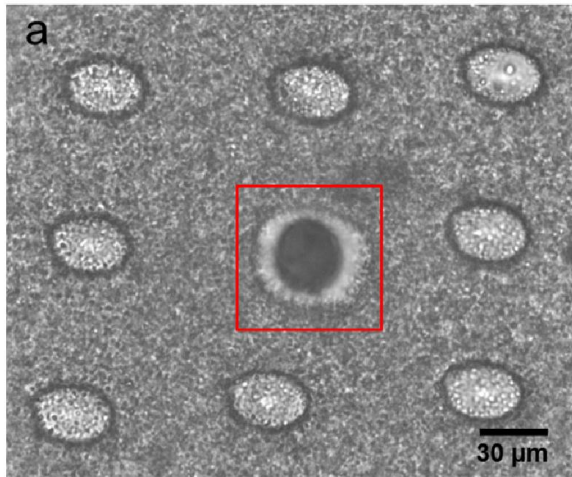


micro-environment in which the central structure contains antibiotic.

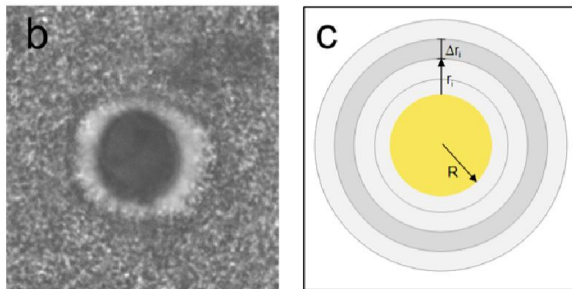


# Guiding bacterial growth in a micro-environment

Study the development of *E. coli* in micro-environments:

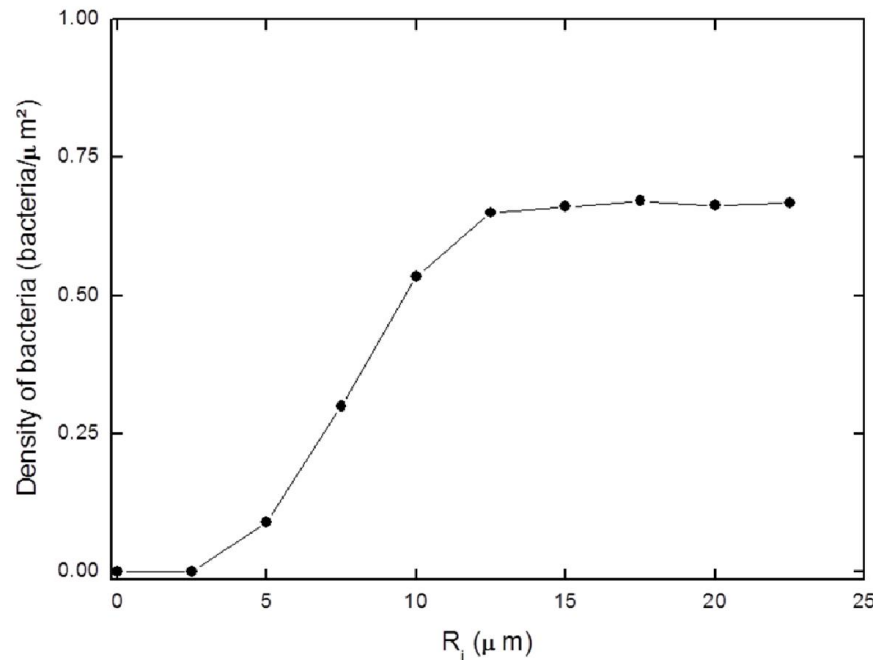


after 3 hours, we observed that a small region around the doped structure does not show bacterial growth.



such inhibition zone was analyzed by determining the bacterial density in concentric rings

# Guiding bacterial growth in a micro-environment



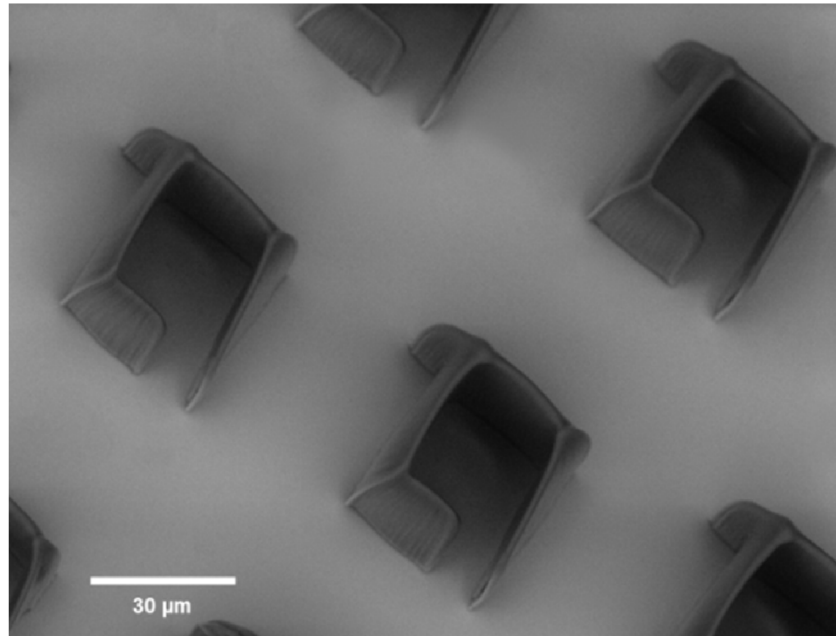
the density of bacteria grows monotonically with  $r_i$

saturation when  $r_i$  reaches approximately 12 μm in about 0.7 bacteria/μm²

the inhibition zone has a maximum range of approximately 10 μm, being more effective as one gets closer to the microstructure impregnated with ciprofloxacin

