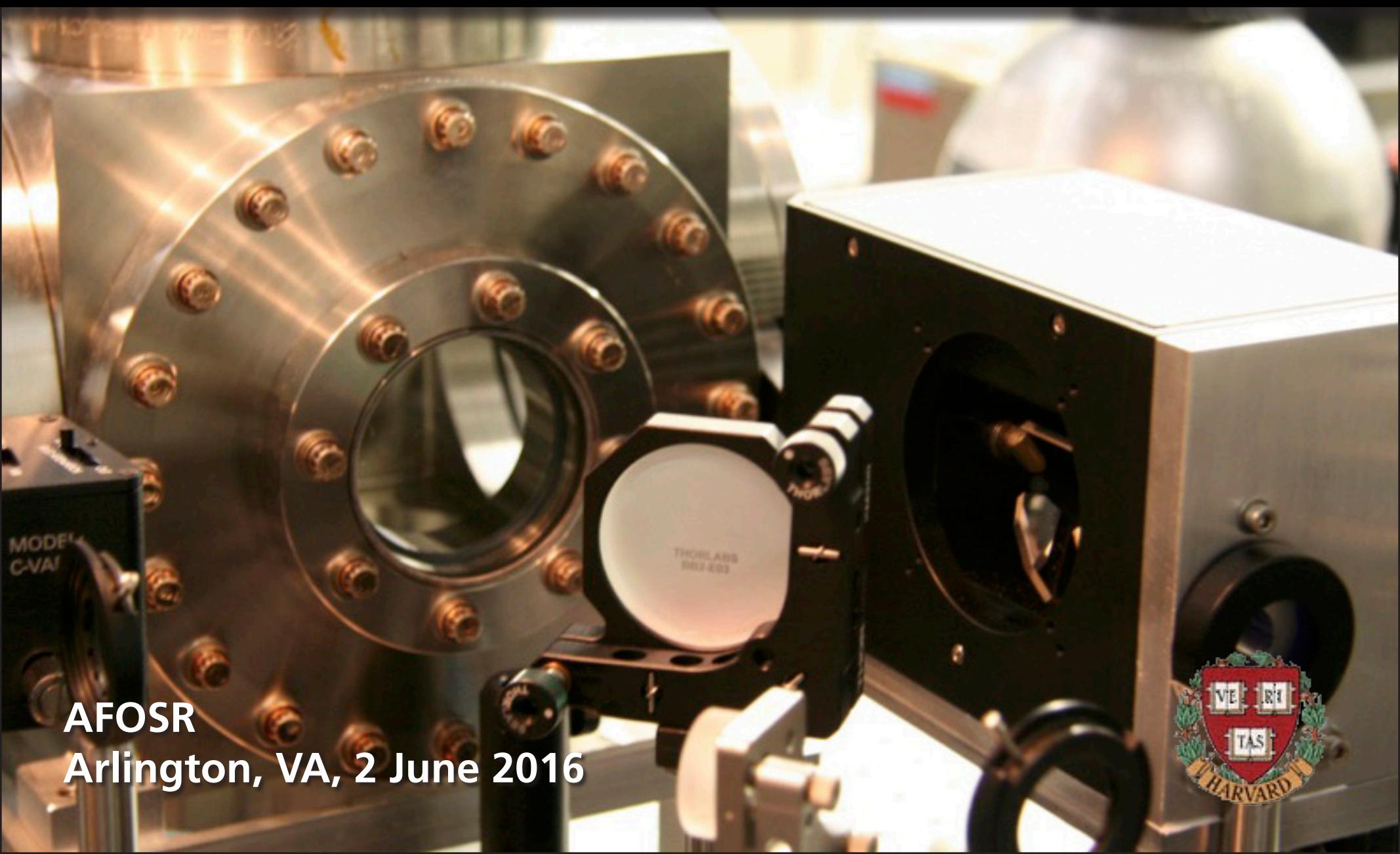


# Non-equilibrium materials by fs-laser texturing and hyperdoping of silicon

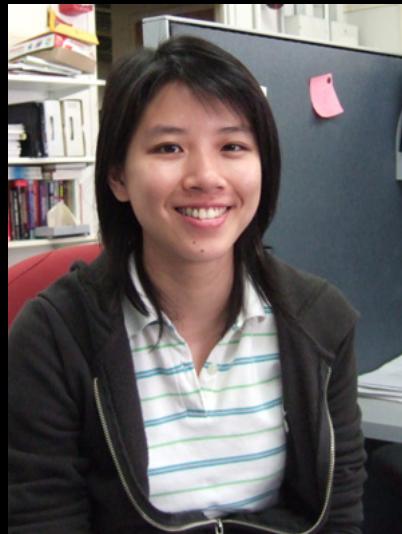


AFOSR  
Arlington, VA, 2 June 2016





Renee Sher



Yu-Ting Lin



Kasey Philips



Ben Franta

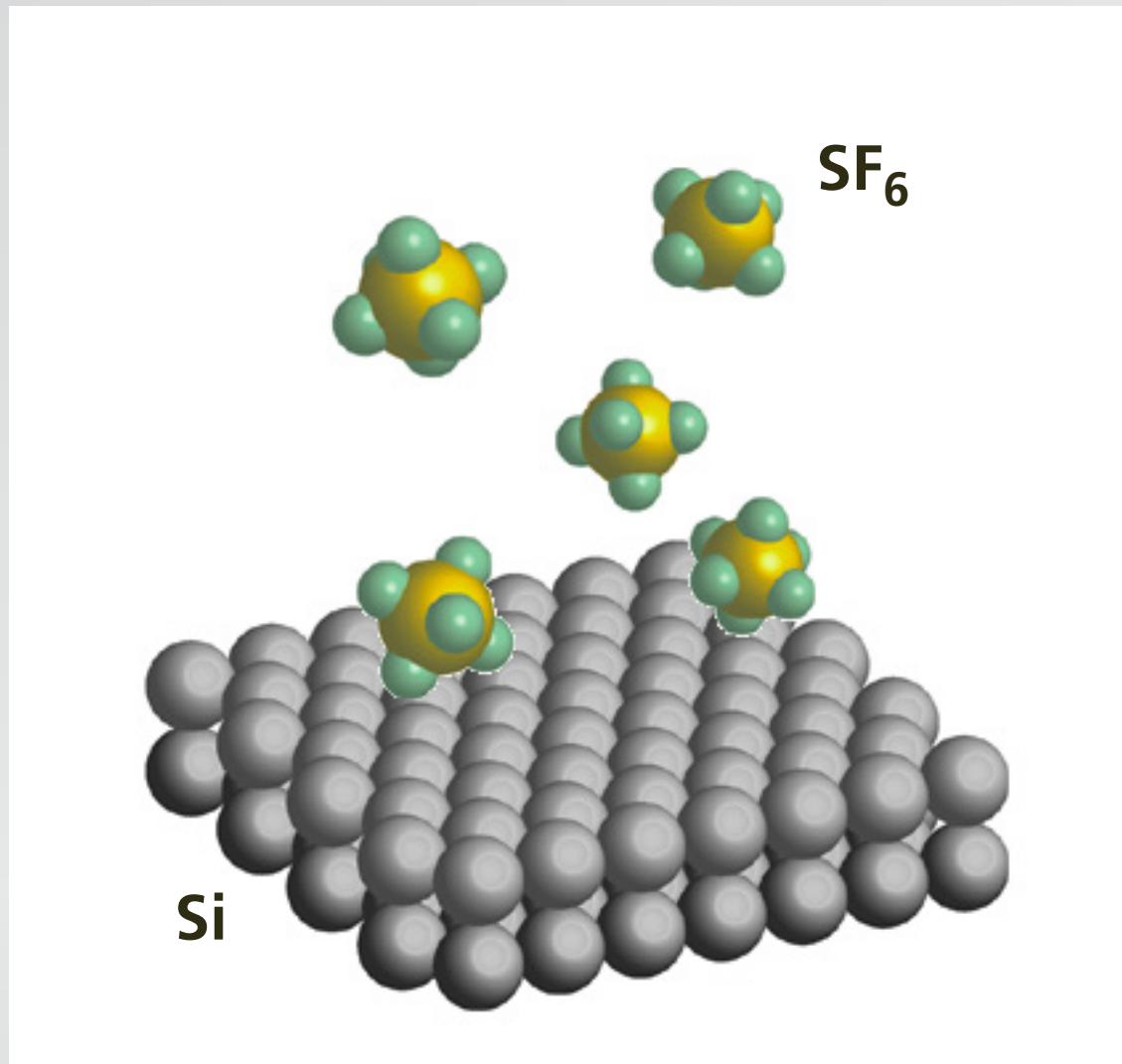


eric\_mazur

and also....

Hemi Gandhi  
Alexander Raymond  
Dr. Marc Winkler  
Dr. Eric Diebold  
Dr. Haifei Albert Zhang  
Dr. Brian Tull  
Dr. Jim Carey (SiOnyx)  
**Prof. Tsing-Hua Her (UNC Charlotte)**  
Dr. Shrenik Deliwala  
Dr. Richard Finlay  
Dr. Michael Sheehy  
Dr. Claudia Wu  
Dr. Rebecca Younkin  
**Prof. Catherine Crouch (Swarthmore)**  
**Prof. Mengyan Shen (Lowell U)**  
**Prof. Li Zhao (Fudan U)**  
  
**Prof. Alan Aspuru-Guzik**  
**Prof. Michael Aziz**  
**Prof. Michael Brenner**  
**Prof. Cynthia Friend**  
**Prof. Howard Stone**

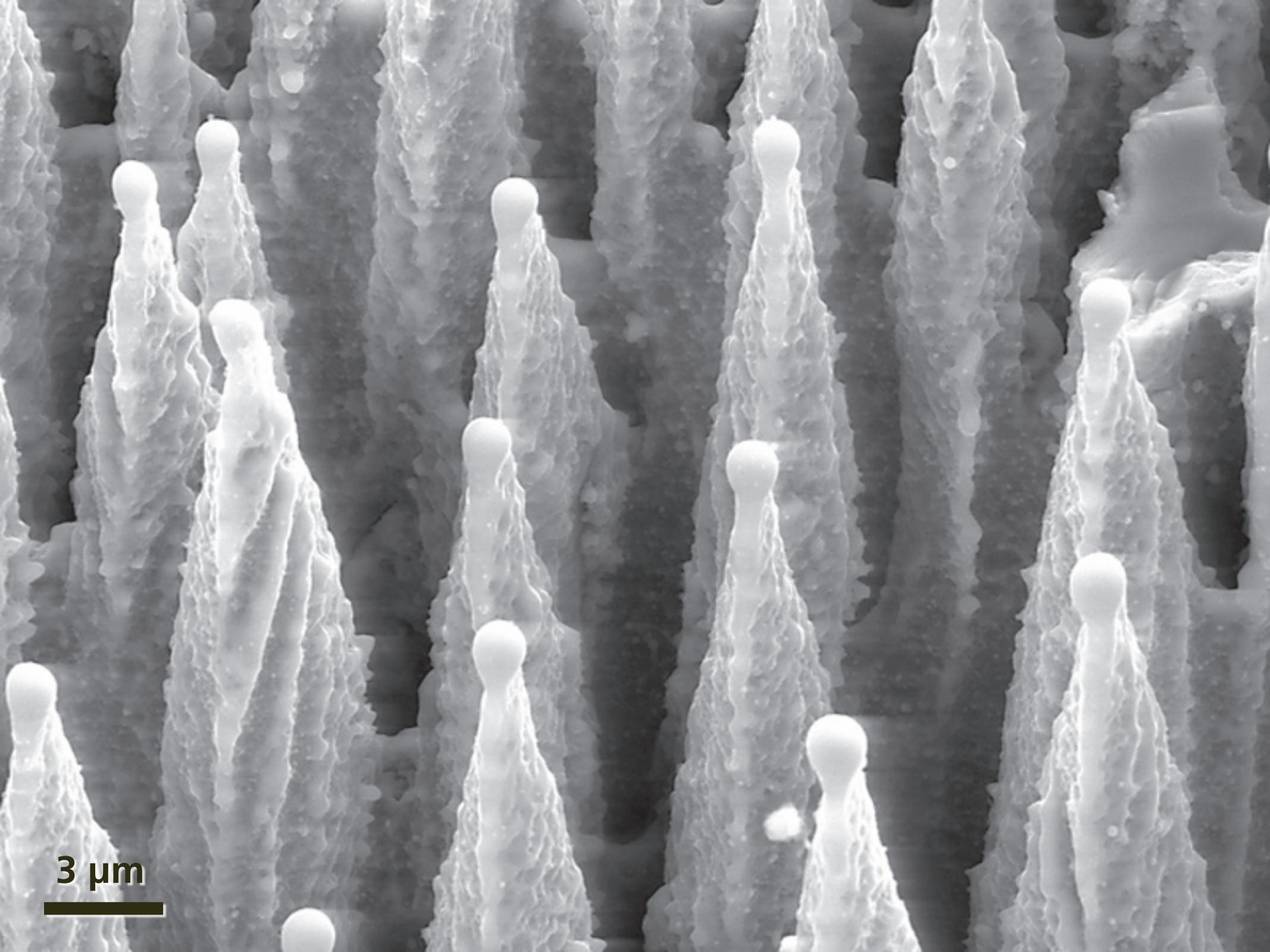
**Prof. Steve Yalisove (Michigan)**  
**Dr. Ben Torralva (Michigan)**  
  
**Prof. Tonio Buonassisi (MIT)**  
**Prof. Silvija Gradecak (MIT)**  
**Prof. Jeff Grossman (MIT)**  
**Dr. Bonna Newman (MIT)**  
**Joe Sullivan (MIT)**  
**Matthew Smith (MIT)**  
  
**Dr. François Génin (LLNL)**  
**Mark Wall (LLNL)**  
  
**Dr. Richard Farrell (RMD)**  
**Dr. Arieh Karger (RMD)**  
**Dr. Richard Meyers (RMD)**  
  
**Dr. Pat Maloney (NVSED)**  
  
**Dr. Jeffrey Warrender (ARDEC)**



irradiate with 100-fs 10 kJ/m<sup>2</sup> pulses

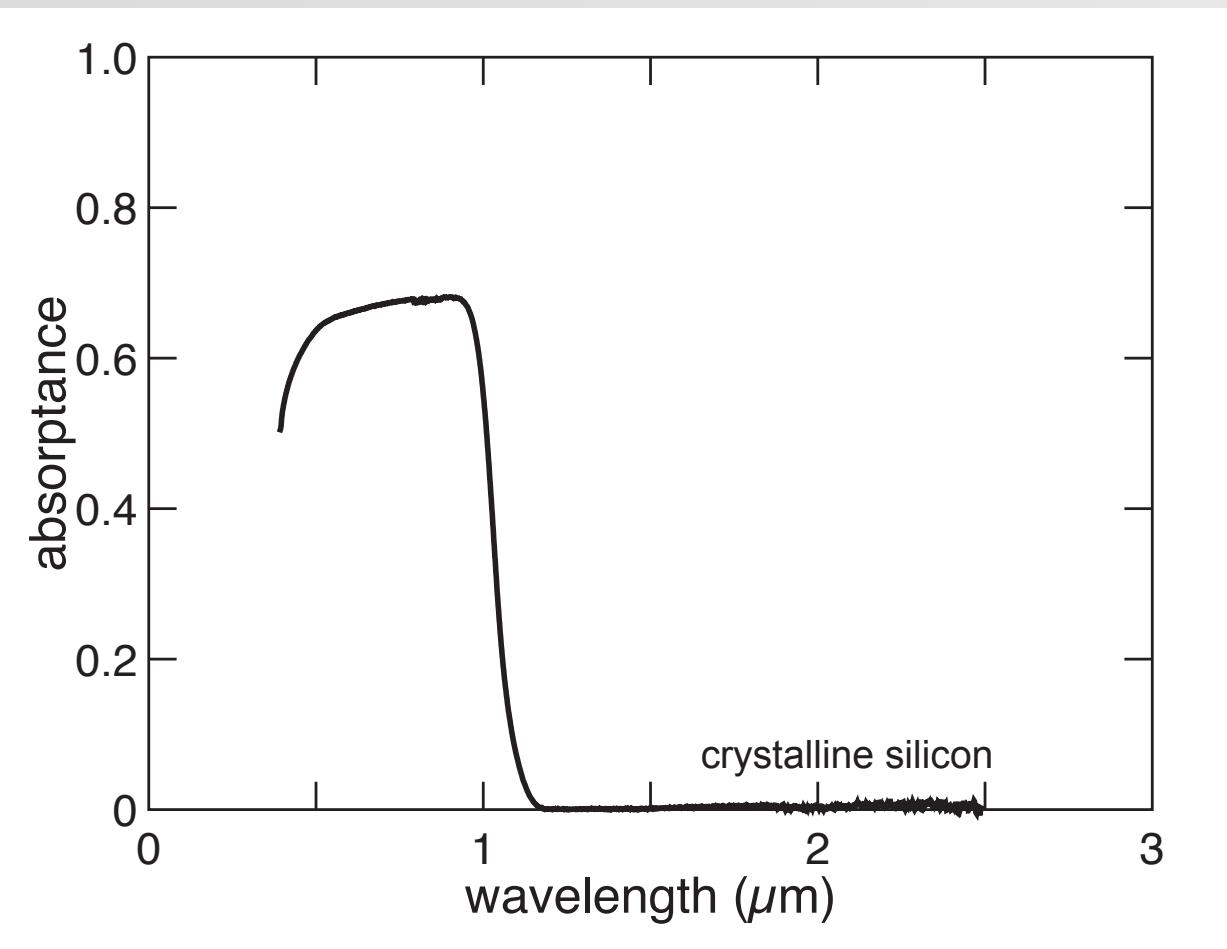


**"black silicon"**

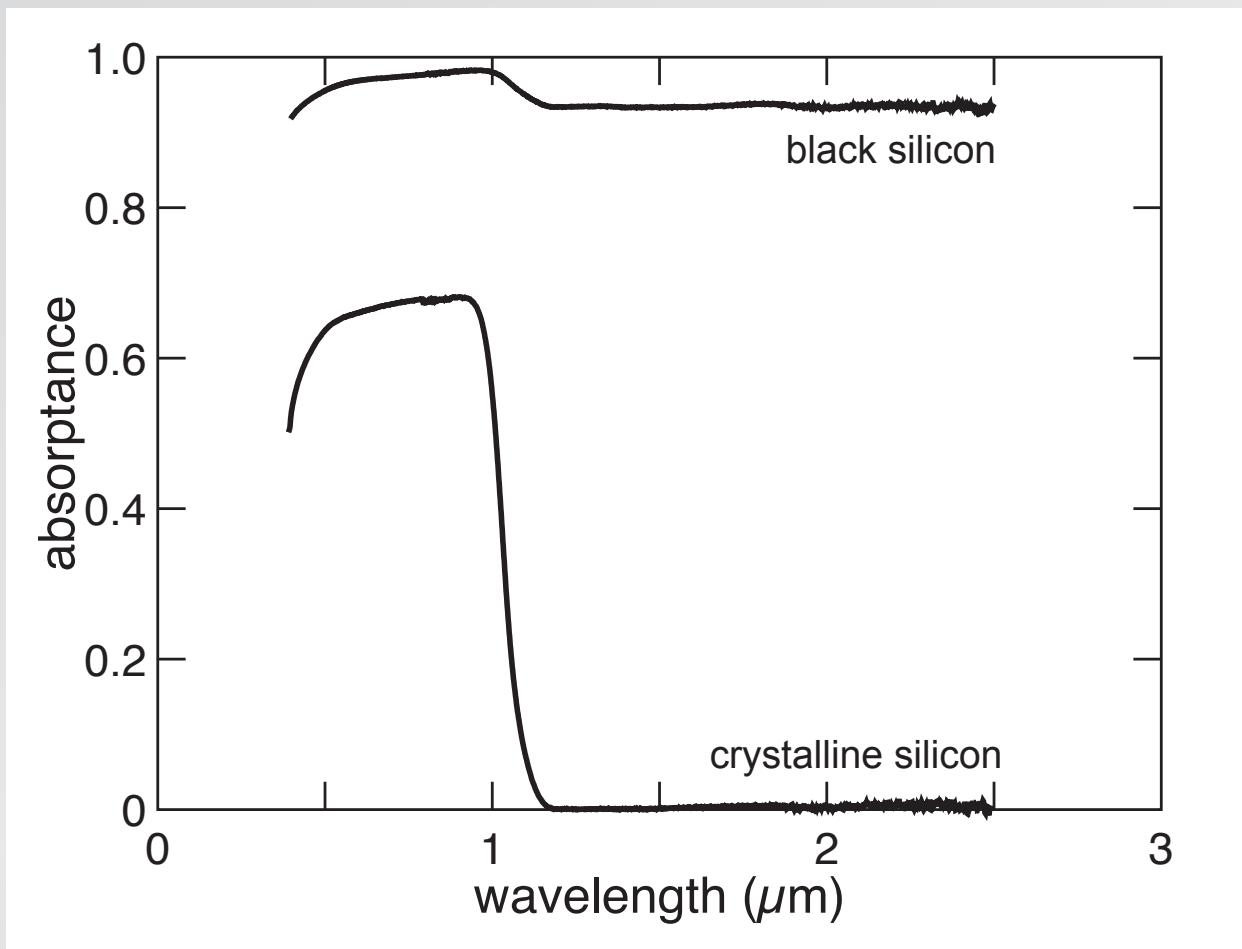


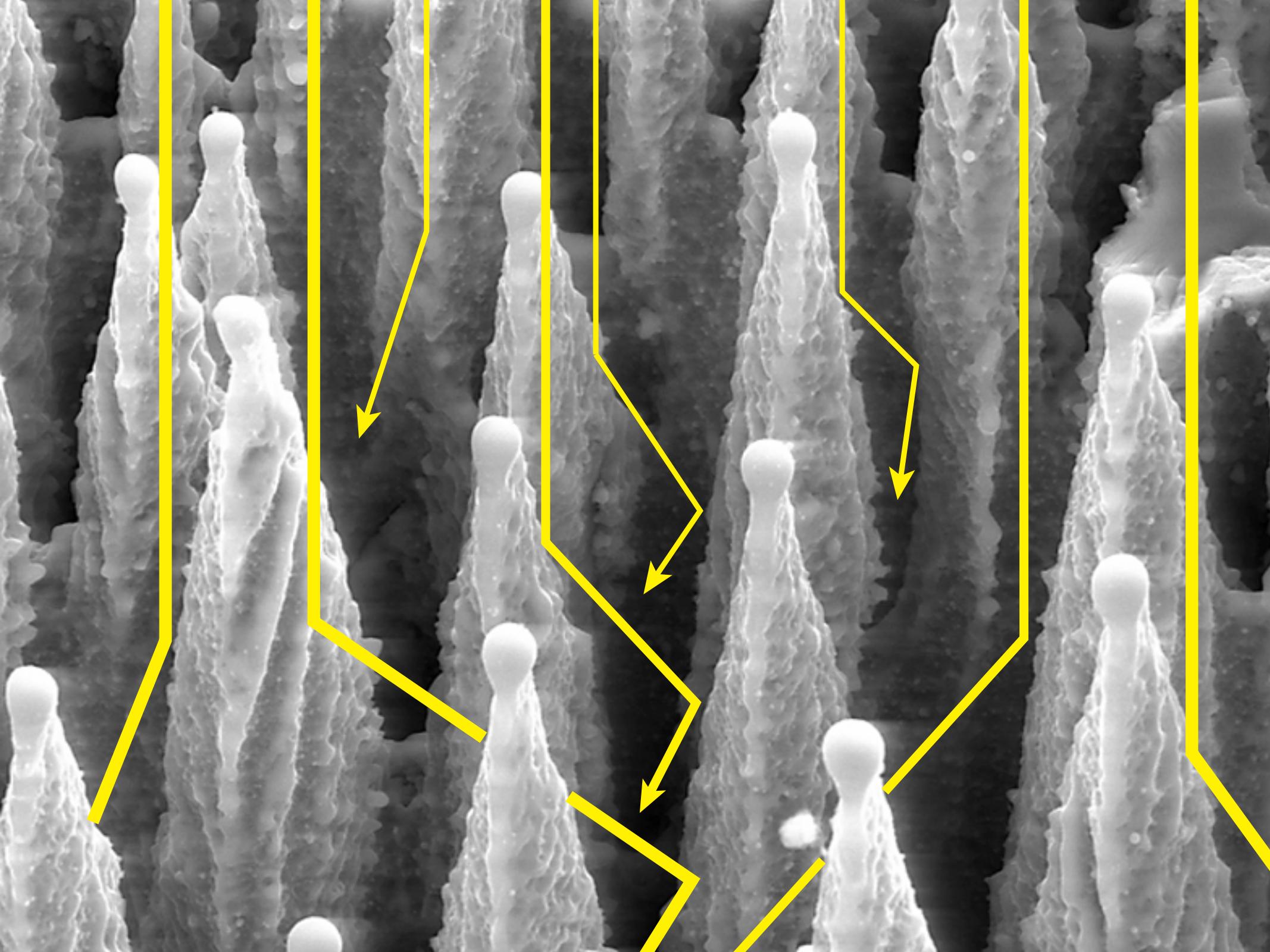
3  $\mu\text{m}$

**absorptance ( $1 - R_{int} - T_{int}$ )**

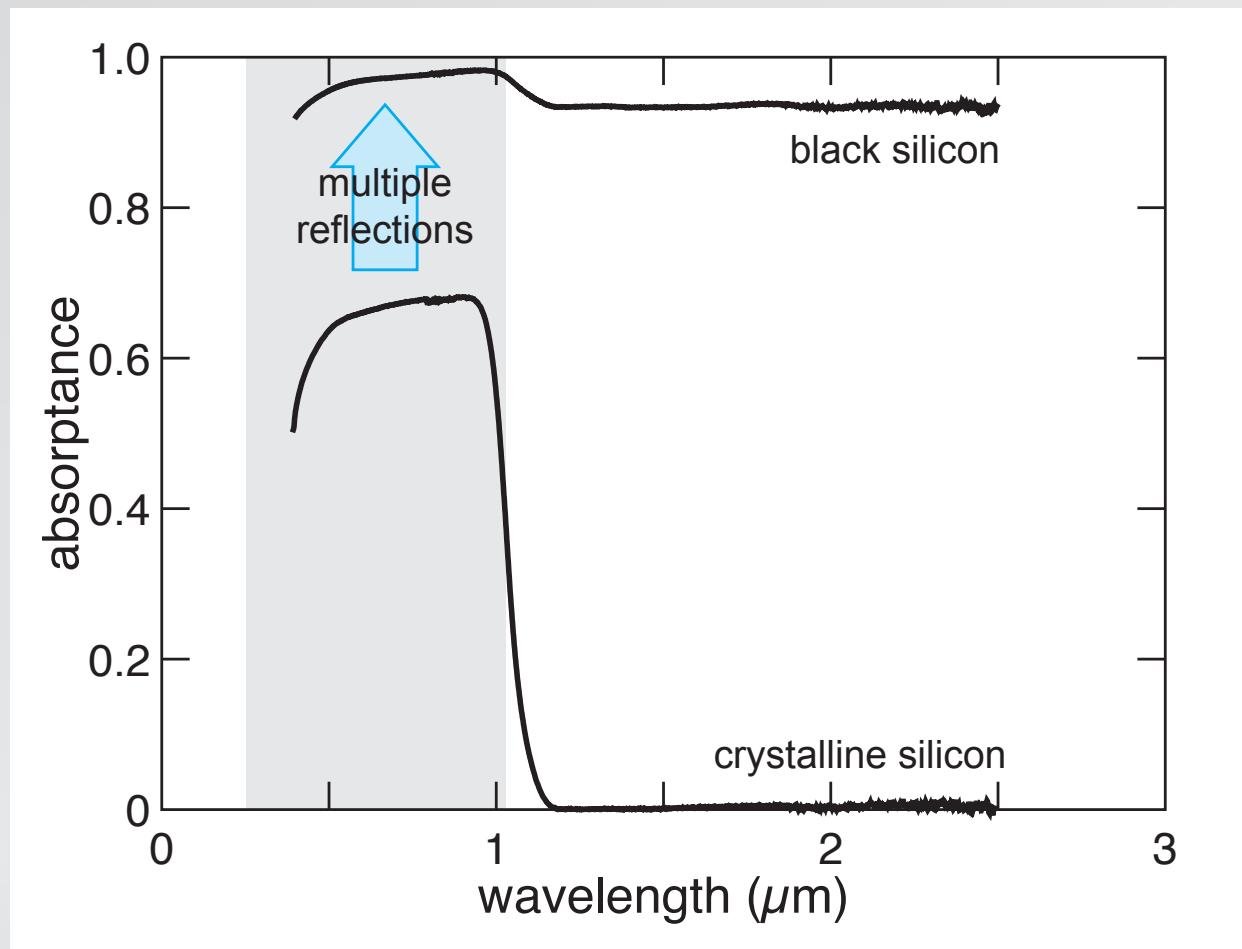


**absorptance ( $1 - R_{int} - T_{int}$ )**

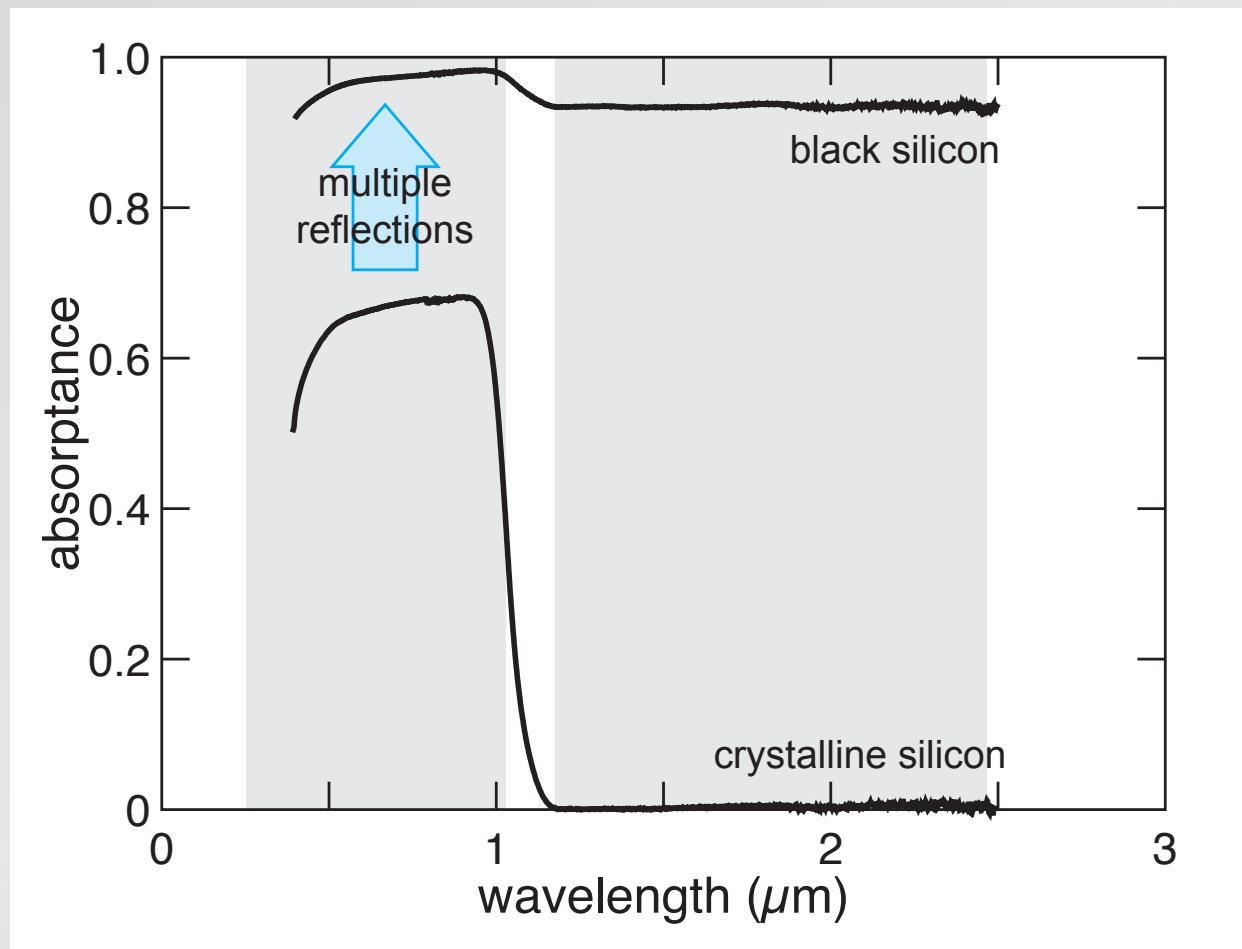




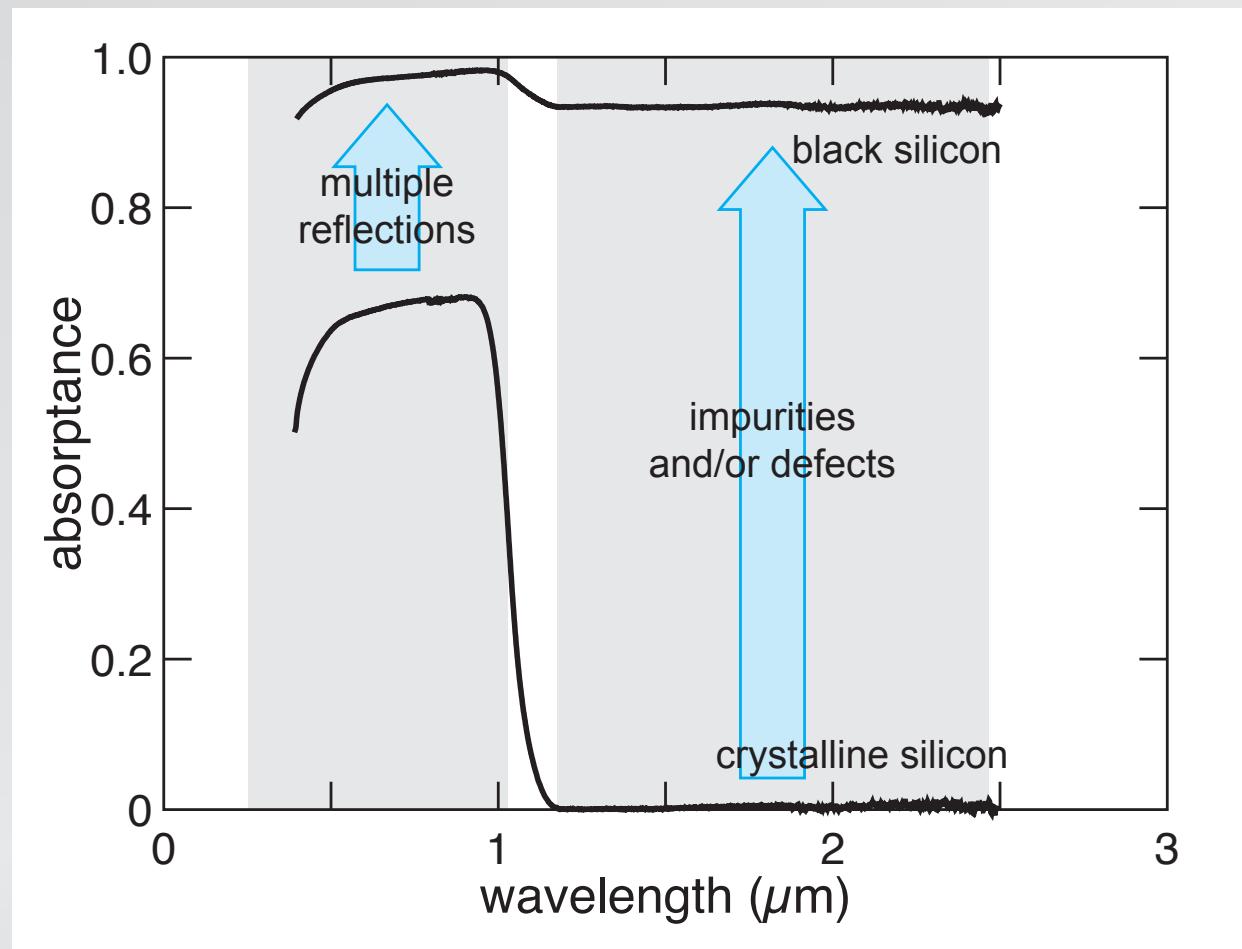
$$\text{absorptance } (1 - R_{int} - T_{int})$$



