Femtosecond laser-assisted microstructuring of silicon for novel detector, sensing, and display technologies

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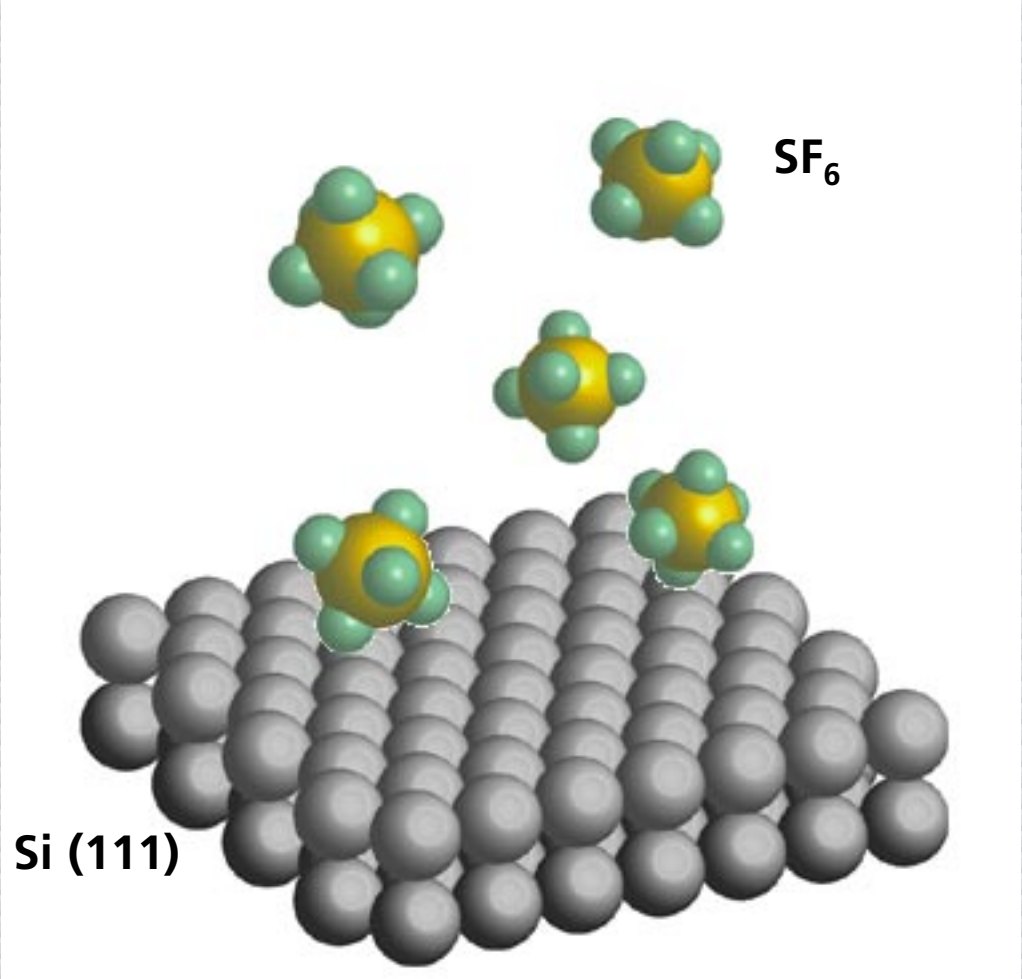
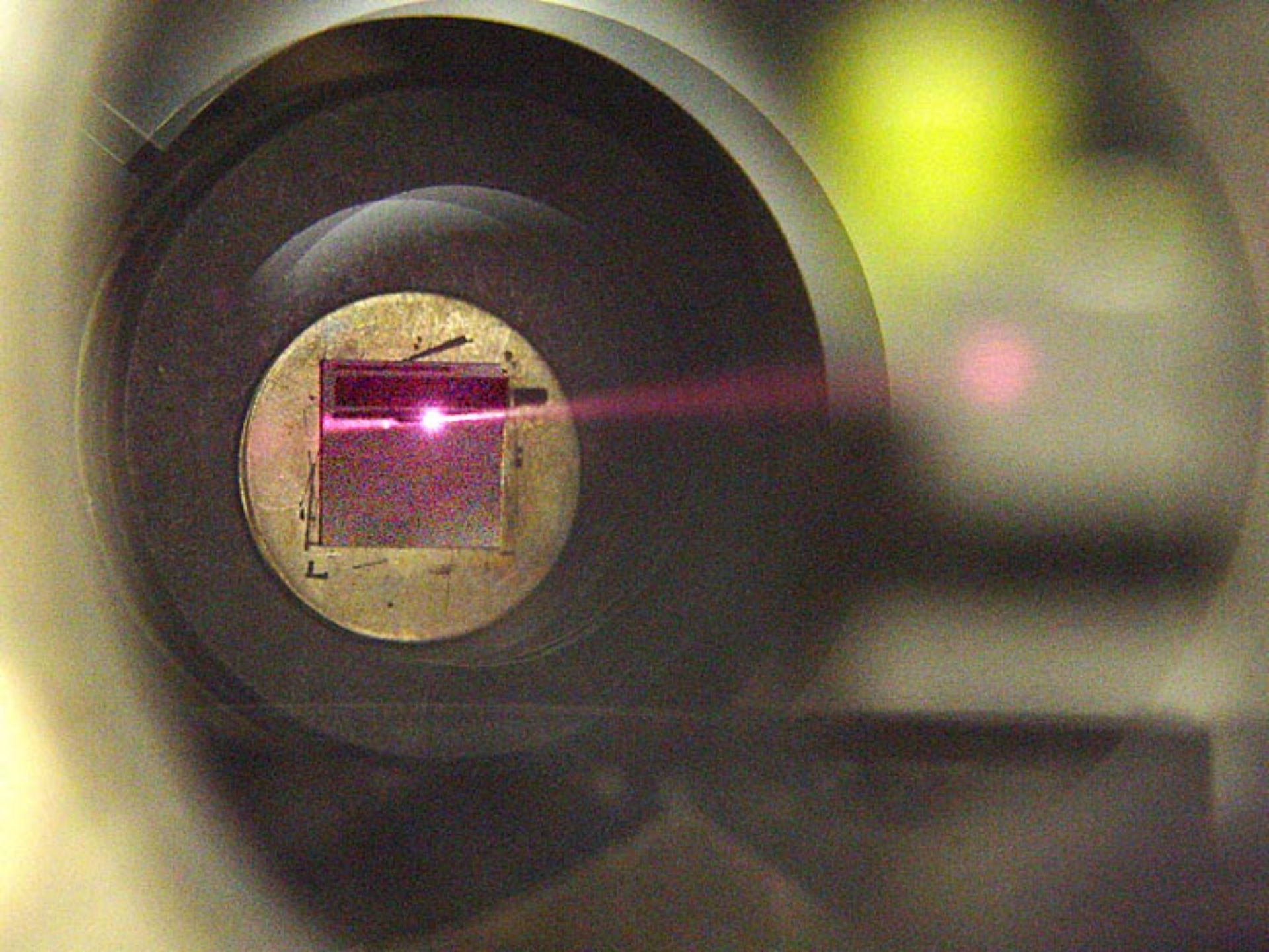
Army Science Board FY03 Summer Study
Washington, DC, 18 March 2003