# Guiding bacterial growth in a micro-environment

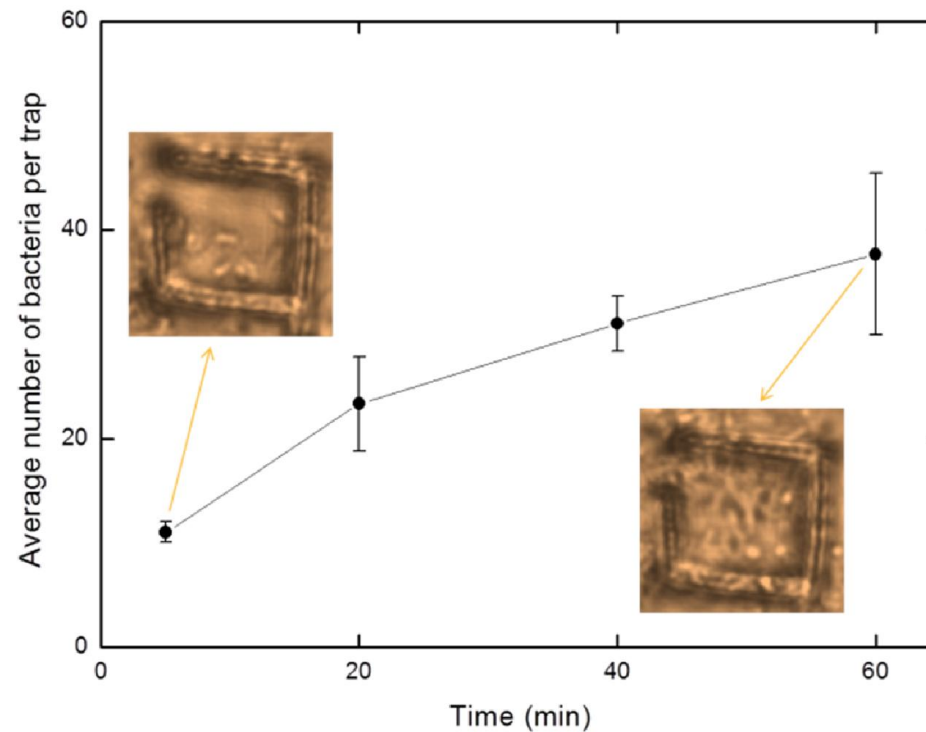
## Bacteria microtraps



using micro-environments to study the dynamics of bacterial migration

# Guiding bacterial growth in a micro-environment

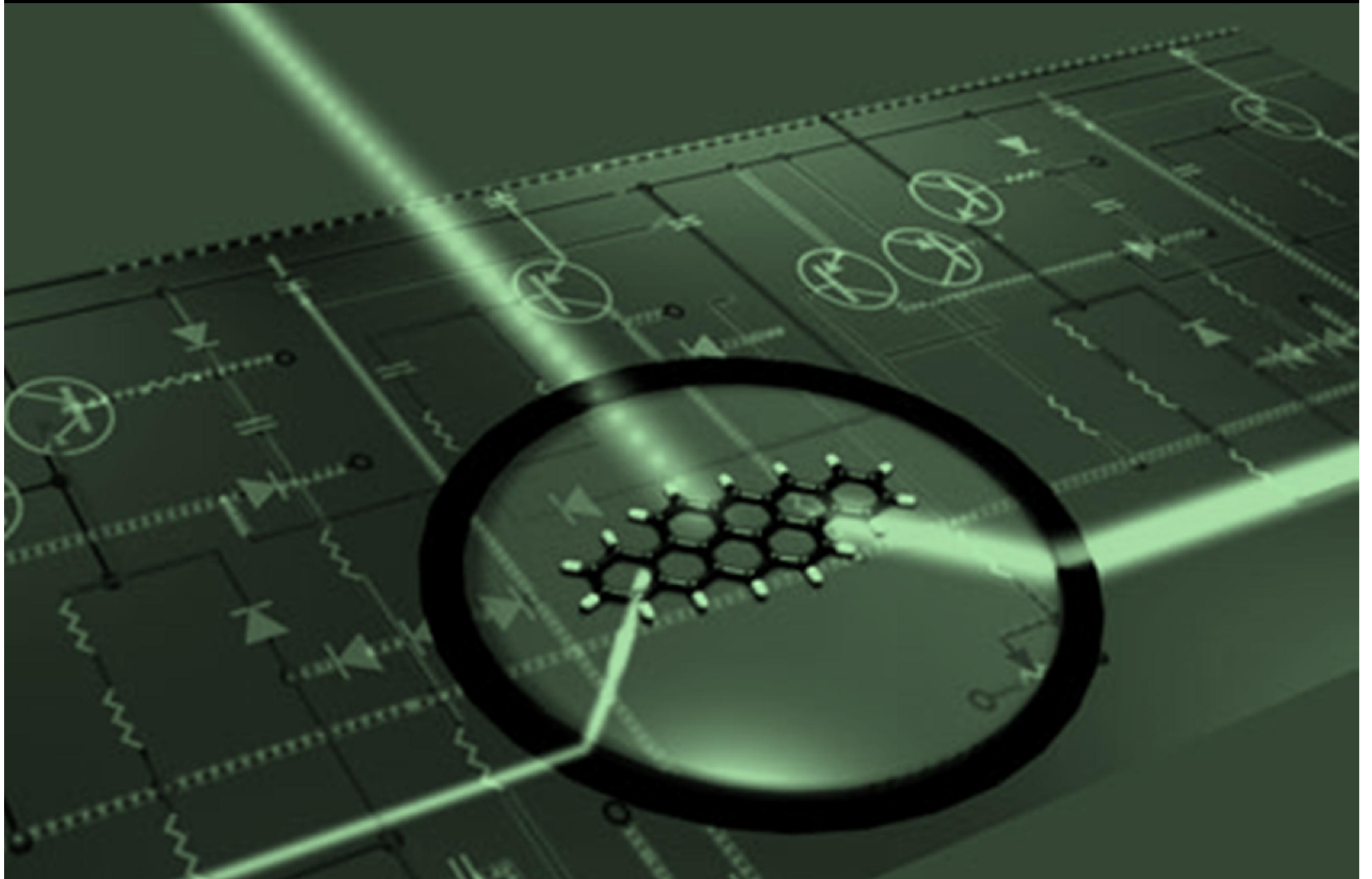
