

08/03/17



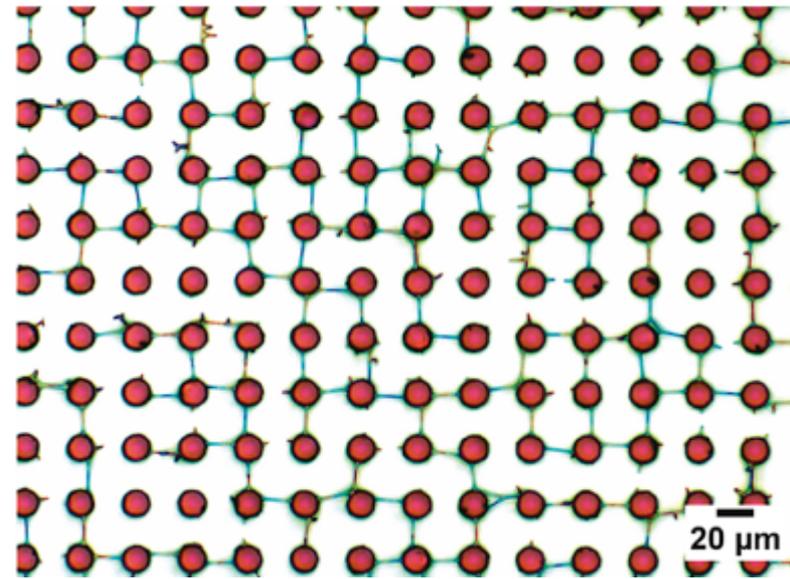
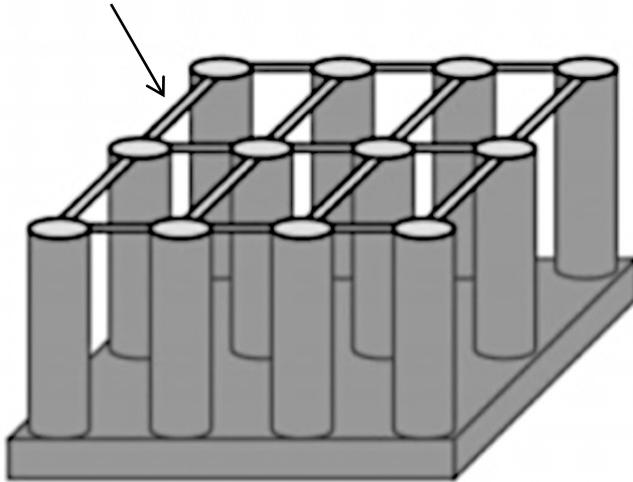
# Laser Assisted Patterning of Free Standing Polystyrene Thin Films

**Presenter: Hiroya Abe**  
**(Tohoku University, Sendai, Japan)**

**Mentor: Dr. Robert W. Cohn**  
**(University of Louisville, Louisville, KY)**



## Suspended polymer fibers



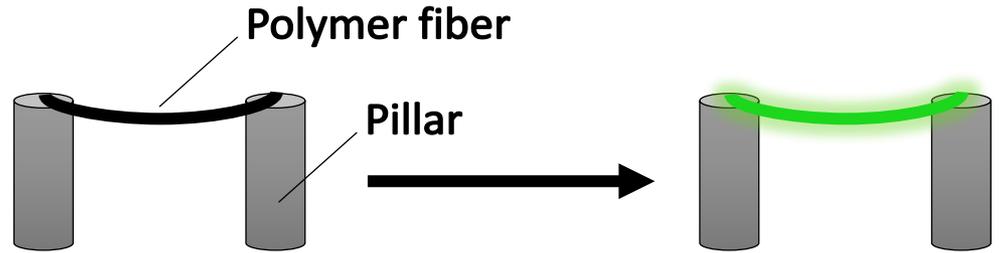
J. M. Rathfon *et al.*, *Macromolecules*, 2009, 42 (17), 6716

Micro/nanoscale polymer fibers have potential application in the micro/nanoscale devices:

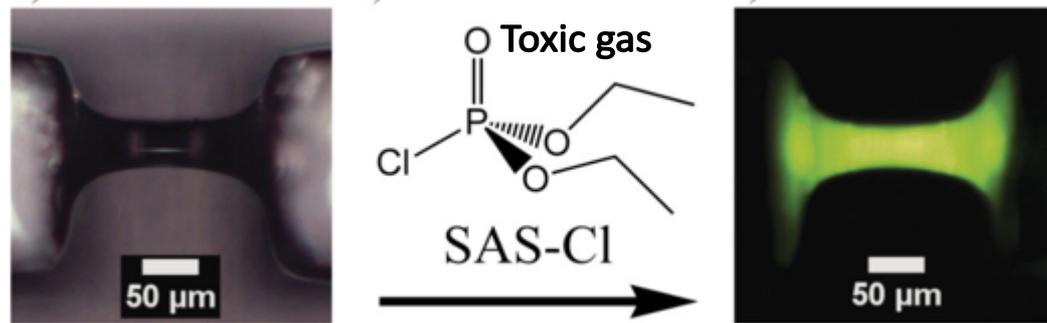
- microelectromechanical systems (MEMS)
- nano-electronics
- nano-optics
- chemical sensors

## Suspended polymer fibers

### Gas sensor



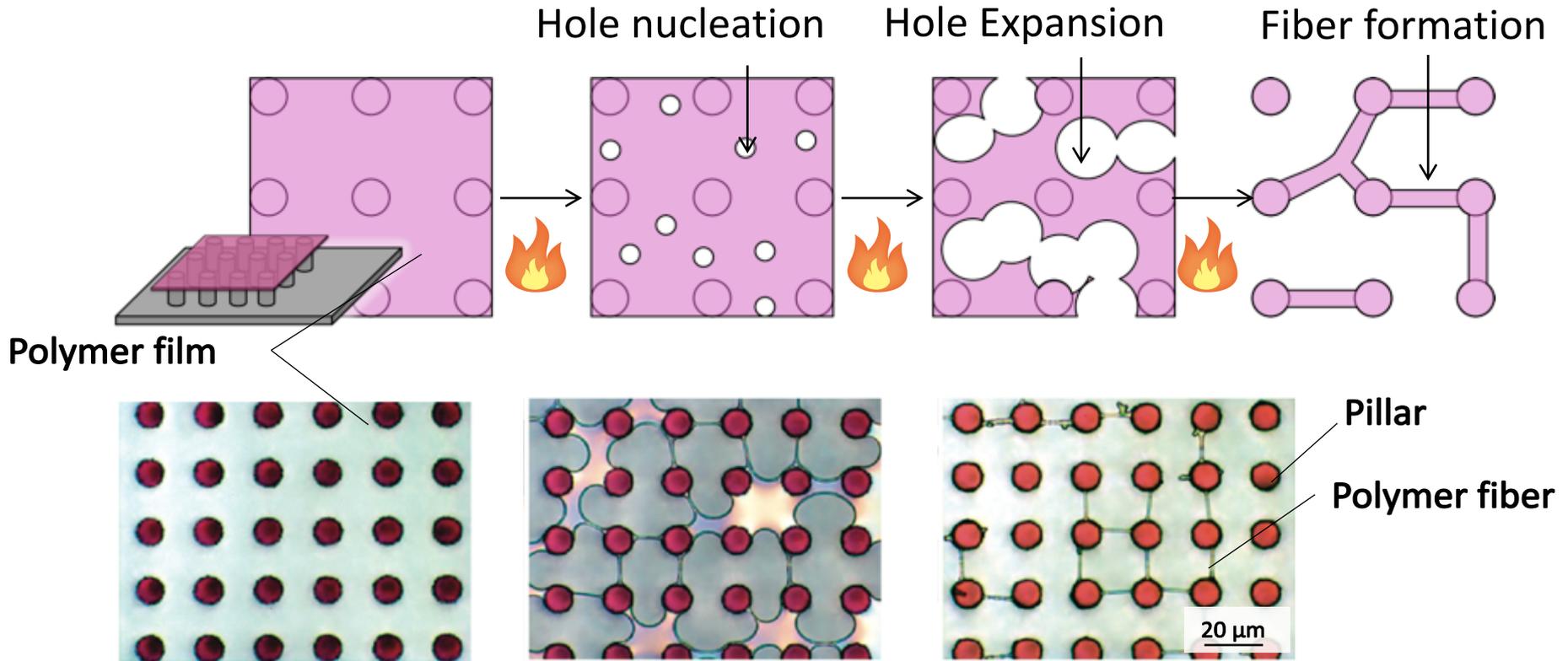
The polymer fiber with sensing molecules



The presence of the fibers increases detection surface area, which can lead to an increase in response time and sensitivity

## Conventional process

J. M. Rathfon *et al.*, *Macromolecules*, 2009, 42 (17), 6716

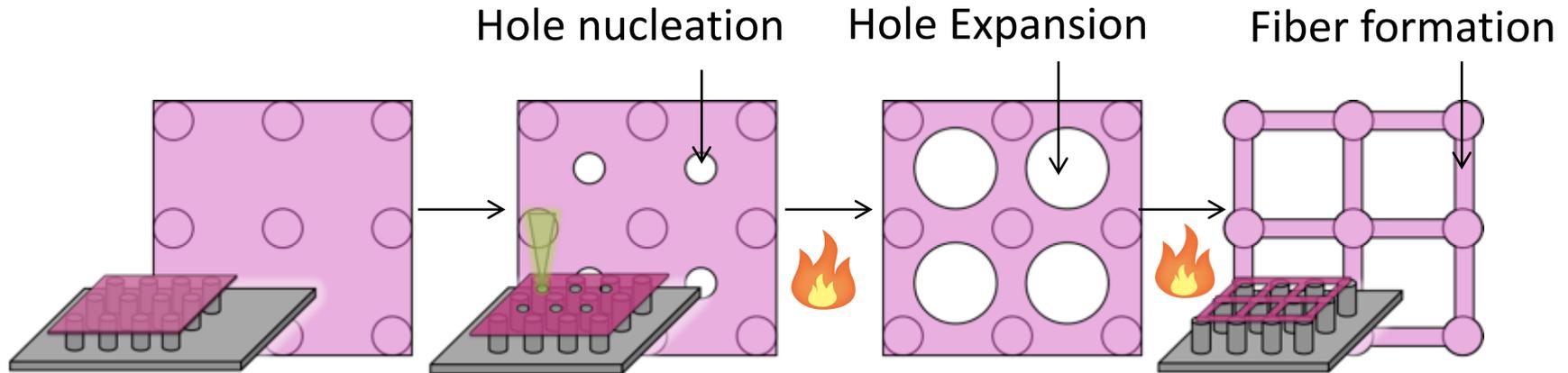


Suspended fibers are self-assembly formed between pillars by temperature annealing.