Introduction



irradiate with 100-fs 10 kJ/m^2 pulses



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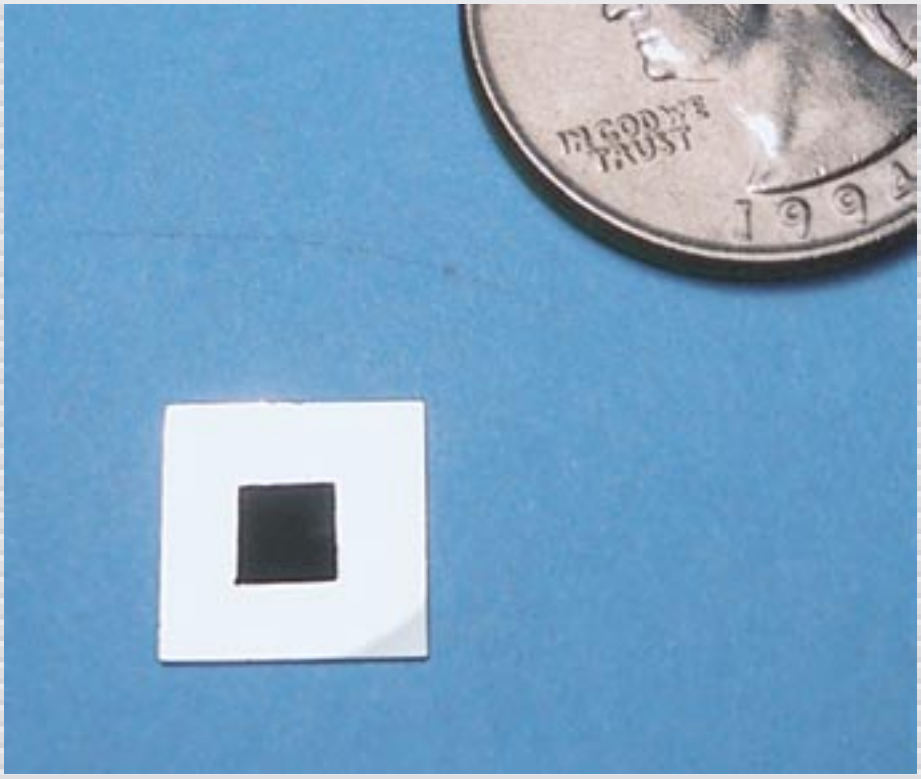
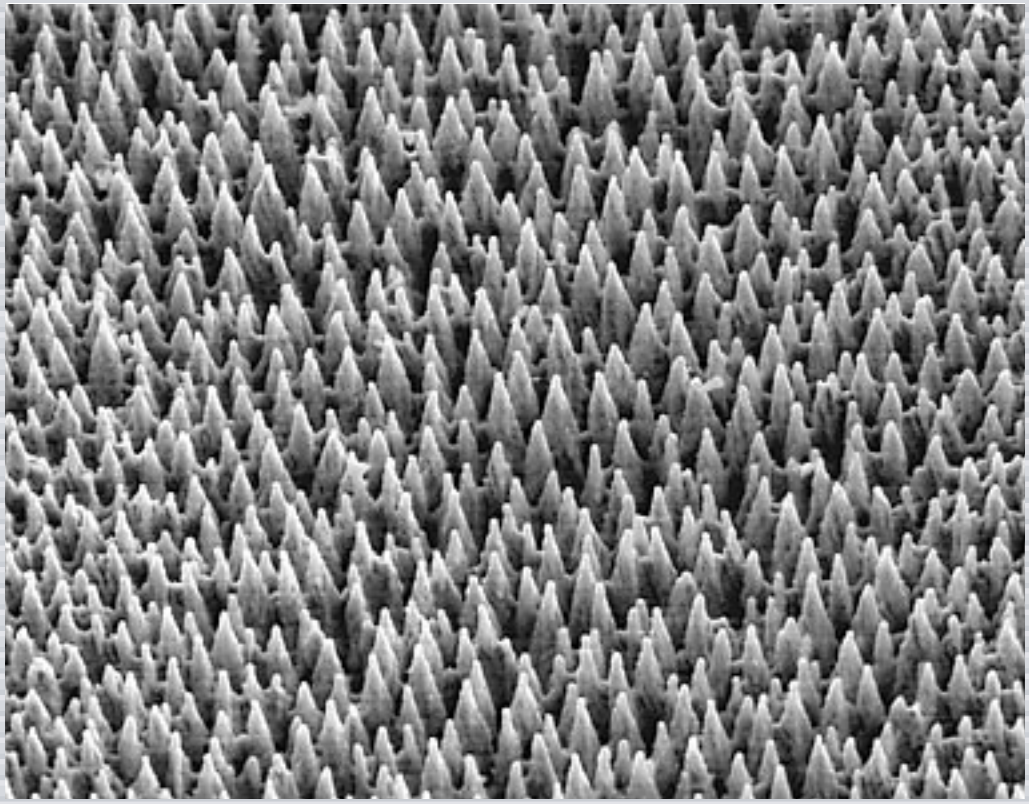