## absorptance ( $1 - R_{int} - T_{int}$ )



## absorptance ( $1 - R_{int} - T_{int}$ )



**laser treatment causes:**

- **surface structuring**
- **inclusion of dopants**

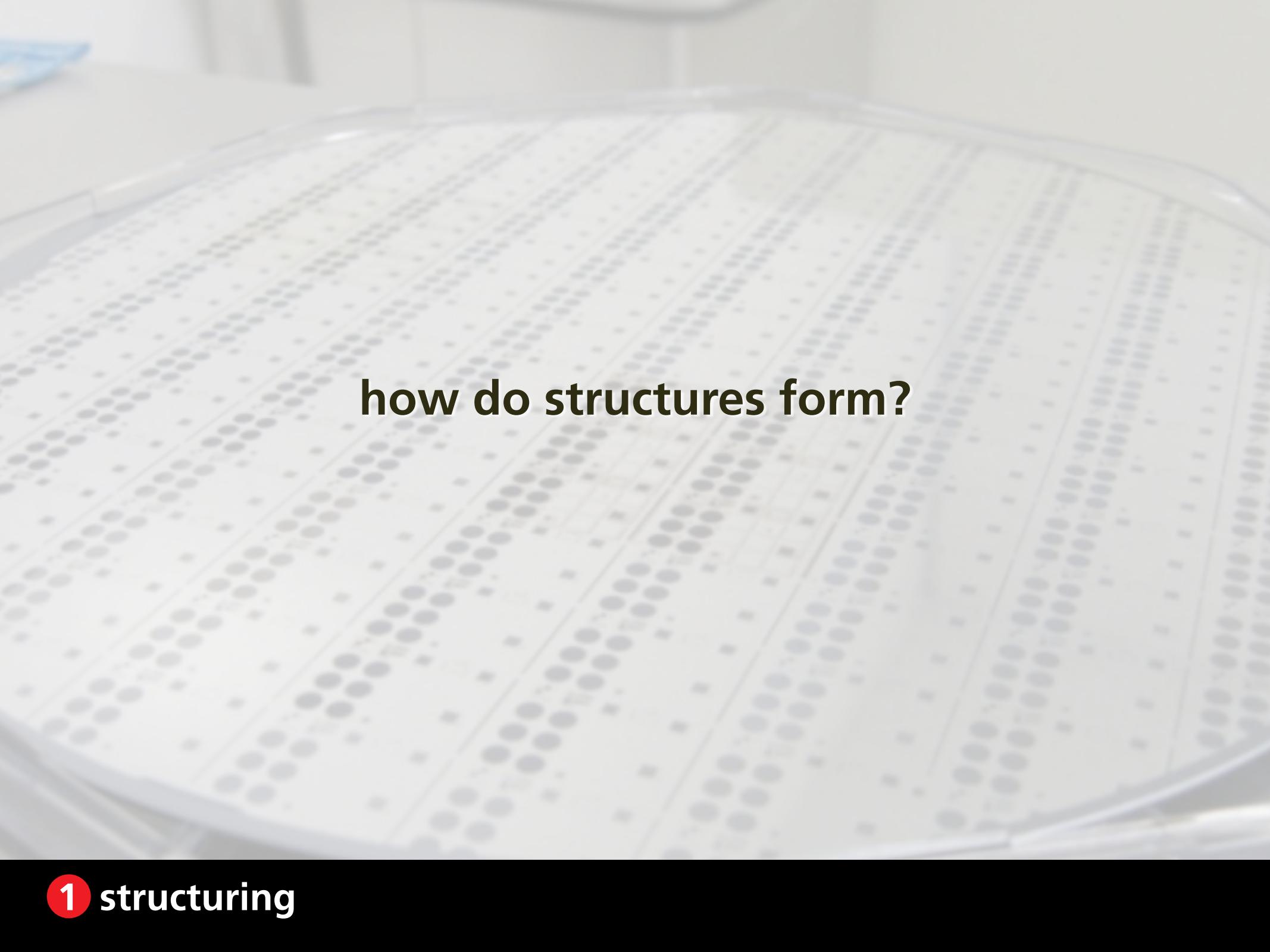


[www.sionyx.com](http://www.sionyx.com)



SiOnyx

# **basic physics of hyperdoped semiconductors**

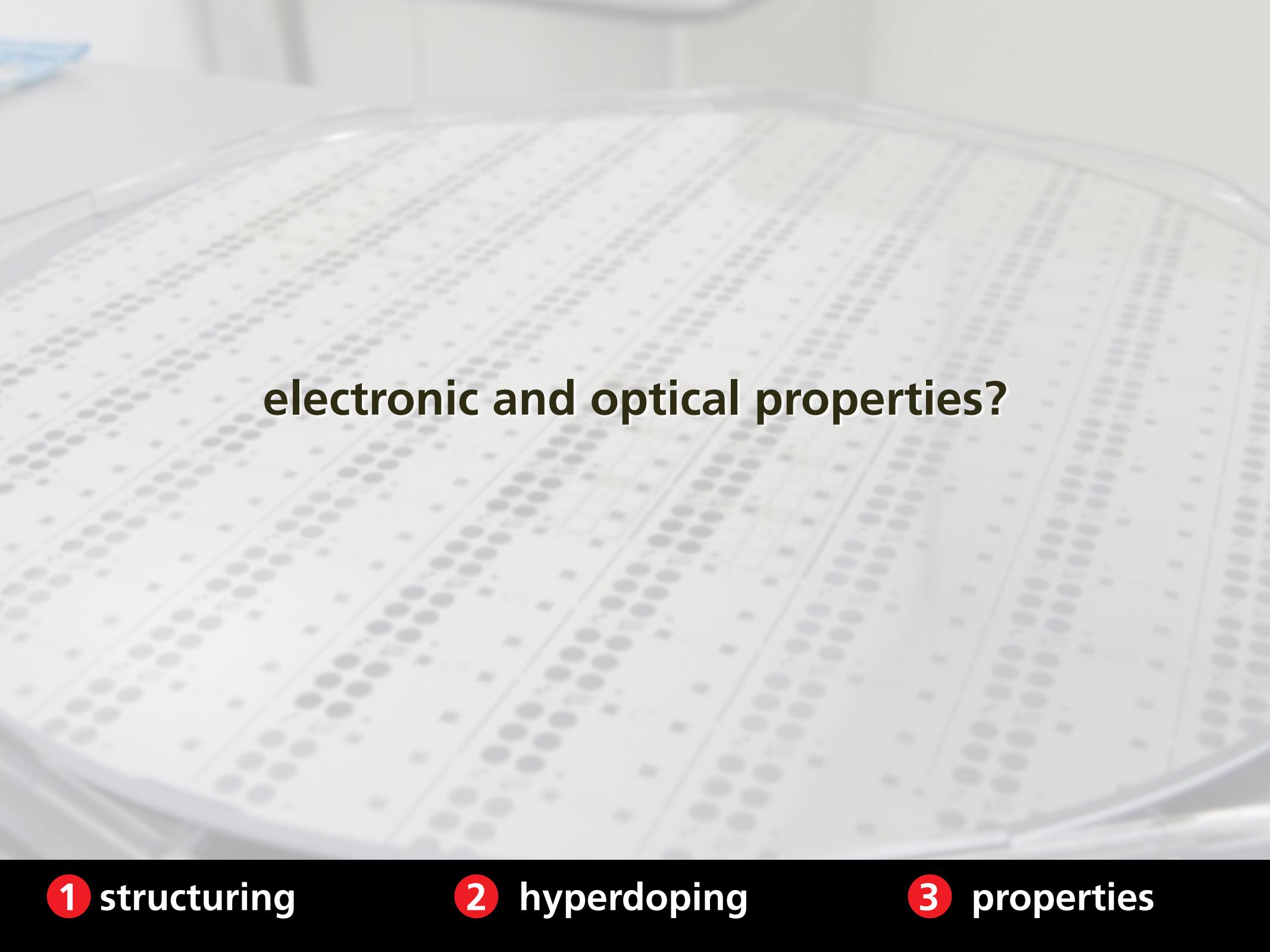


**how do structures form?**

# process of hyperdoping?

1 structuring

2 hyperdoping

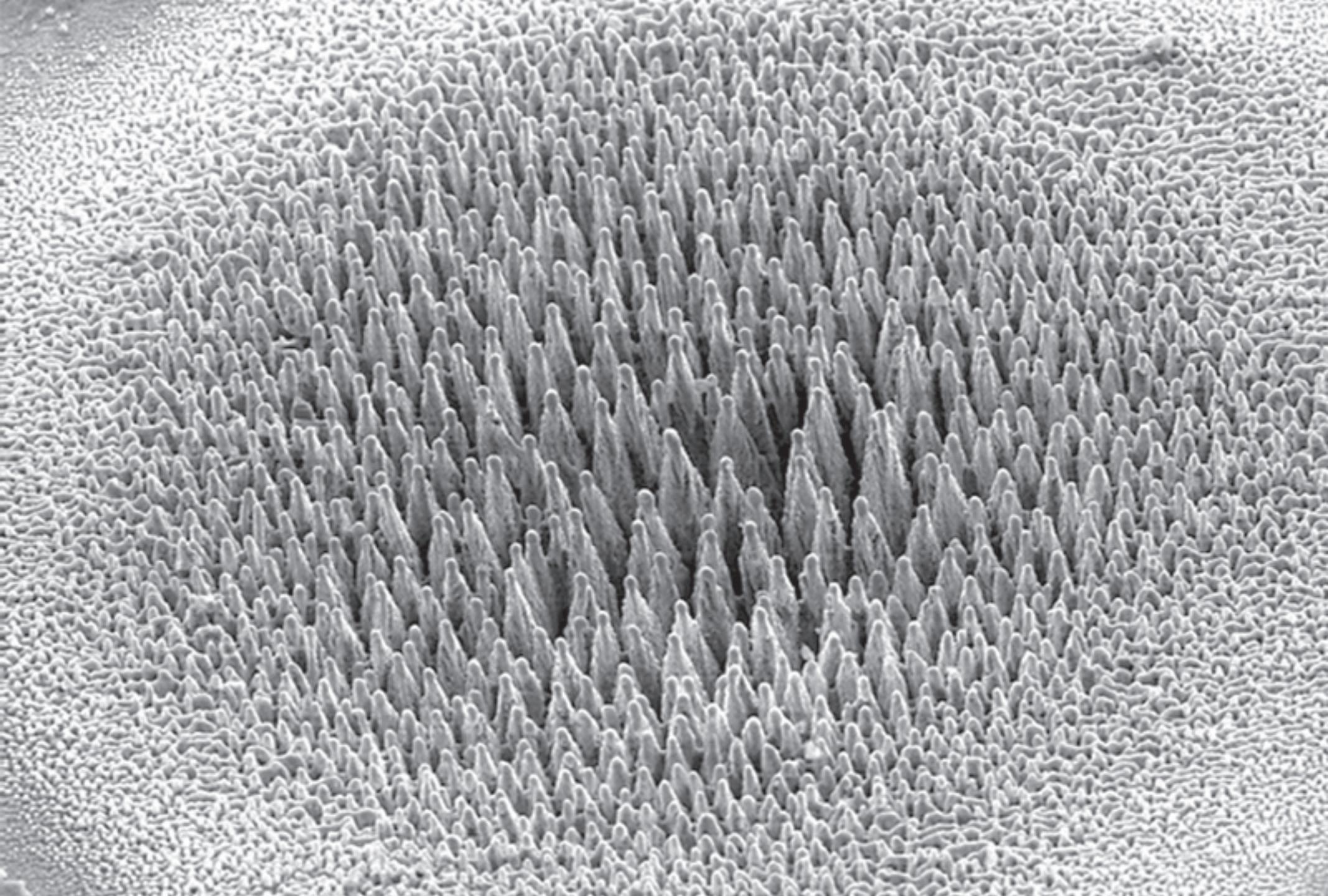


# electronic and optical properties?

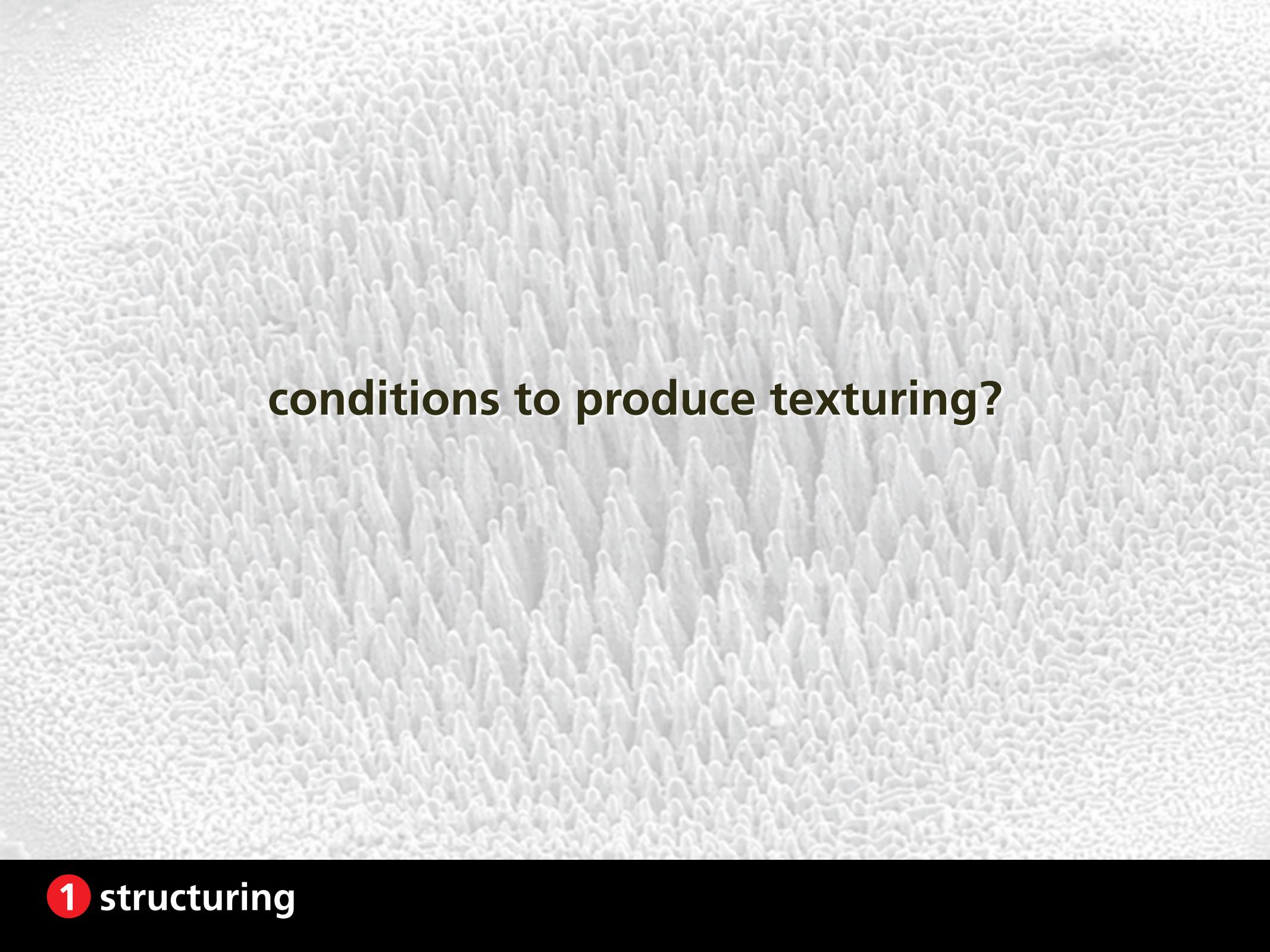
1 structuring

2 hyperdoping

3 properties

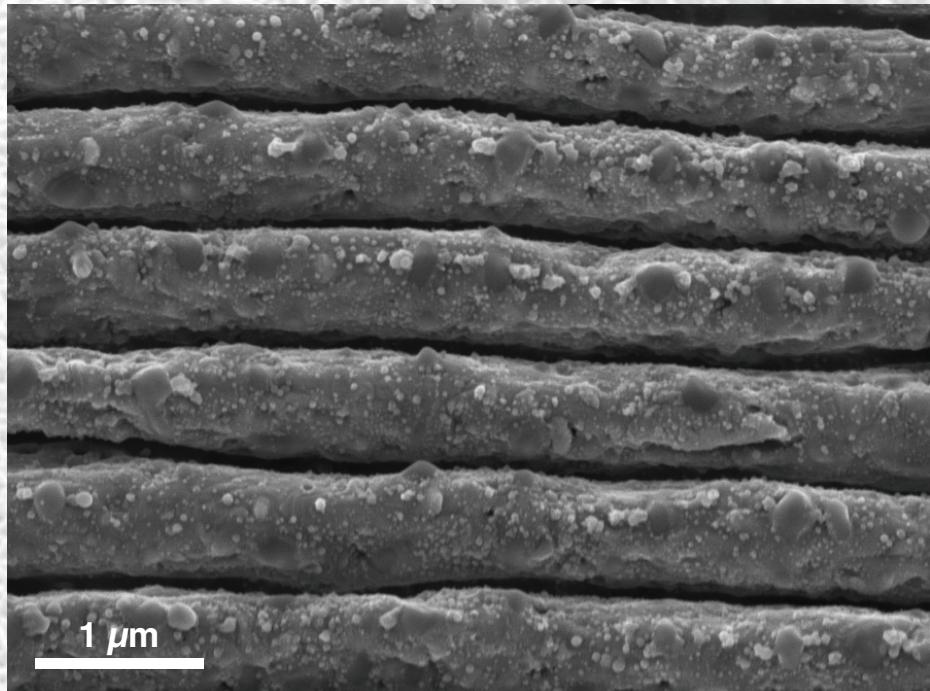


1 structuring

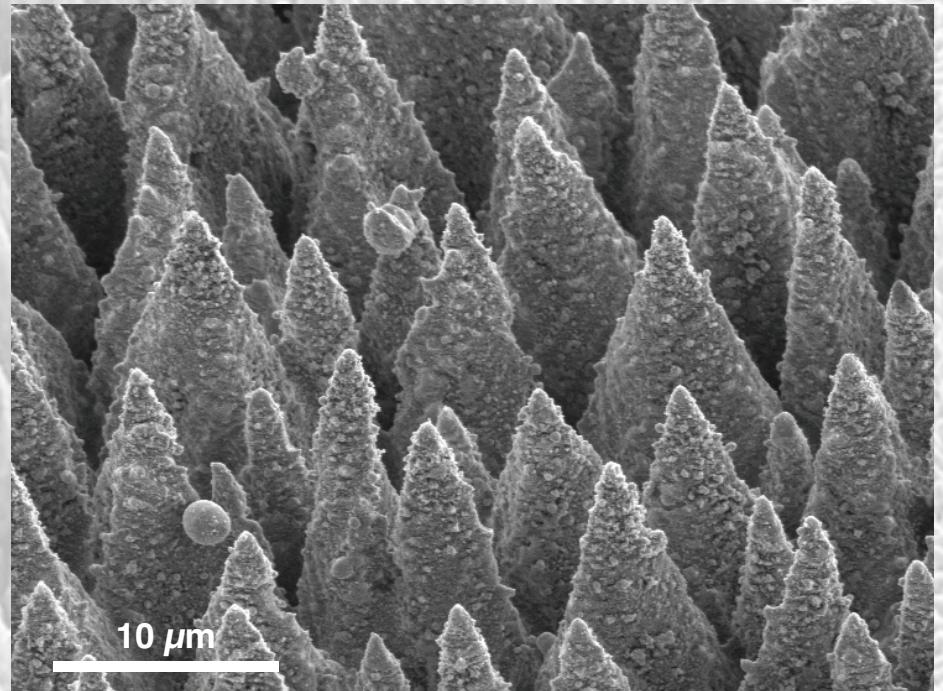


**conditions to produce texturing?**

surface ripples



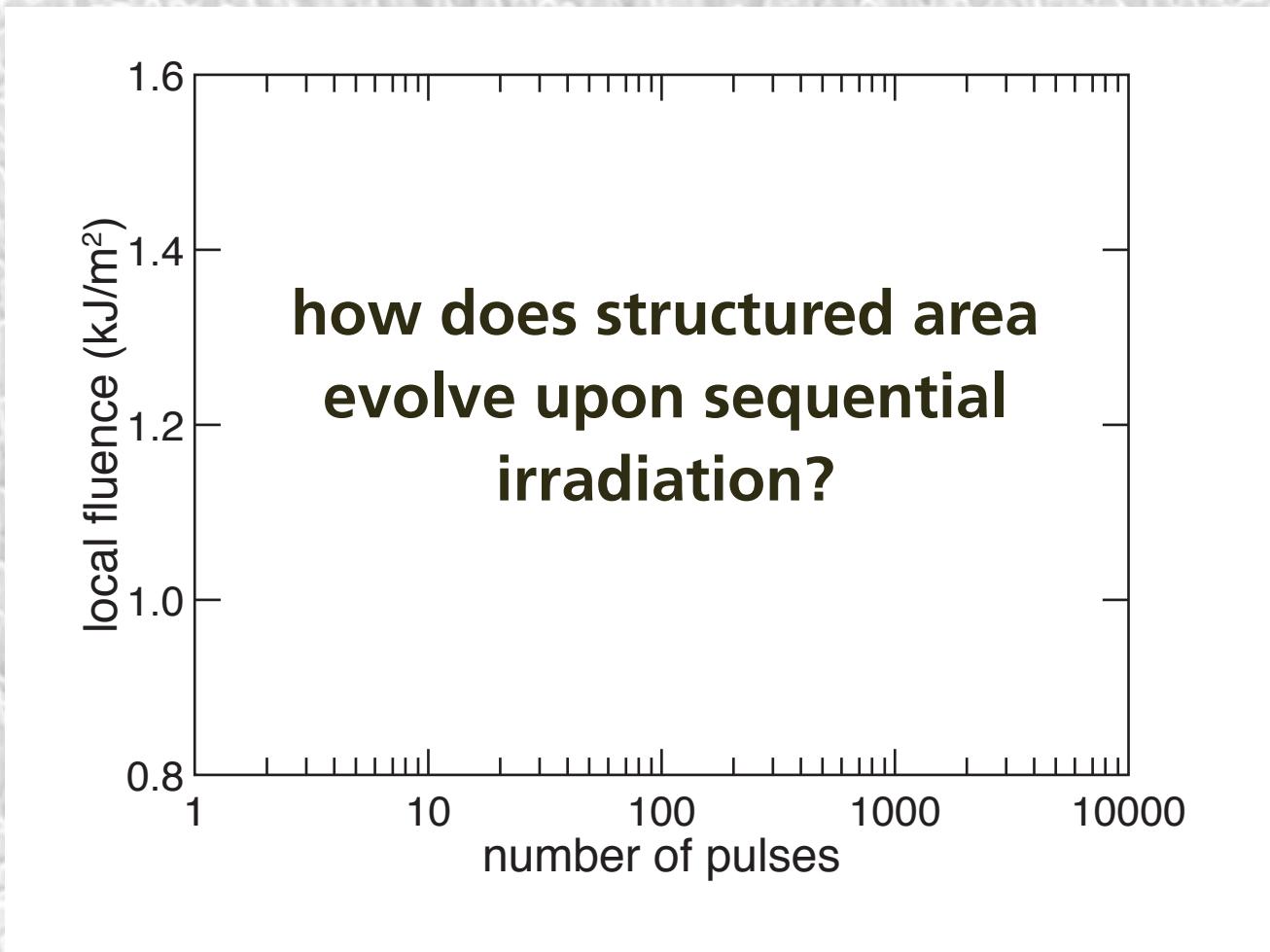
heavy texturing



Franta, PhD Thesis (2016)

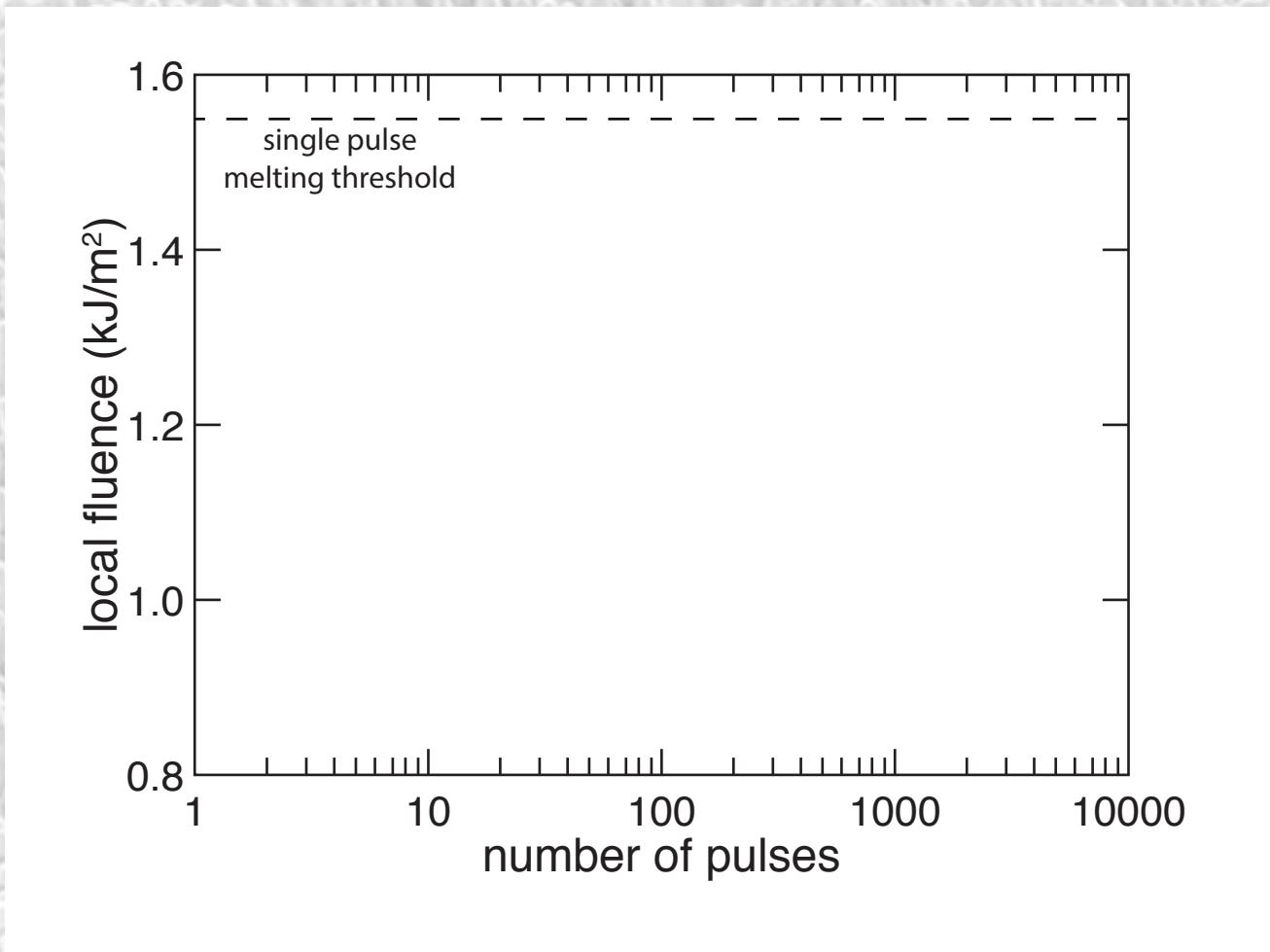
1 structuring

# surface ripples



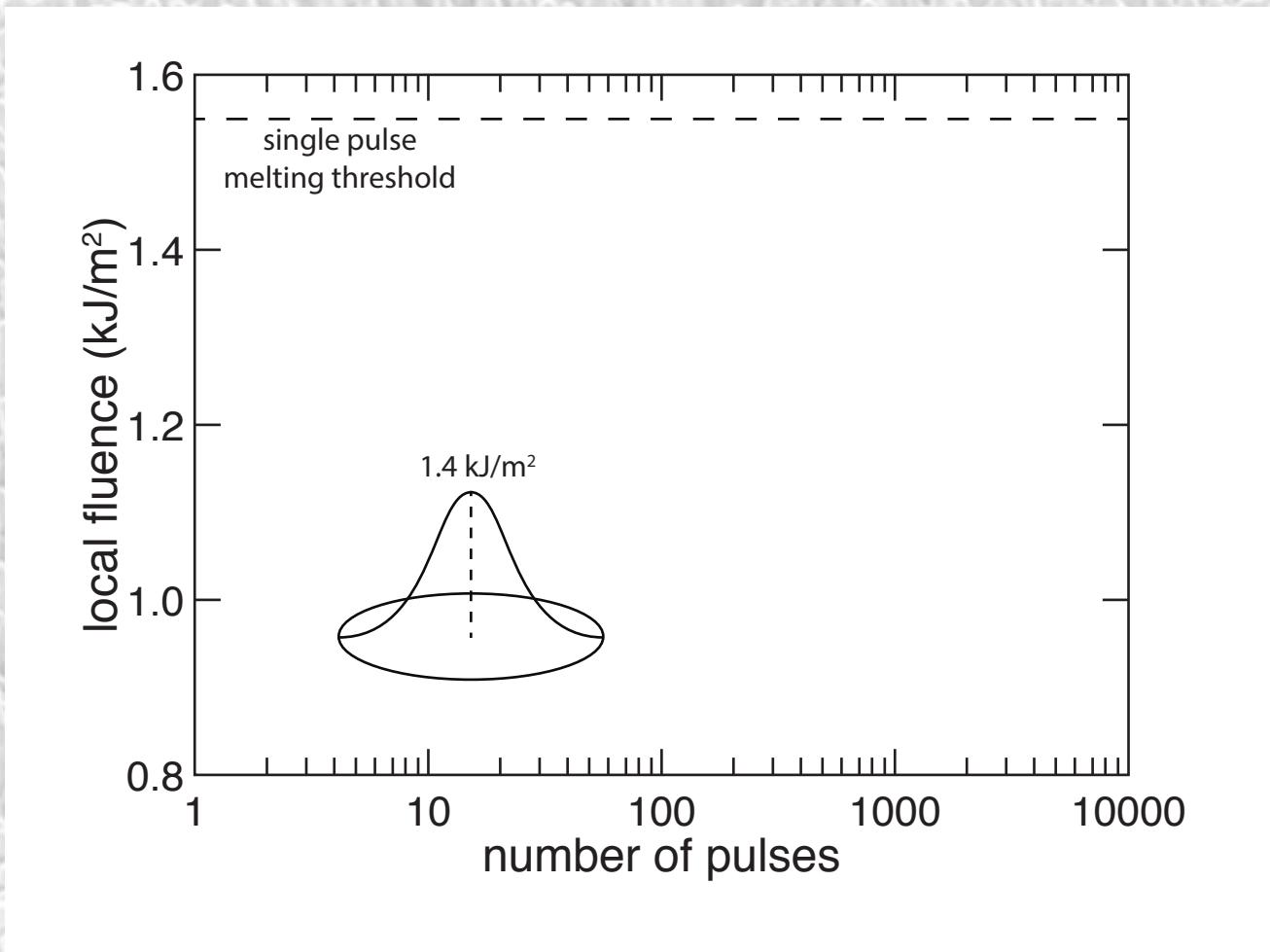
Franta, PhD Thesis (2016)