## Bacteria microtraps

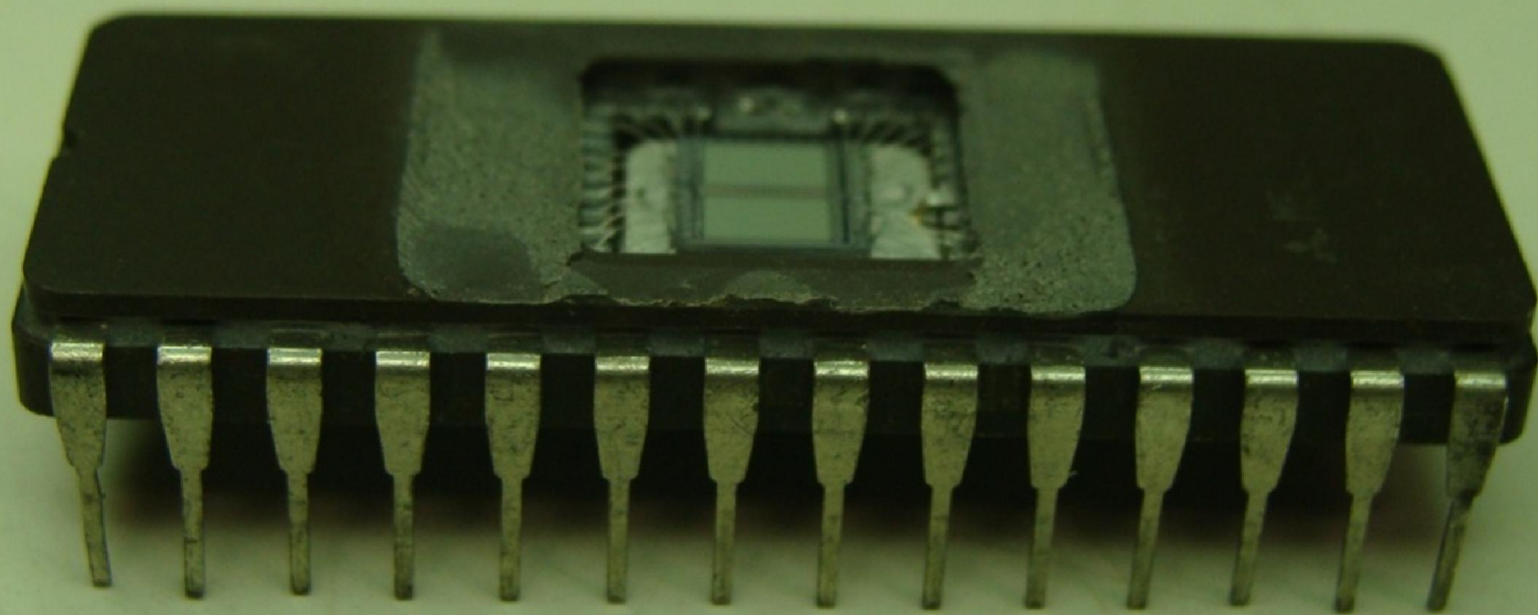


using micro-environments to study the dynamics of bacterial migration

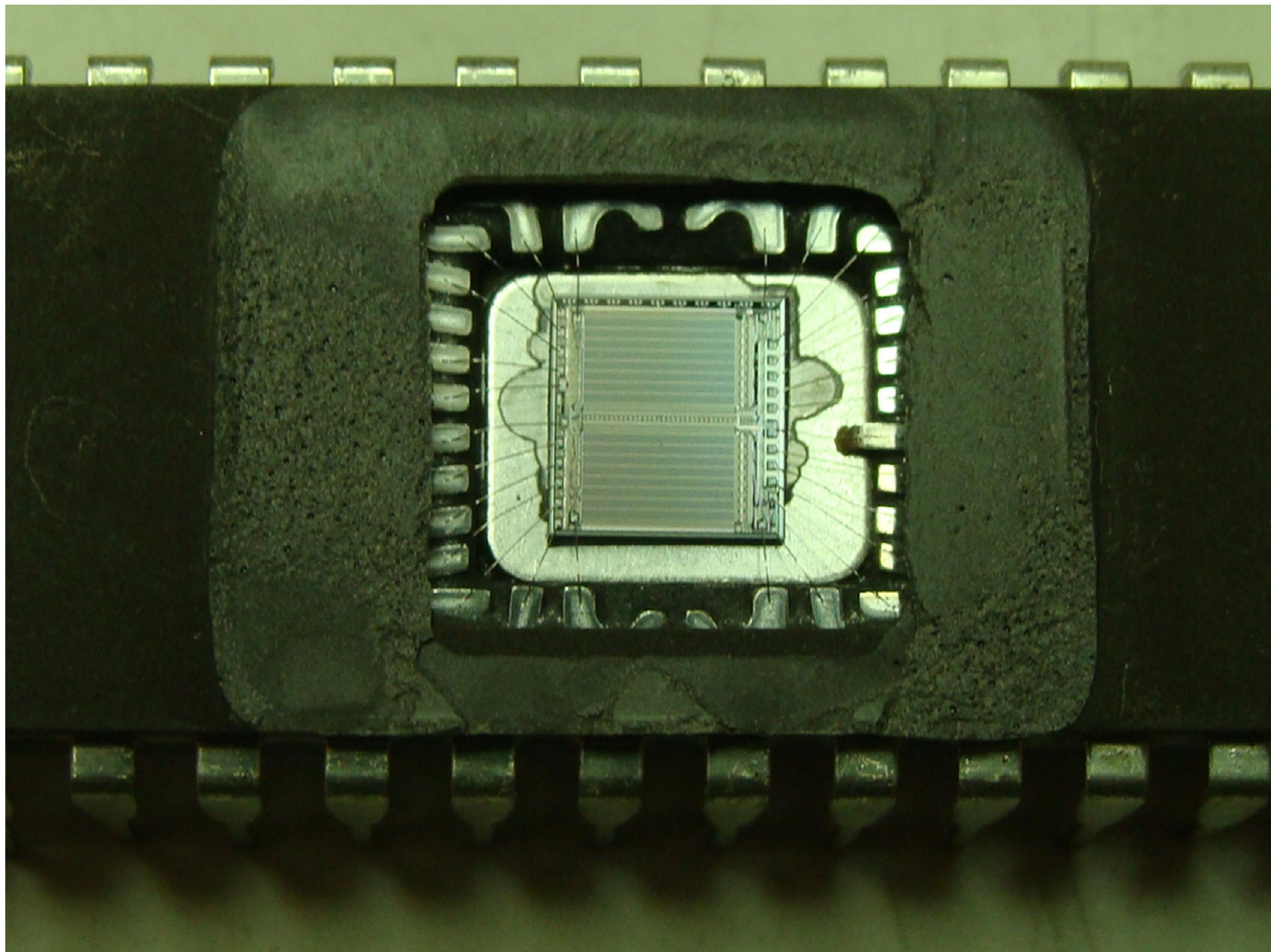


# Optical circuit



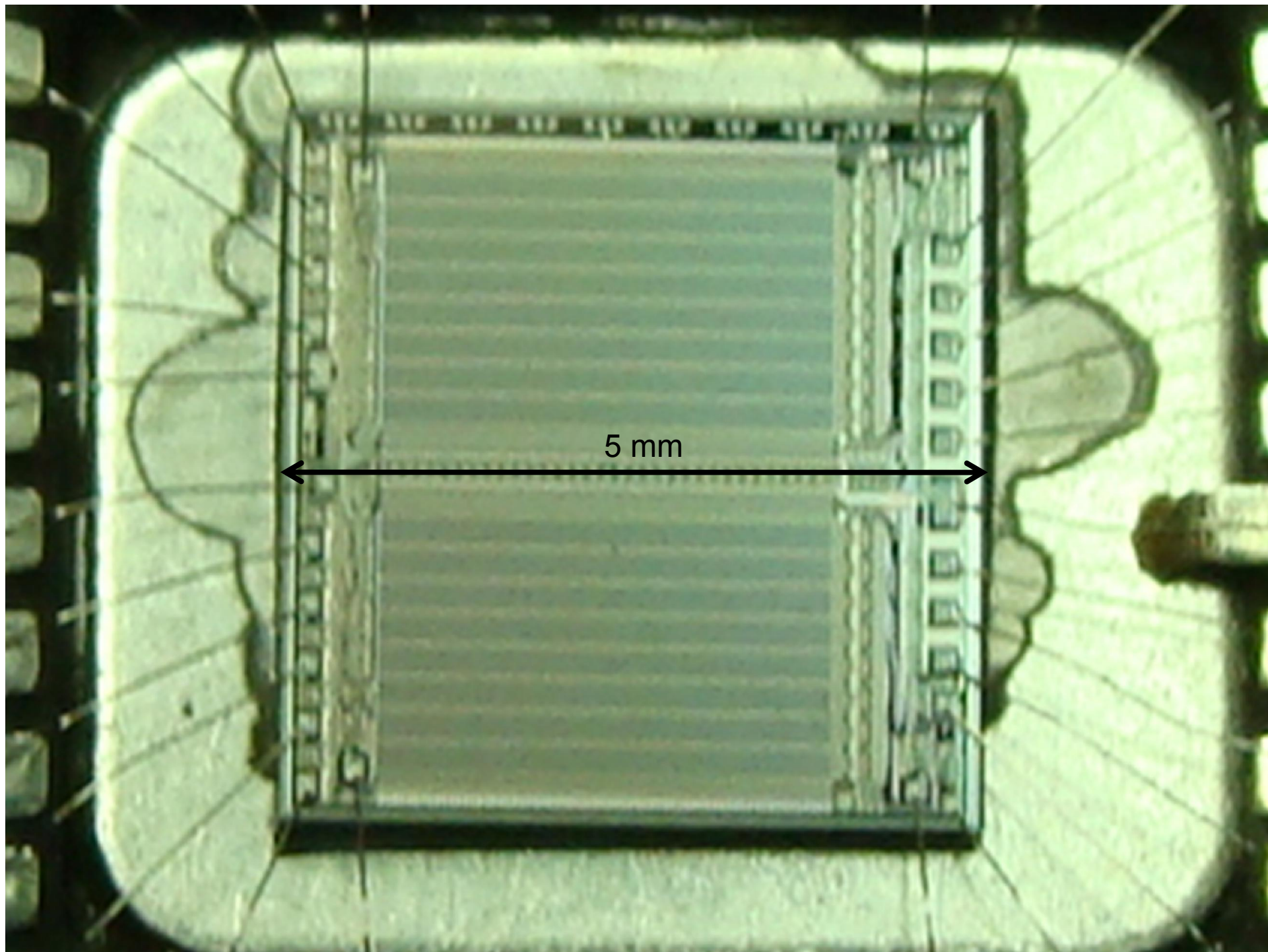
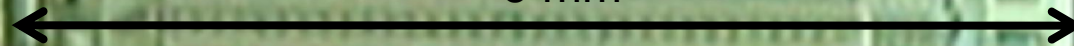