‘black silicon’

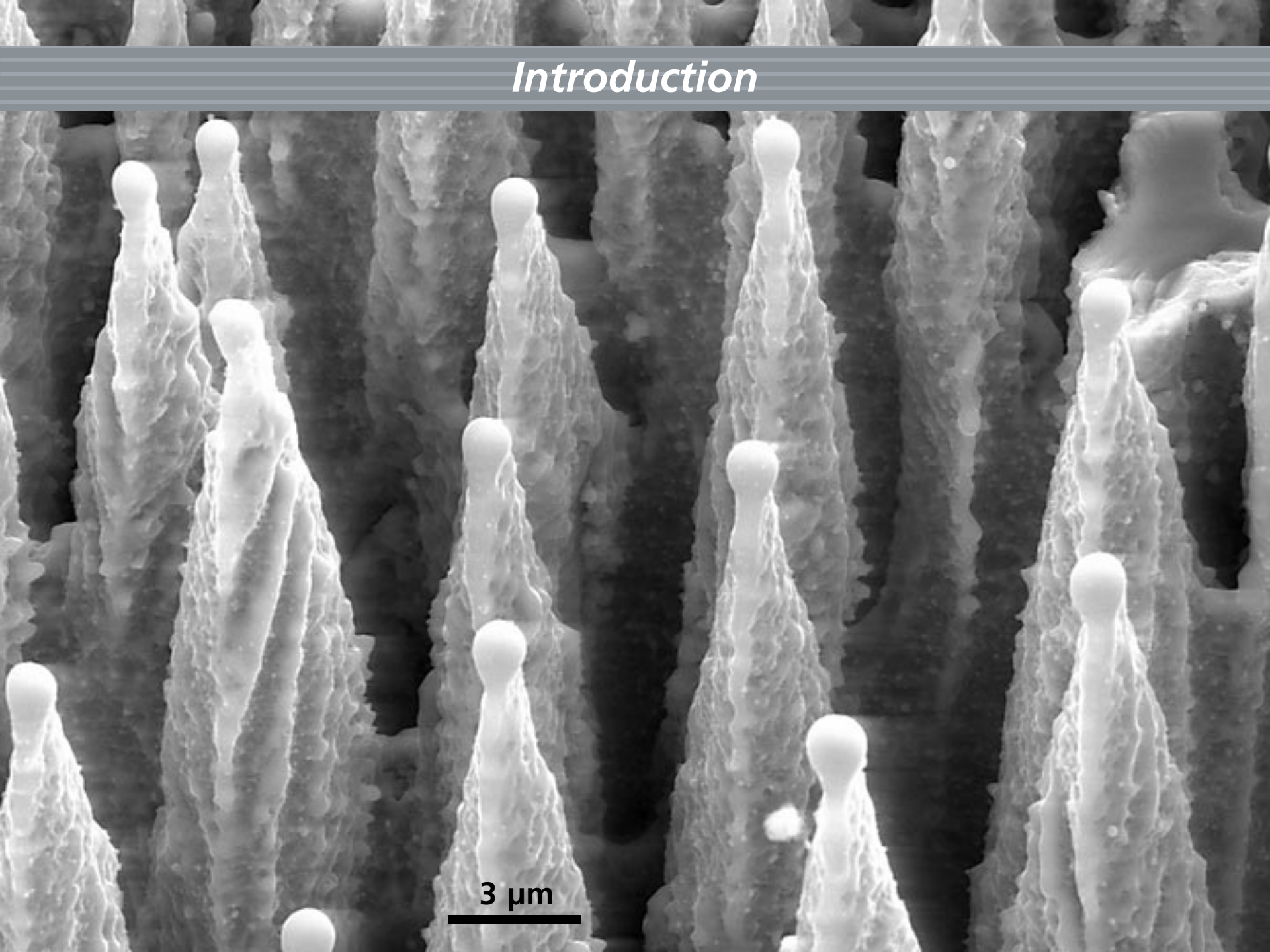
***Appl. Phys. Lett.* 73, 1673 (1998)**

Introduction



20 μm

Introduction