However

Since hole nucleation occurs randomly, controlling fiber formation is difficult and yield of fibers is low

## This study



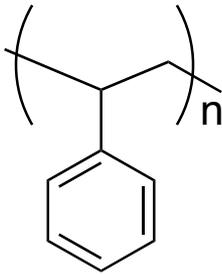
By introducing **laser ablation process**, we expect :

- to gain control over the suspended PS fiber formation process
- to be able to form custom arrangements of suspended nanostructures

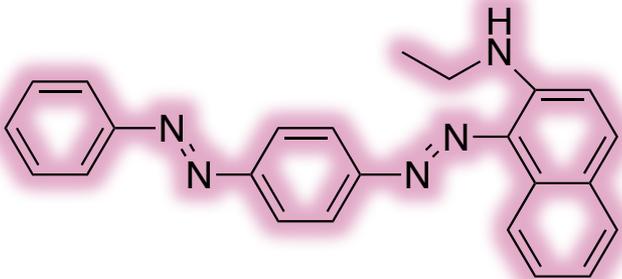
## However

Common polymer (Polystyrene) do not absorb a laser light at 532 nm.

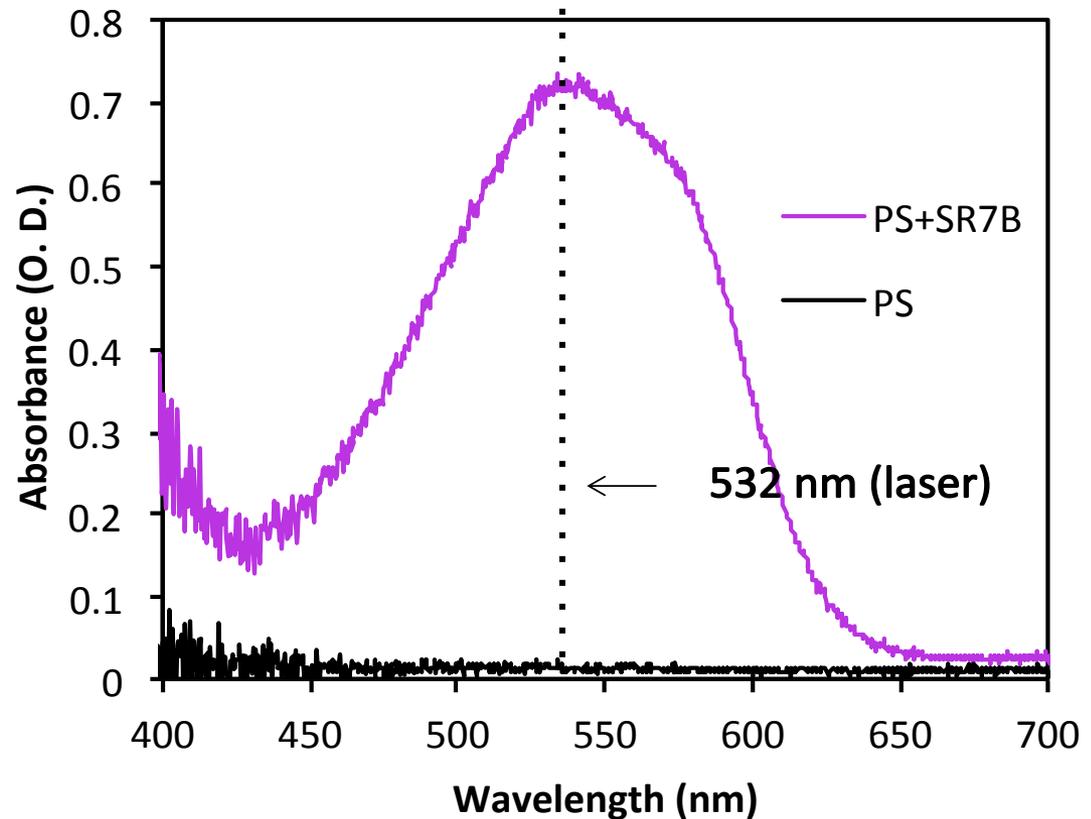
**Polymer**  
Polystyrene (PS)



**Dye**  
Sudan Red 7B (SR7B)



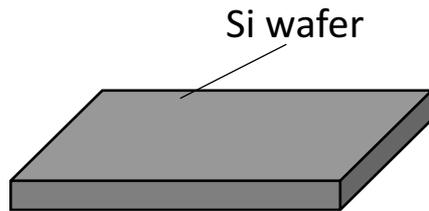
## Absorbance curves



SR7B can increase the absorption at 532 nm, which support PS films to easily laser-ablate

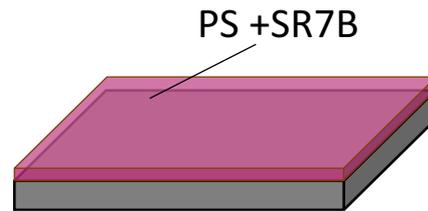
## (1) Cleaning

- Acetone bath
- Toluene bath

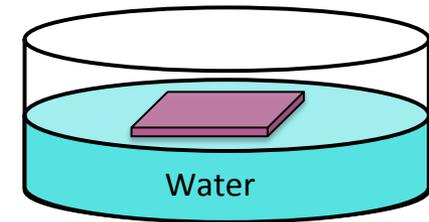


## (2) Spin-coating

- 0.75 wt% PS
- + 1.5 wt% SR7B
- in toluene



## (3) Floating



(1)

Si wafer



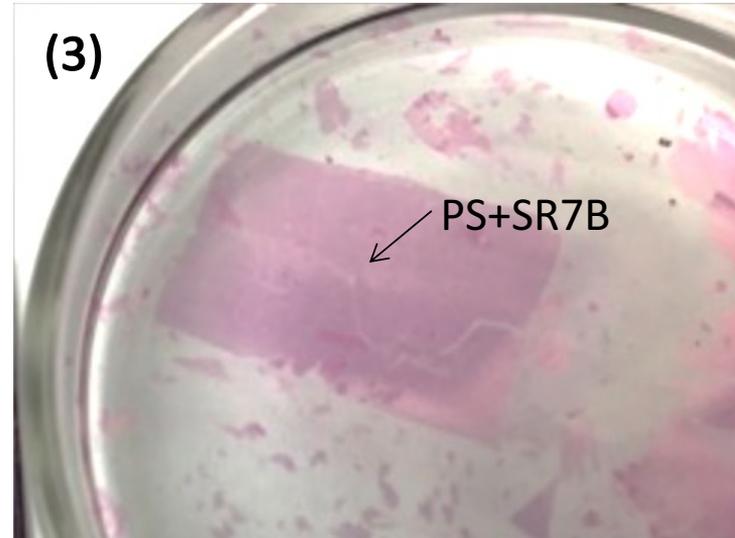
(2)

PS+SR7B



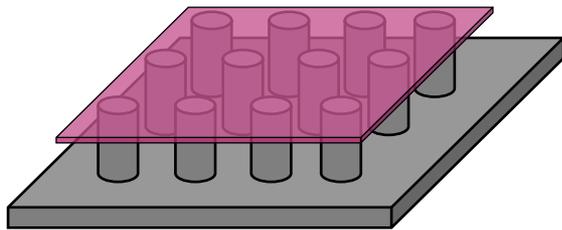
(3)