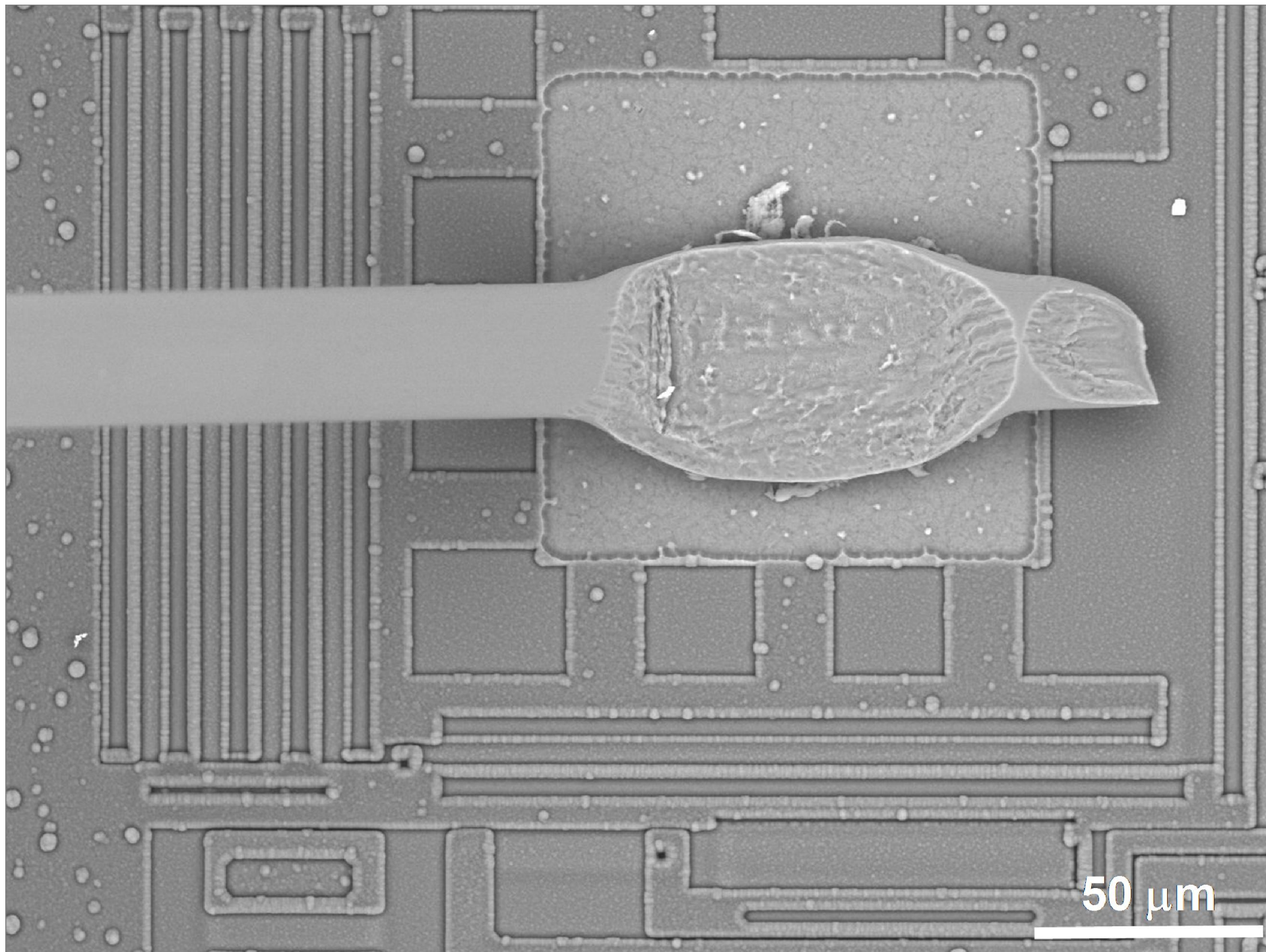




5 mm







# Optical circuit

- microfabrication
- silica nanowires
- coupling microstructures

50  $\mu\text{m}$



# Silica nanowires

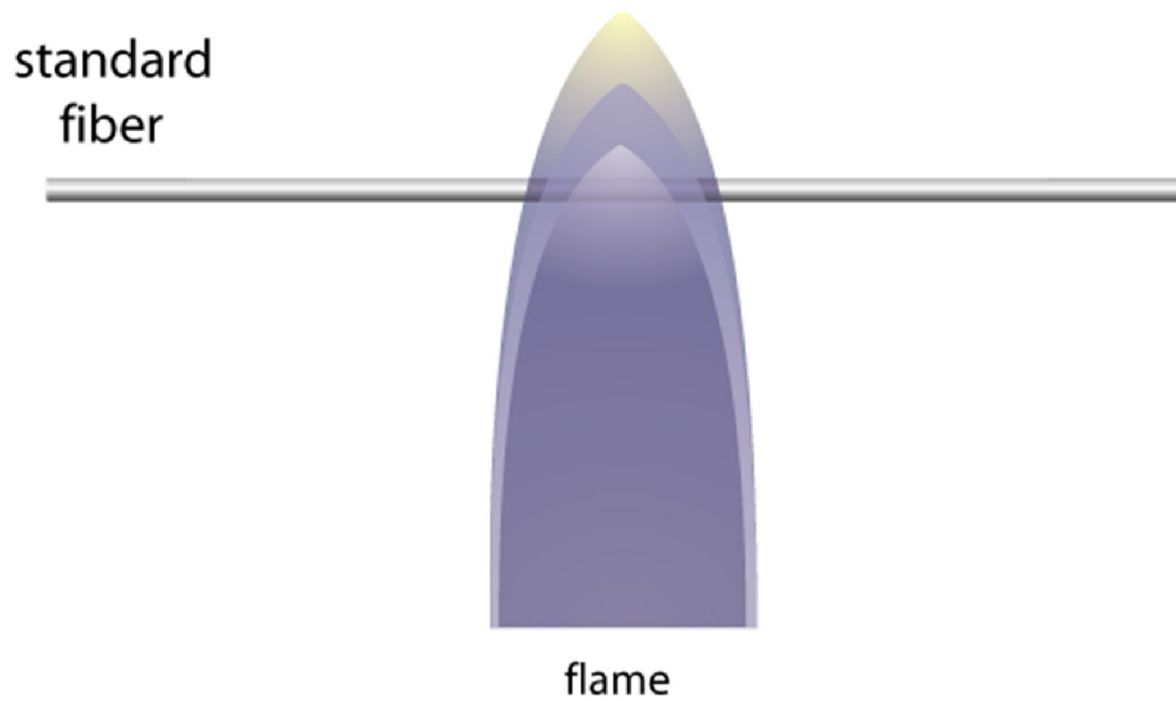
## nanowires fabrication process

standard  
fiber



# Silica nanowires

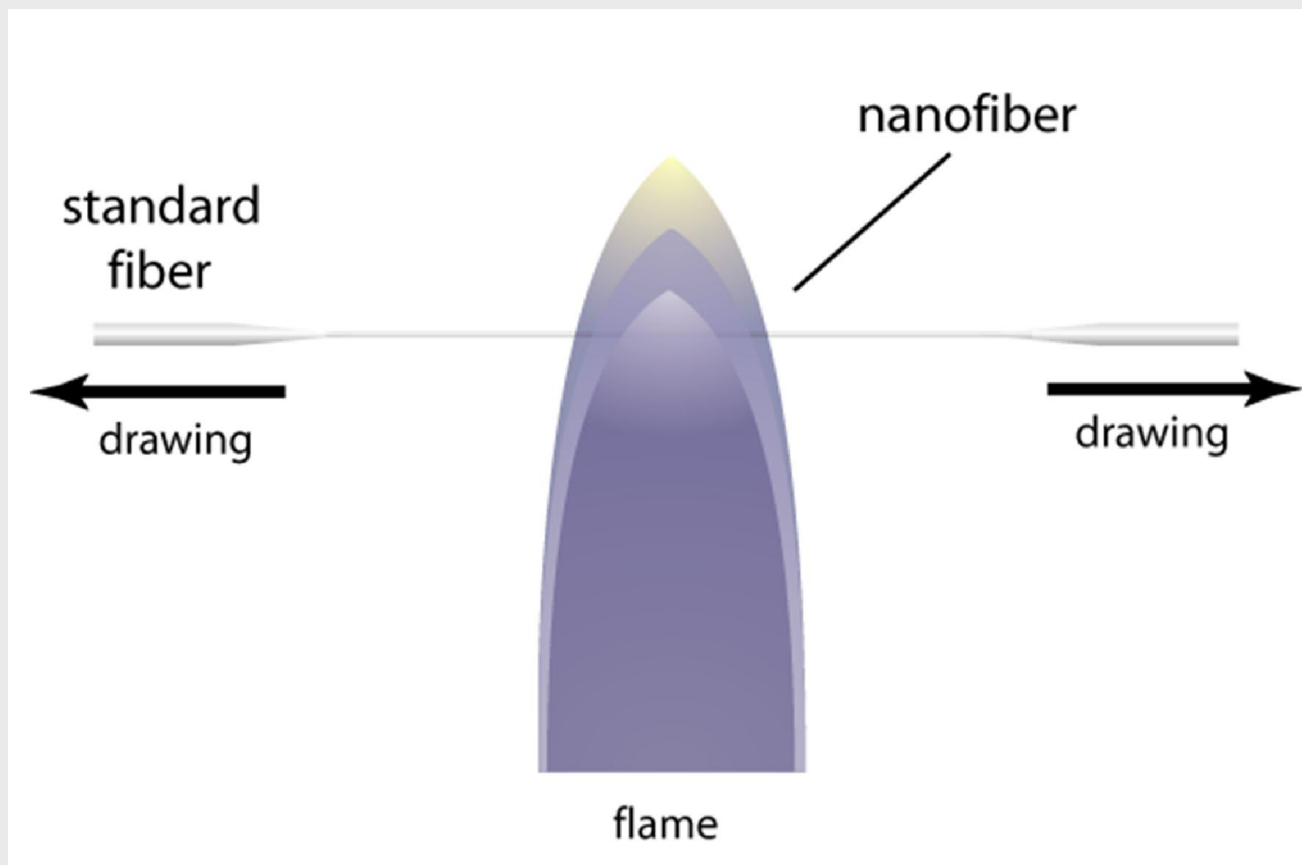
nanowires fabrication process