# surface ripples



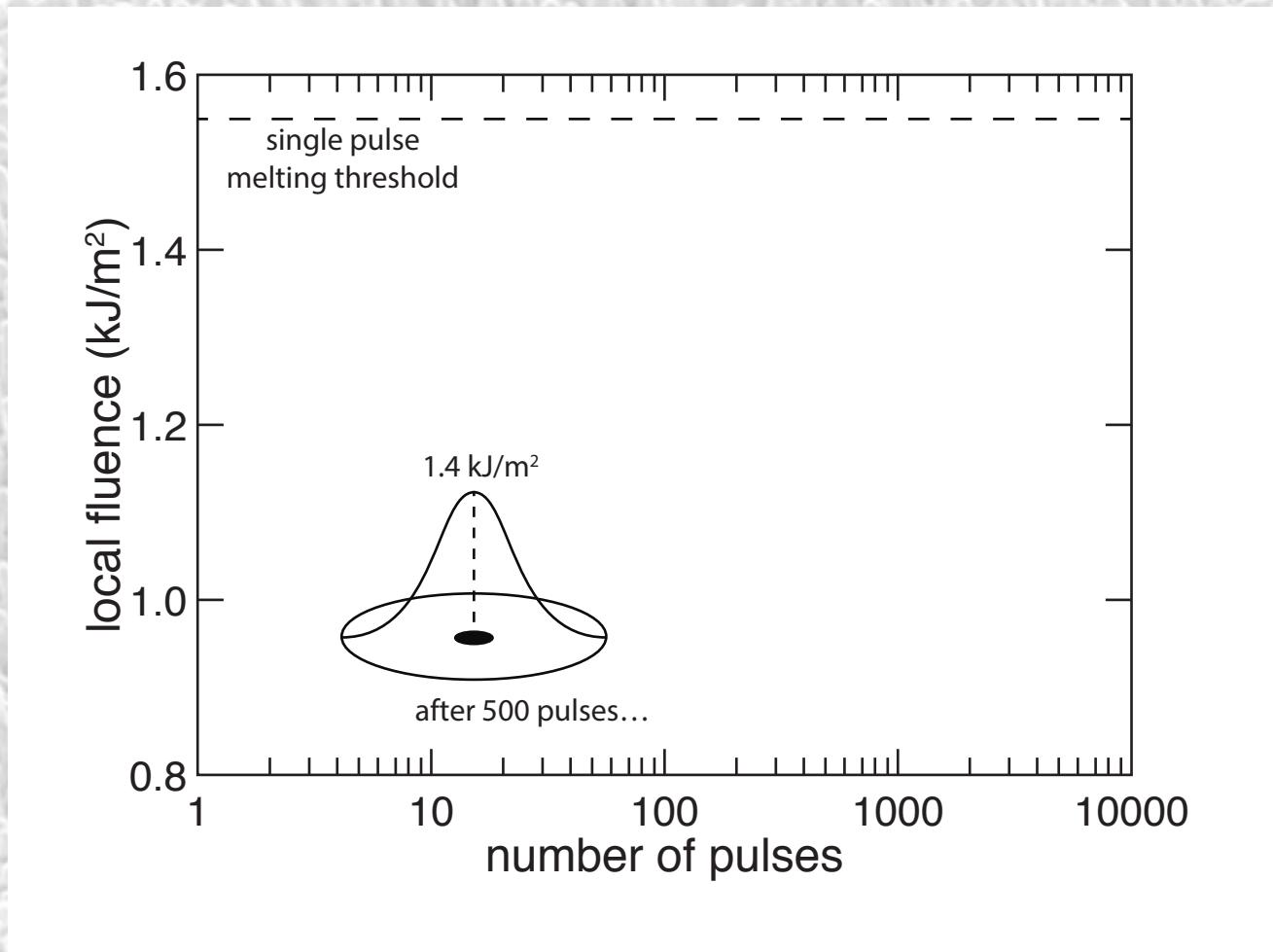
Franta, PhD Thesis (2016)

# surface ripples



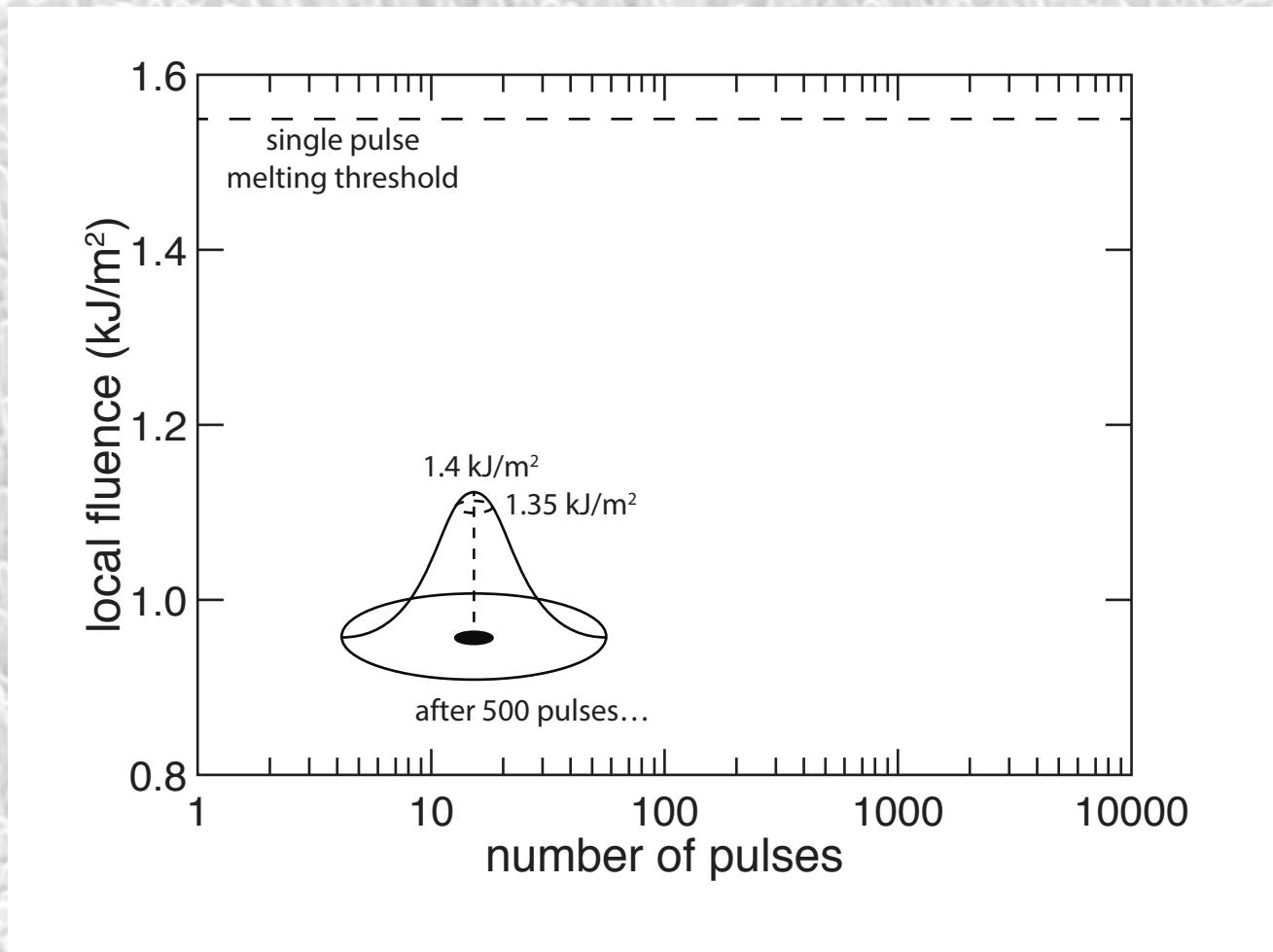
Franta, PhD Thesis (2016)

# surface ripples



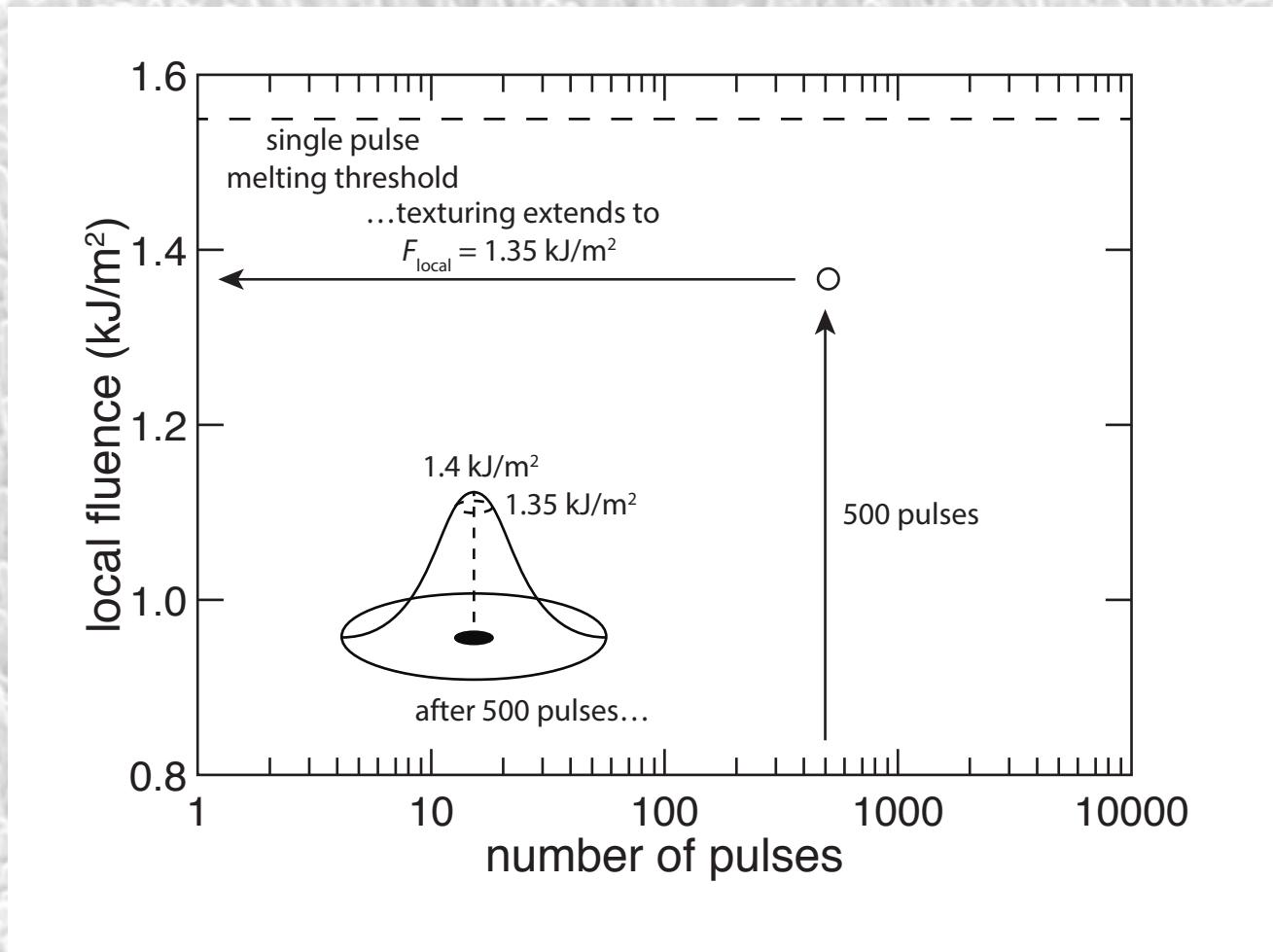
Franta, PhD Thesis (2016)

# surface ripples



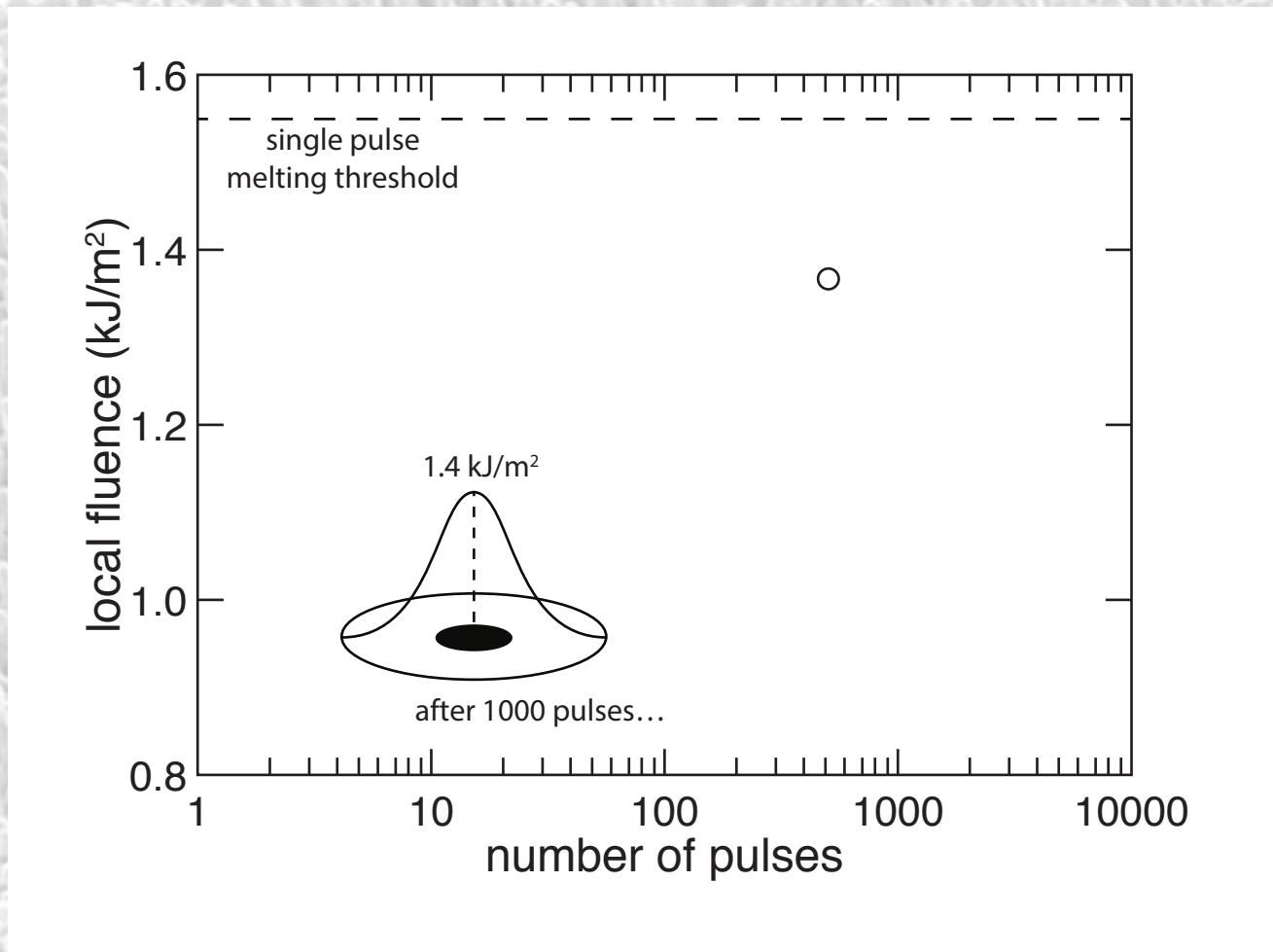
Franta, PhD Thesis (2016)

# surface ripples



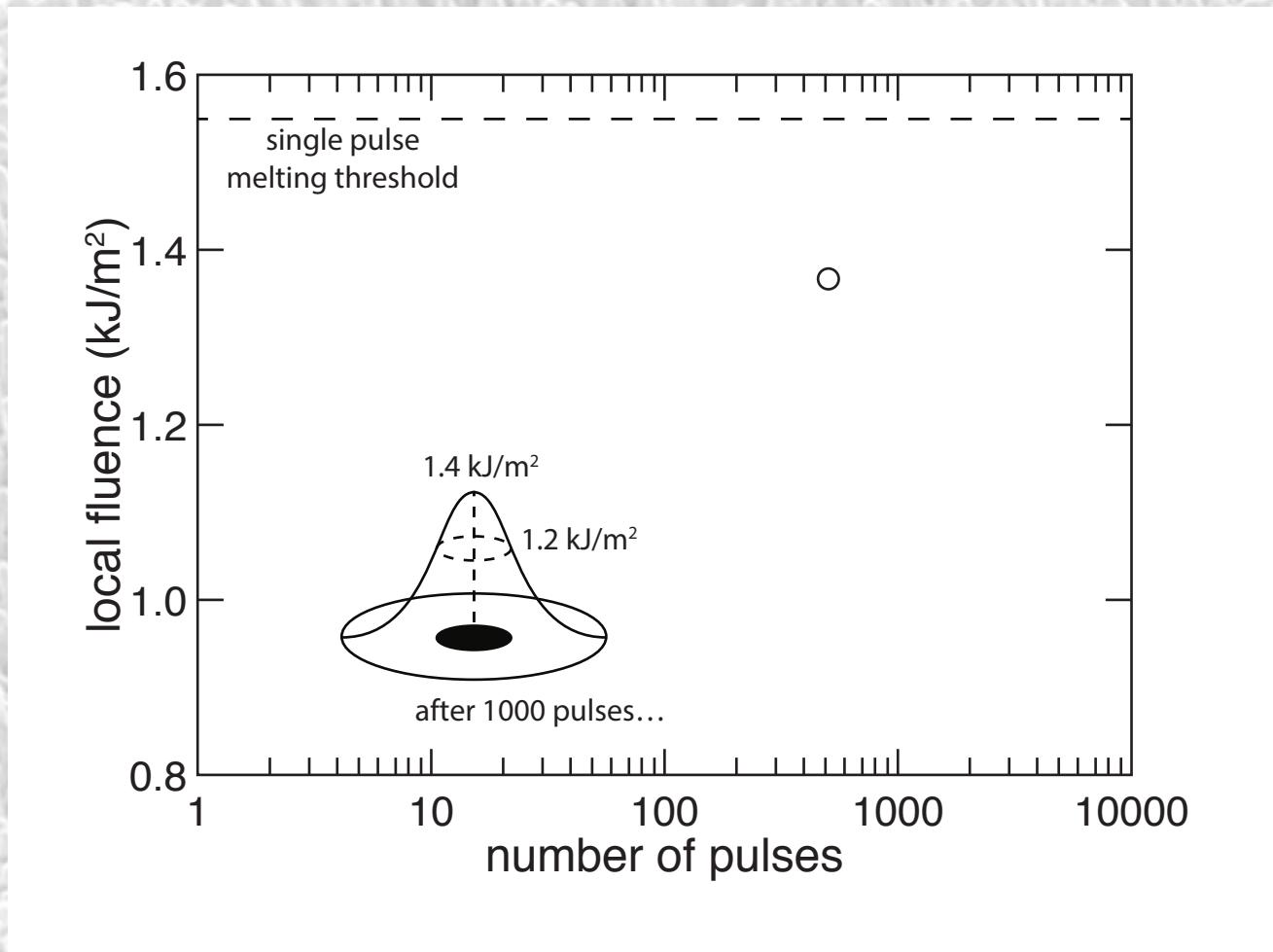
Franta, PhD Thesis (2016)

# surface ripples



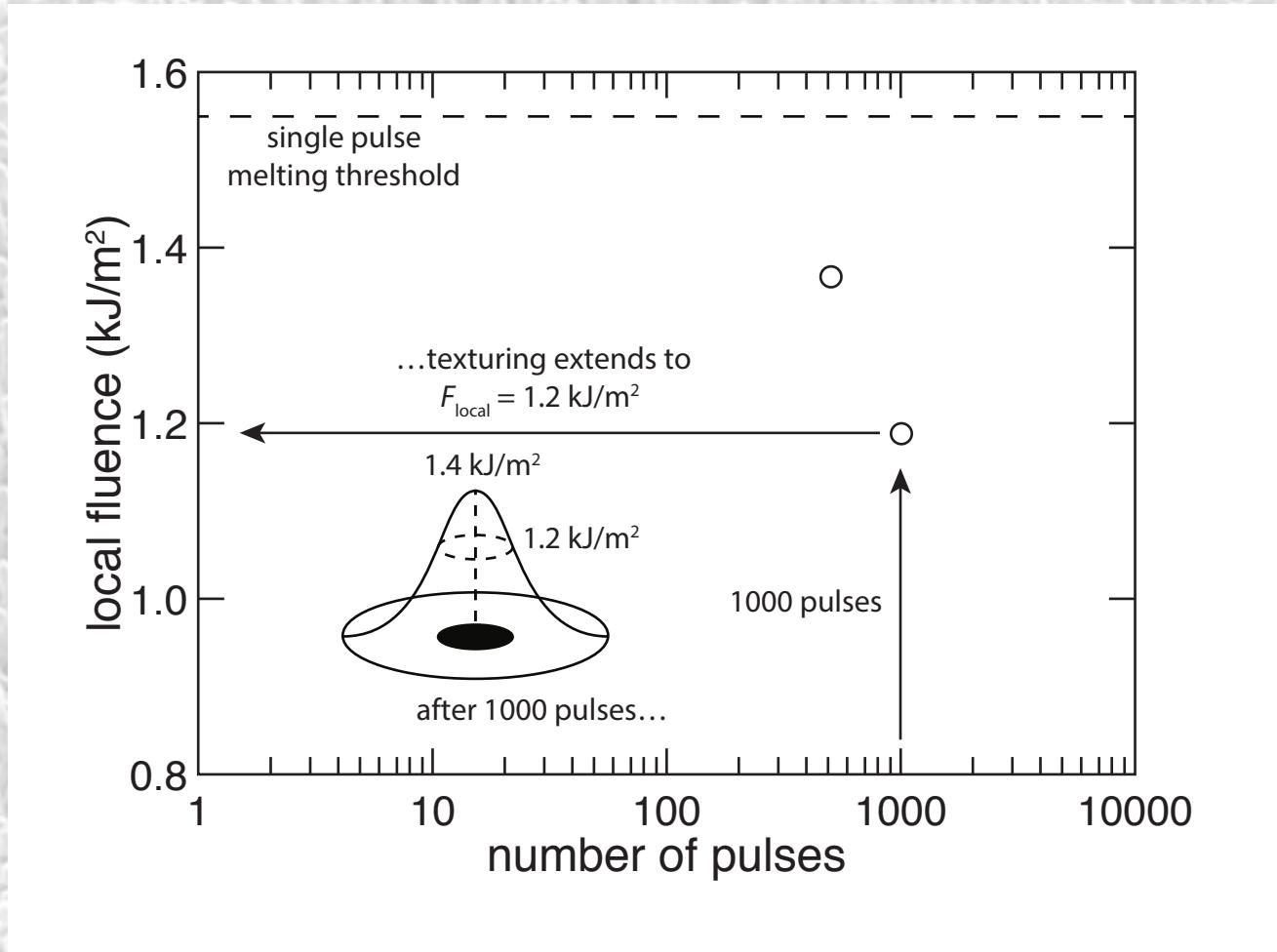
Franta, PhD Thesis (2016)

# surface ripples



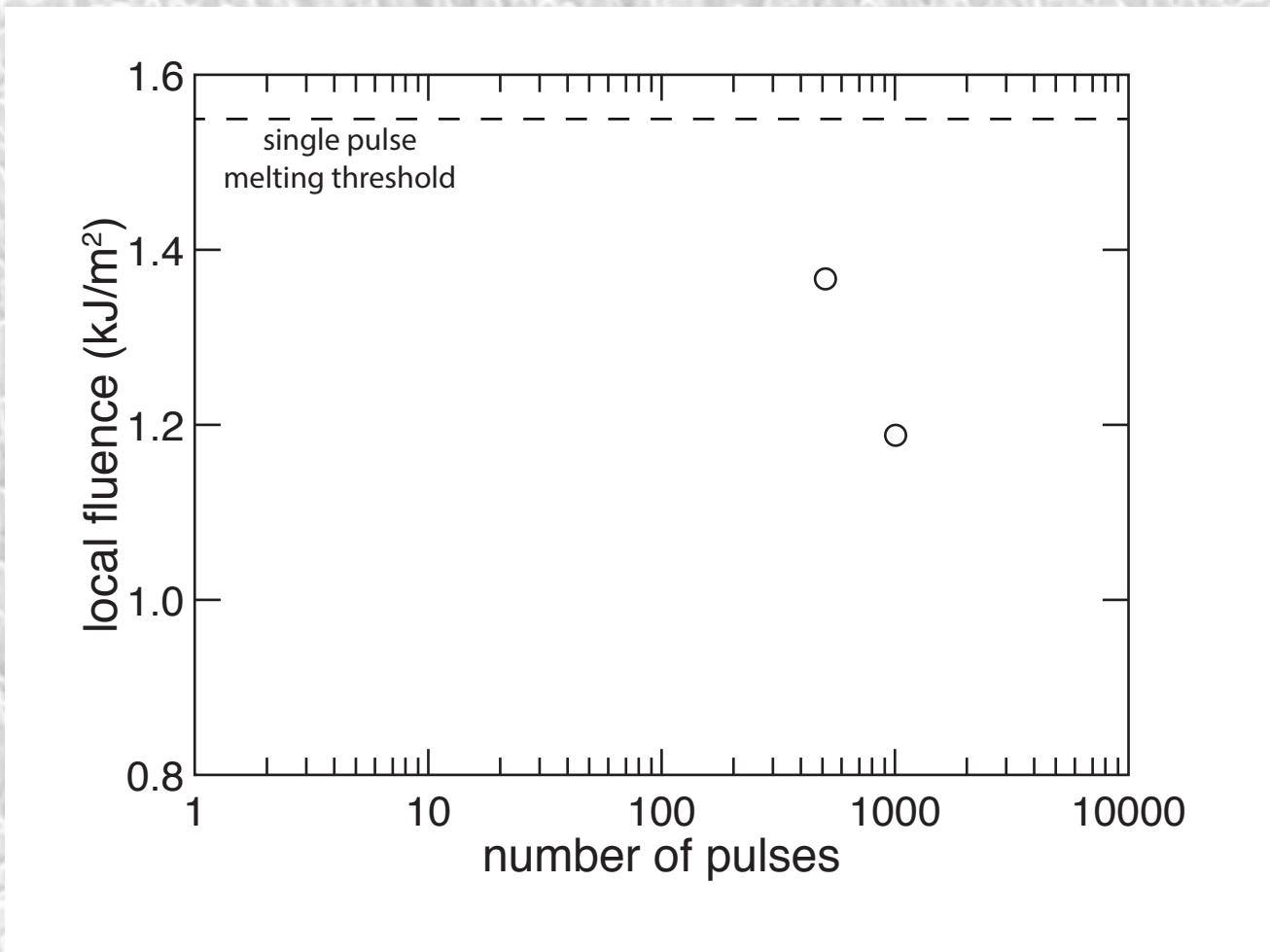
Franta, PhD Thesis (2016)

# surface ripples



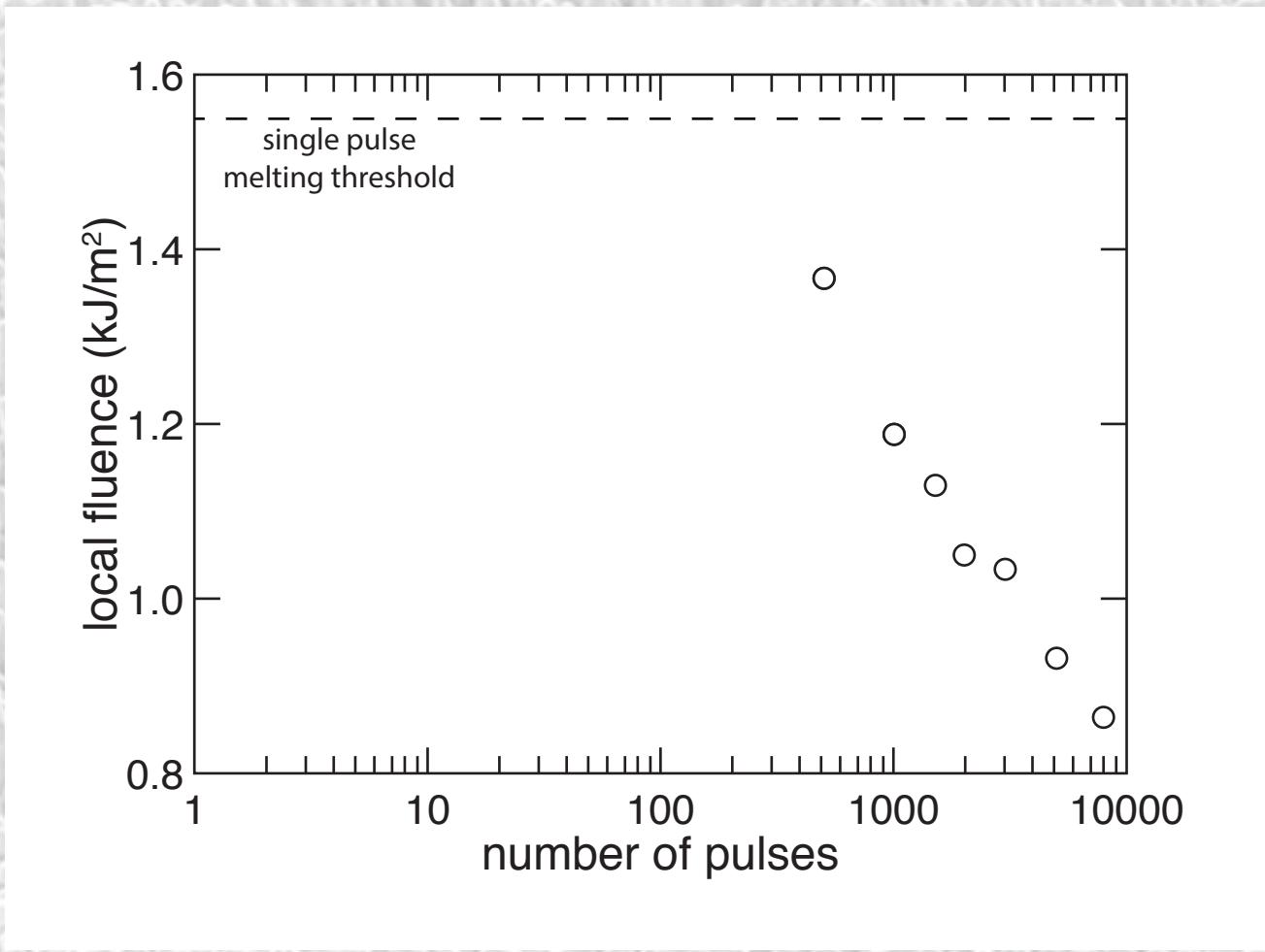
Franta, PhD Thesis (2016)