PS+SR7B

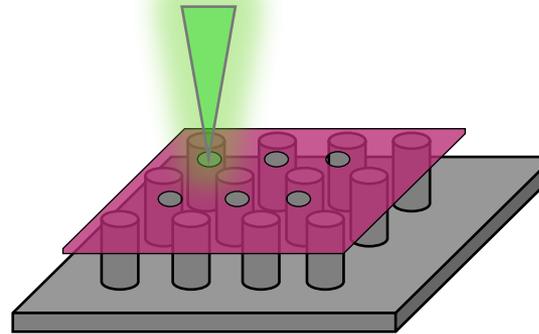


We successfully obtained the floated films

(4) Transferring

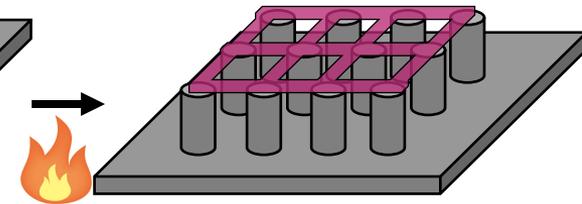


(5) Laser-Ablating

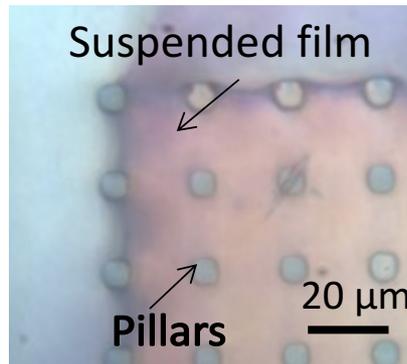
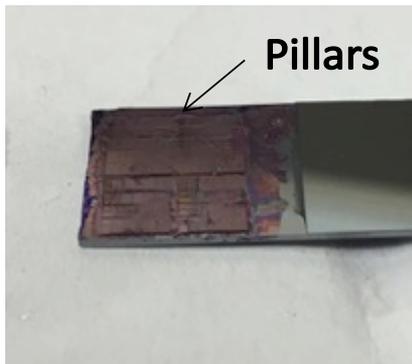


(6) Annealing

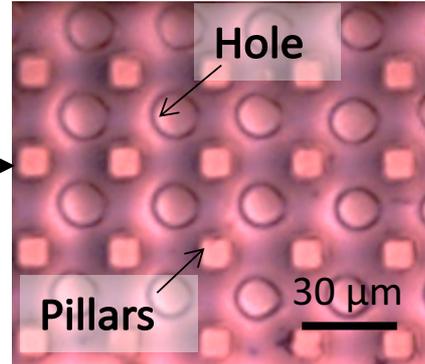
55 °C, 10 min



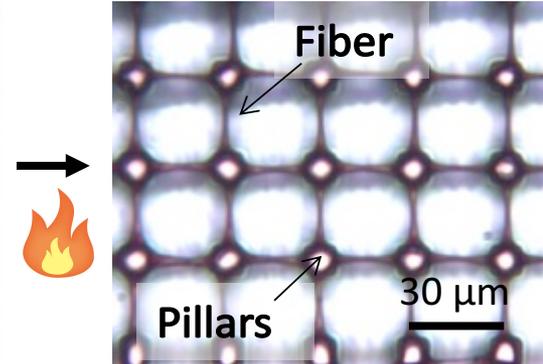
(4) Transferring



(5) Laser-Ablating

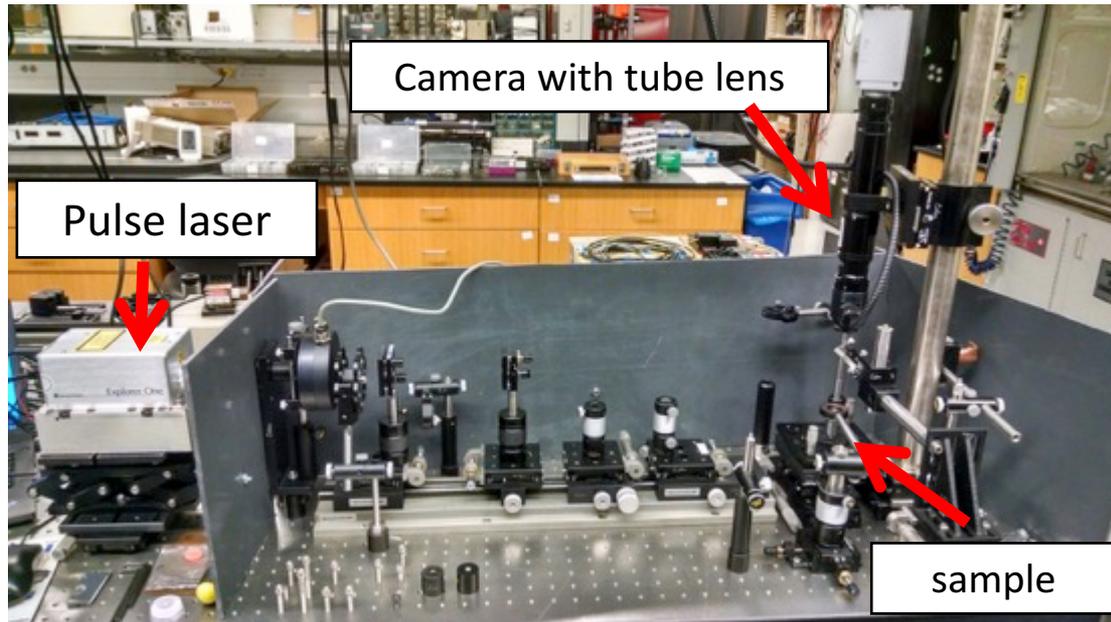
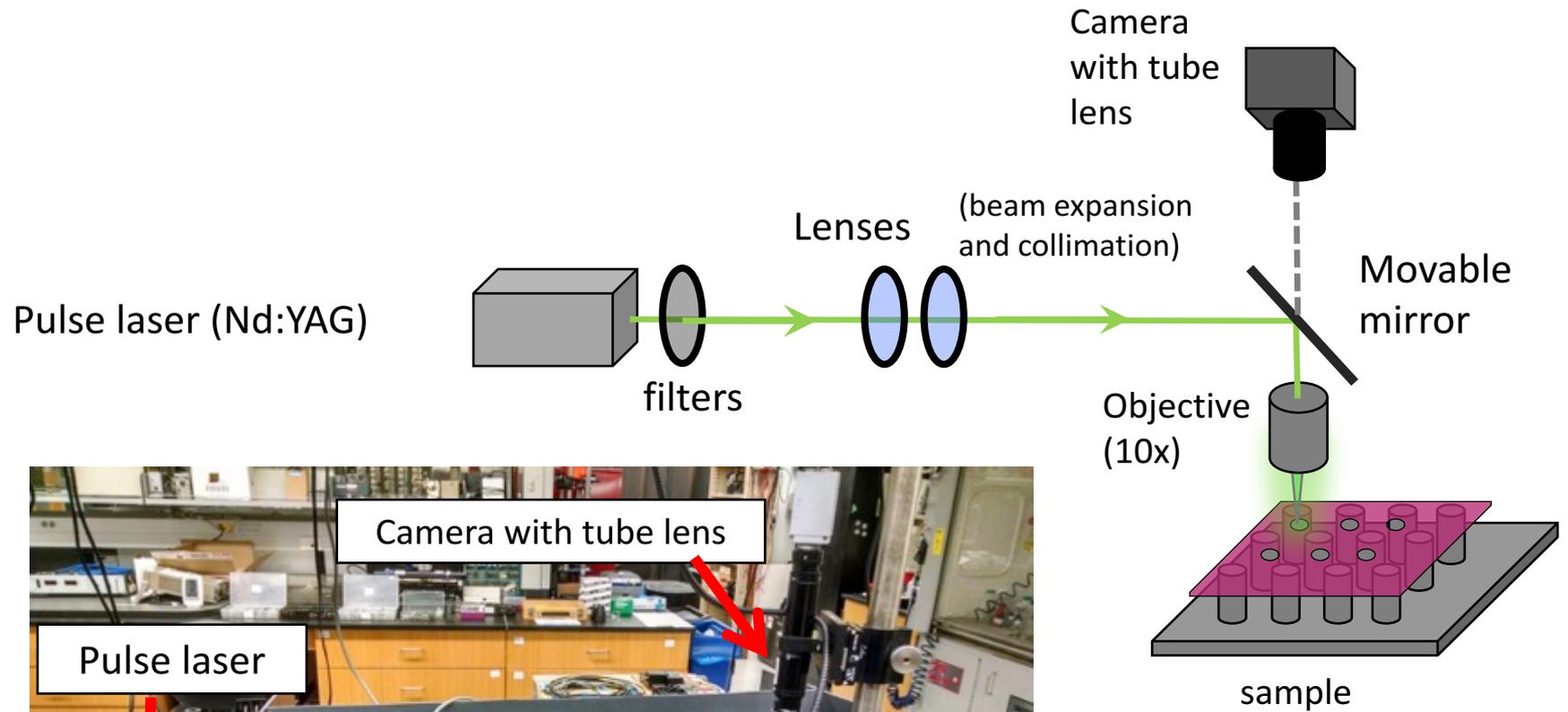