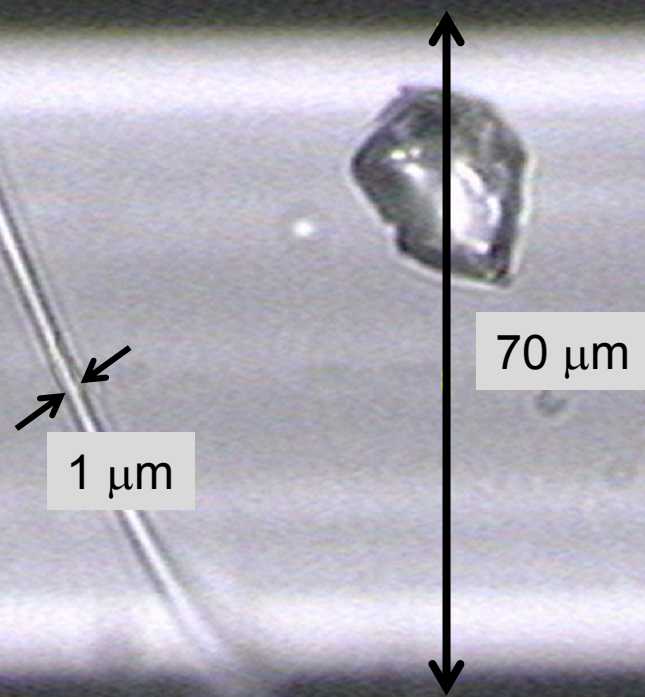


# Silica nanowires

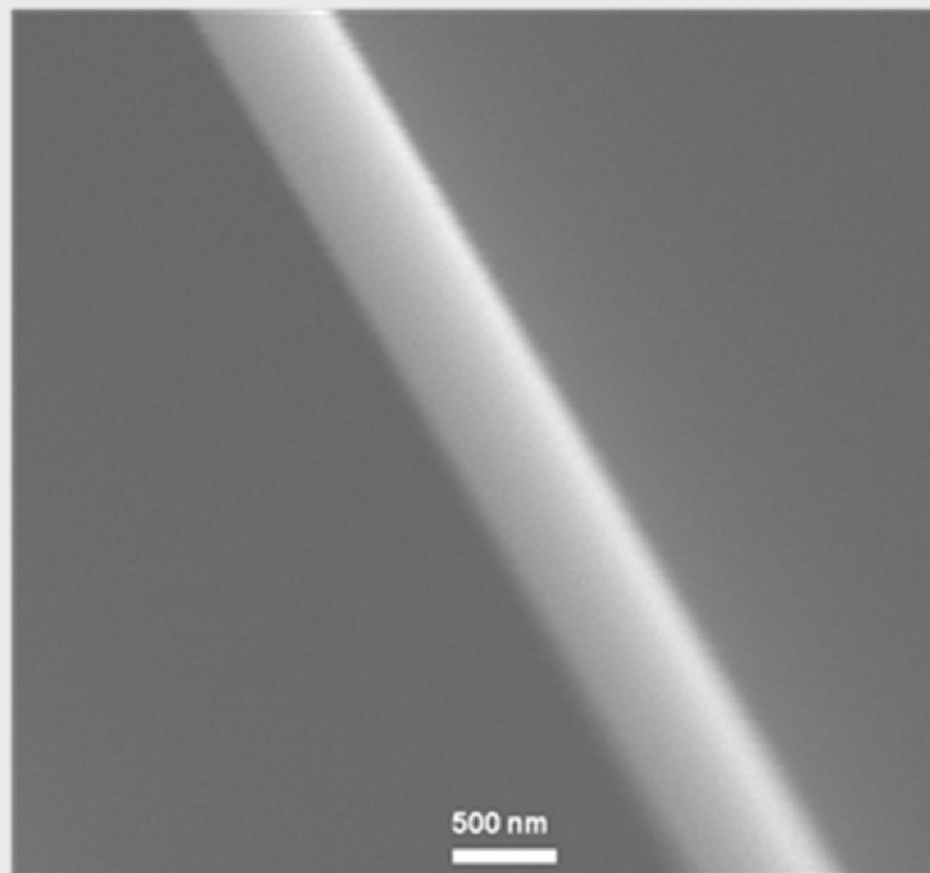
nanowires fabrication process



# Silica nanowires

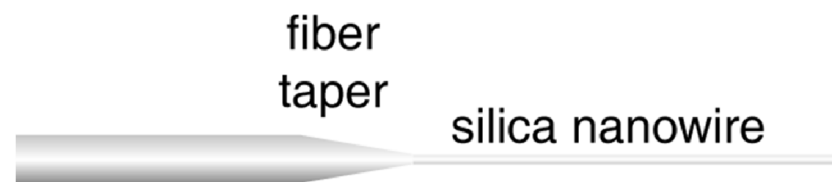


# Silica nanowires



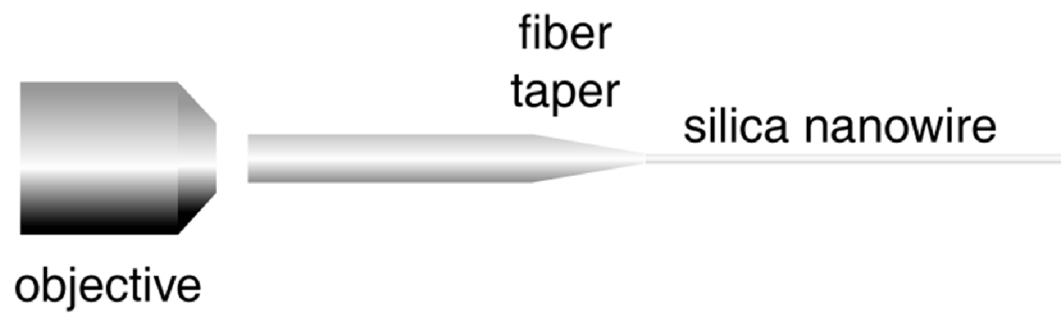
# Silica nanowires

coupling light into nanowires



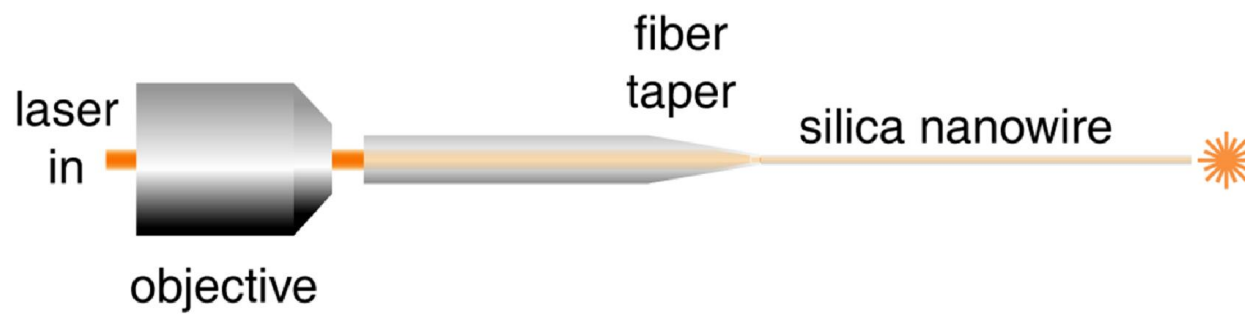