# surface ripples



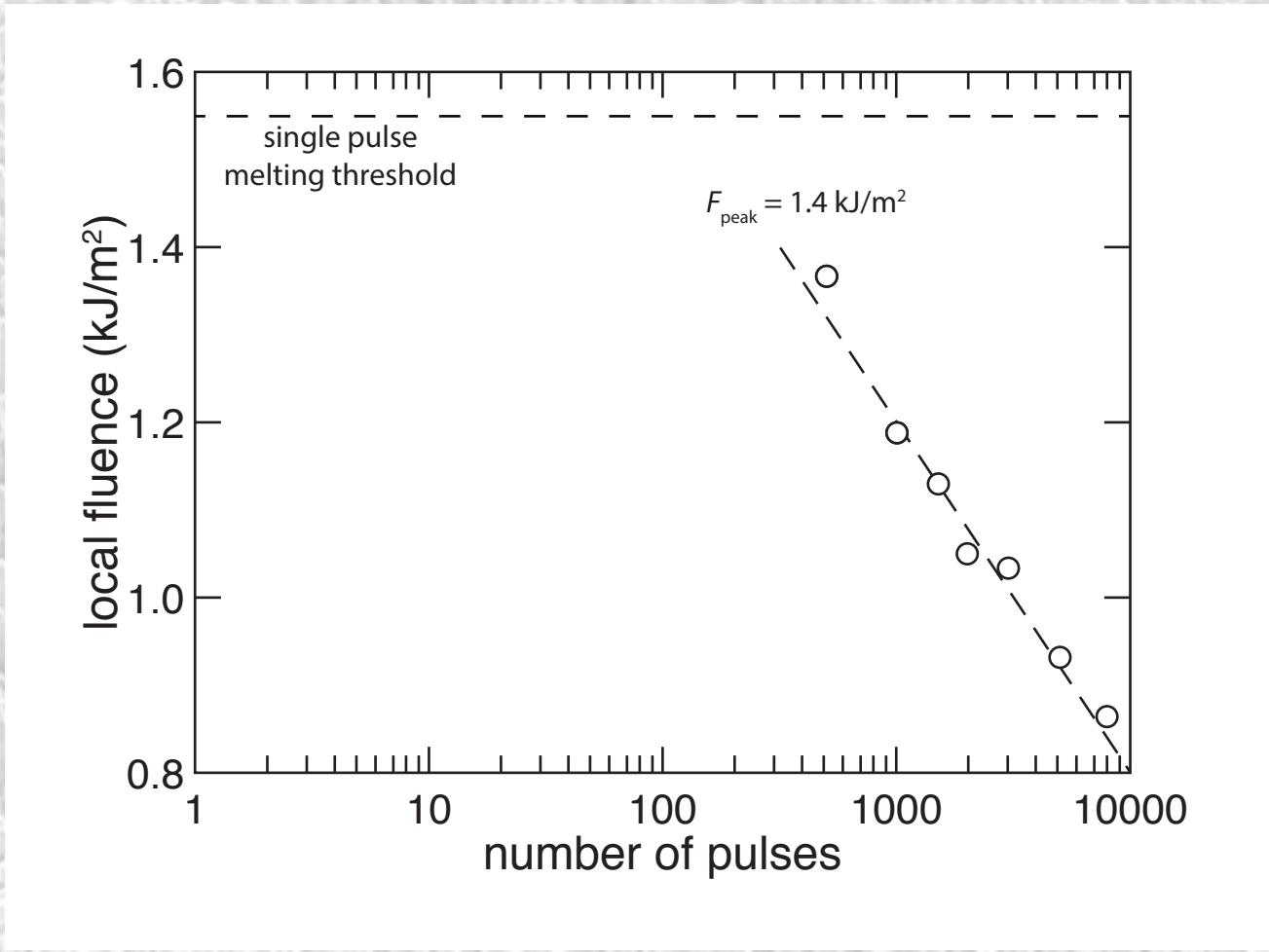
Franta, PhD Thesis (2016)

# surface ripples



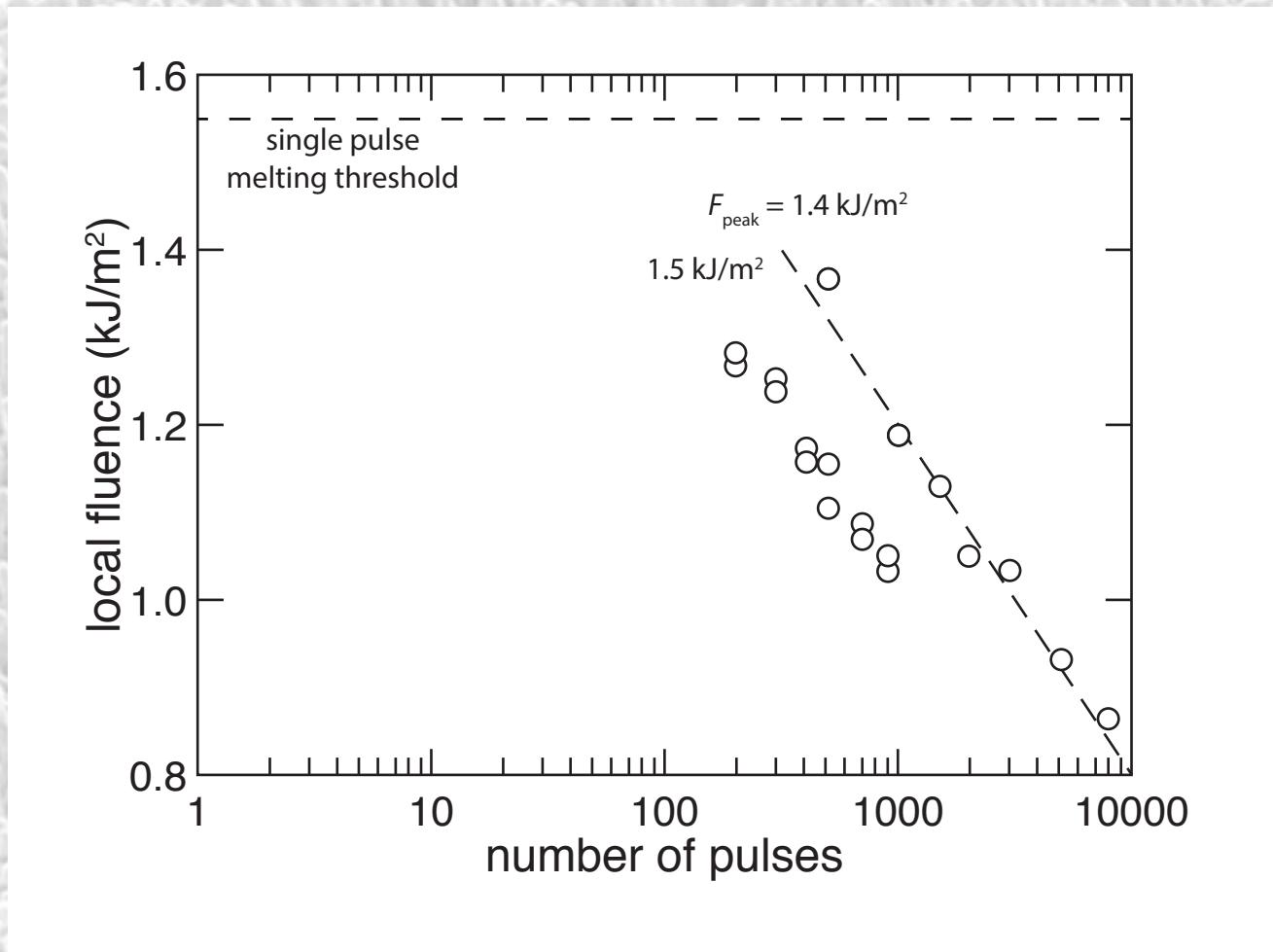
Franta, PhD Thesis (2016)

# surface ripples



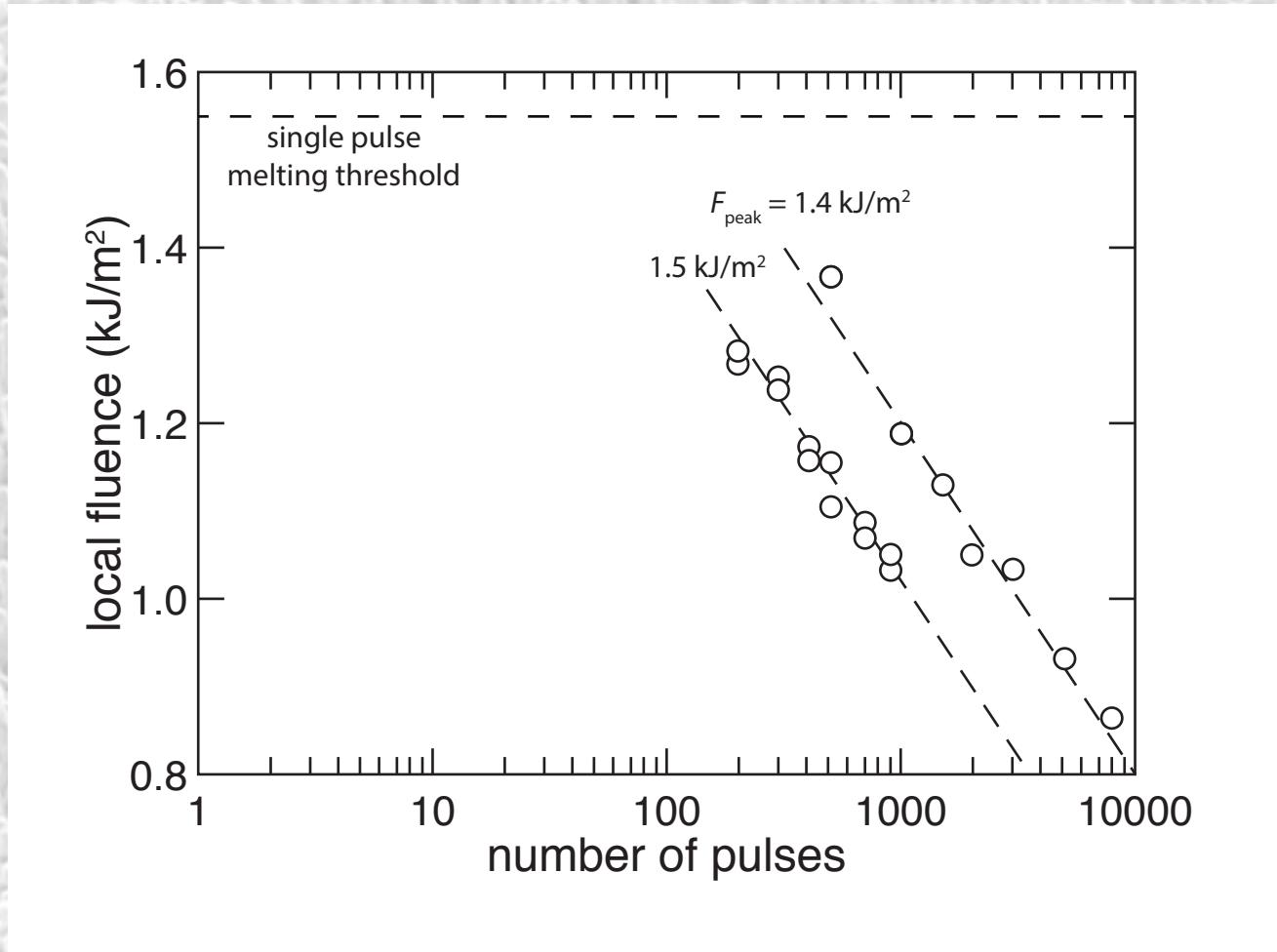
Franta, PhD Thesis (2016)

# surface ripples

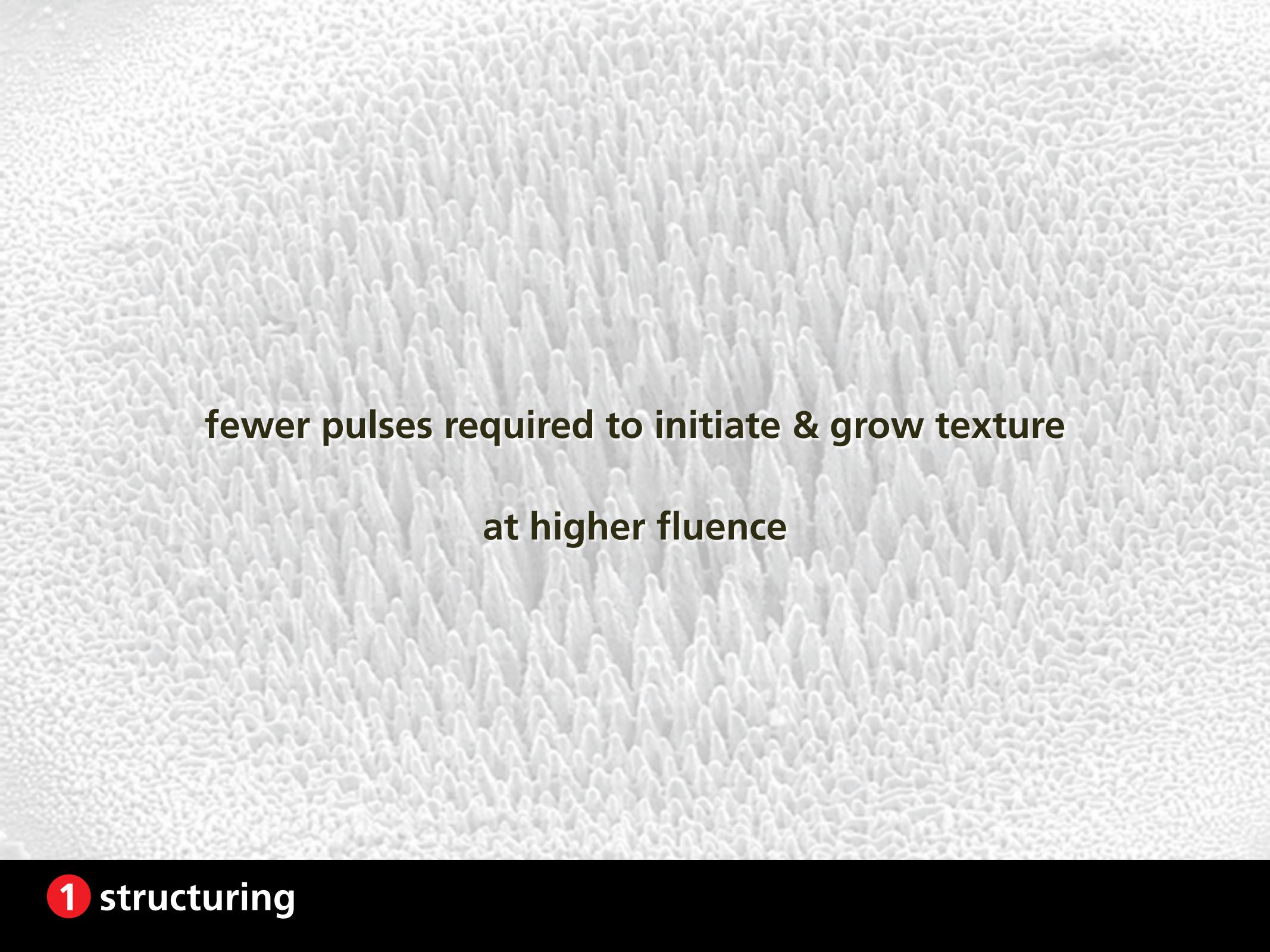


Franta, PhD Thesis (2016)

# surface ripples



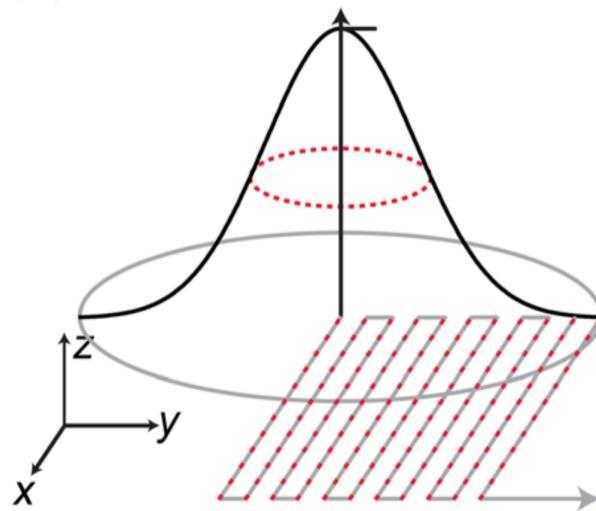
Franta, PhD Thesis (2016)



**fewer pulses required to initiate & grow texture**

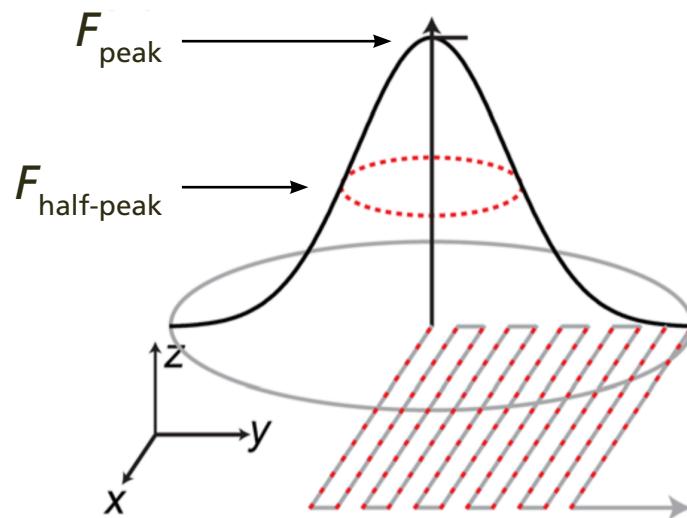
**at higher fluence**

# raster scanning



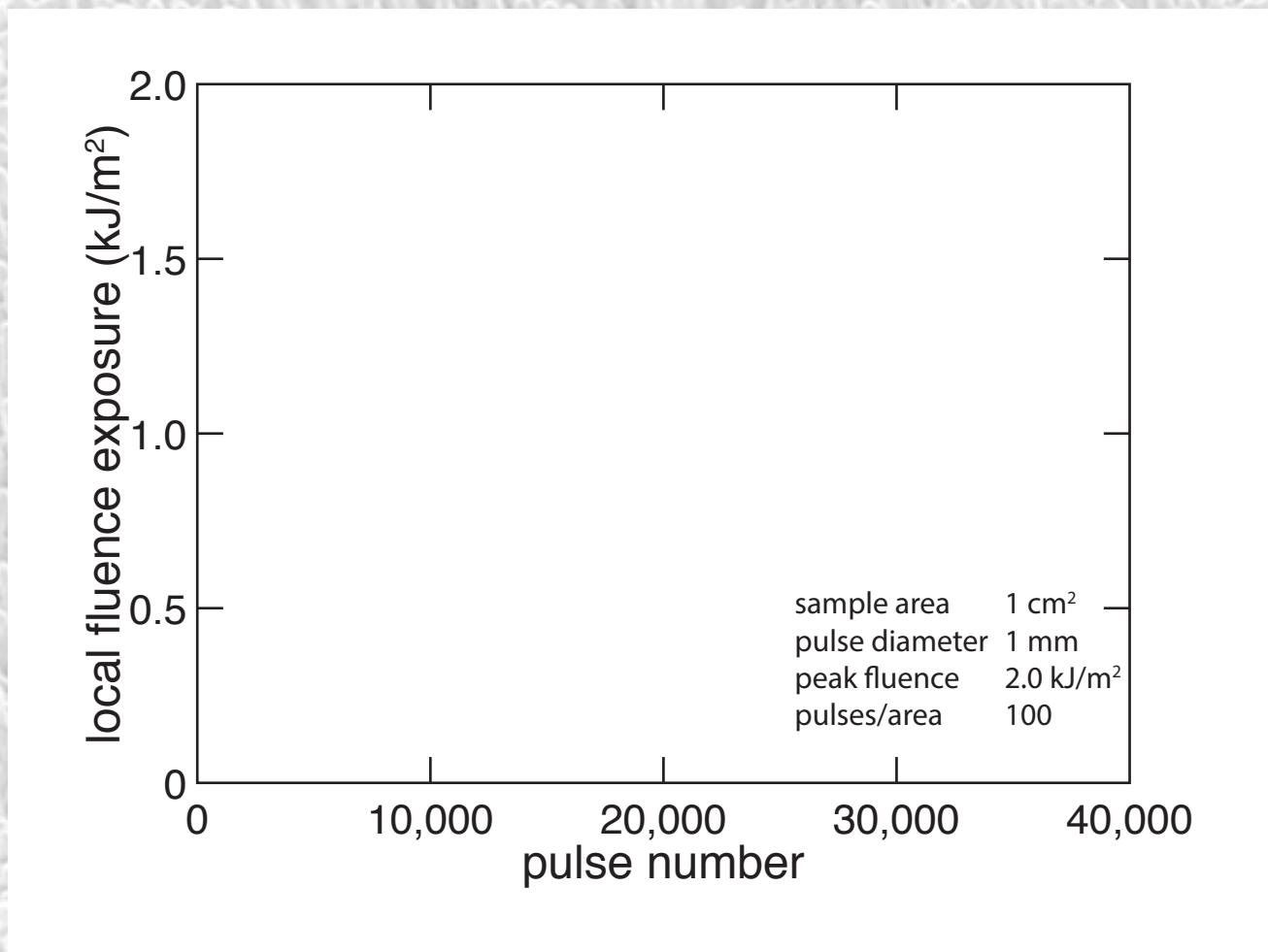
# raster scanning

shots/area = #pulses between  $F_{\text{peak}}$  and  $F_{\text{half-peak}}$



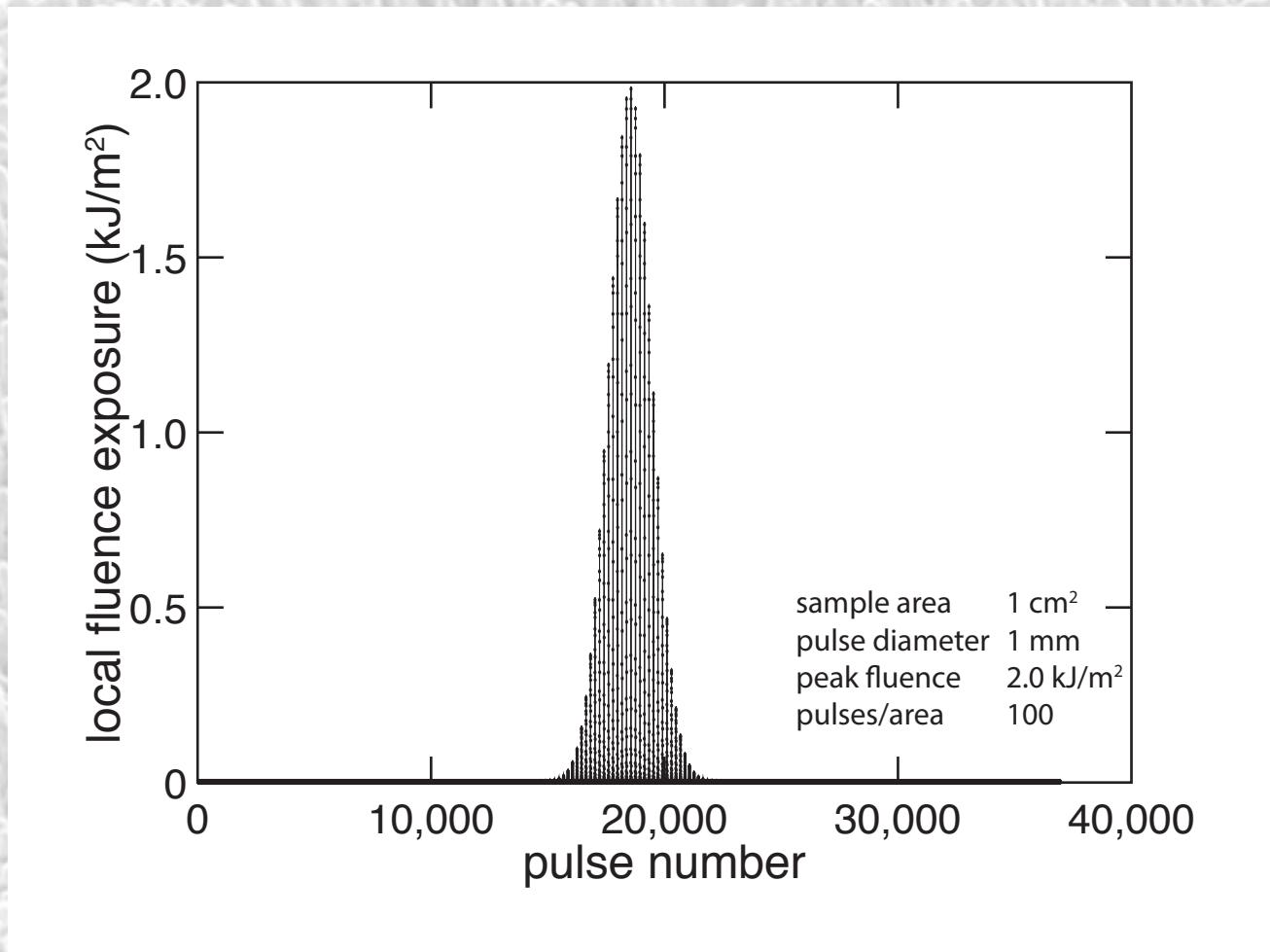
Smith, Sher, Franta, et al., *J. Appl. Phys.* **112** (2012)

# raster scanning



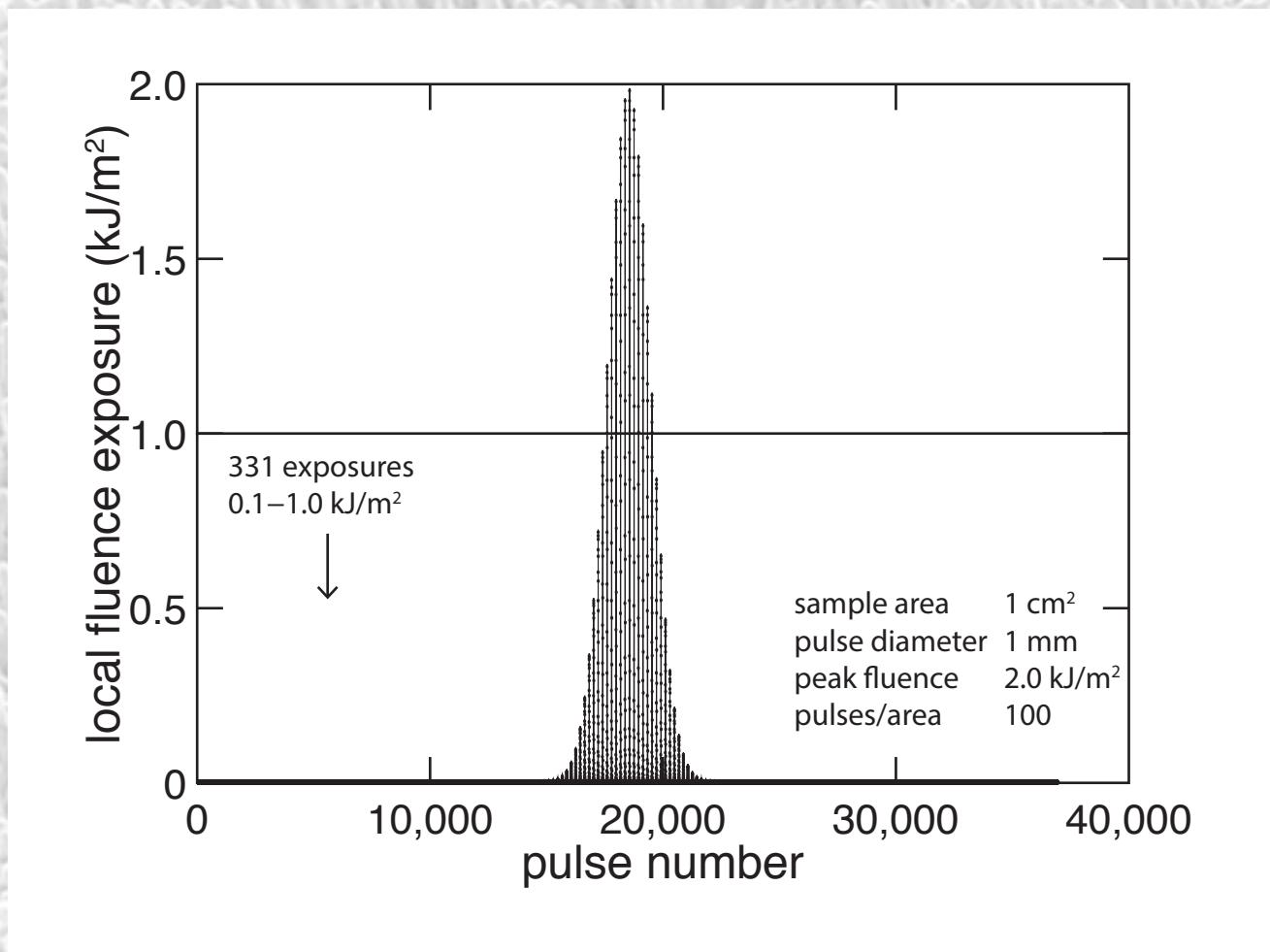
Franta, PhD Thesis (2016)

# raster scanning



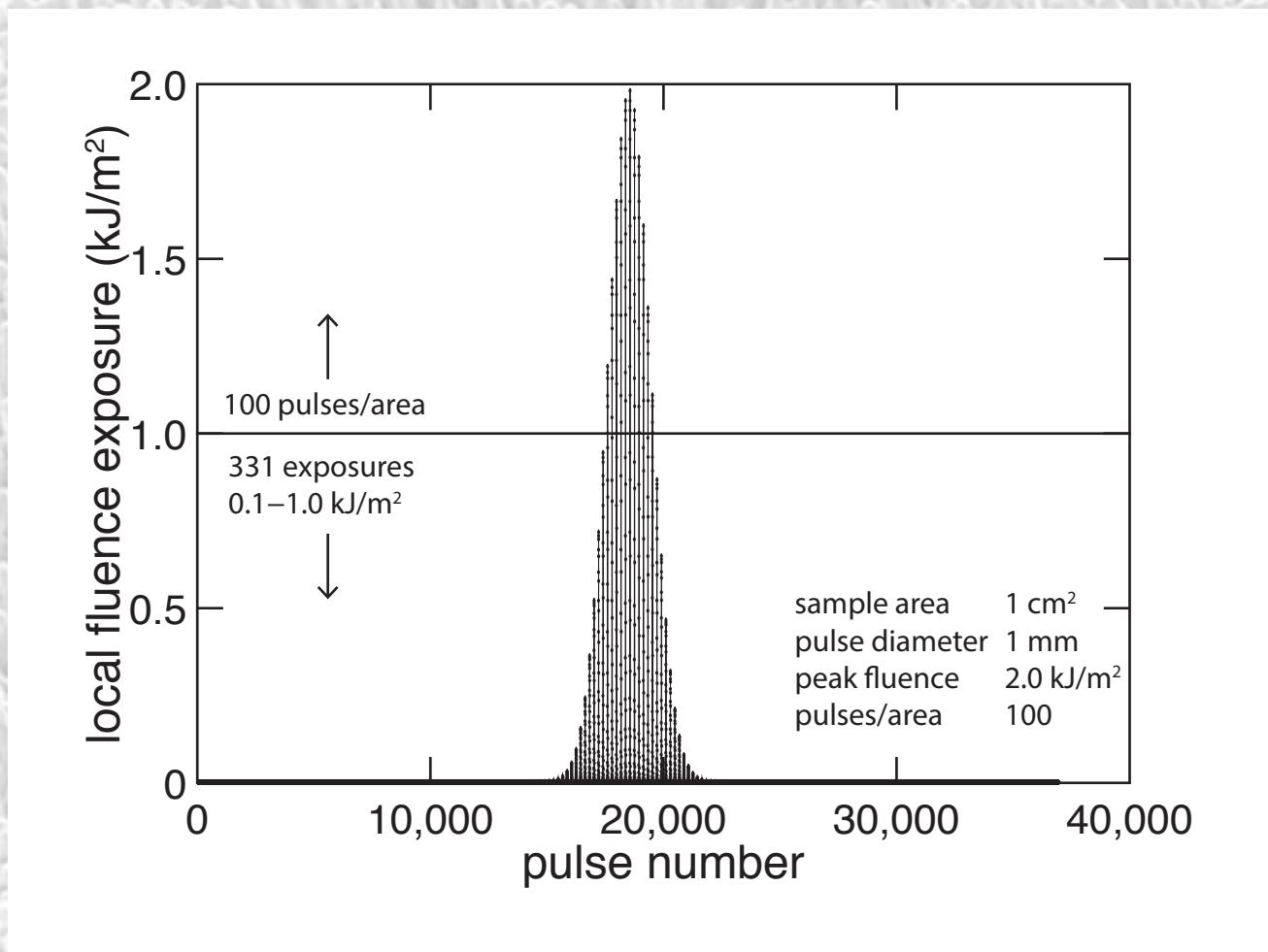
Franta, PhD Thesis (2016)