(6) Annealing



We successfully obtained the suspended fibers

# Experimental set – up for the laser patterning



Hole size: 10 – 15  $\mu\text{m}$

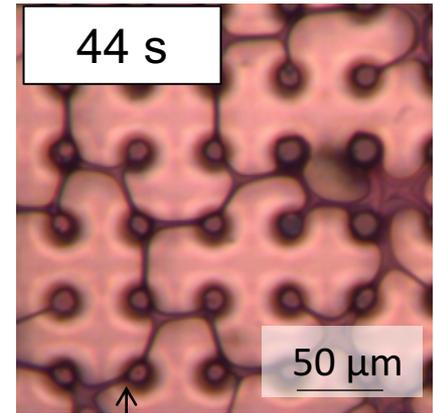
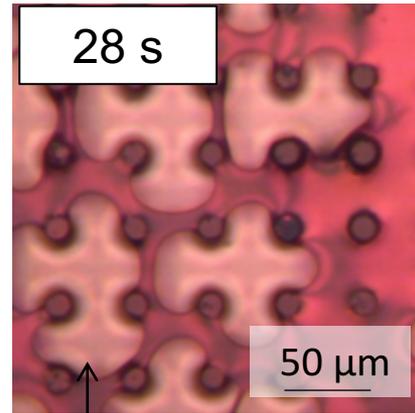
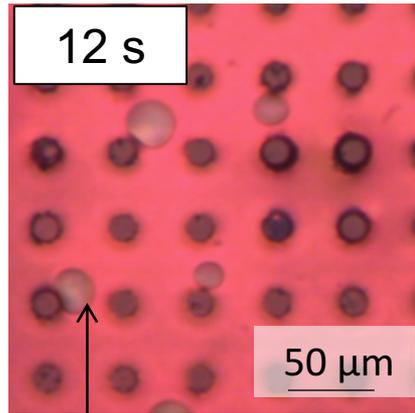
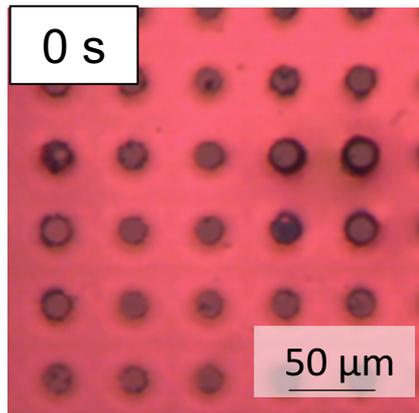
Pulse Laser: Spectra Physics EON-532-200 , 532 nm, max power = 2 W

## Without laser-ablation

Film thickness: 100 nm  
Annealing temperature: 55 °C

Before

After annealing



Hole nucleation

Hole Expansion

Fiber formation

Since hole nucleation occurs randomly



- yield of fibers is low
- controlling the fiber location is difficult

## Without laser-ablation

4 x

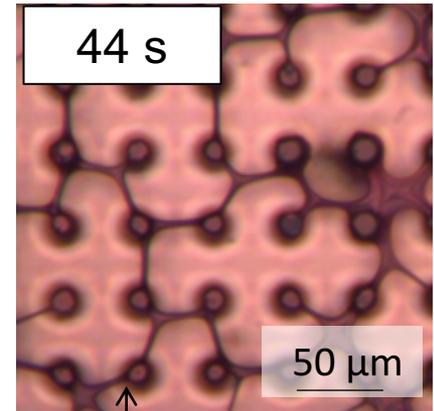
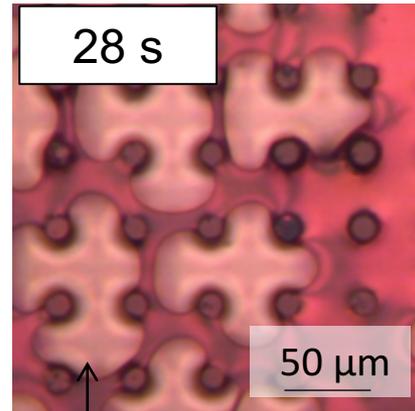
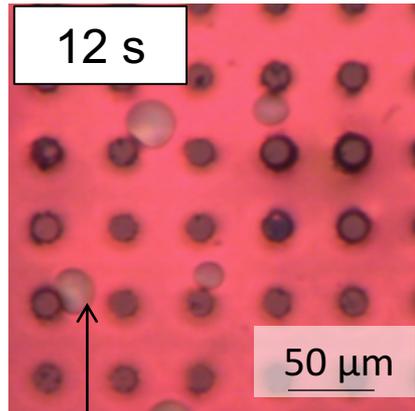
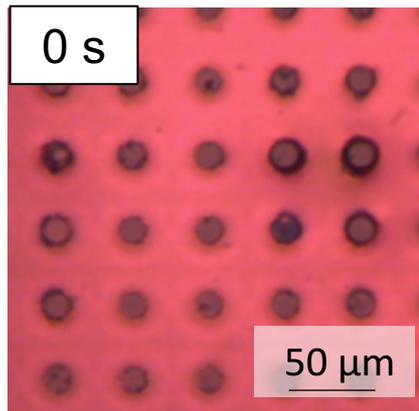


## Without laser-ablation

Film thickness: 100 nm  
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Before

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Hole nucleation

Hole Expansion

Fiber formation

Since hole nucleation occurs randomly



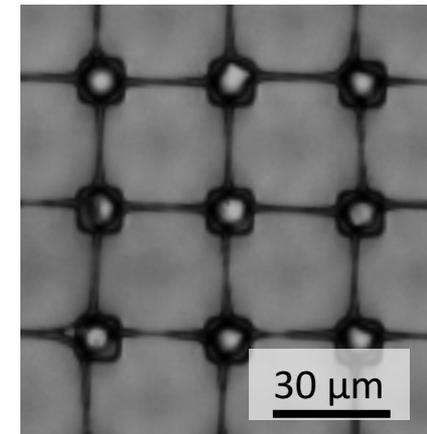
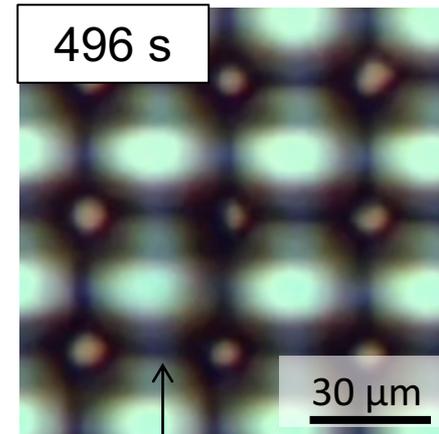
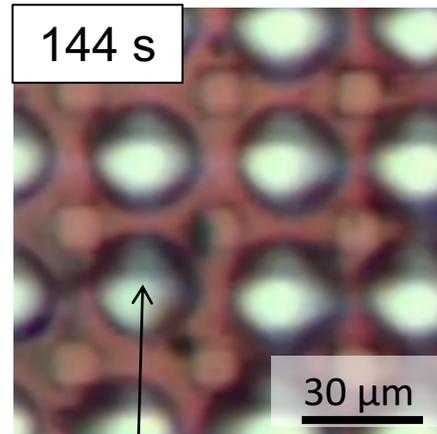
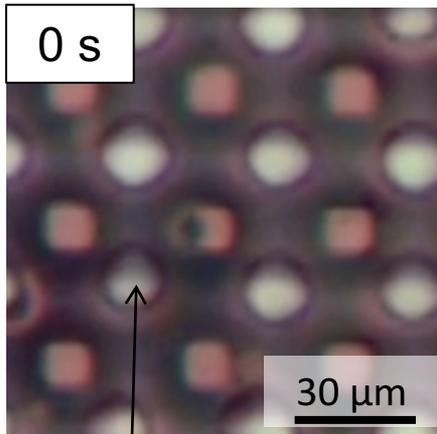
- yield of fibers is low
- controlling the fiber location is difficult

## With laser-patterning

Film thickness: 100 nm  
Annealing temperature: 55 °C

Before

After annealing



Hole  
(formed by laser  
ablation)

Hole Expansion

Fiber formation

Holes expansion initiated from ablated spots.

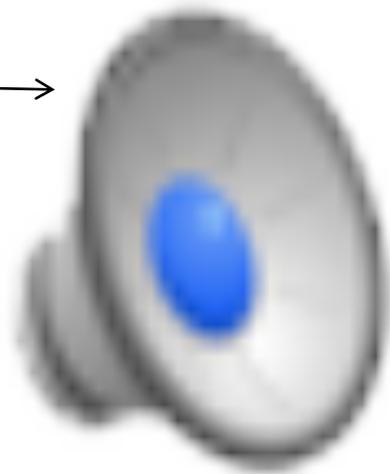
Fibers formed between pillars during temp. annealing.

**Laser ablation conditions:** Energy dose per pulse = 25 μJ, pulse width = 35 ns,  
# of pulses = 10 – 50, approximate beam size = 5 μm (at the surface of the polymer film)

# With laser-patterning

**16 x**

Hole  
(formed by laser  
ablation)



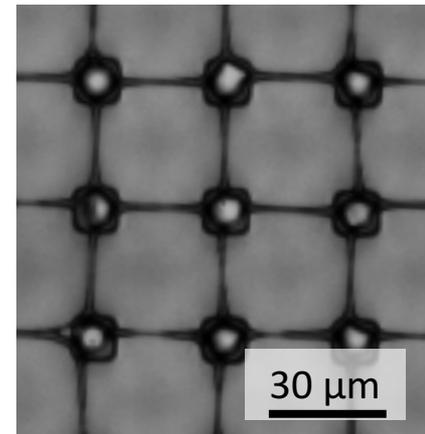
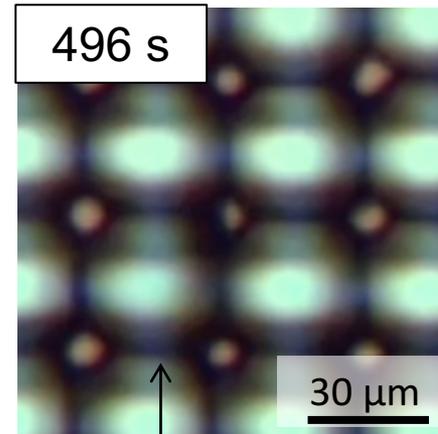
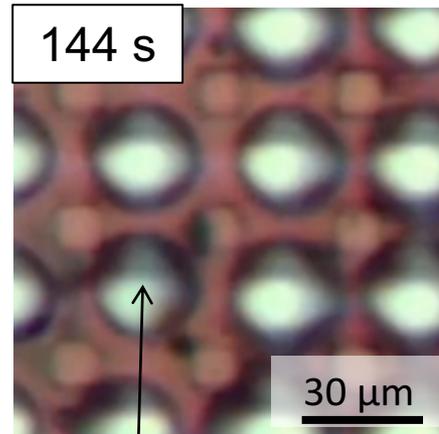
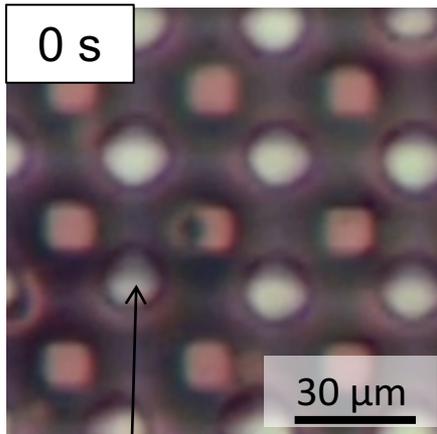
← Fiber

## With laser-patterning

Film thickness: 100 nm  
Annealing temperature: 55 °C

Before

After annealing



Hole  
(formed by laser  
ablation)

Hole Expansion

Fiber formation

Holes expansion initiated from ablated spots.