# Silica nanowires

coupling light into nanowires



# Silica nanowires

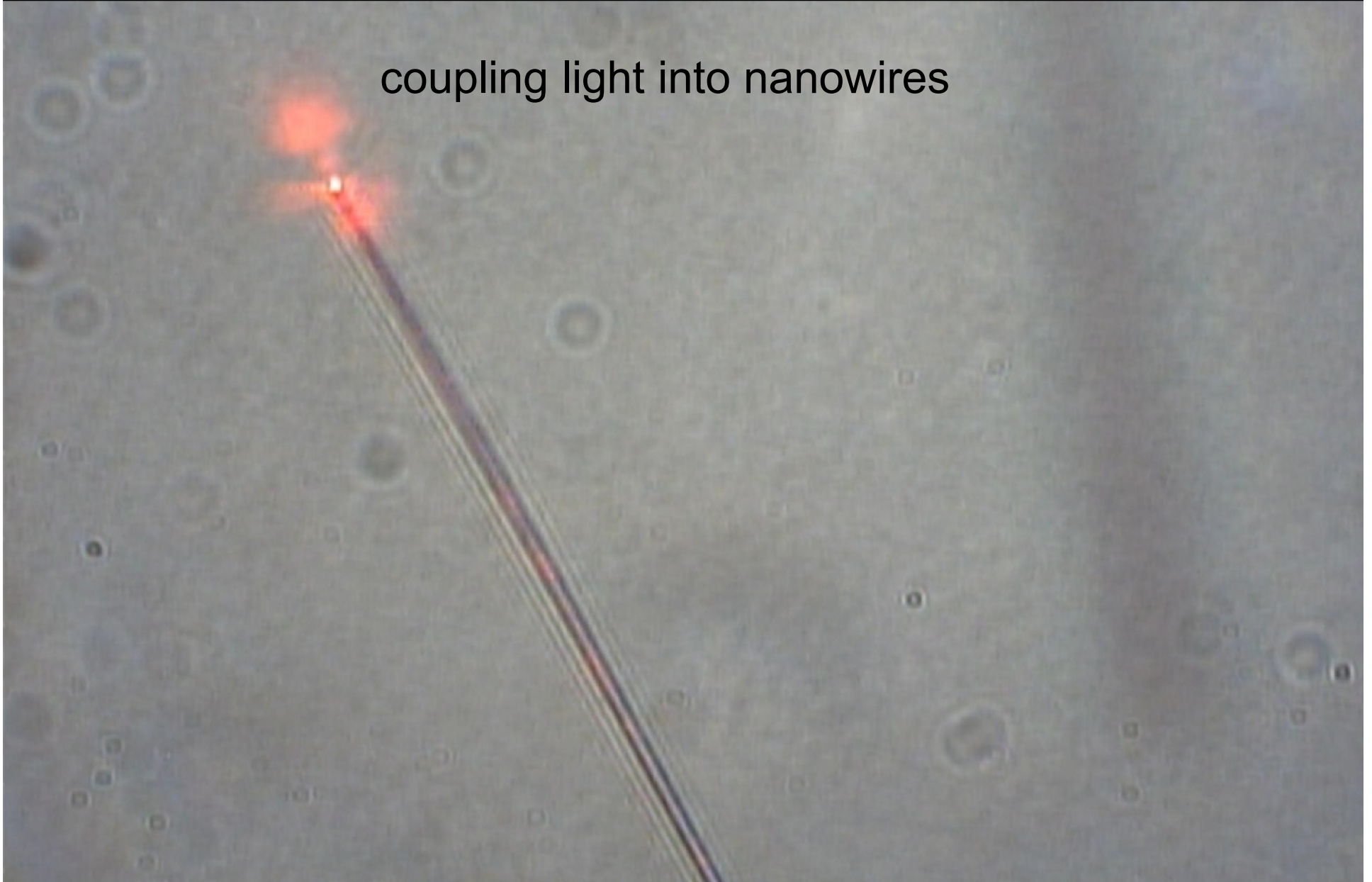
coupling light into nanowires



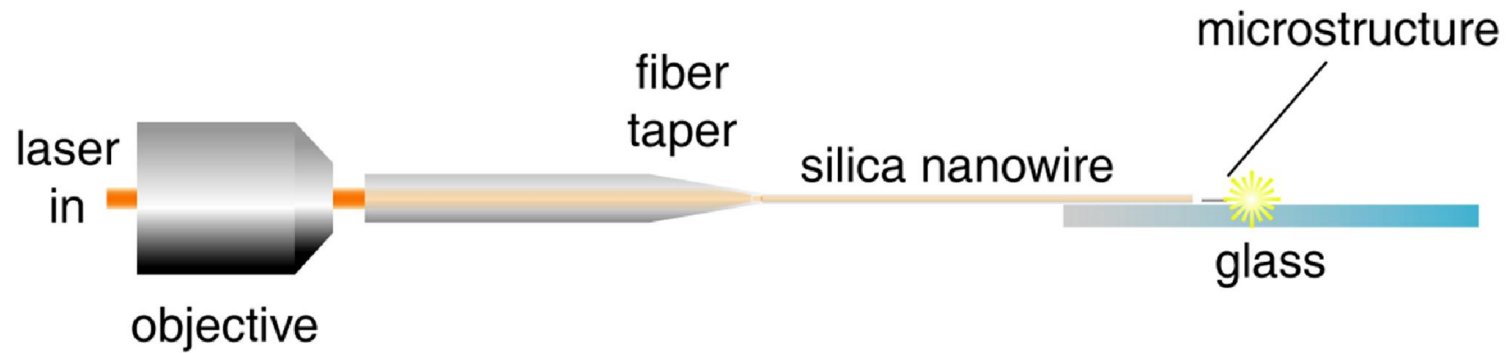


## Silica nanowires

coupling light into nanowires

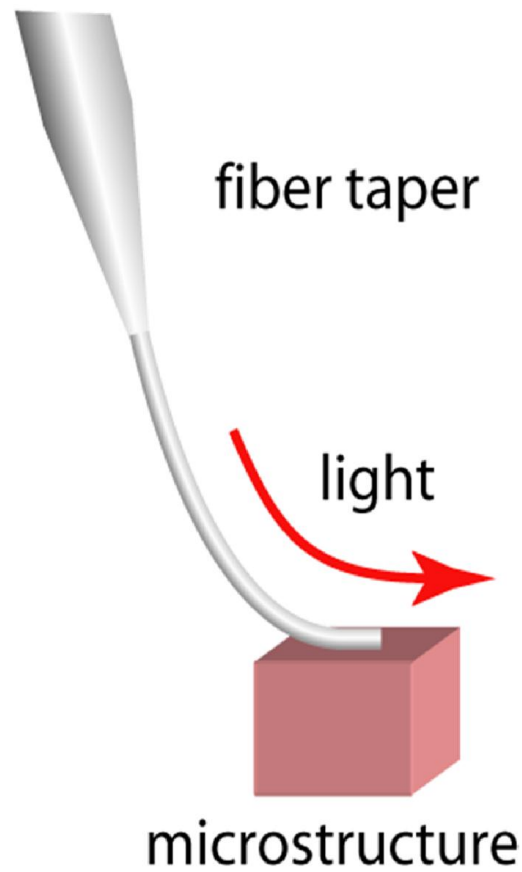


# Coupling microstructures

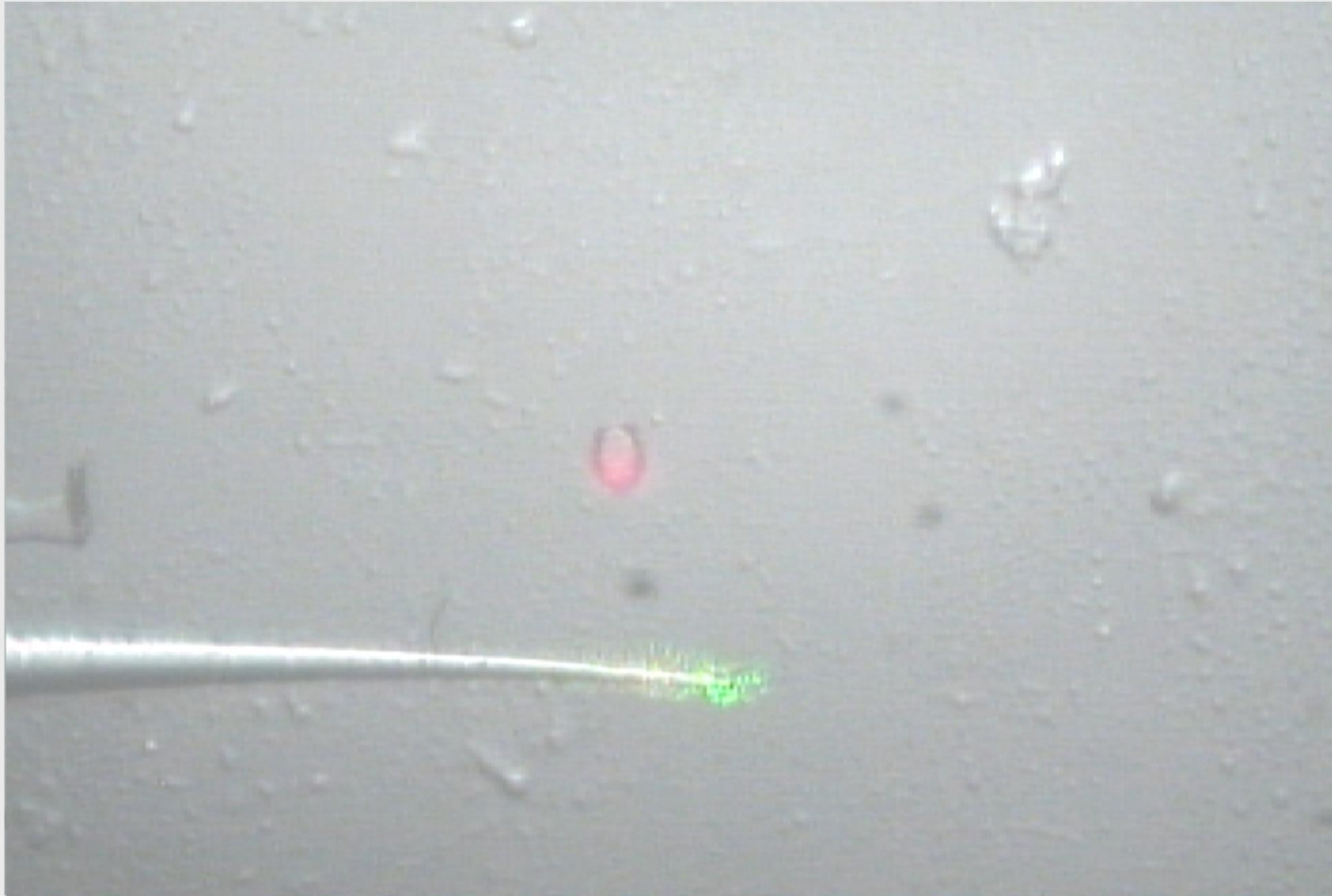