# raster scanning



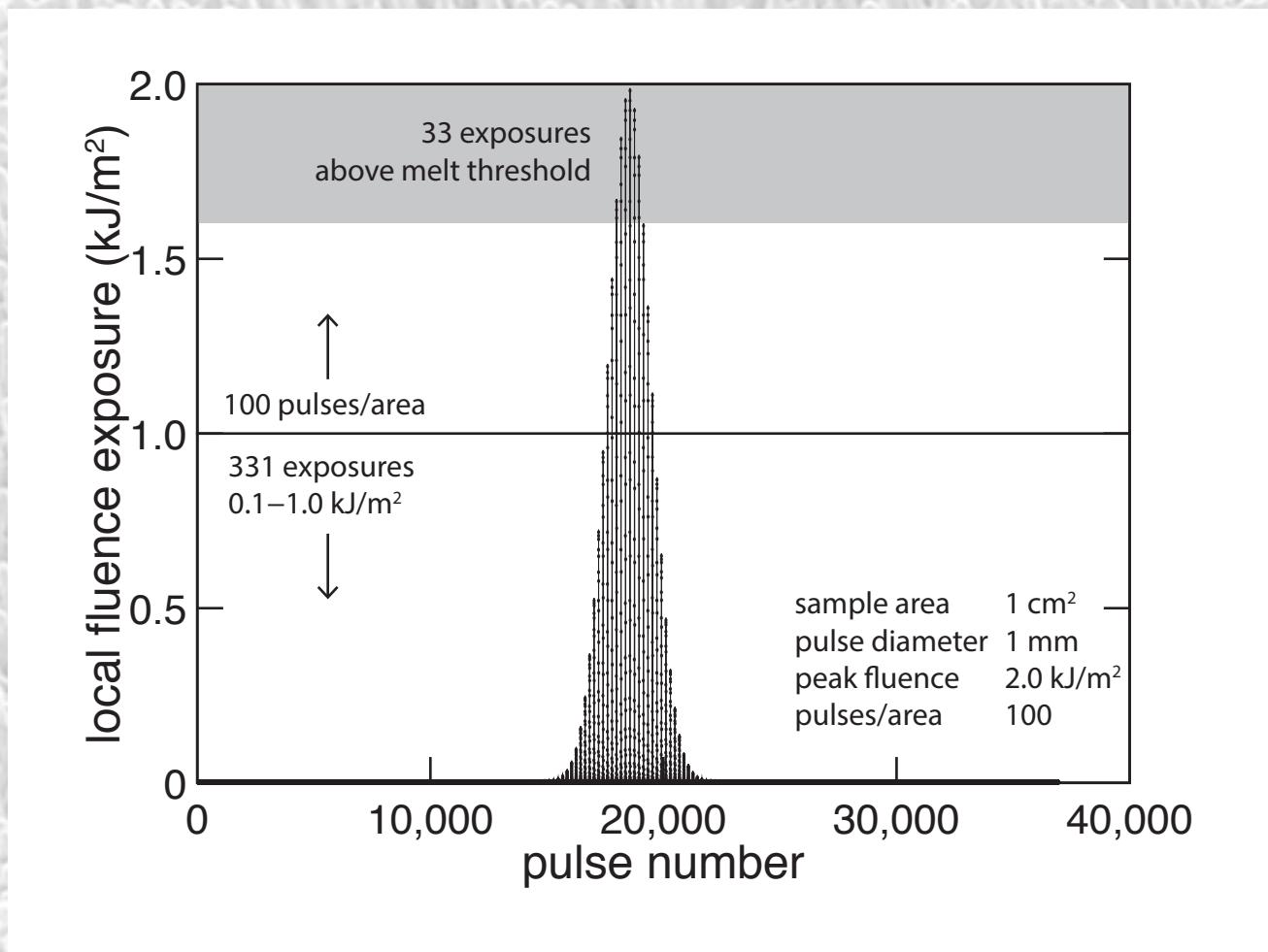
Franta, PhD Thesis (2016)

# raster scanning



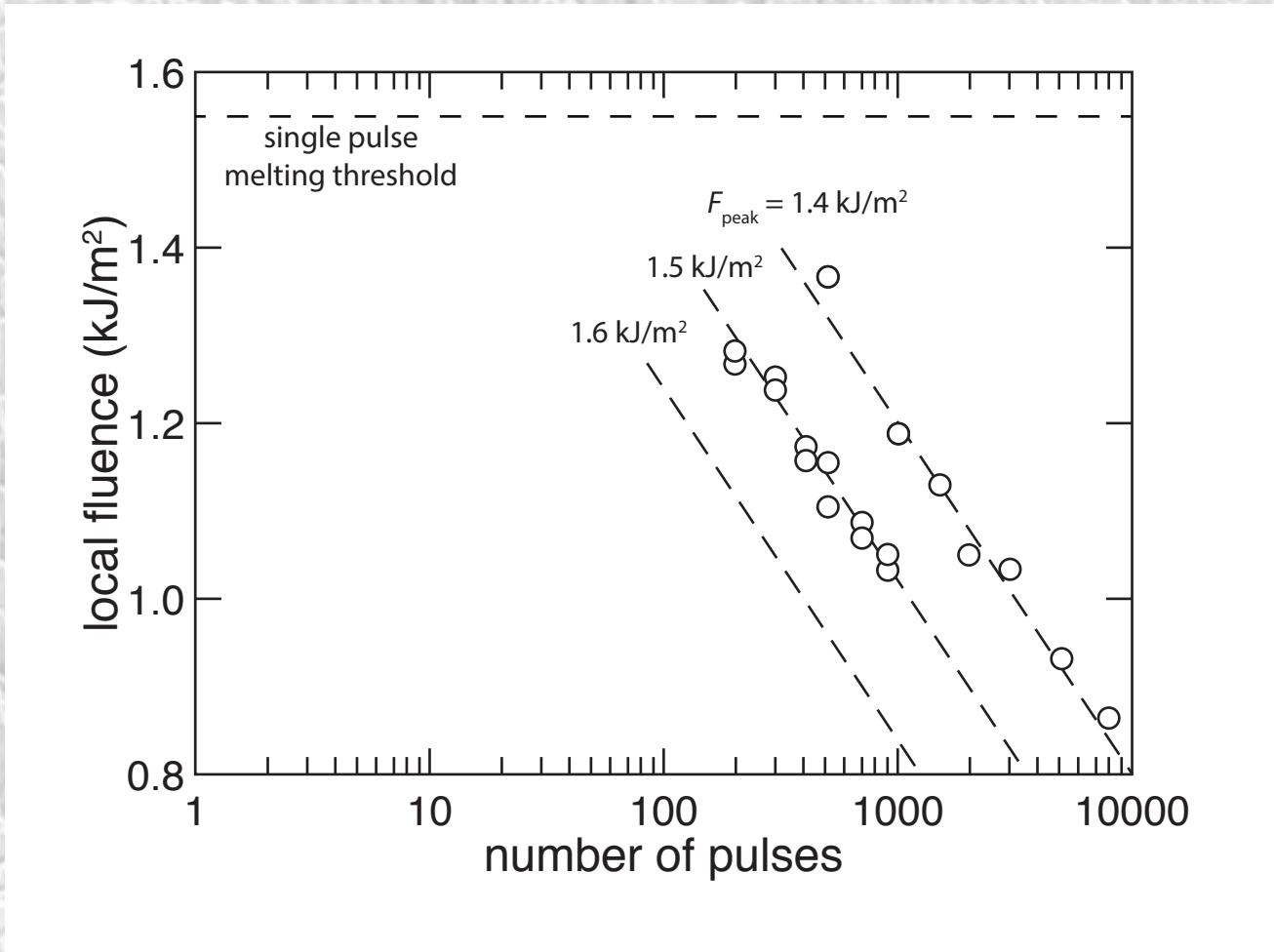
Franta, PhD Thesis (2016)

# raster scanning

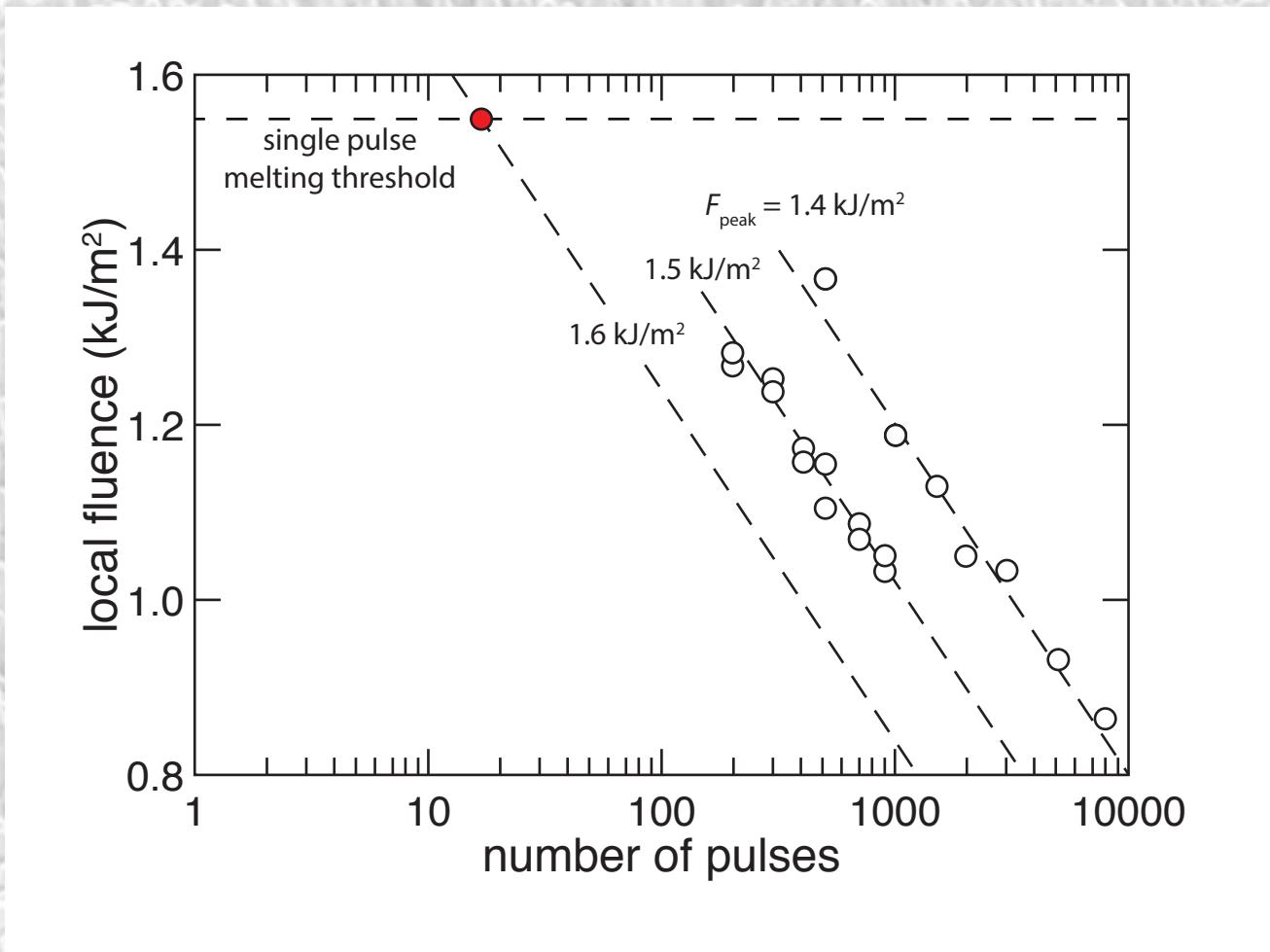


Franta, PhD Thesis (2016)

# surface ripples

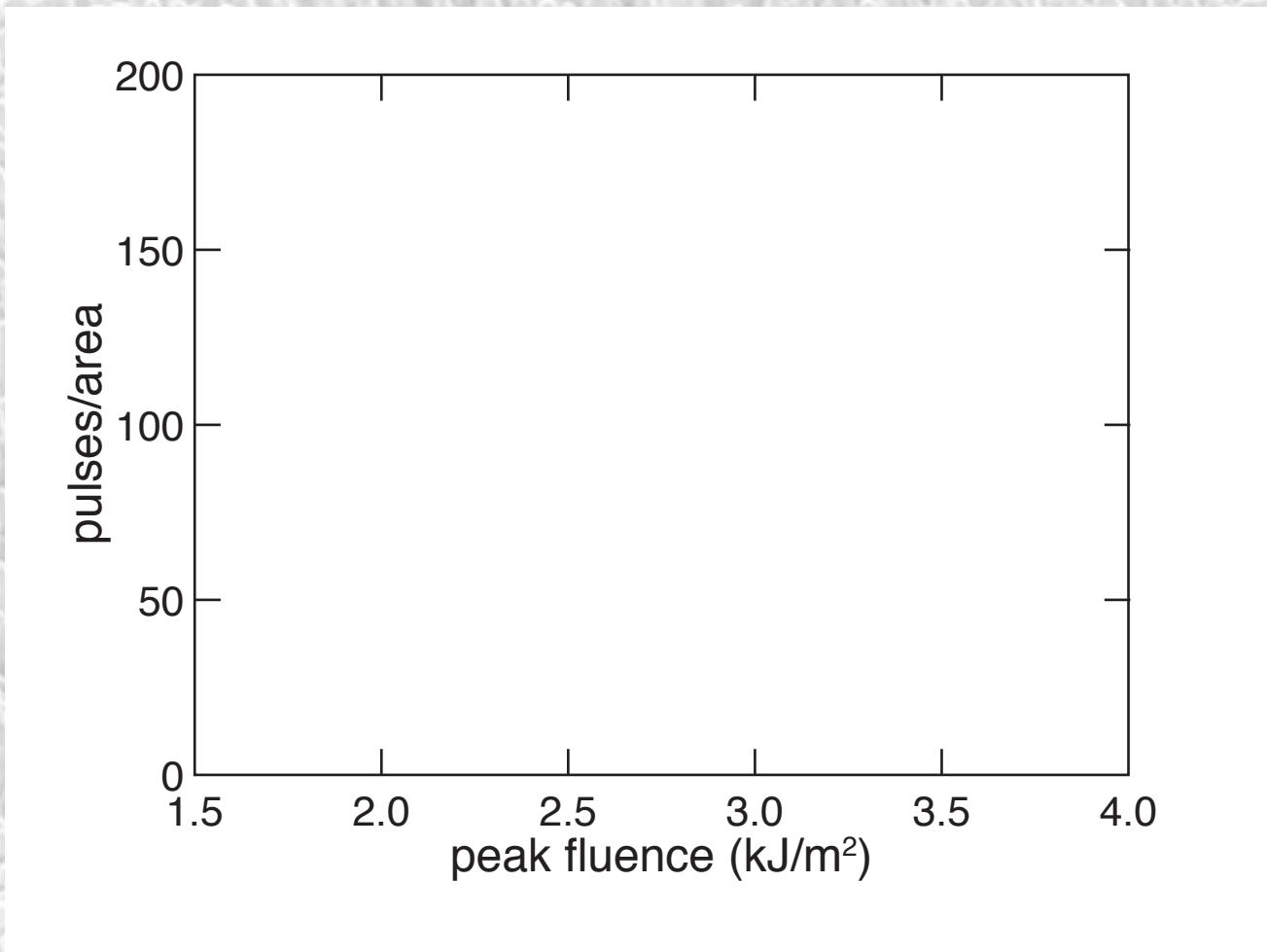


# surface ripples



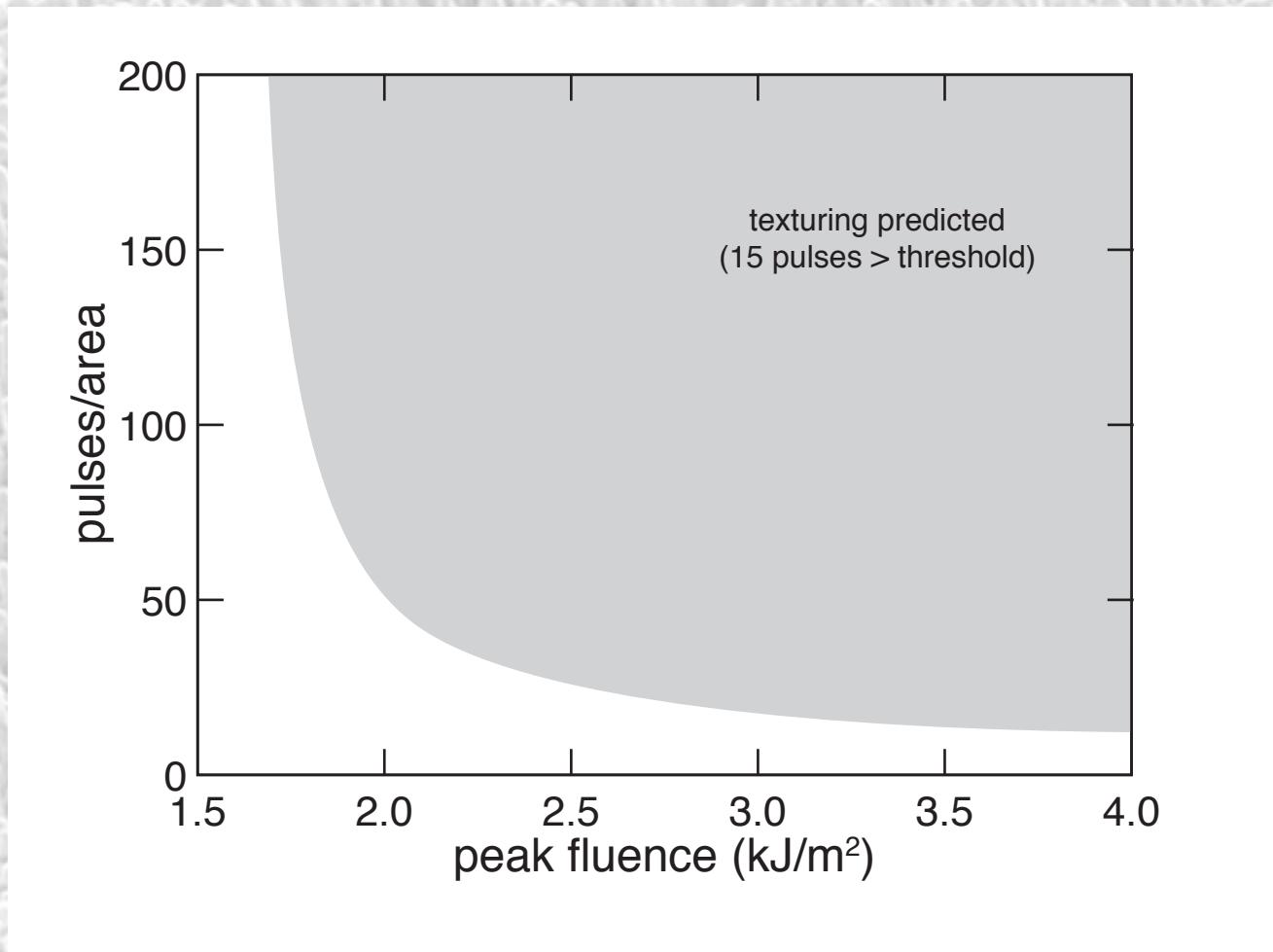
Franta, PhD Thesis (2016)

# surface ripples



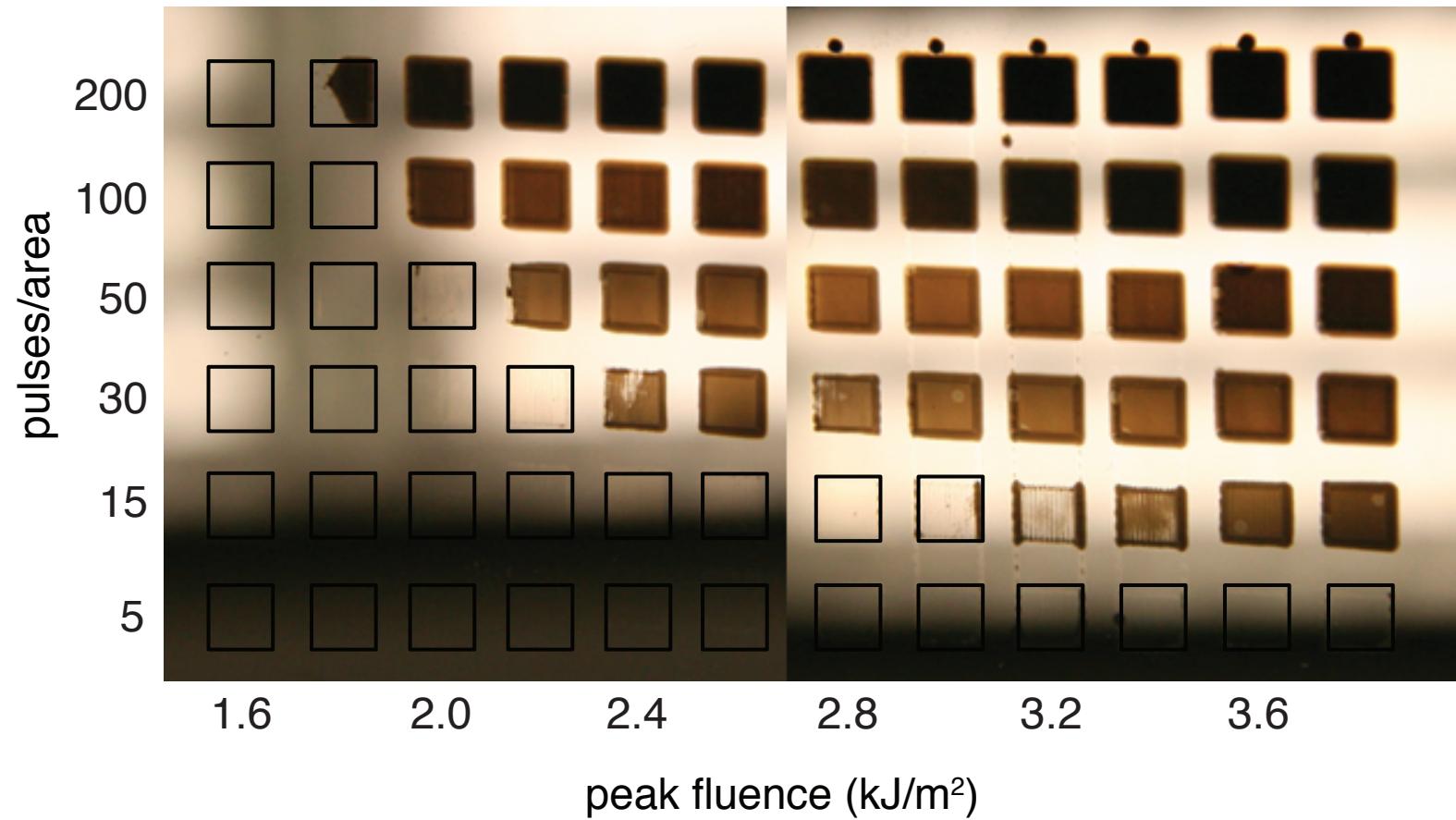
Franta, PhD Thesis (2016)

# surface ripples



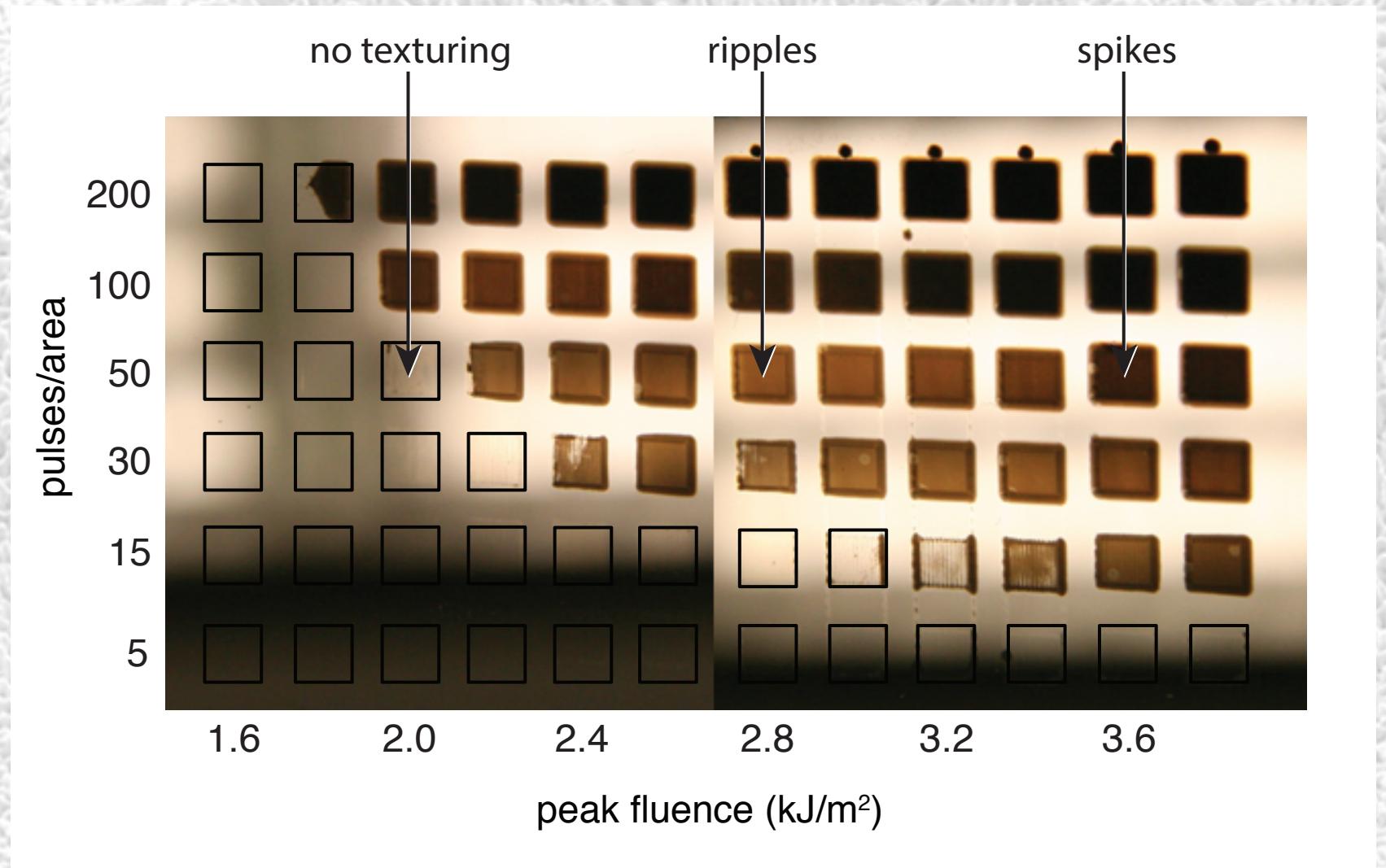
Franta, PhD Thesis (2016)

## raster scanning samples



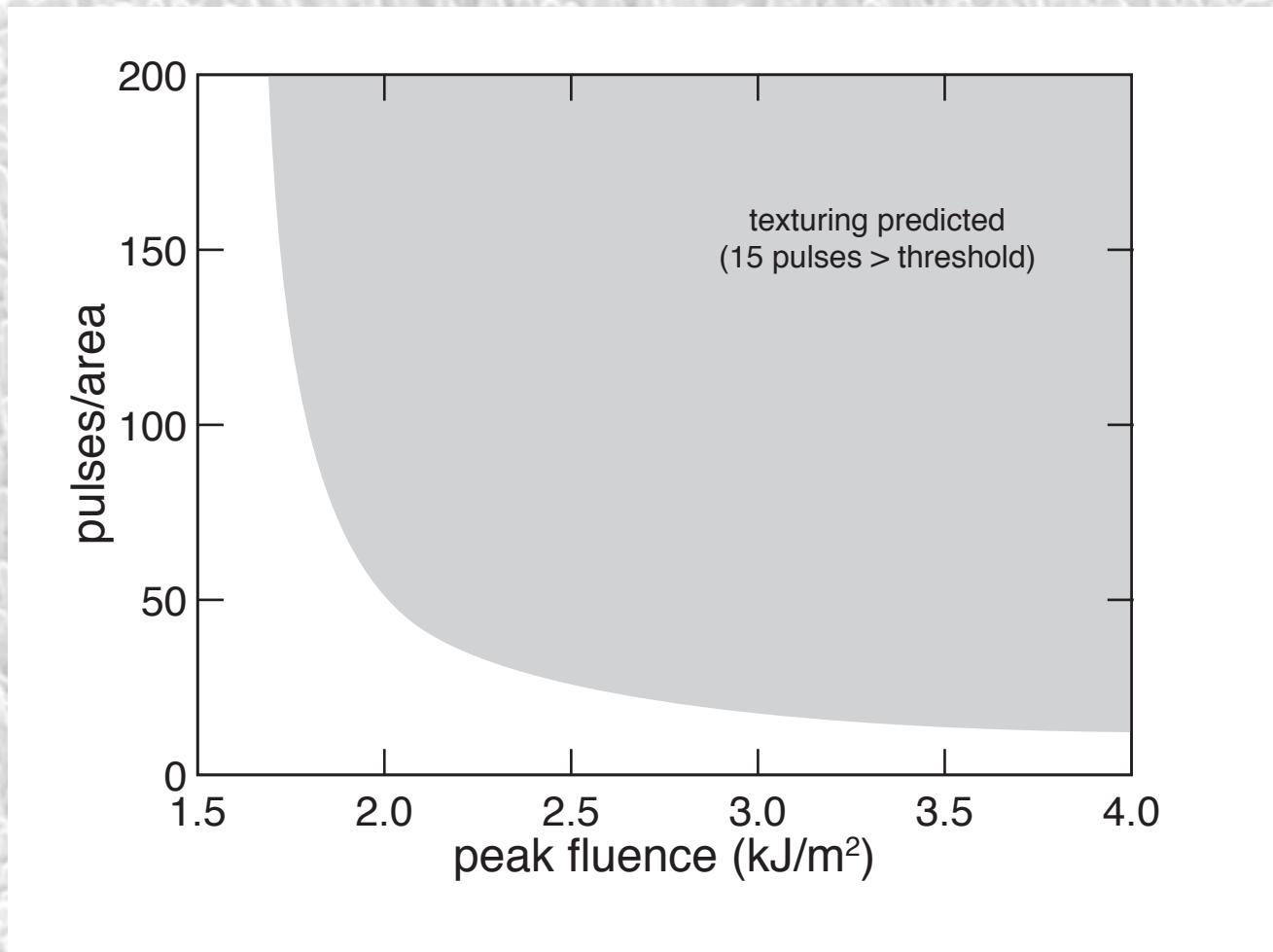
Franta, PhD Thesis (2016)

## raster scanning samples



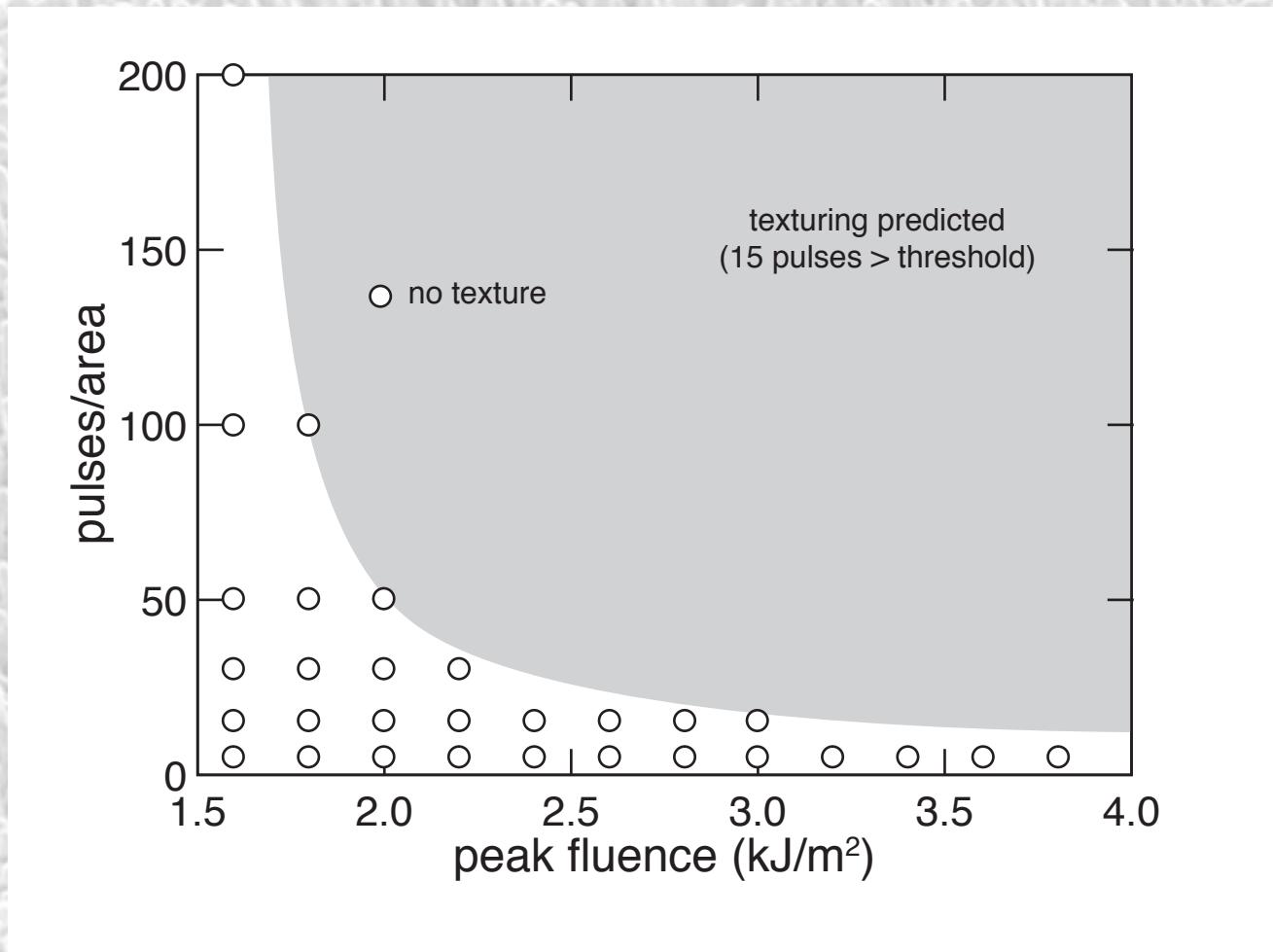
Franta, PhD Thesis (2016)