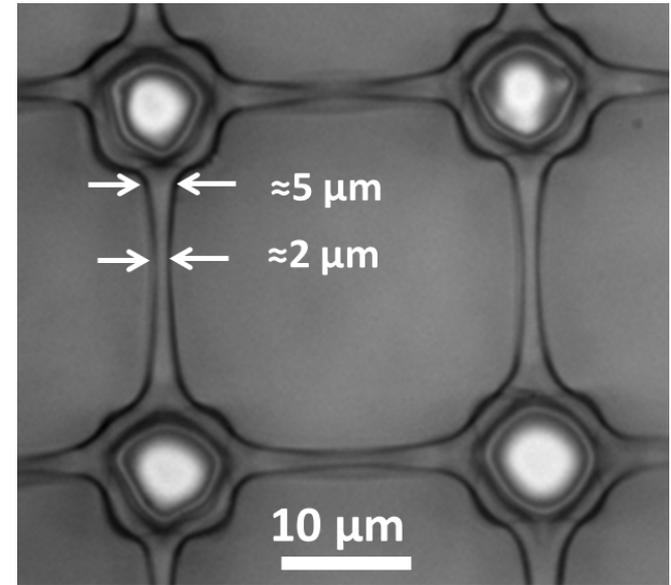
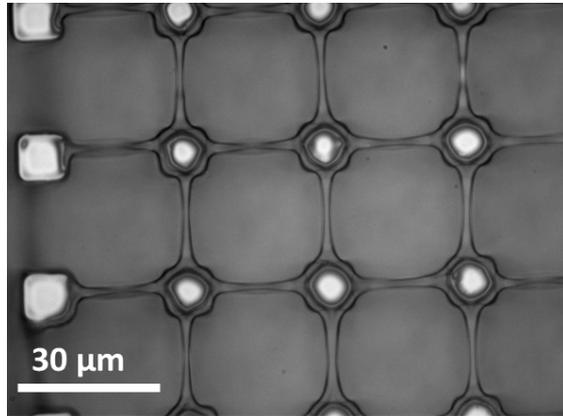
Fibers formed between pillars during temp. annealing.

**Laser ablation conditions:** Energy dose per pulse = 25  $\mu$ J, pulse width = 35 ns,  
# of pulses = 10 – 50, approximate beam size = 5  $\mu$ m (at the surface of the polymer film)

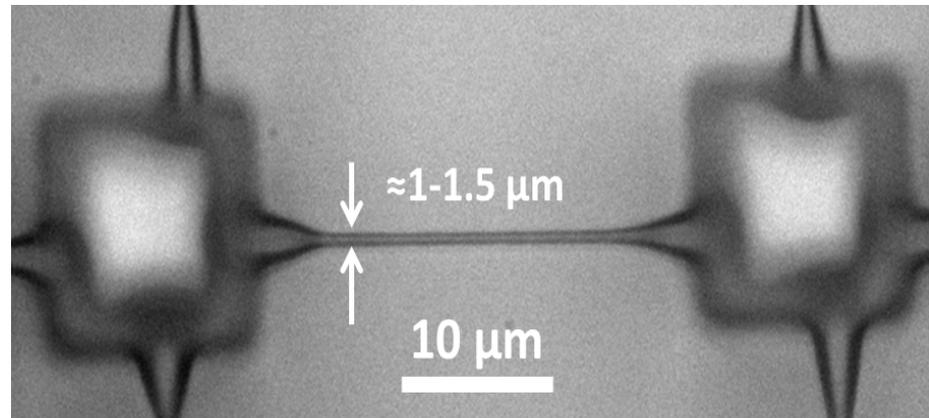
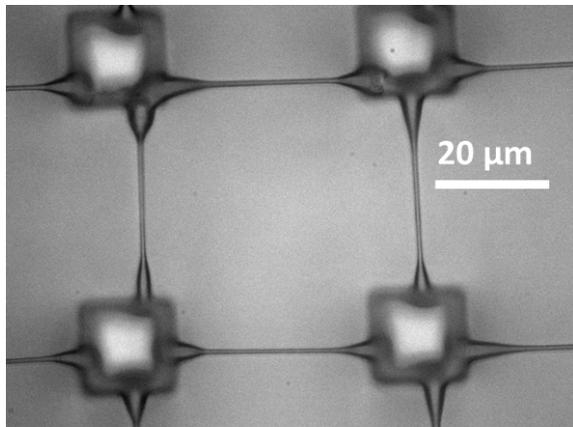


# Results – Shapes depending on the pillar structure

Pillar 1 (Distance between pillars: **30  $\mu\text{m}$** )

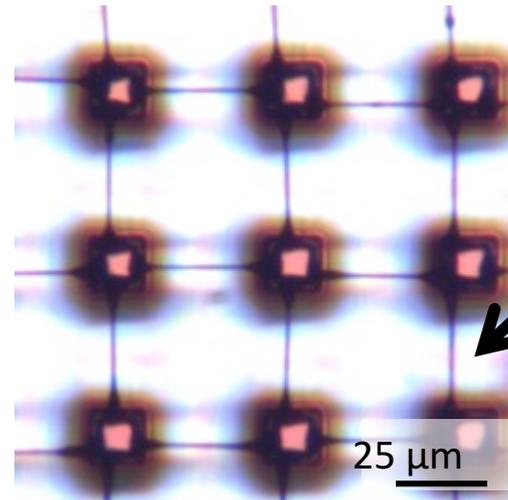
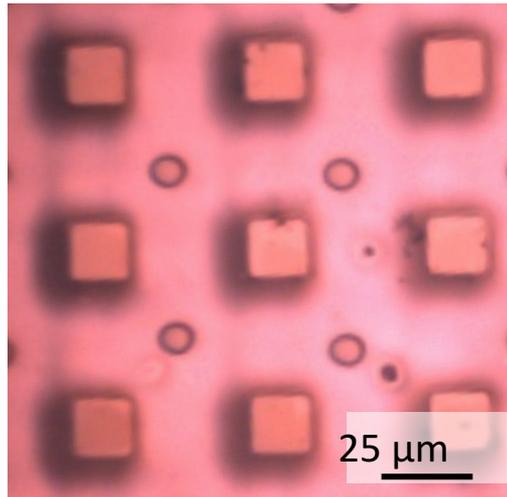


Pillar 2 (Distance between pillars: **60  $\mu\text{m}$** )



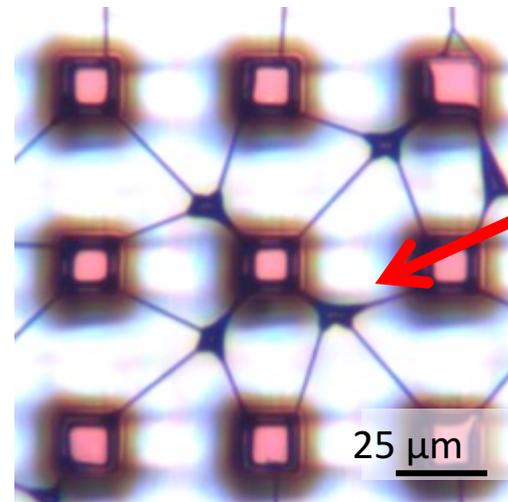
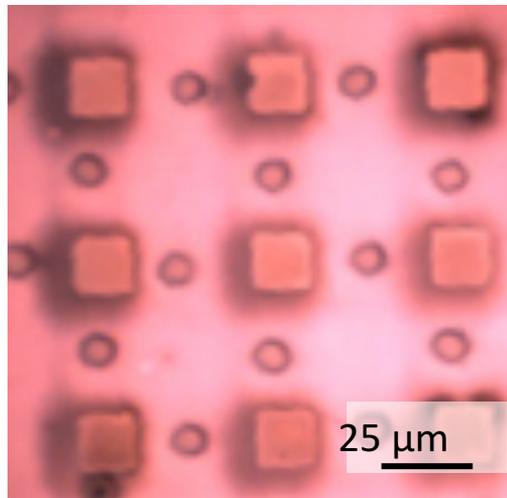
Shapes and fiber dimension depended on the pillar structure