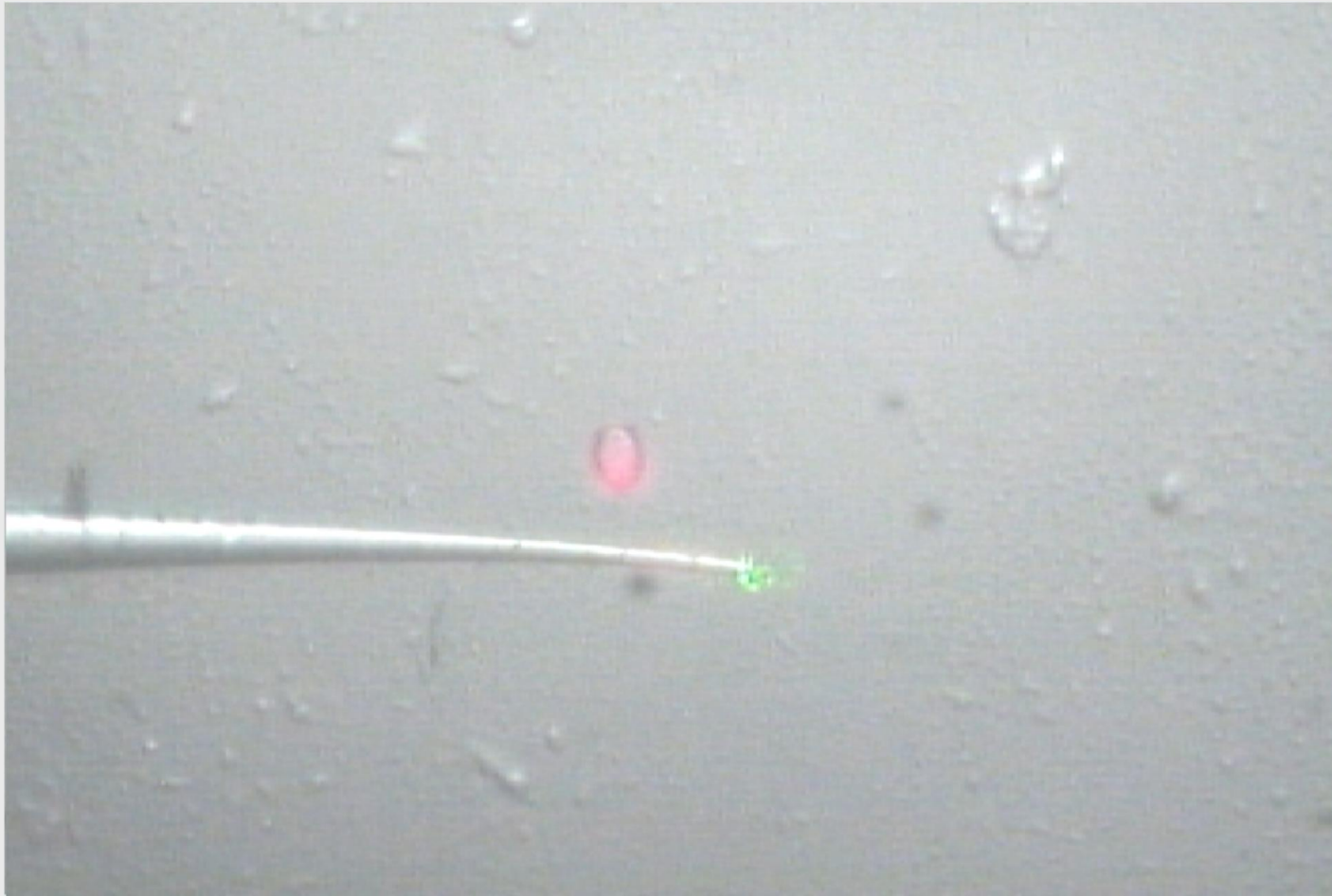
# Coupling microstructures



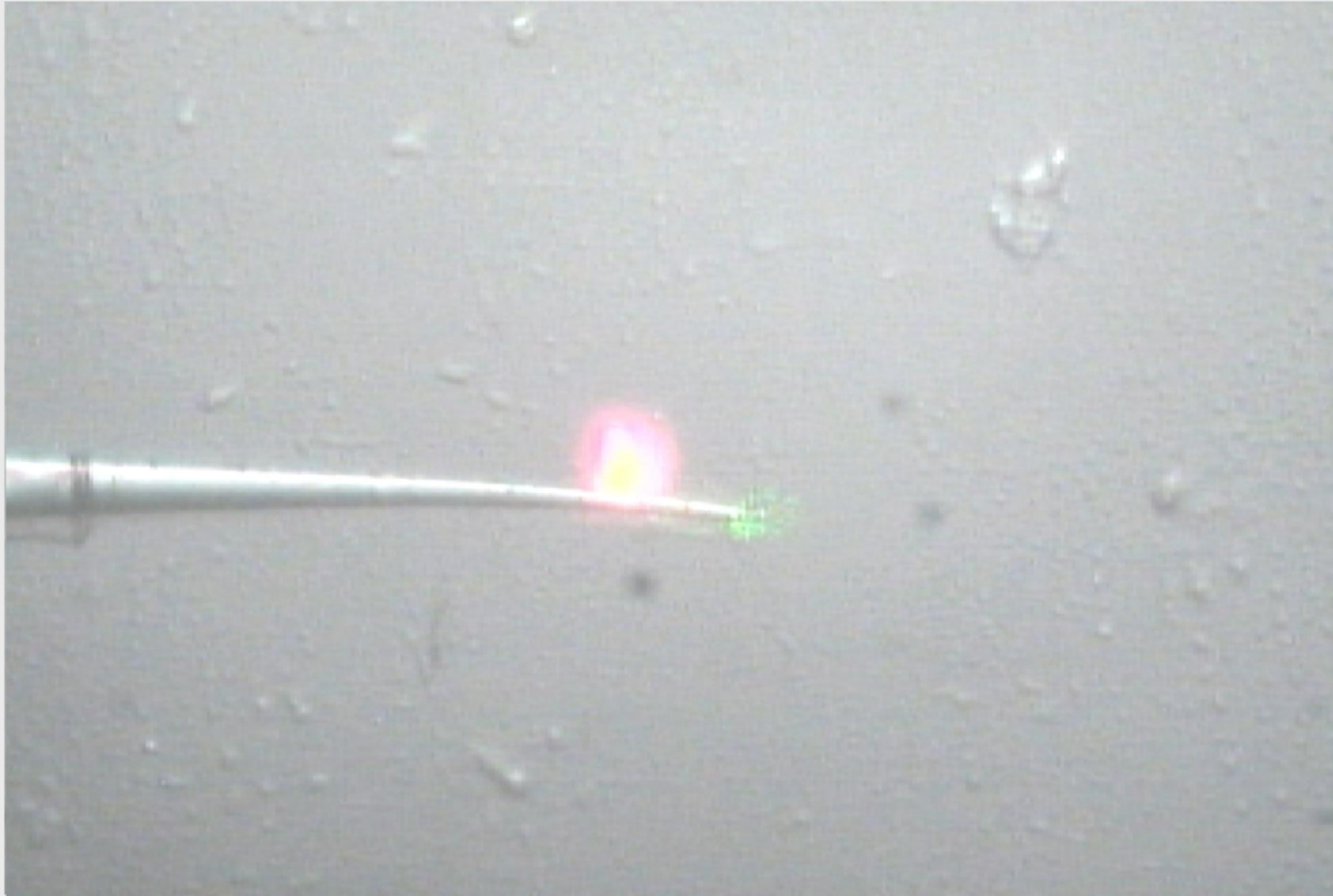
## Coupling microstructures



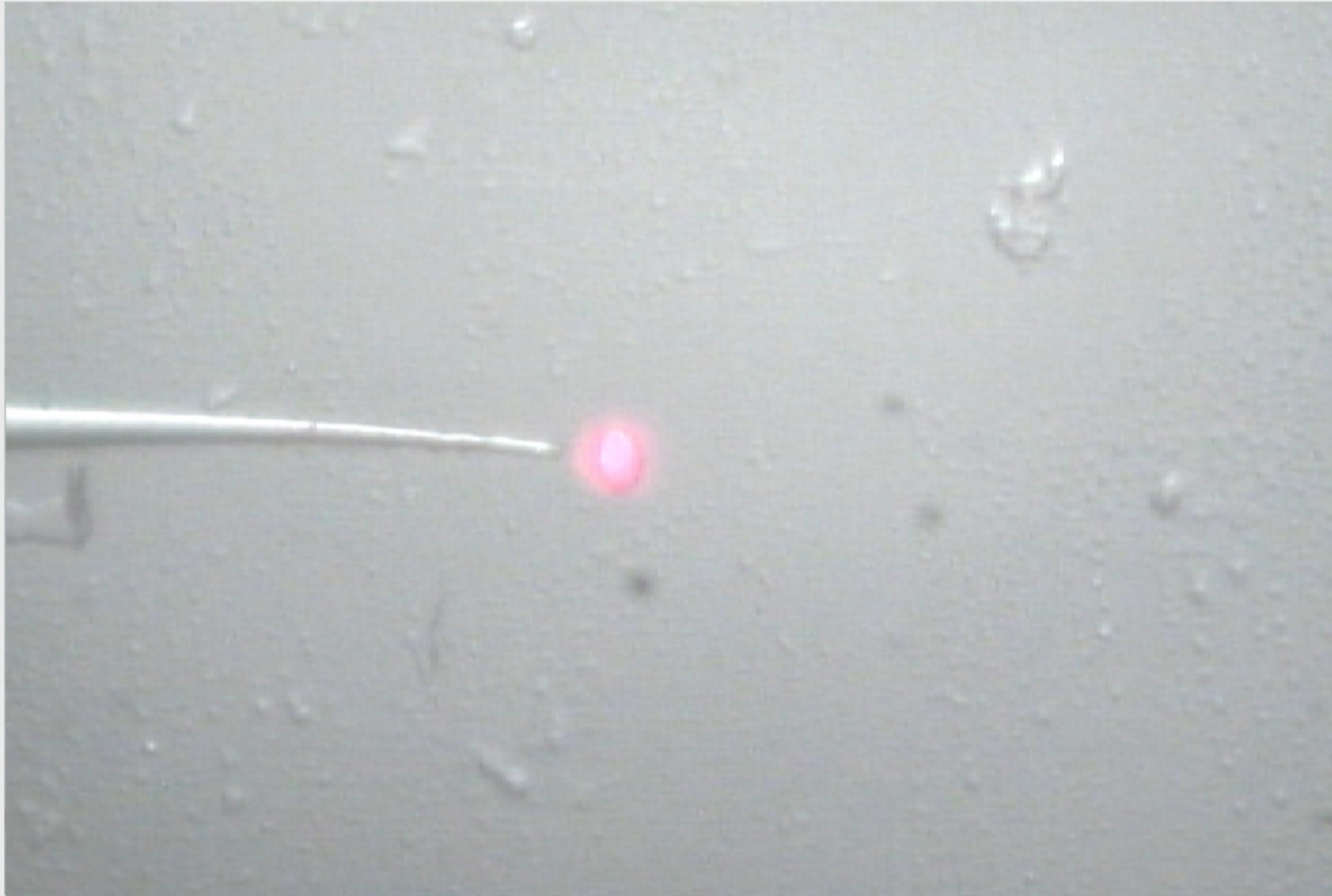
## Coupling microstructures



## Coupling microstructures

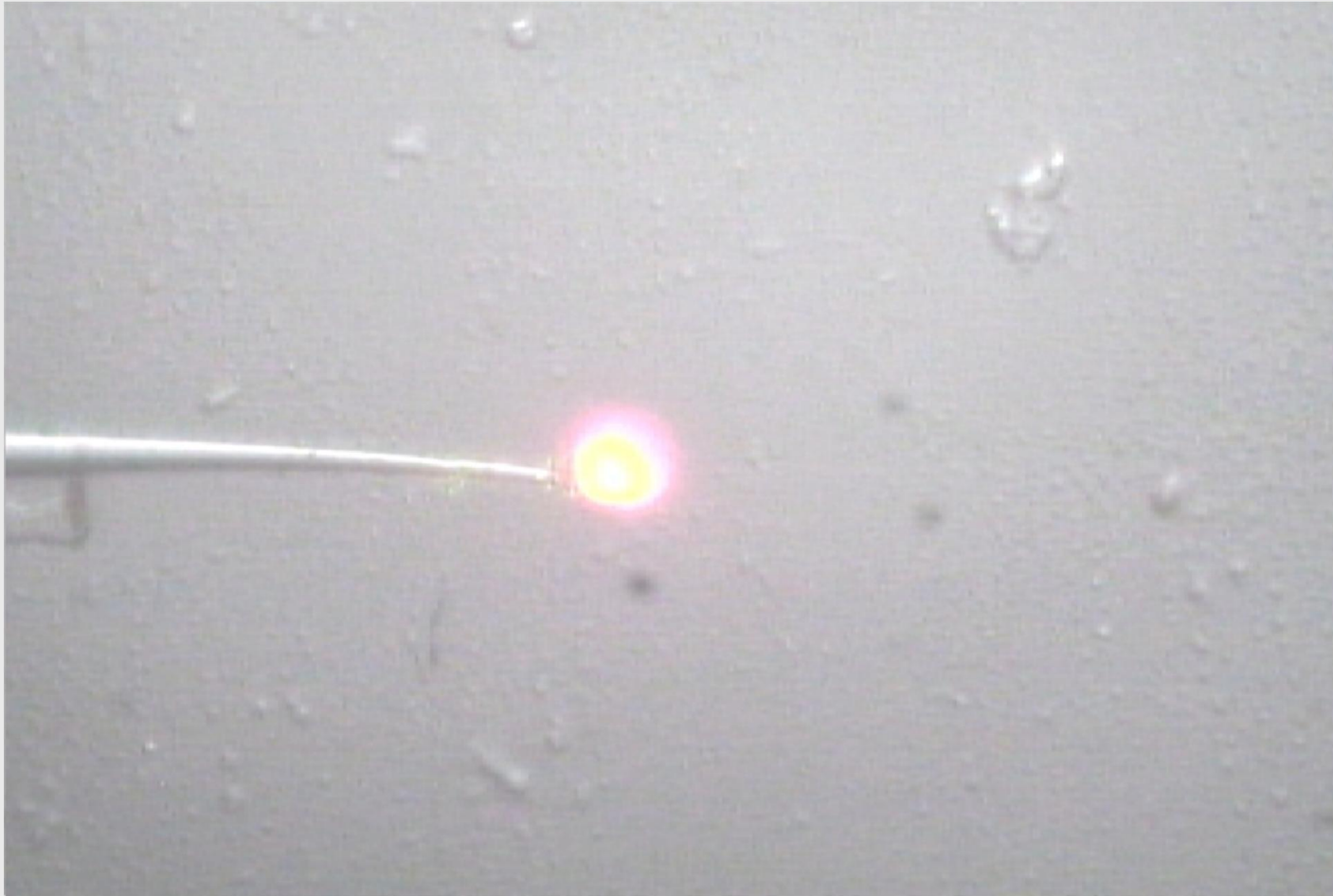


## Coupling microstructures

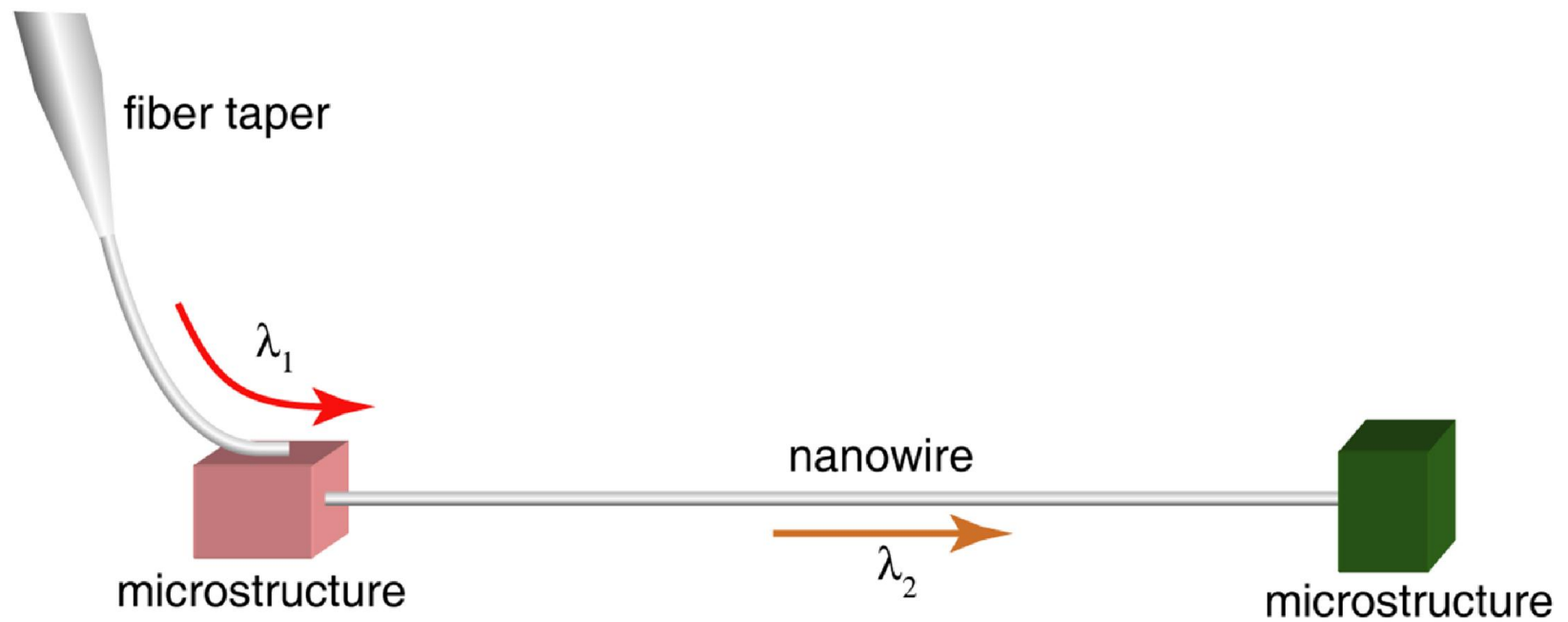




## Coupling microstructures



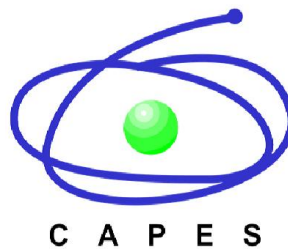
# Coupling microstructures



# Acknowledgments

## *Team*

Daniel S Correa  
Marcos R Cardoso  
Juliana Almeida  
*Adriano Otuka*  
*Gustavo Almeida*  
Vinicius Tribuzi  
Ruben Fonseca  
Renato Martins  
Paulo H. D. Ferreira



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