# surface ripples



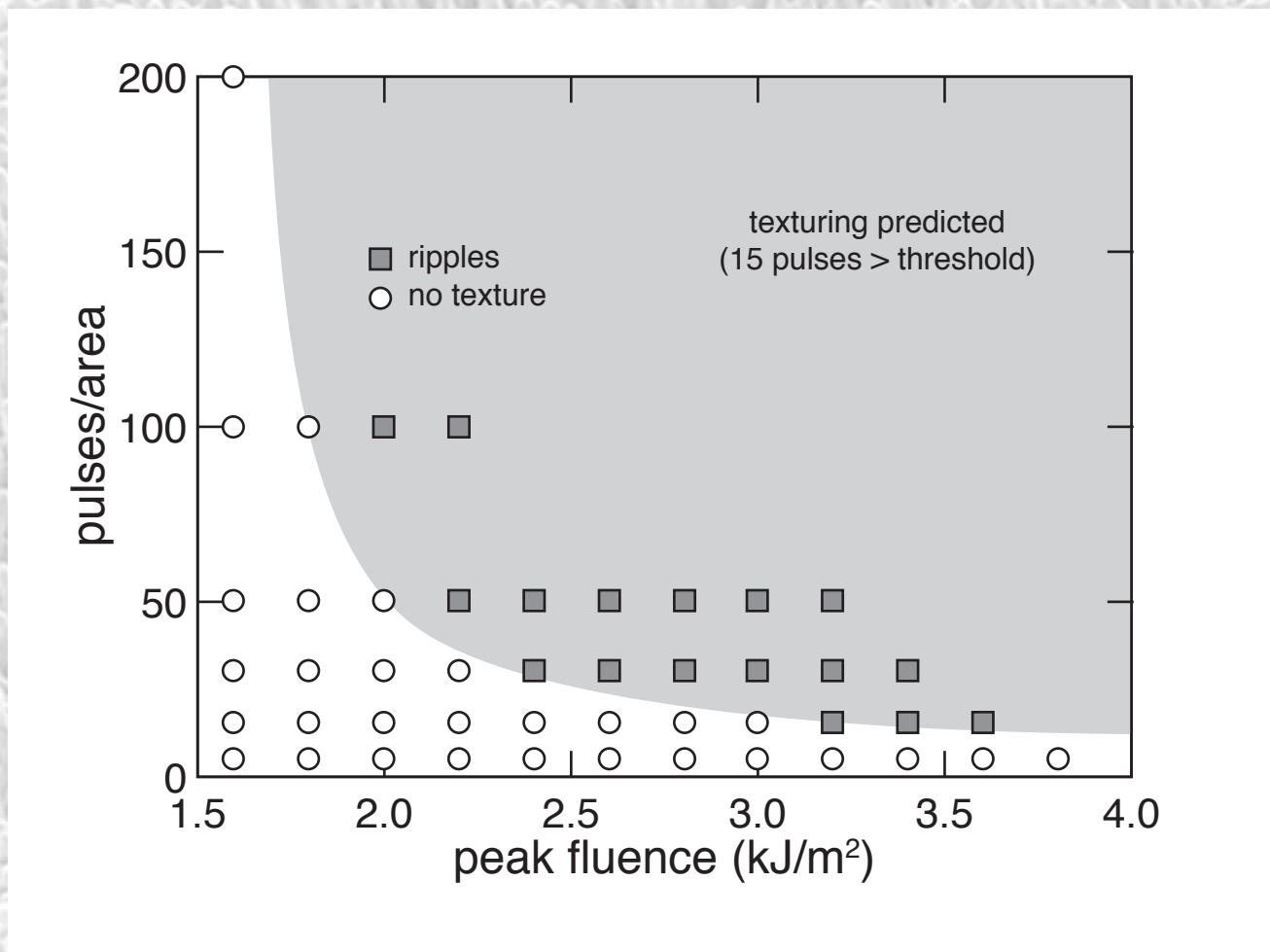
Franta, PhD Thesis (2016)

# surface ripples



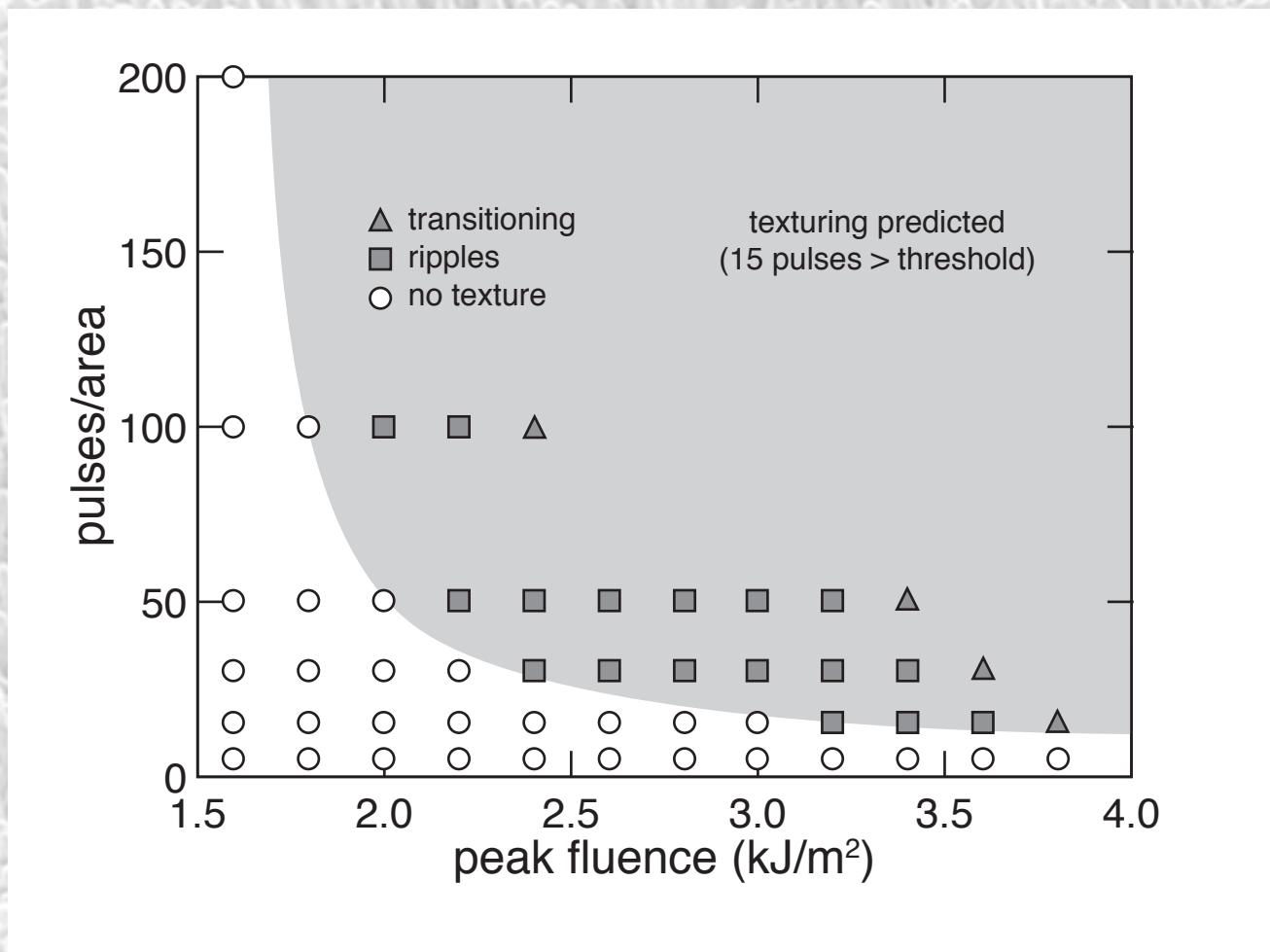
Franta, PhD Thesis (2016)

# surface ripples



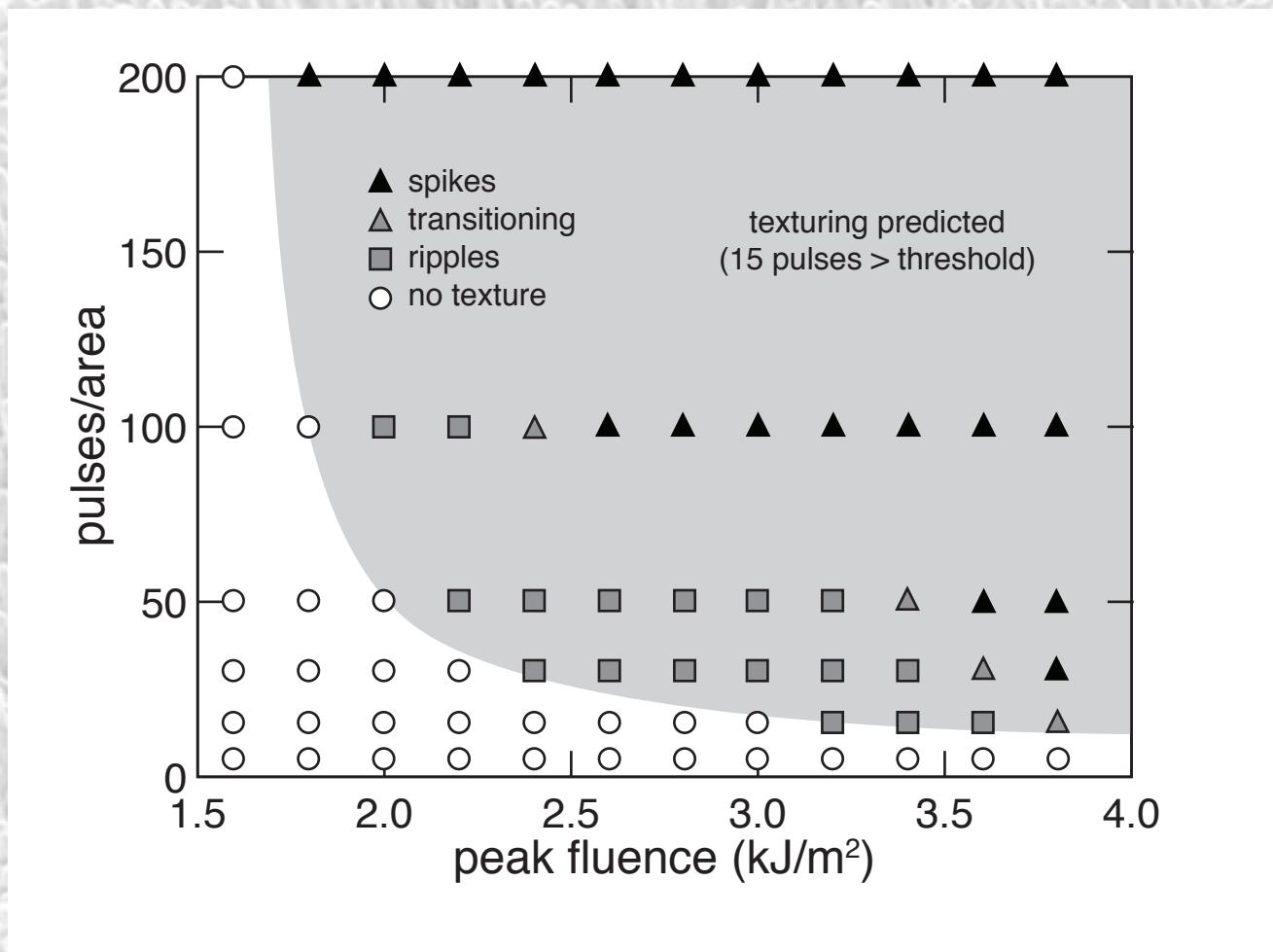
Franta, PhD Thesis (2016)

# surface ripples



Franta, PhD Thesis (2016)

# surface ripples

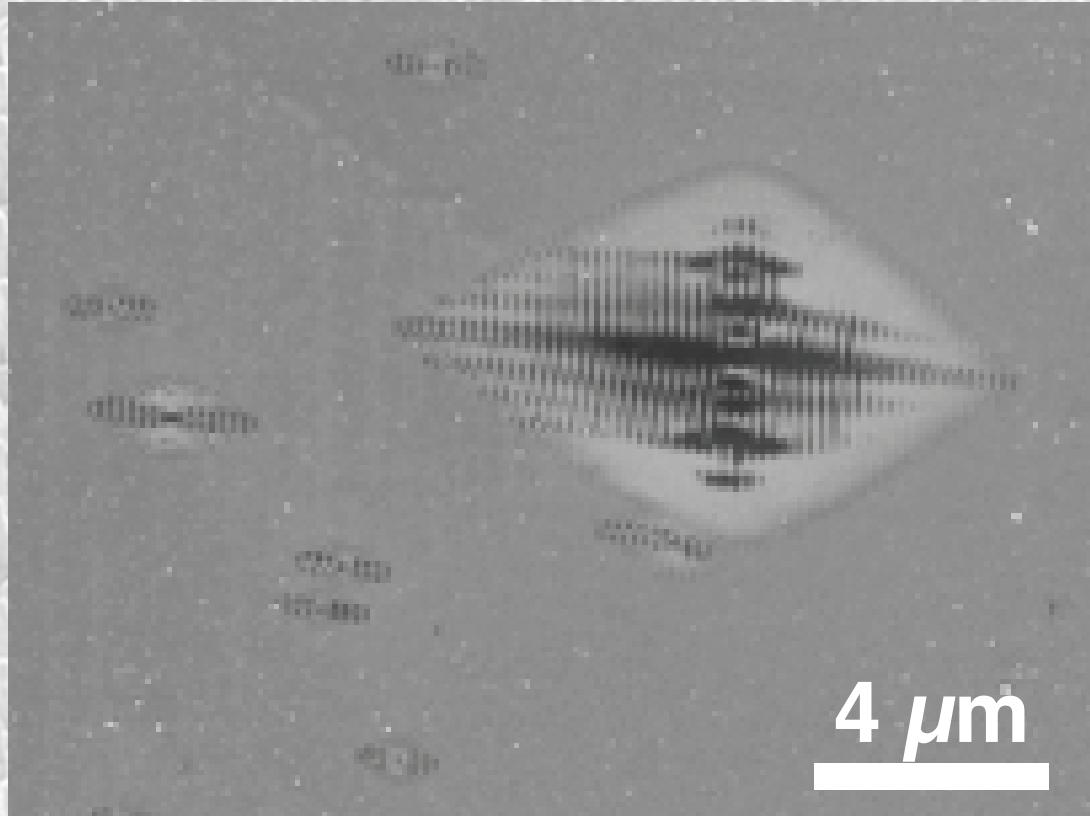


Franta, PhD Thesis (2016)

## What we learned

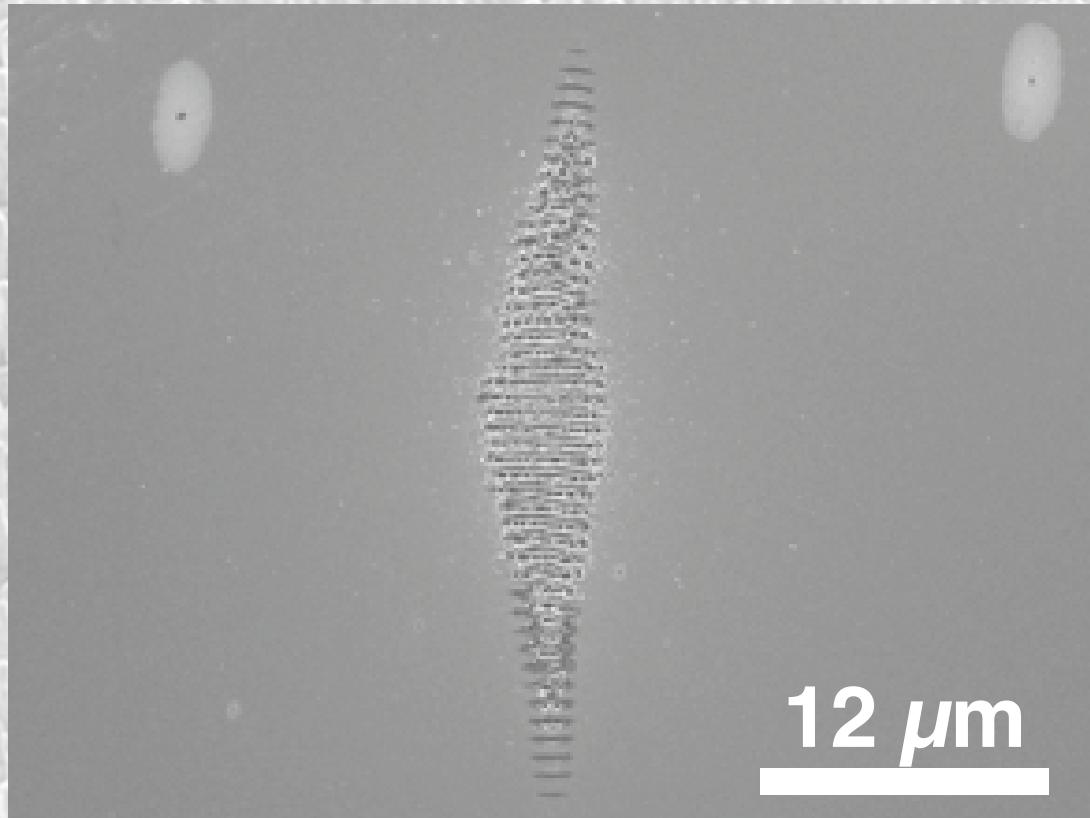
- texture onset depends on peak fluence
- texture onset does not depend on atmosphere
- quantitative agreement standing/scanning texturing

# formation of structures



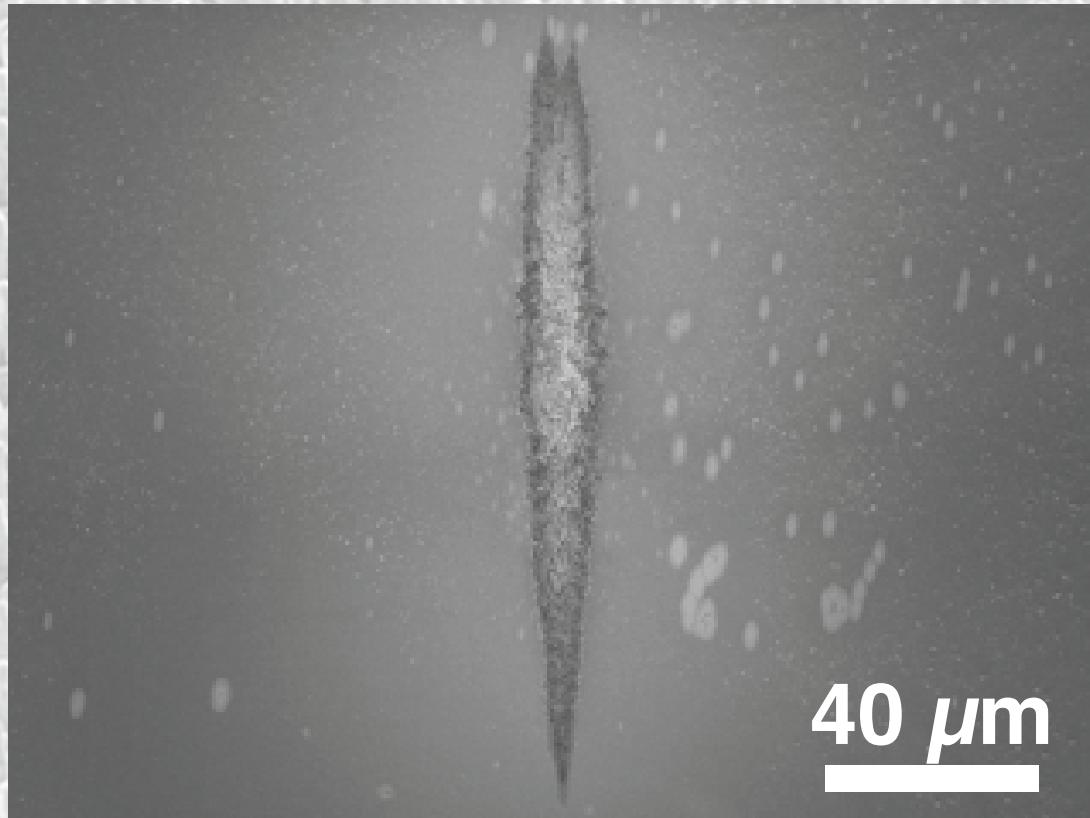
110 pulses, 20 Torr N<sub>2</sub> gas, 1.5 kJ/m<sup>2</sup>

## formation of structures



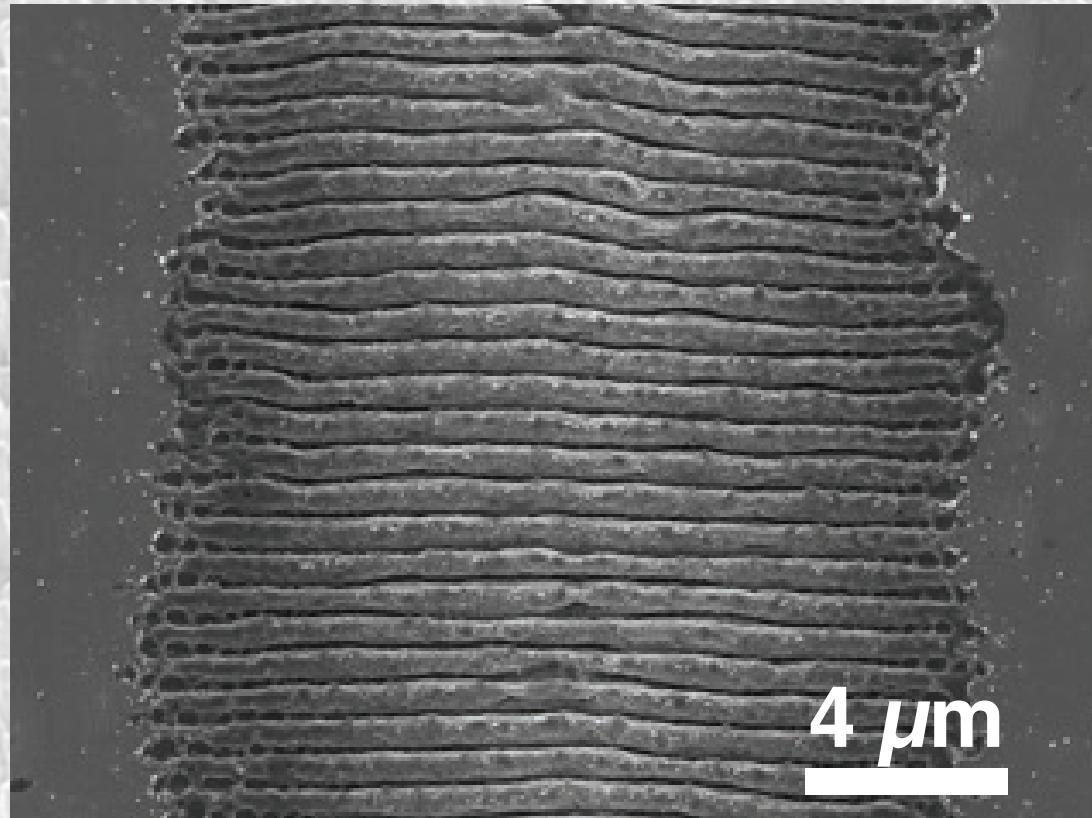
110 pulses, 20 Torr N<sub>2</sub> gas, 1.5 kJ/m<sup>2</sup>

## formation of structures



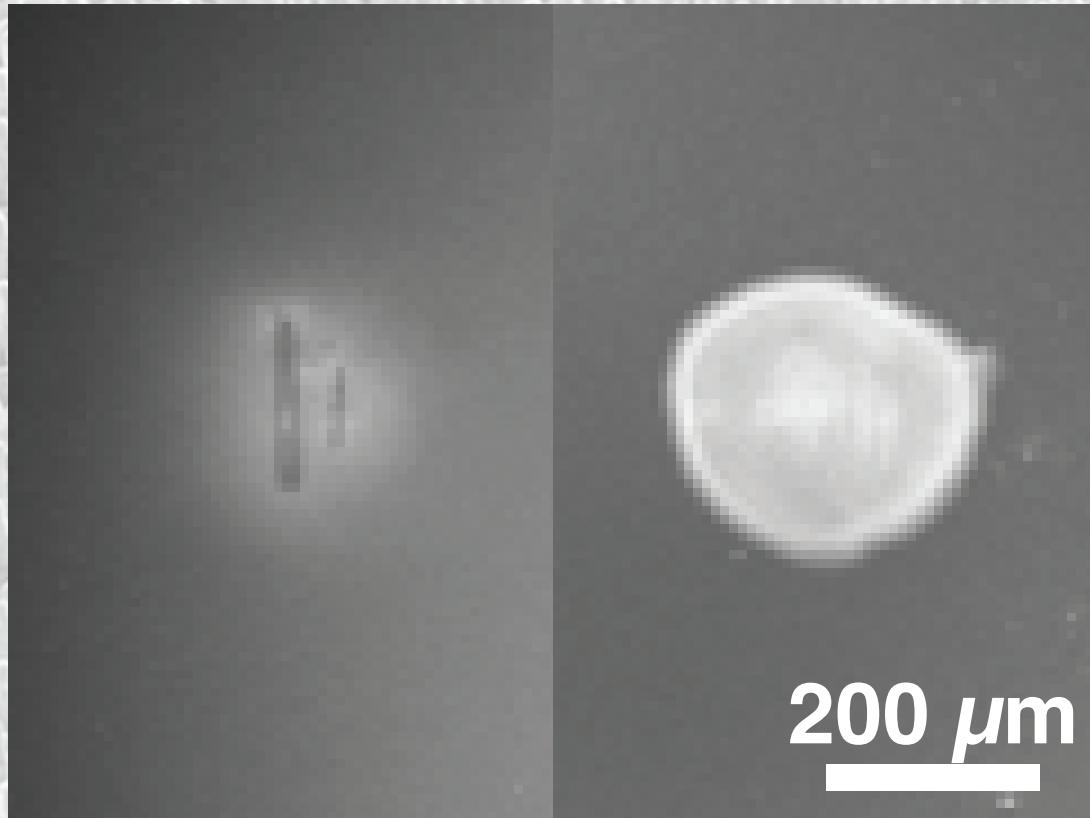
140 pulses, 760 Torr air, 1.5 kJ/m<sup>2</sup>

## formation of structures



140 pulses, 760 Torr air, 1.5 kJ/m<sup>2</sup>

## formation of structures



110 pulses, 20 (left)/760 (right) Torr N<sub>2</sub> gas, 1.5 kJ/m<sup>2</sup>

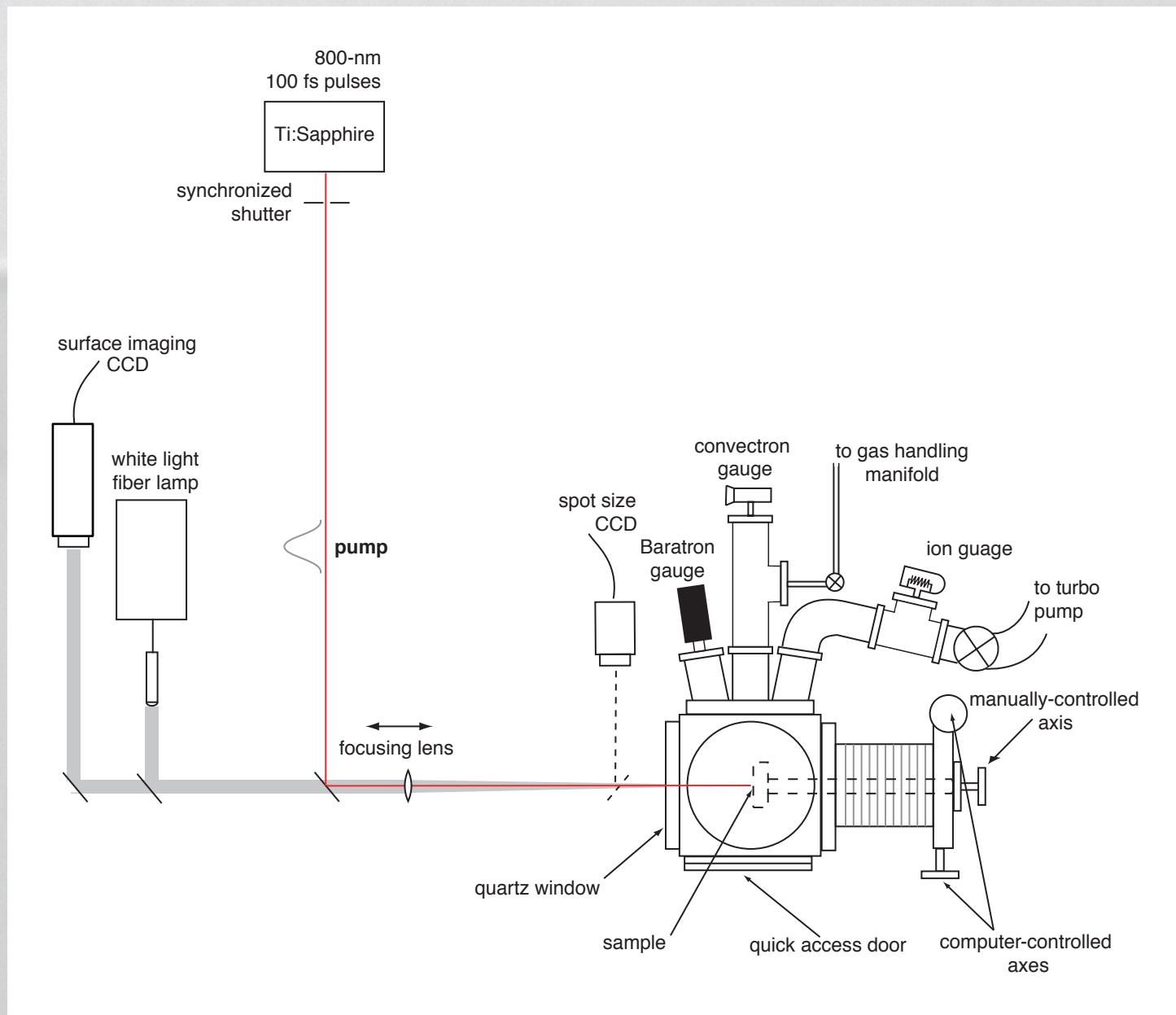
## Questions

- What determines initial, random surface modification?
- What is role of surface plasmon polaritons?
- What is mechanism behind gas pressure effect?
- How can process be time resolved?