Pattern 1



Fiber

Pattern 2

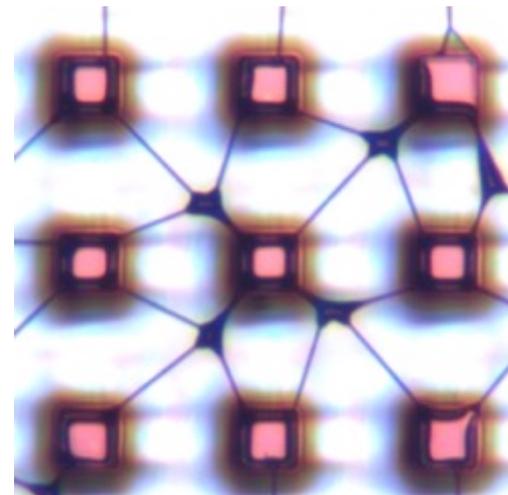
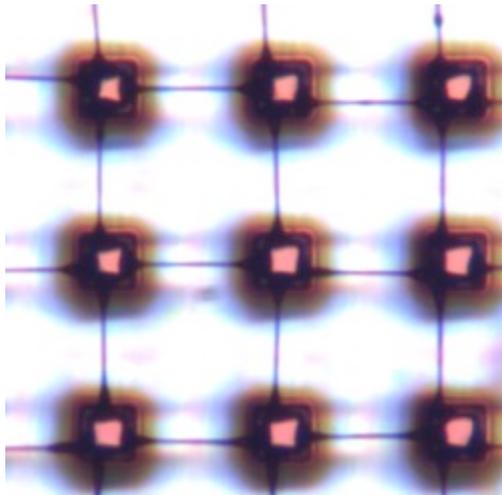


Branched fibers

The various fiber structures could be formed depending on the hole patterns – however further work is needed for a better control.

We obtained the suspended fibers at high yield (94 %) by laser-patterning of the polymer thin films

We showed that the proposed method could be used in the fabrication of the various fiber structures (fiber patterns)





This research was supported by

- IMPACT Research Experience for Undergraduates (REU) (Award ID: 1542164)
- NNCI/NIMS Graduate Exchange Fellowship program, Nanotechnology Platform - NIMS, Japan
- Fellows from the Japan Society for the Promotion of Science
- Institute for International Advanced Research and Education

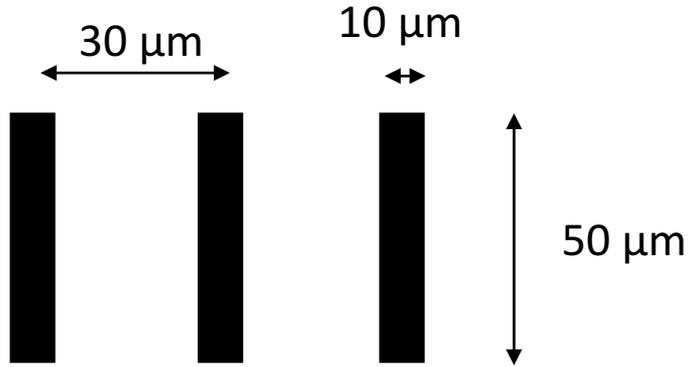
I would like to acknowledge

- Dr. Robert W. Cohn for his guidance this project, at UoL
- Dr. Andriy Sherehiy for assistance, at UoL,
- impact REU program staffs and members

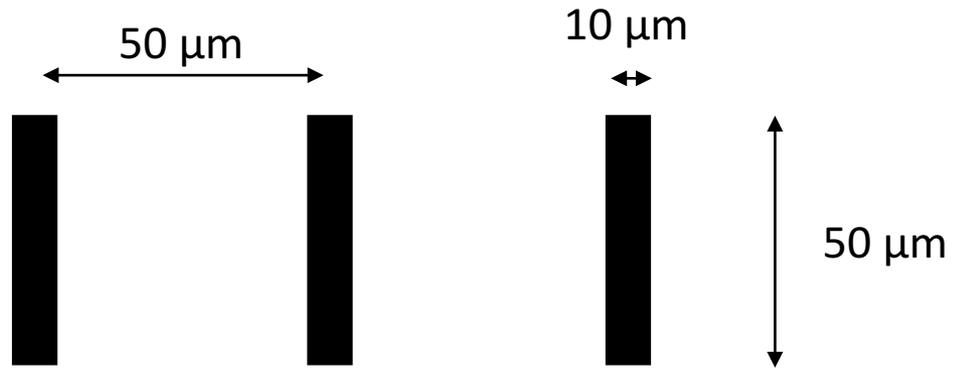


# Supporting information

12



15



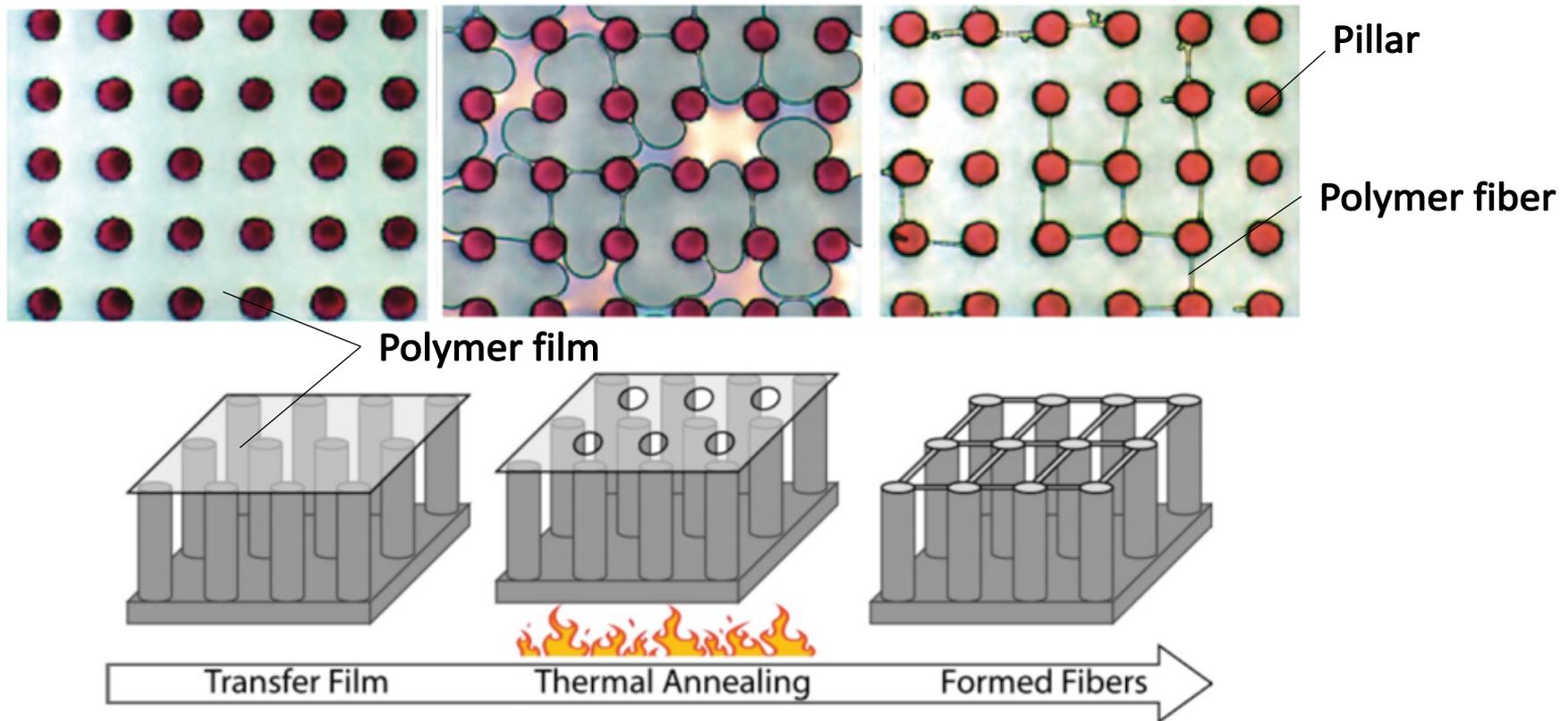
none





## Conventional method for fabrication of the suspended fibers

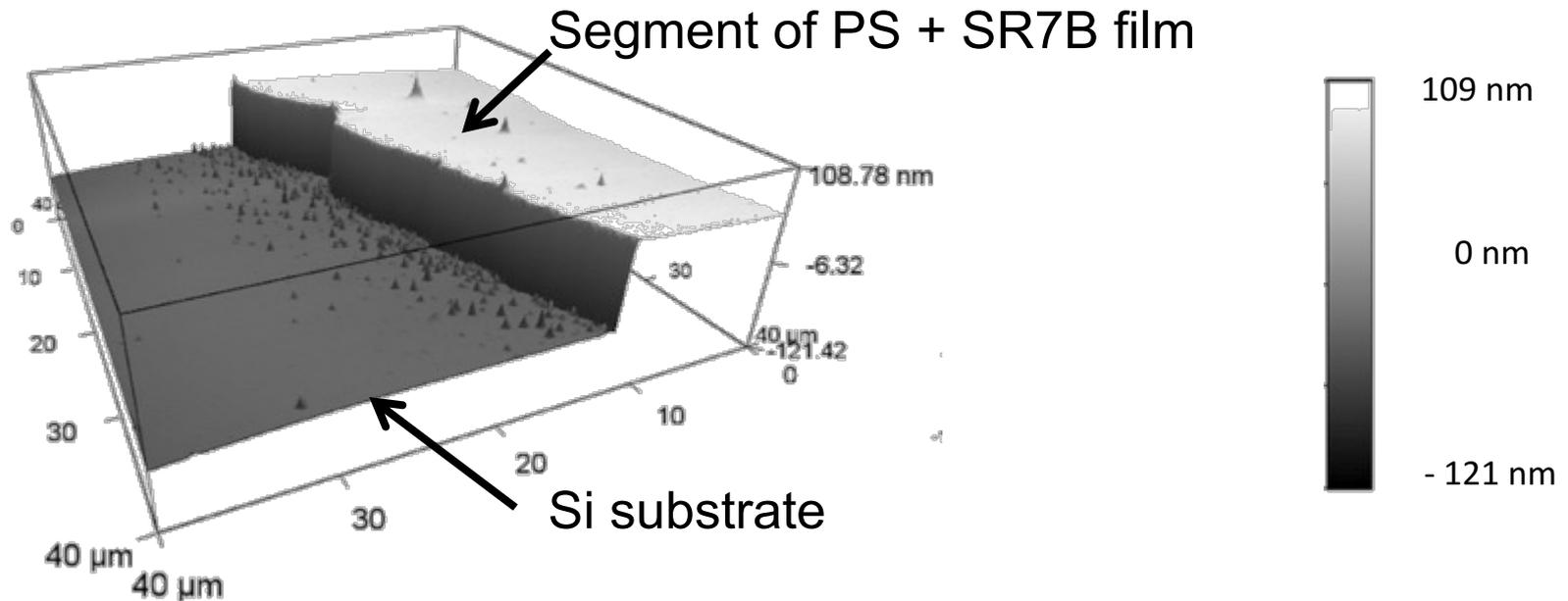
J. M. Rathfon *et al.*, *Macromolecules*, 2009, 42 (17), 6716



Suspended fibers are self-assembly formed between pillars by temperature annealing of PS thin film.

However conventional method was limited control of the process.

Atomic force microscopy (AFM) image

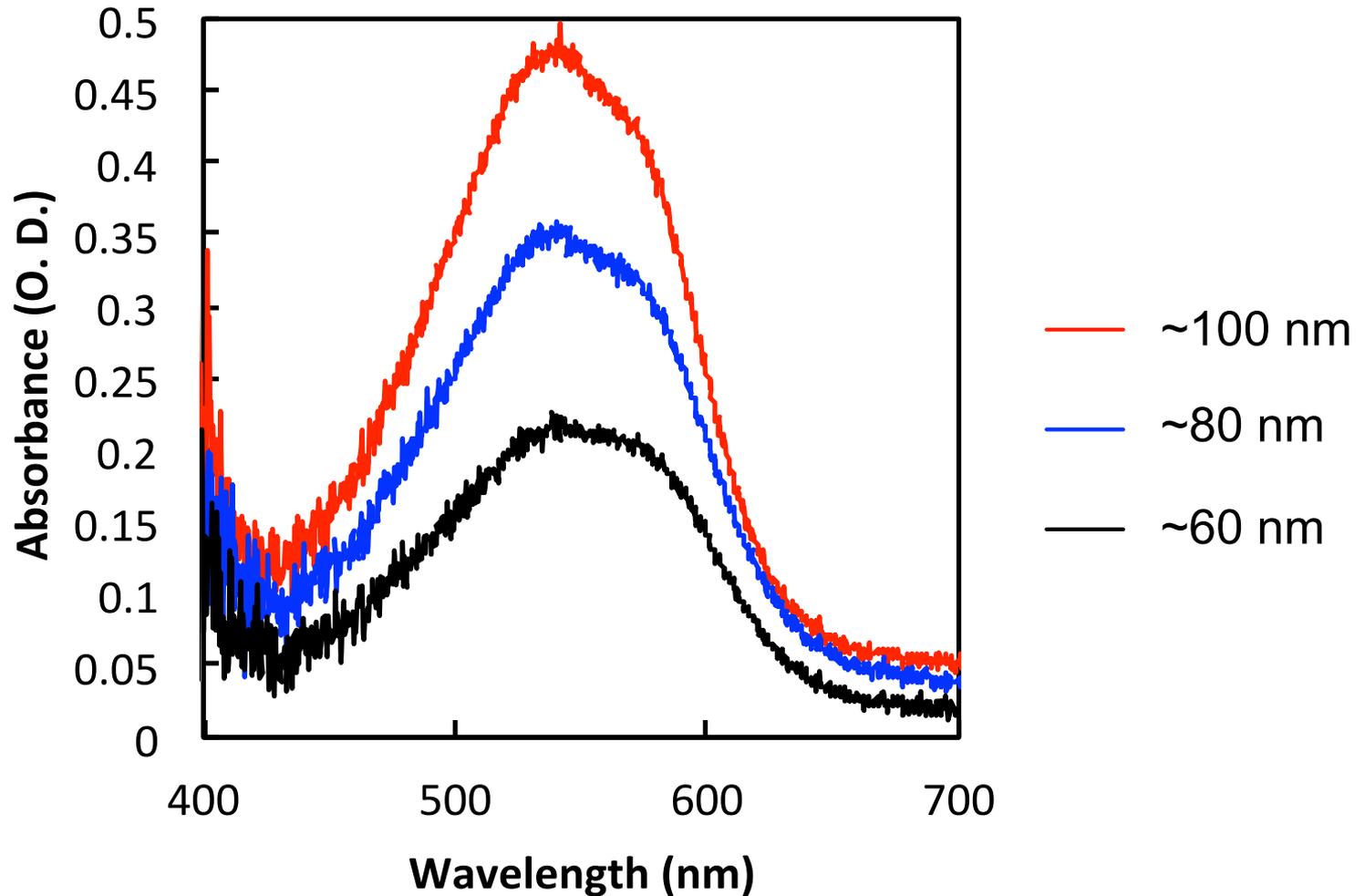


An average thickness of the film was determined by AFM.  
(The AFM consists of a cantilever with a nanoscale probe at its end that is used to scan the surface.)

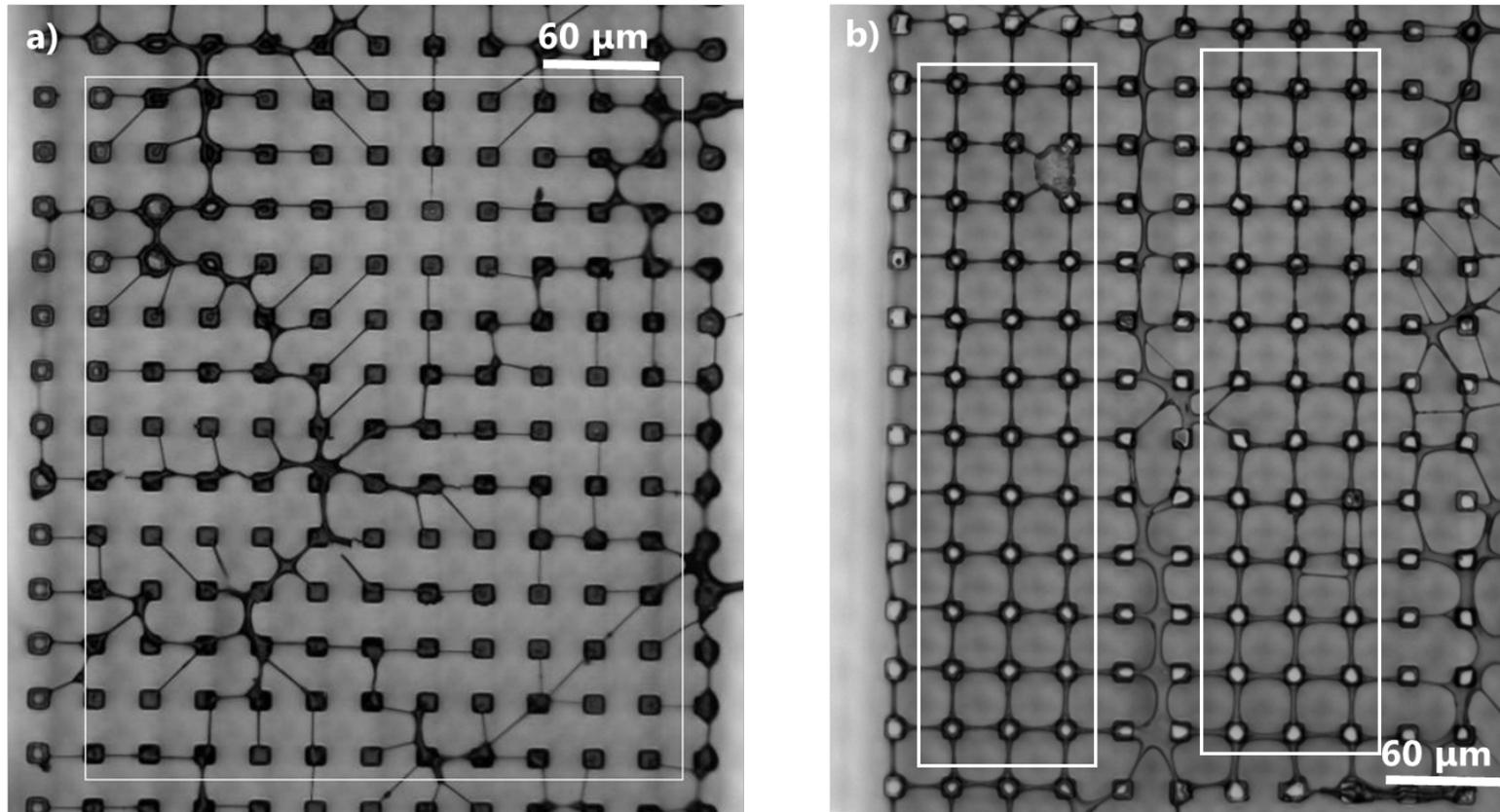
The average thickness for given film is  $93 \pm 7$  nm