**1** structuring

**2** hyperdoping

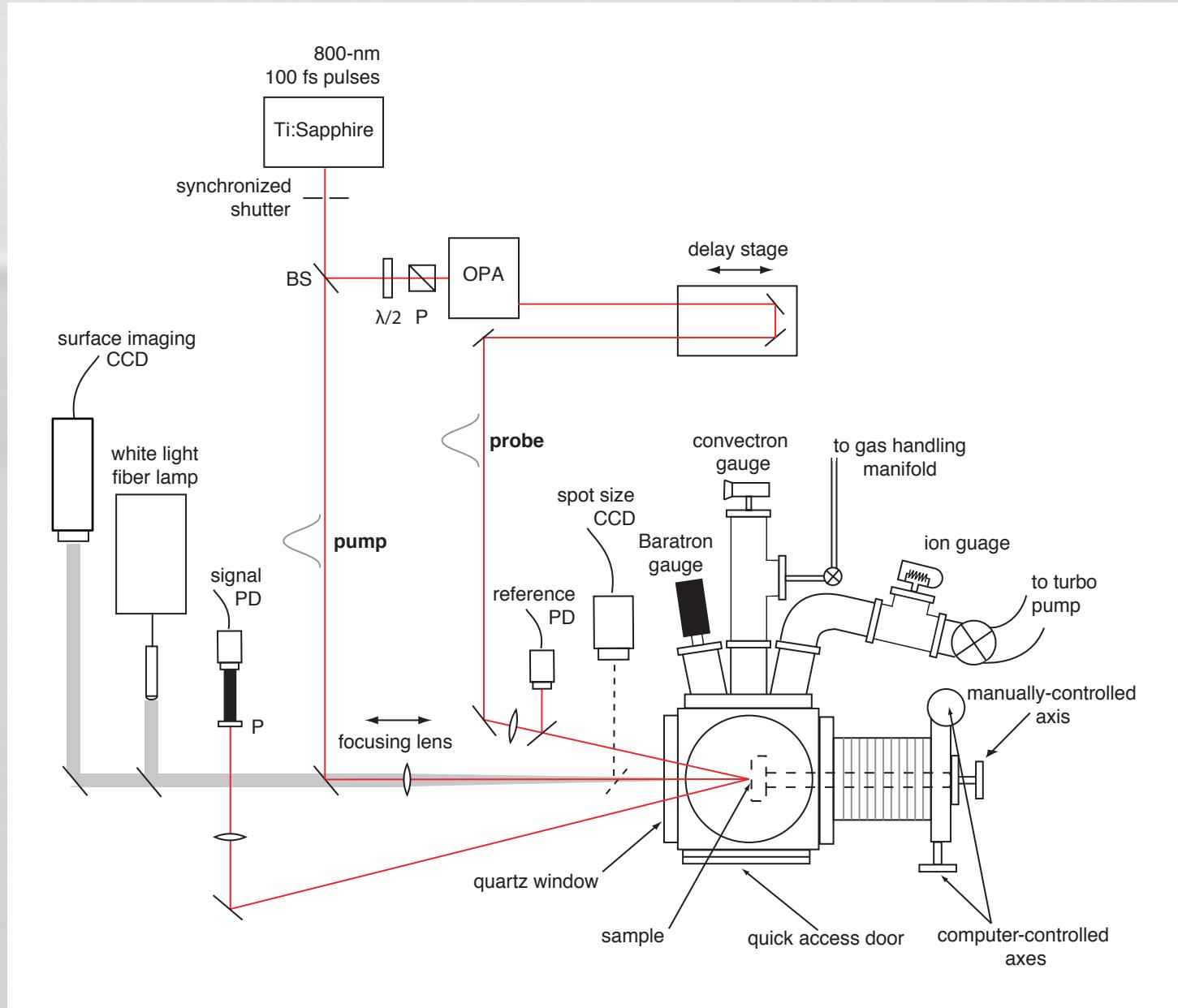
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

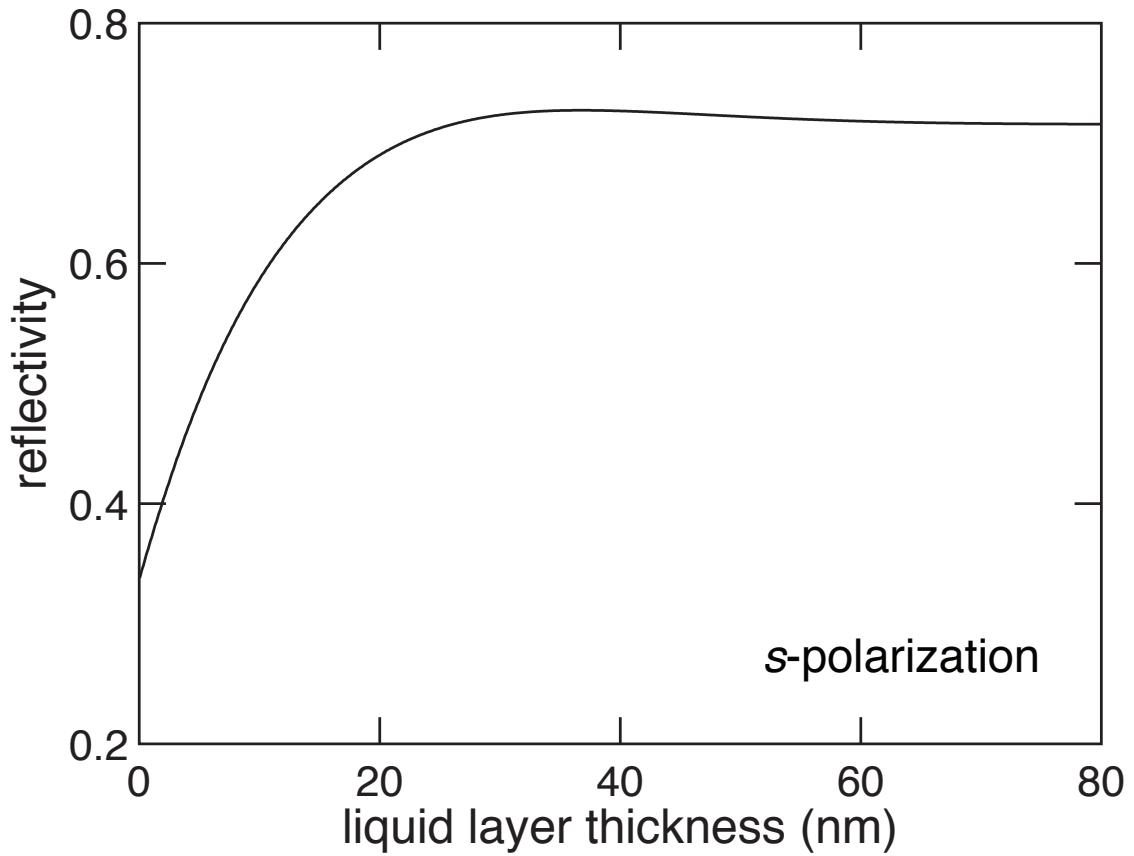
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

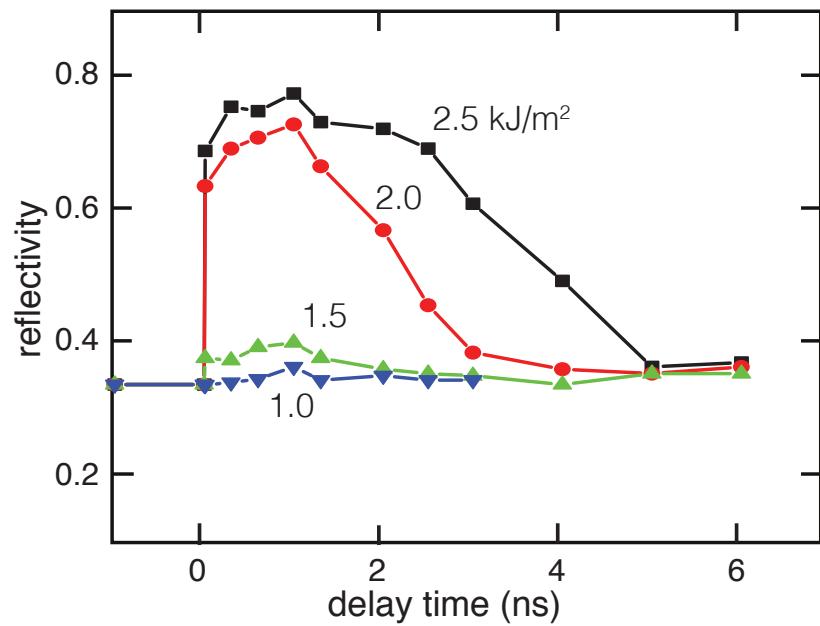
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

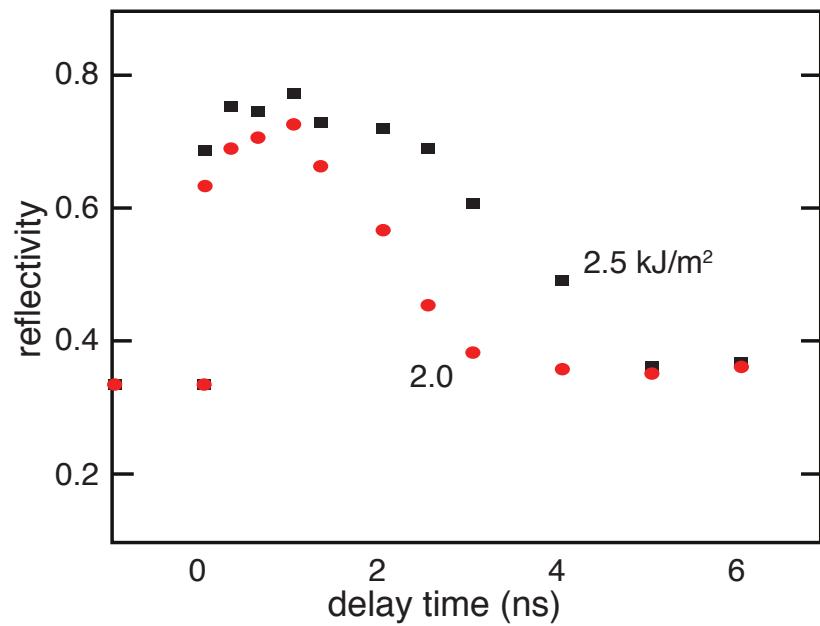
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

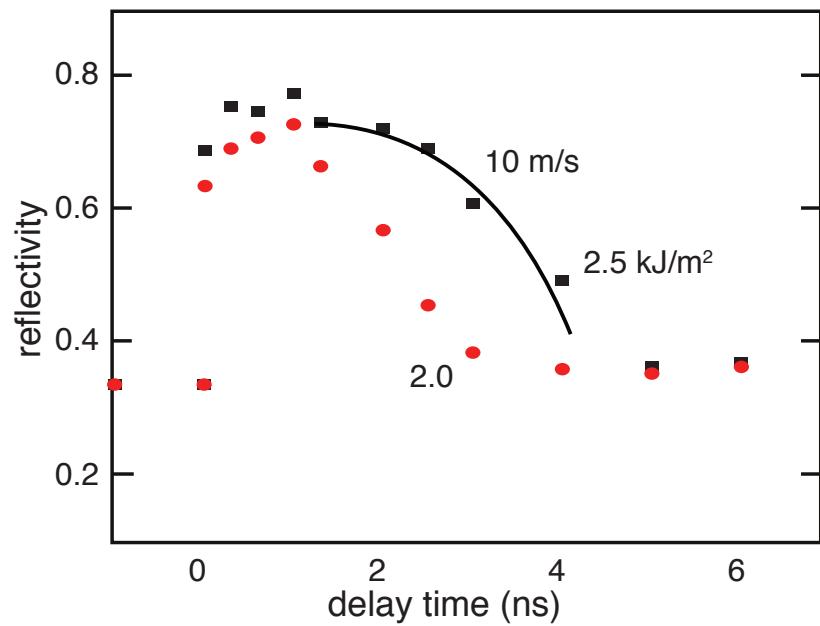
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

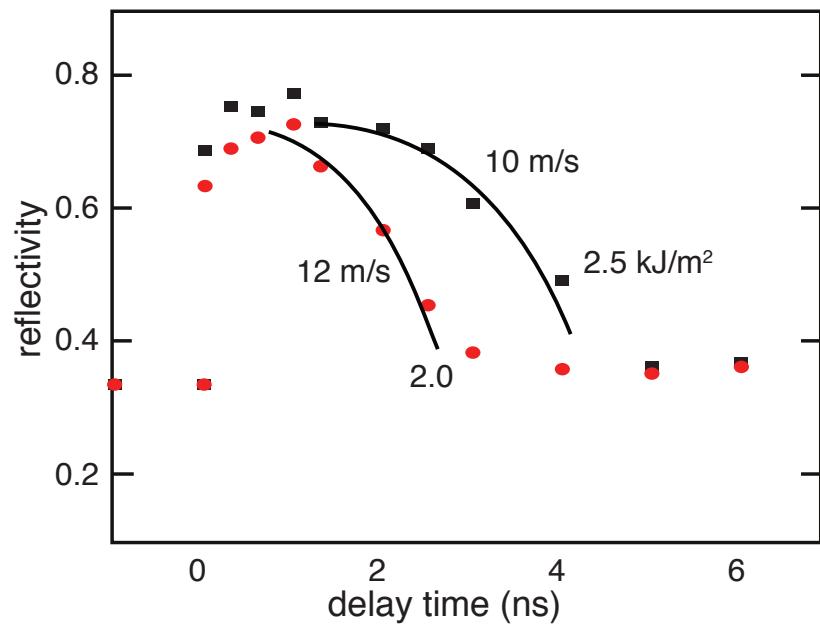
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

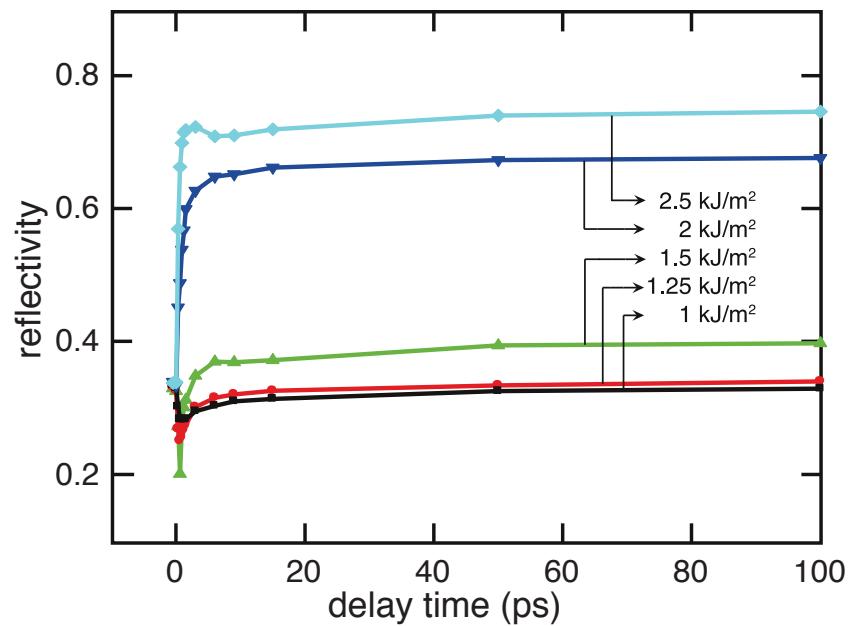
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

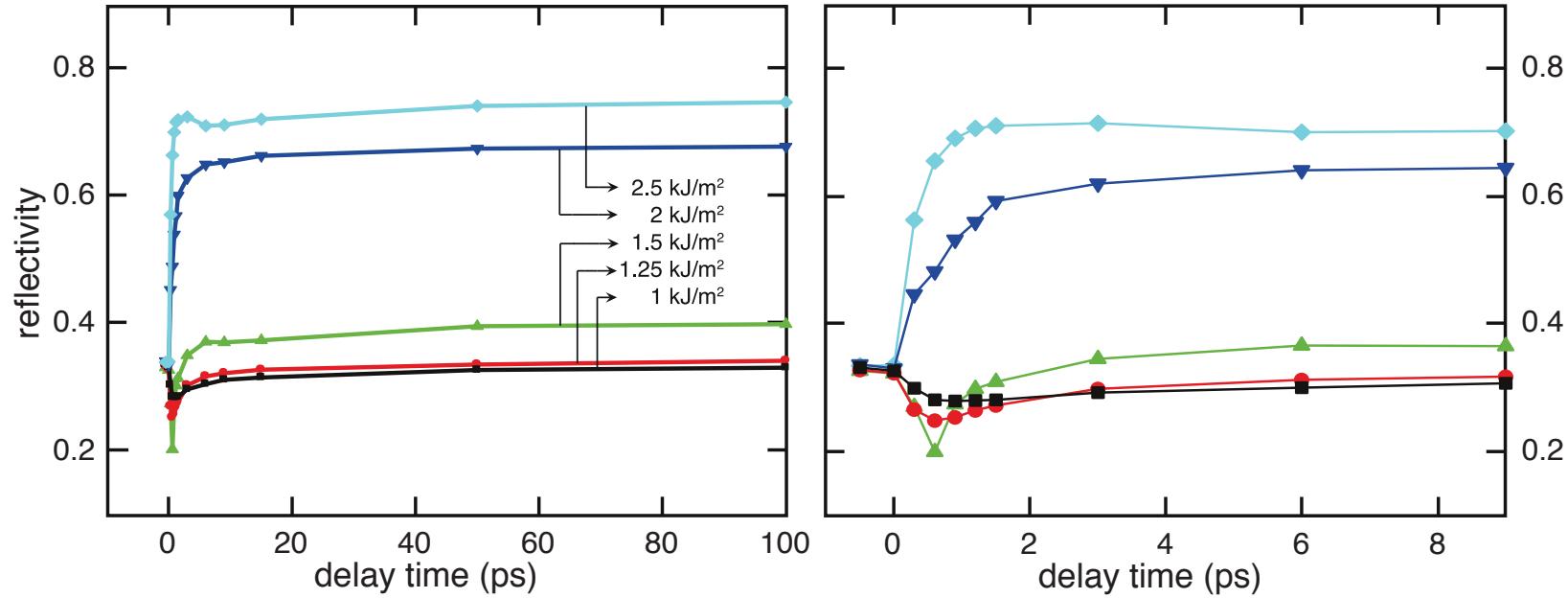
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

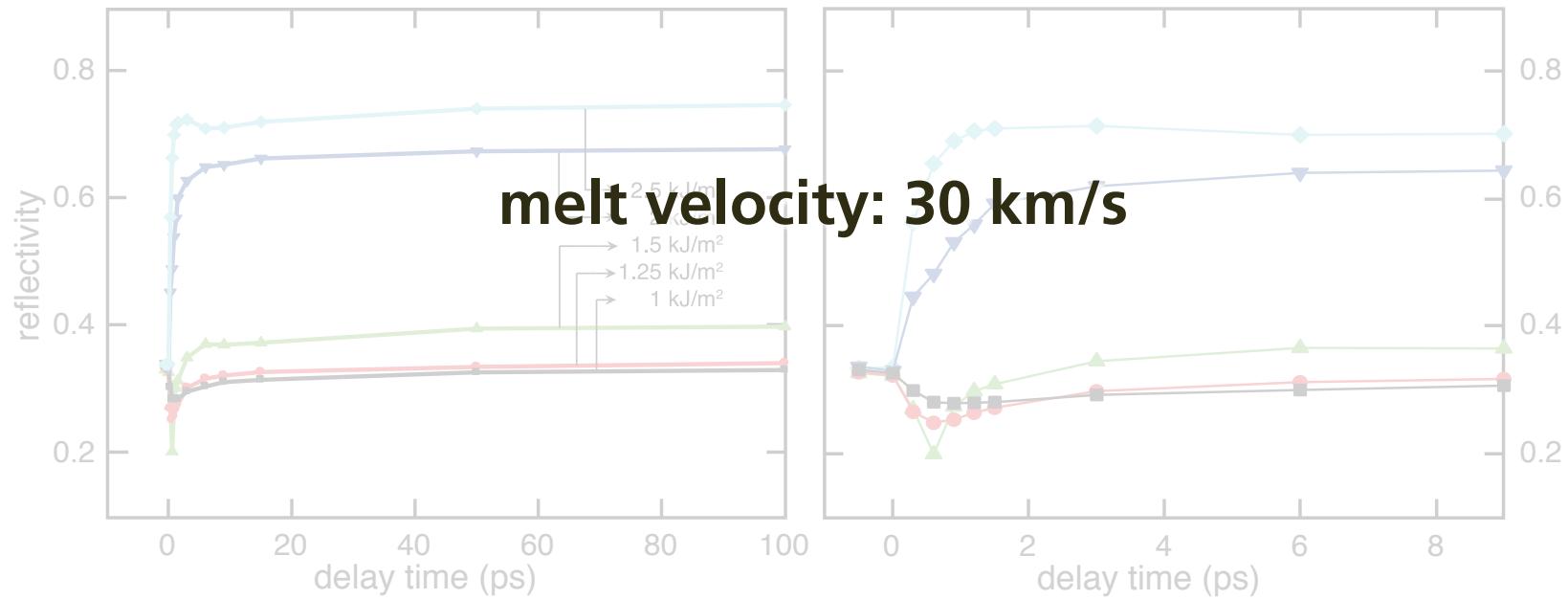
# fs pump-probe reflectometry



1 structuring

2 hyperdoping

# fs pump-probe reflectometry



1 structuring

2 hyperdoping

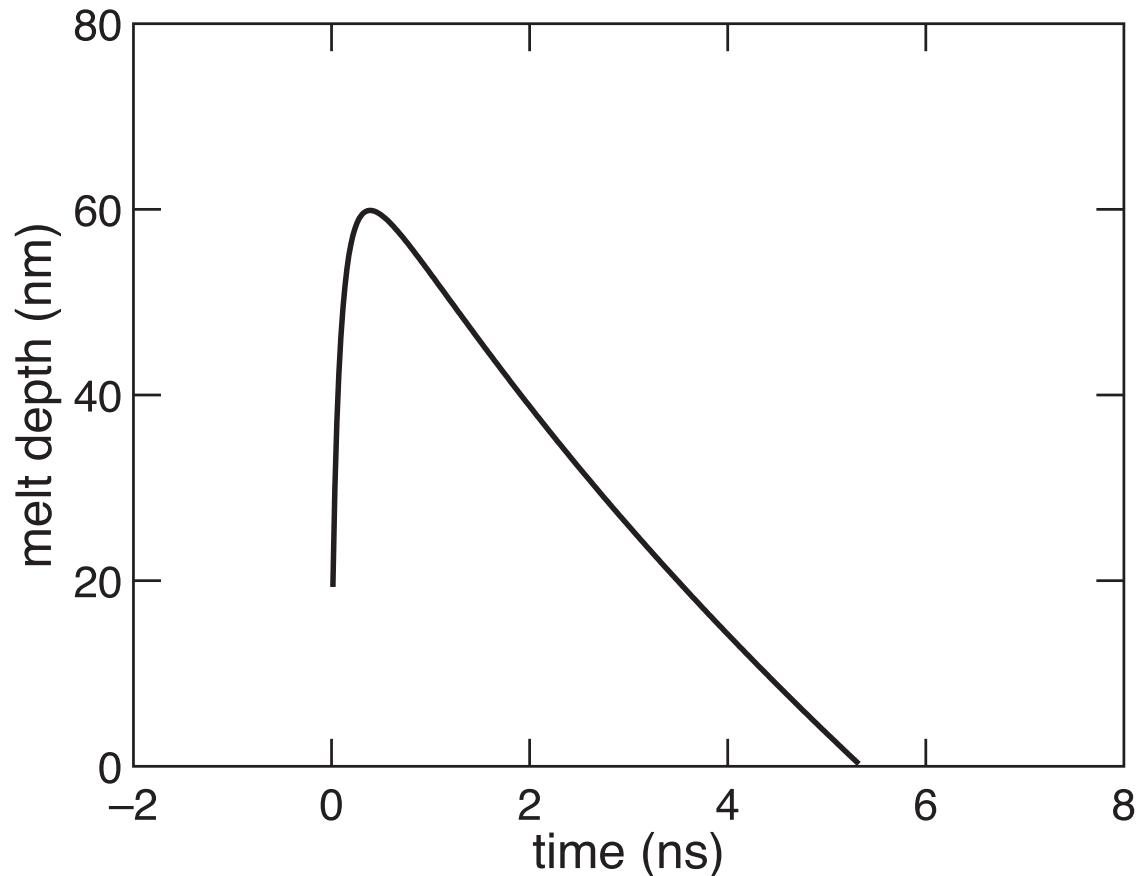
# **fs pump-probe reflectometry**

**melt velocity**      **30 km/s (athermal)**

**melt duration**      **1–10 ns**

**resolidification velocity**      **10–16 m/s**

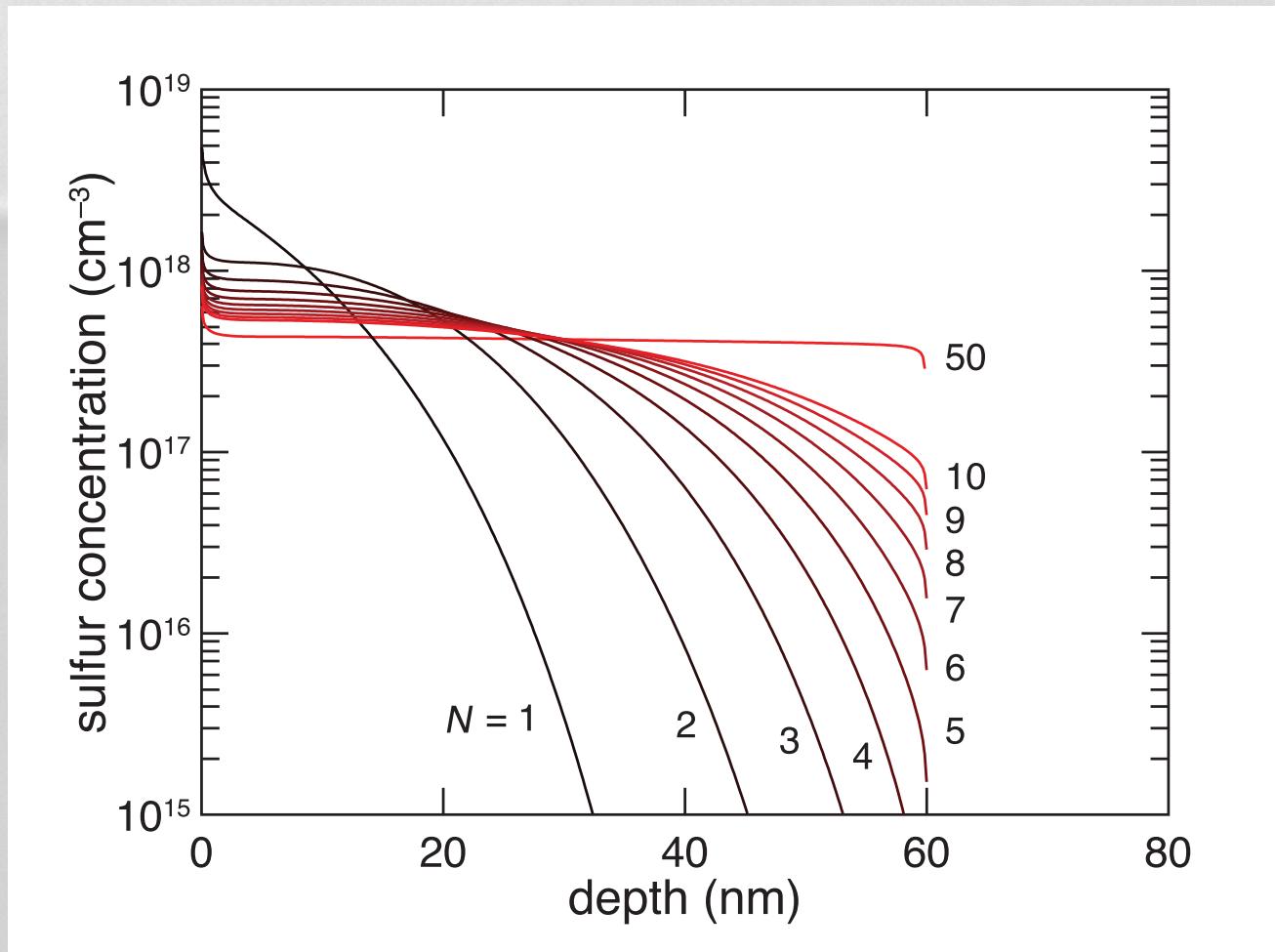
# diffusion model simulation



1 structuring

2 hyperdoping

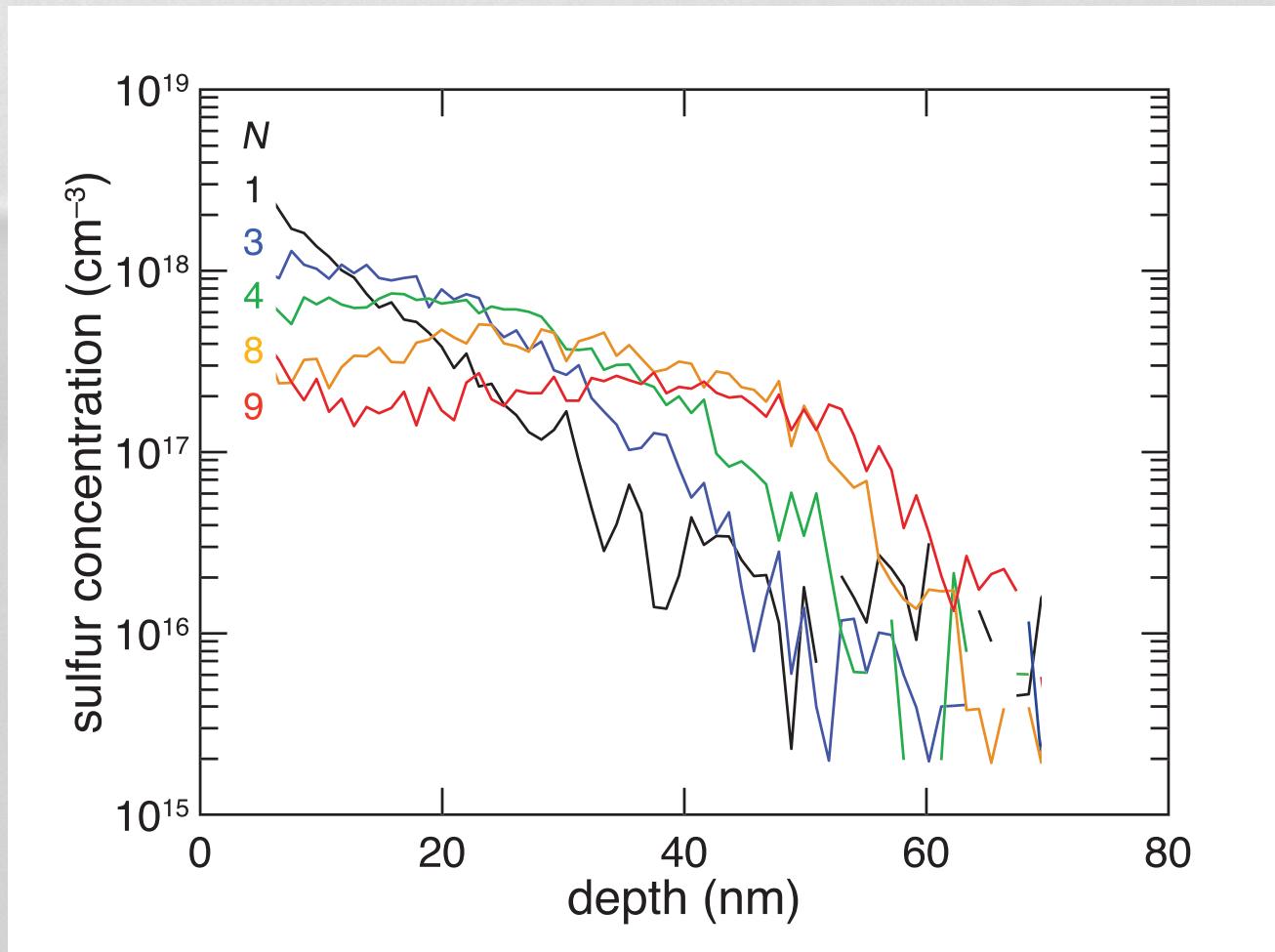
# diffusion model simulation



1 structuring

2 hyperdoping

# diffusion model simulation

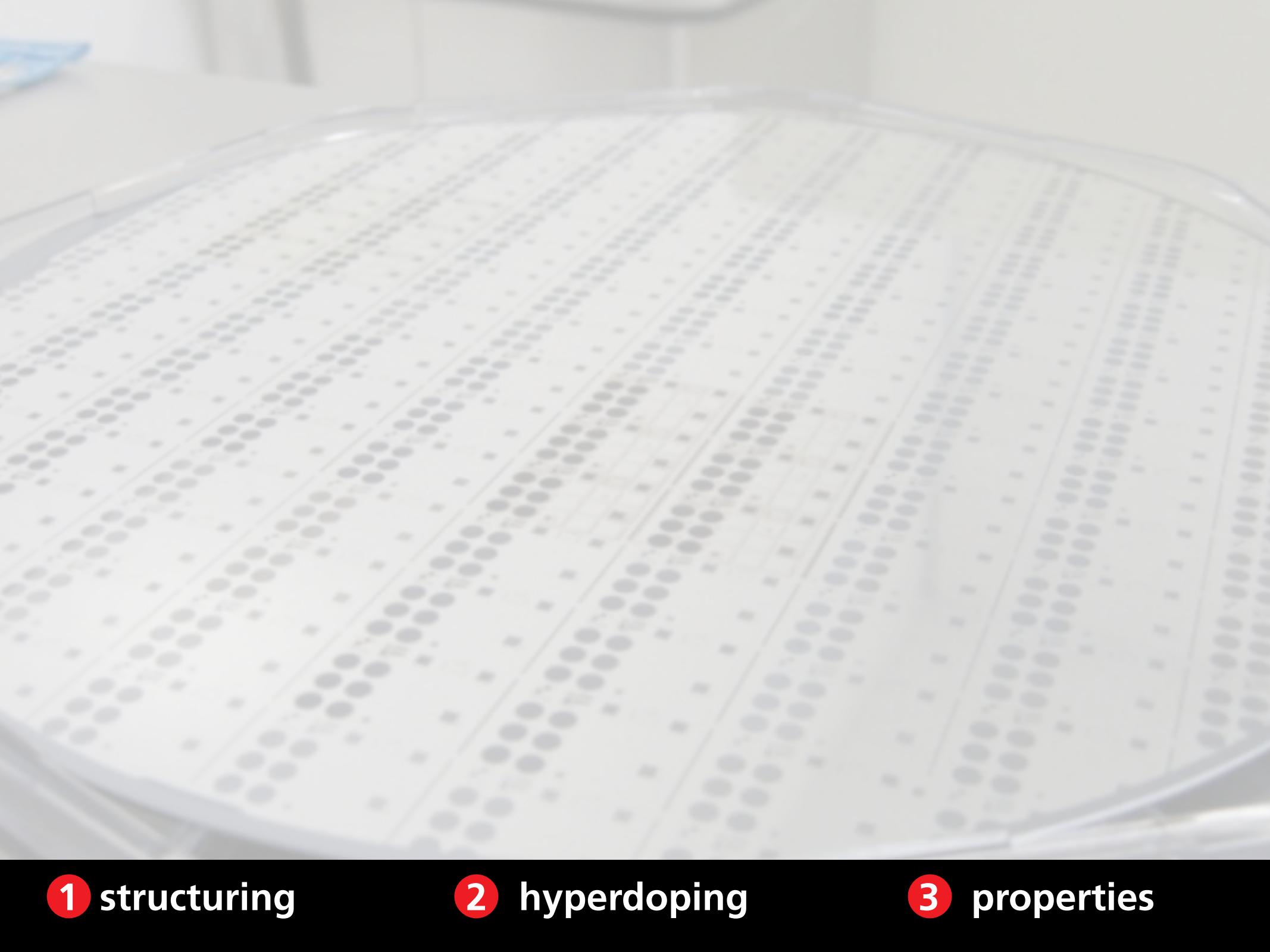


1 structuring

2 hyperdoping

## What we learned

- melting via ultrafast lattice destabilization (athermal)
- resolidification velocity in range of critical velocity for amorphization (15 m/s)
- resolidification can be controlled by fluence (high fluence yields lower velocity)
- dopant profile can be described by classical diffusion
- dopant profile can be controlled and flattened

The background of the slide features a subtle, abstract pattern of light gray diagonal lines and small circular dots, creating a sense of depth and texture.

**1** structuring

**2** hyperdoping

**3** properties

# Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin

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Hyperdoping has emerged as a promising method for designing semiconductors with unique optical and electronic properties, although such properties currently lack a clear microscopic explanation. Combining computational and experimental evidence, we probe the origin of sub-band-gap optical absorption and metallicity in Se-hyperdoped Si. We show that sub-band-gap absorption arises from direct defect-to-conduction-band transitions rather than free carrier absorption. Density functional theory predicts the Se-induced insulator-to-metal transition arises from merging of defect and conduction bands, at a critical concentration, demonstrate that correlation is important to describing the transition accurately, and suggest that it is a classic impurity-driven Mott transition.

PACS numbers: 71.30.+h, 61.72.sd, 73.61.Cw, 78.20.Bh

Of all the experimentally measurable physical properties of materials, electronic conductivity exhibits the largest variation, spanning a factor of  $10^{31}$  from the best metals to the strongest insulators [1]. Over the last century, the puzzle of why some materials are conductors and others insulators, and the mechanisms underlying the transformation from one to the other, have been carefully scrutinized; yet even after such a vast body of research over such a long period, the subject remains the object of controversy. In 1956, Mott introduced a model for the insulator-to-metal transition (IMT) in doped semiconductors, in which long-ranged electron correlations are the driving force [2]. Hyperdoping (doping beyond the solubility limit) creates a new materials playground to explore defect-mediated IMTs in semiconductors. In this Letter, we identify a defect-induced IMT in silicon hyperdoped with selenium to concentrations exceeding  $10^{20} \text{ cm}^{-3}$  (compared to the equilibrium solubility limit [ $5 \times 10^{16} \text{ cm}^{-3}$ ]) and we detailed nature of the transition. We find that the IMT is transition and most resembles a Mott transition. Additionally, we

silicon appears to justify such interest. While isolated S and Se dopants are well-established deep double donors in silicon [3,14], the enhanced optical properties of hyperdoped silicon (in which these chalcogenic impurities are present at much higher concentrations) are not yet well understood. Further, unlike the prototypical system of phosphorus-doped silicon for which the IMT has been extensively studied and characterized [15,16], there are very few studies of an IMT resulting from deep defects such as chalcogens [17].

We prepared Se-doped silicon (Se:Si) samples using ion implantation followed by nanosecond pulsed-laser melting (PLM) and rapid resolidification. The PLM process enables chalcogen doping with concentrations exceeding 1% atomic; such samples exhibit unexplained optical properties including broad, featureless absorption of photons with energy lower than the band gap of silicon [9]. Silicon substrates (boron doped,  $\rho \approx 25 \Omega \text{ cm}$ ) were ion implanted with Se to nominal doses of  $3 \times 10^{15}$  and  $1 \times 10^{16} \text{ cm}^2$  using an ion beam energy of 176 keV. The implanted samples were exposed to four laser pulses (fluences of 1.7, 1.7, 1.7 and  $1.8 \text{ J cm}^{-2}$ ). This fluence regimen results in a slightly shallower dopant profile, and higher Se concentration, than reported previously [18]. The  $10^{16} \text{ cm}^2$  sample is electrically isolated from the crystalline substrate, as measured by capacitance-voltage (C-V) measurement.

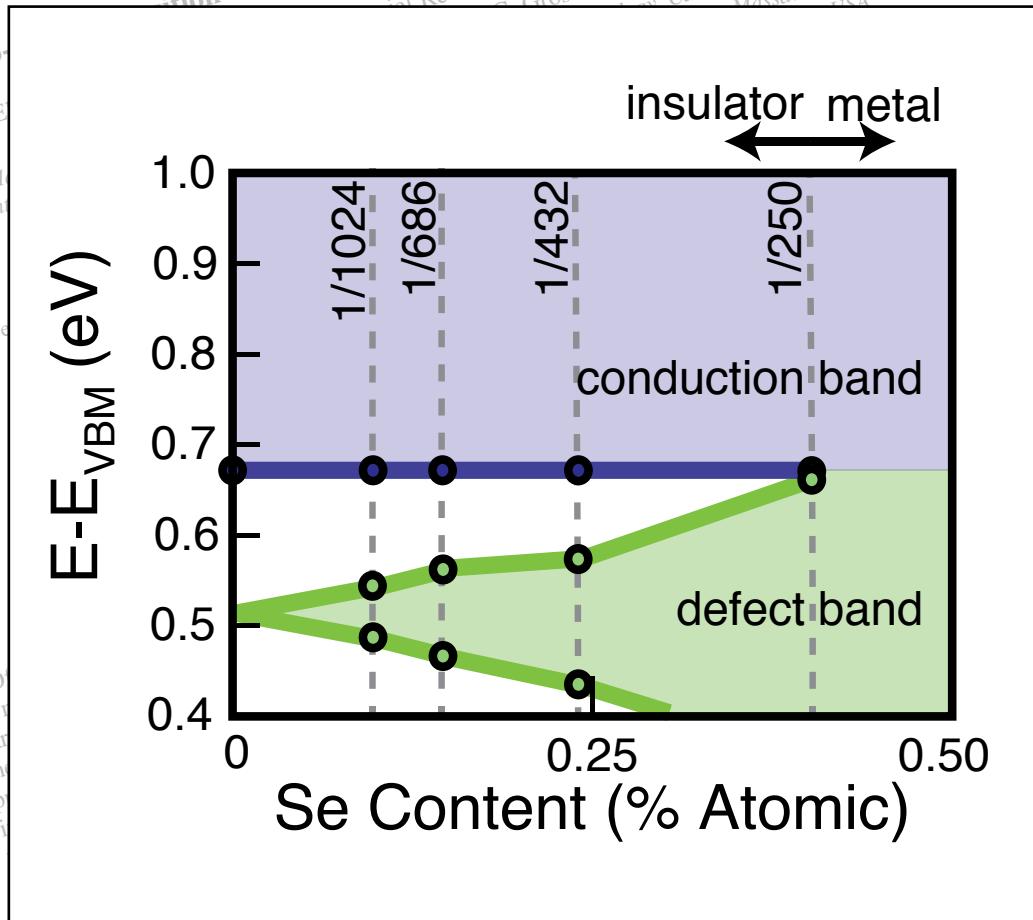
Ertekin et al., Phys. Rev. Lett. 108, 026401 (2012)

# intermediate band

PRL 108, 026401 (2012)

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PHYSICAL REVIEW LETTERS  
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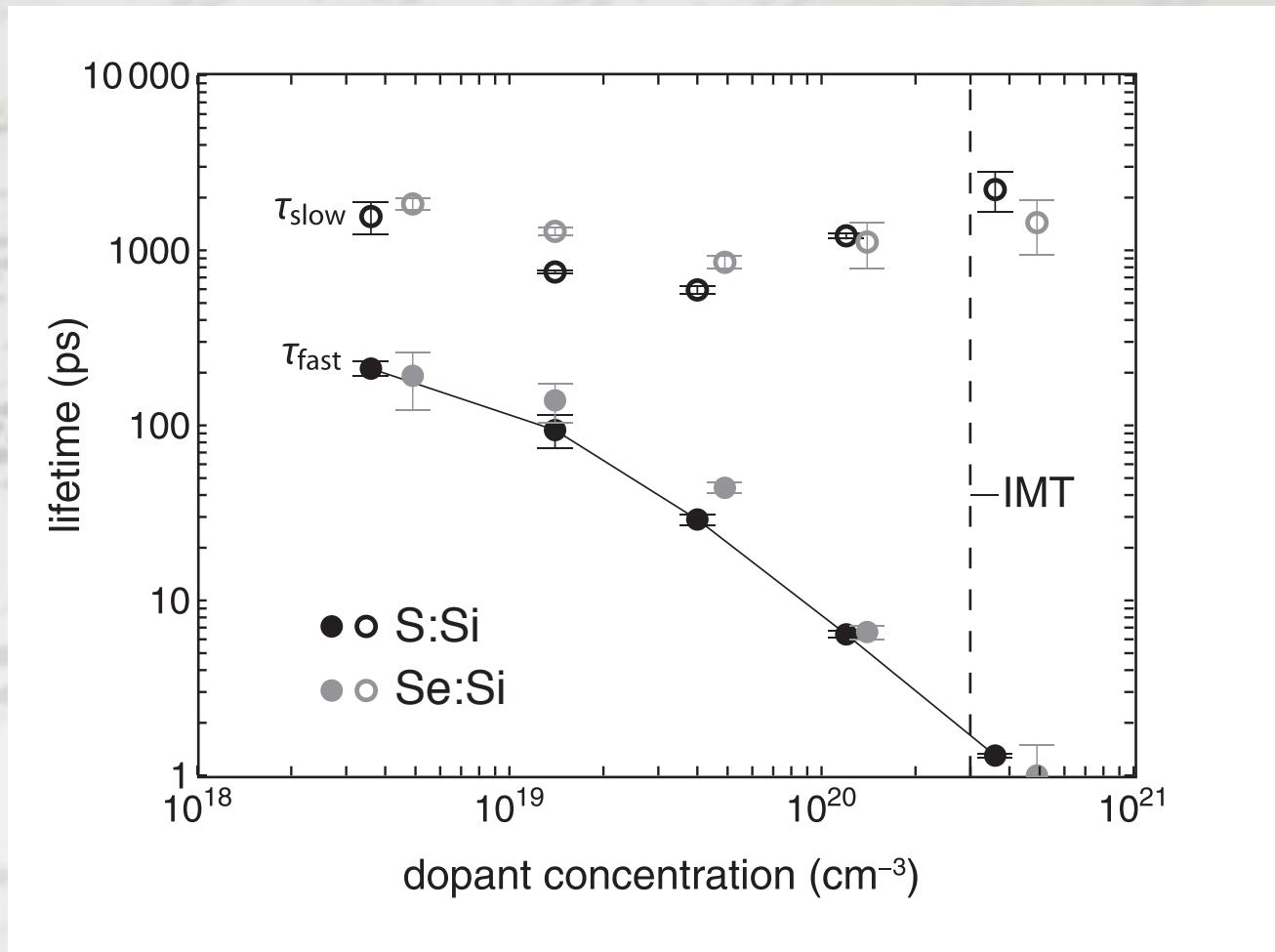
Ertekin et al., Phys. Rev. Lett. 108, 026401 (2012)

1 structuring

2 hyperdoping

3 properties

# carrier lifetime



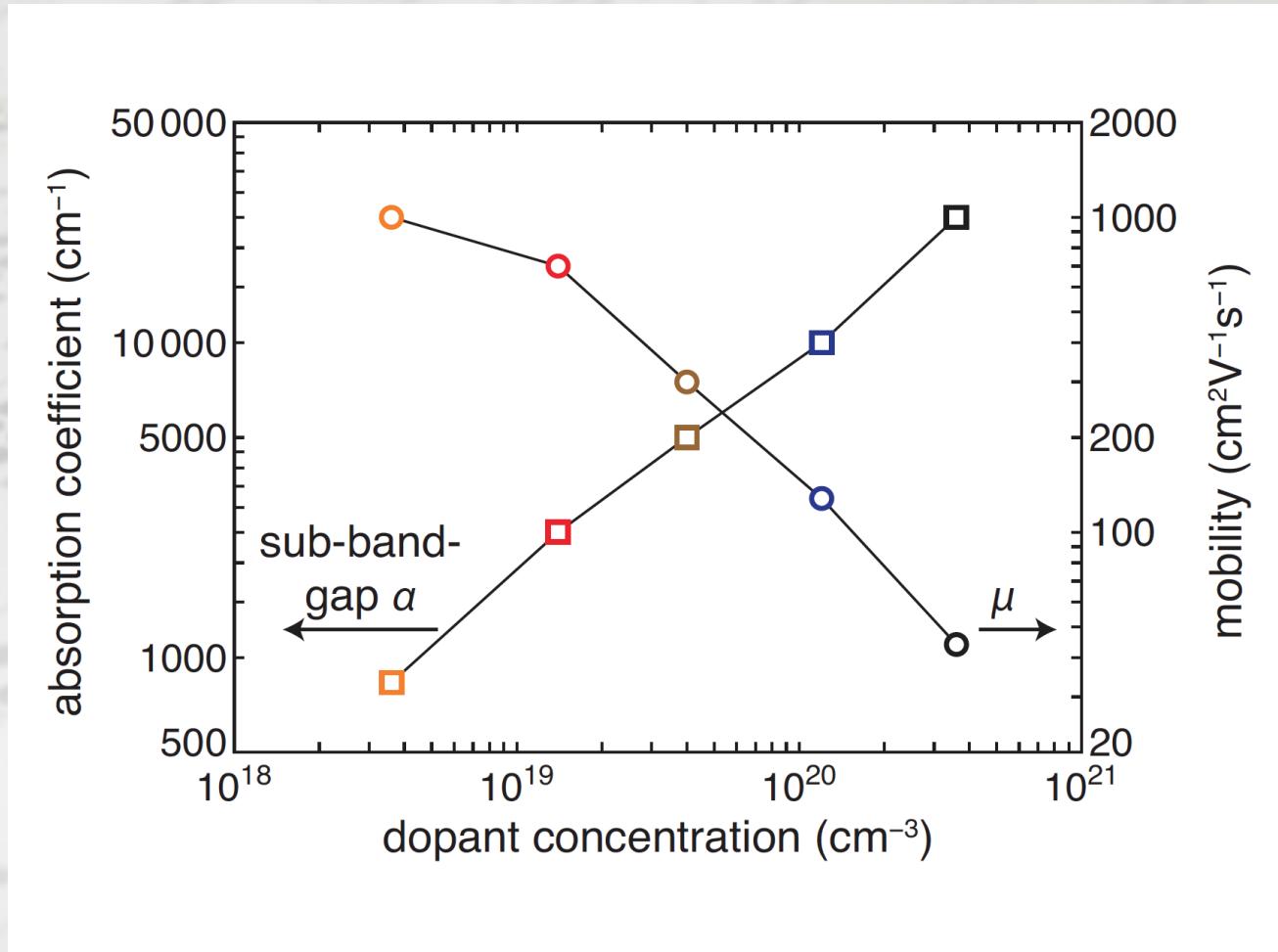
Sher et al., Appl. Phys. Lett. (2014)

1 structuring

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# absorption coefficient and mobility



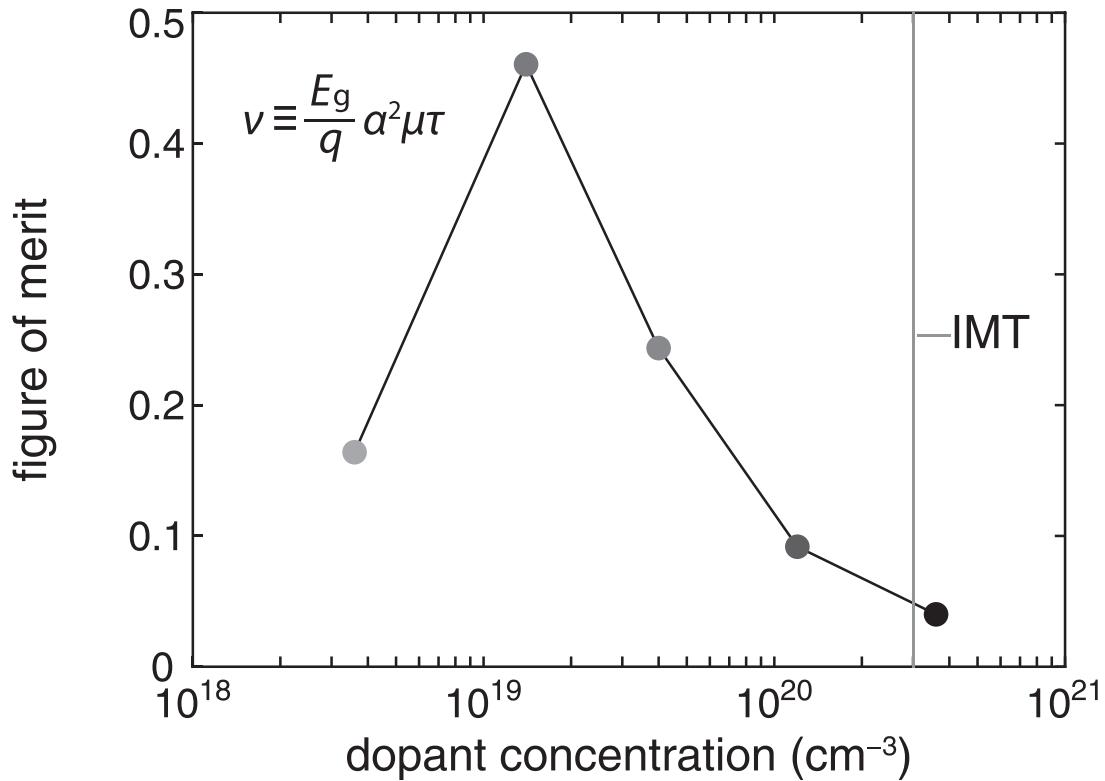
Sher et al., Appl. Phys. Lett. (2014)

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# carrier transport



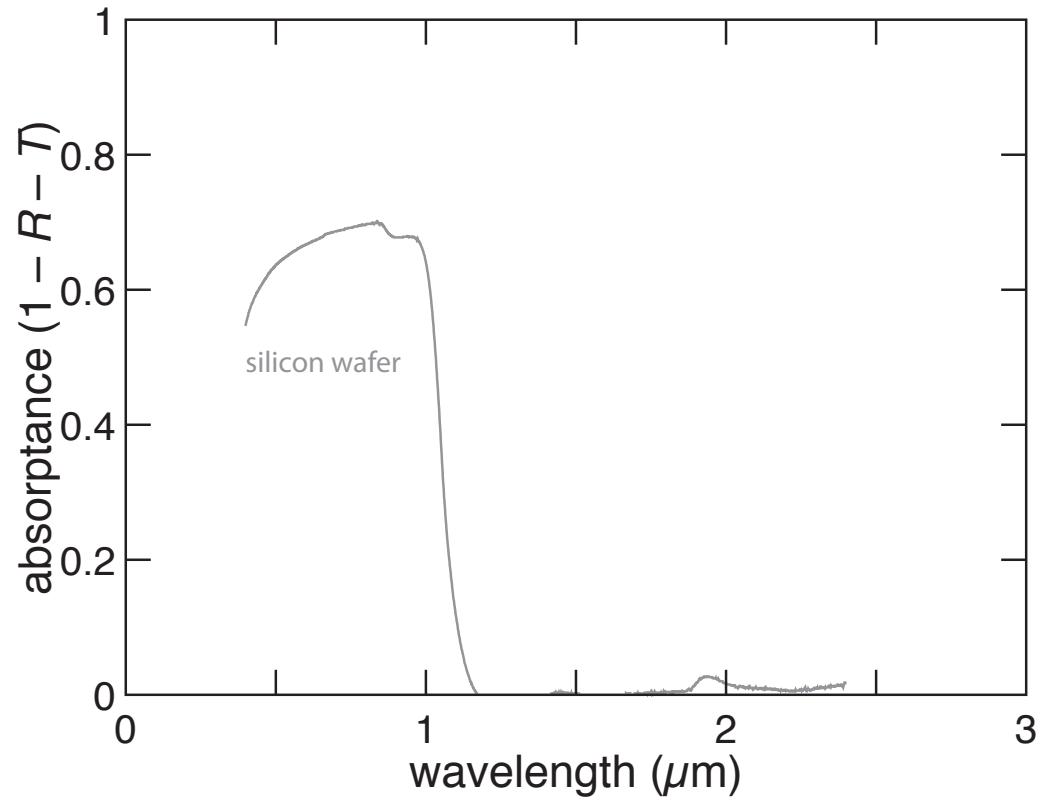
Sher et al., Appl. Phys. Lett. (2014)

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3 properties

# optical deactivation/reactivation

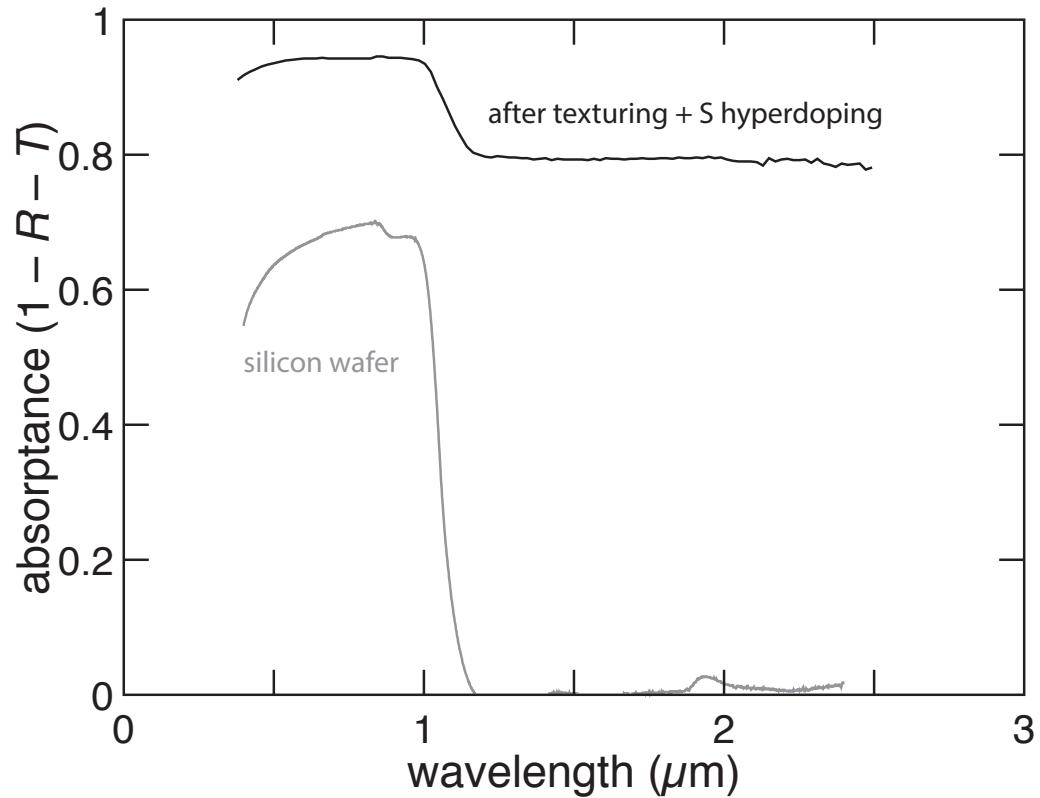


1 structuring

2 hyperdoping

3 properties

# optical deactivation/reactivation



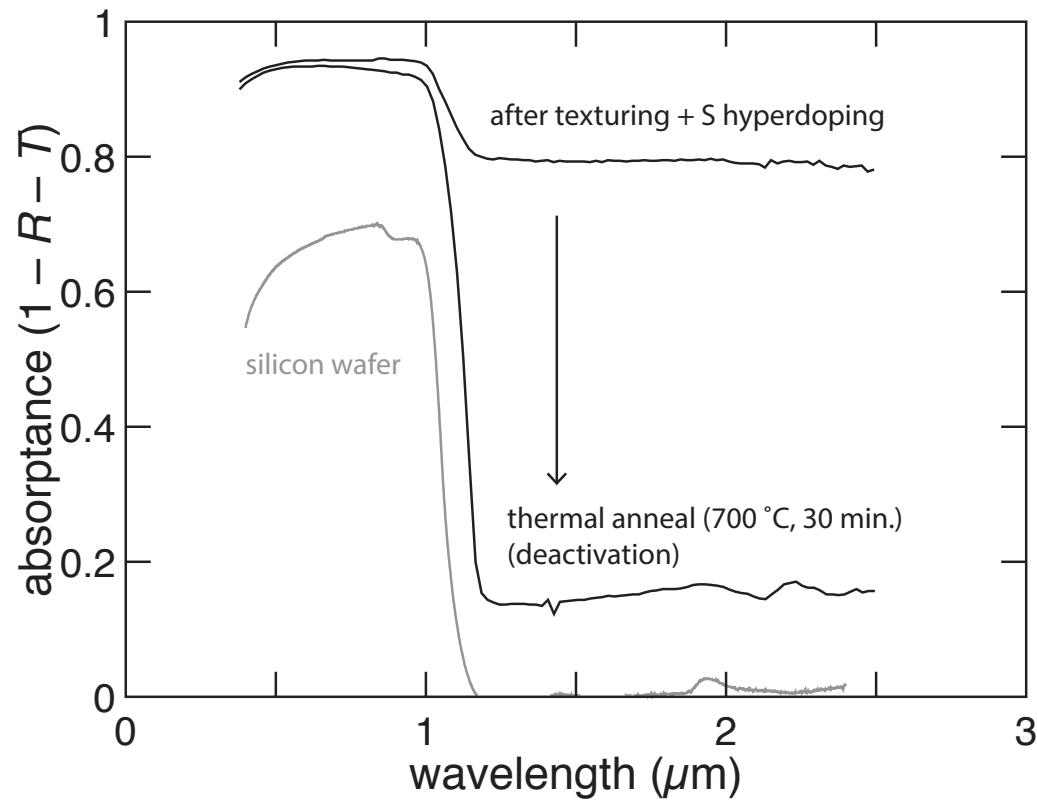
Franta et al., Appl. Phys. Lett. 118 (2015)

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# optical deactivation/reactivation



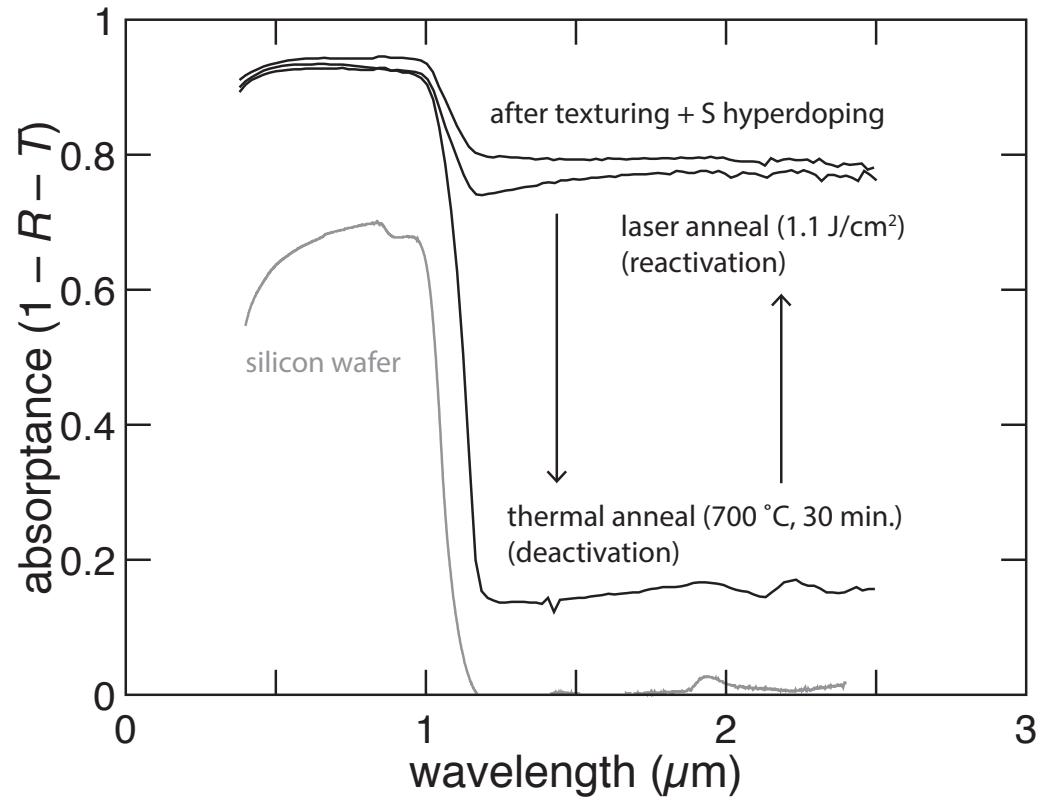
Franta et al., Appl. Phys. Lett. 118 (2015)

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# optical deactivation/reactivation



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# optical deactivation/reactivation

## What we learned

- carrier lifetime 1–100 ps
- lifetime decreases with increasing dopant concentration
- optical activity can be reversibly activated and deactivated
- dopant behavior depends on cooling rate

# Work Supported

## Publications

- Franta, B. Fabrication techniques for femtosecond laser textured and hyperdoped silicon. Doctoral dissertation, Harvard University.
- Franta, B., D. Pastor, H. Gandhi., P. Rekemeyer., S. Grade ak, M. Aziz, E. Mazur . Increasing the crystallinity and optical absorptance of hyperdoped black silicon using nanosecond laser annealing. *Journal of Applied Physics*, 2015. 118, p. 225303.
- Fabbri, F., Lin, Y.-T., Bertoni, G., Rossi, F., Smith, M. Gradecak, S., Mazur, E., Salviati, G. Origin of the visible emission of black silicon microstructures. *Applied Physics Letters*. 107, p. 021907-1-021907-4.
- Lin, Y.-T., et al., Creating femtosecond-laser-hyperdoped silicon with a homogeneous doping profile. *Applied Physics Letters*, 2015. 106(6): p. 062105.
- Lin, Yu-Ting. 2014. Femtosecond-laser hyperdoping and texturing of silicon for photovoltaic applications. Doctoral dissertation, Harvard University.
- Smith, M., Sher, M.-J., Franta, B., Lin, Y.,-T., Mazur, E., Gradecak, S. Improving Dopant Incorporation During Femtosecond-Laser Doping of Si with a Se Thin-Film Dopant Precursor. *Applied Physics A*. 114, p. 1009-1016.

## Patents/disclosures

- Aziz, M., Franta, B., Mazur, E, Pastor, D., US Patent Application 62/166,617
- Aziz, M., Franta, B., Mazur, E, Pastor, D., PCT/US 15/60385
- Mazur, E., Gandhi, H., ROI Oct 2014

## **Future work**

- **time-resolved measurements of Si structures**
- **tomographic measurements of reactivated dopants**
- **intermediate band formation in Ge**
- **ultrafast laser texturing of Ge**



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