(PS 0.75 wt% + SR7B 1.5 wt% in toluene solution, 3000 rpm)

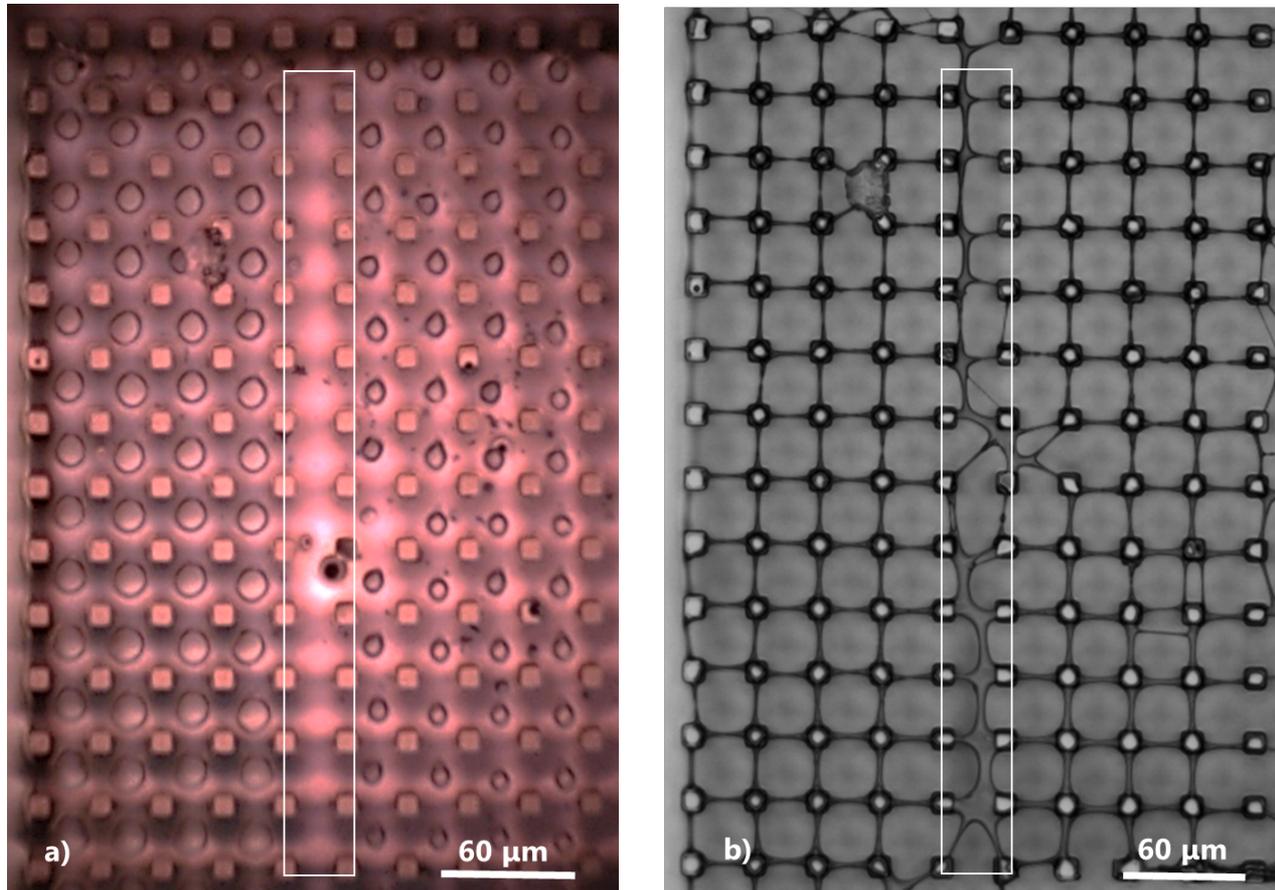
The absorbance at 532 nm depends on the film thickness



(When absorbance is 0.5 OD – about 32 % of the incident light is transmitted)



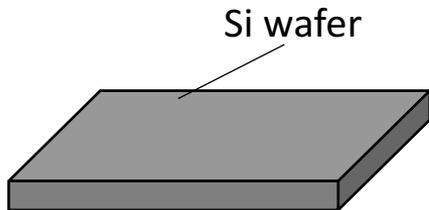
PS+SR7B thin film (thickness 100 nm) on the pillar structure after the thermal annealing: a) without laser patterning (conventional method), b) with laser patterning. Selected area (white rectangles) was used to determine the # of the fibers yield. Both pillar structures are the same.



PS + SR7B thin films (thickness 100 nm) on the pillar structure with laser patterning:  
Before a) and after annealing b).

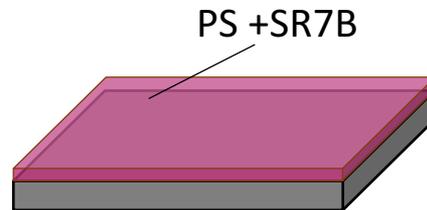
## (1) Cleaning

- Acetone bath
- Toluene bath

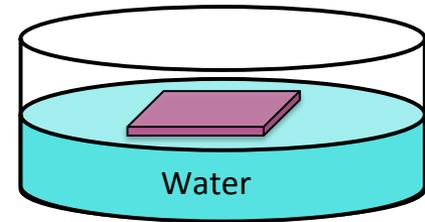


## (2) Spin-coating

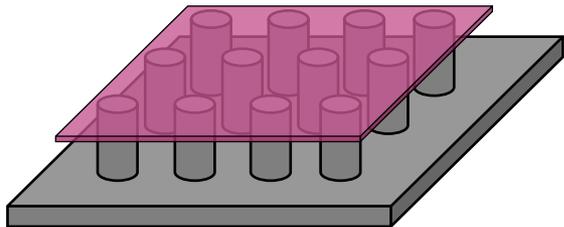
- 0.75 wt% PS
- + 1.5 wt% SR7B
- in toluene



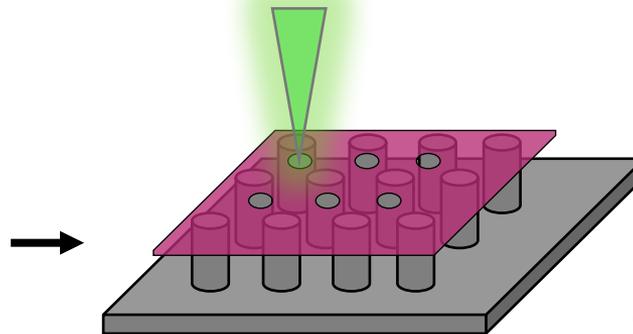
## (3) Floating



## (4) Transferring

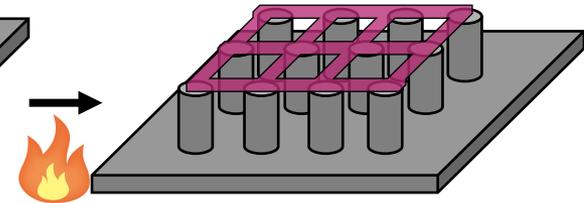


## (5) Laser-Ablating



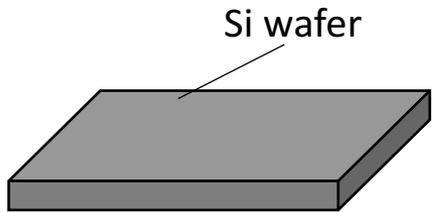
## (6) Annealing

55 °C, 10 min



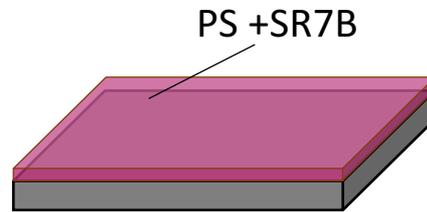
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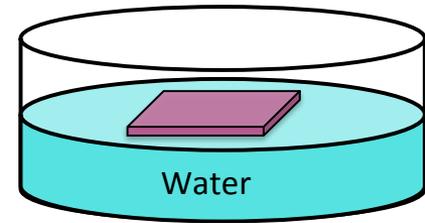


## (2) Spin-coating

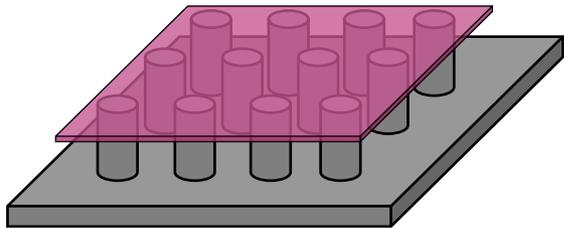
- 0.75 wt% PS
- + 1.5 wt% SR7B
- in toluene



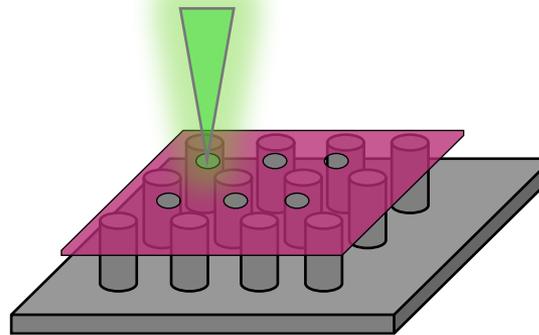
## (3) Floating



## (4) Transferring



## (5) Laser-Ablating



## (6) Annealing

55 °C, 10 min