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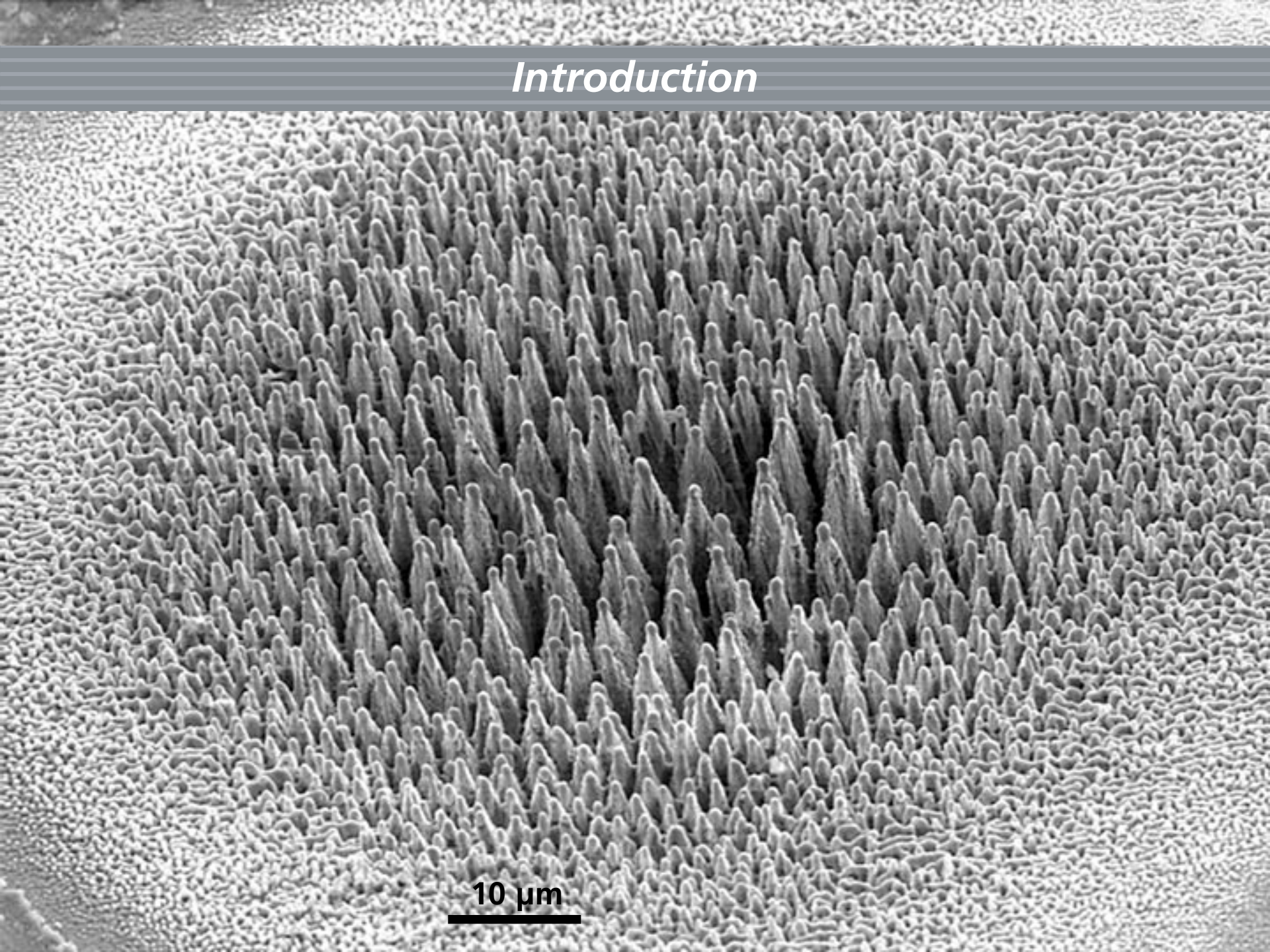

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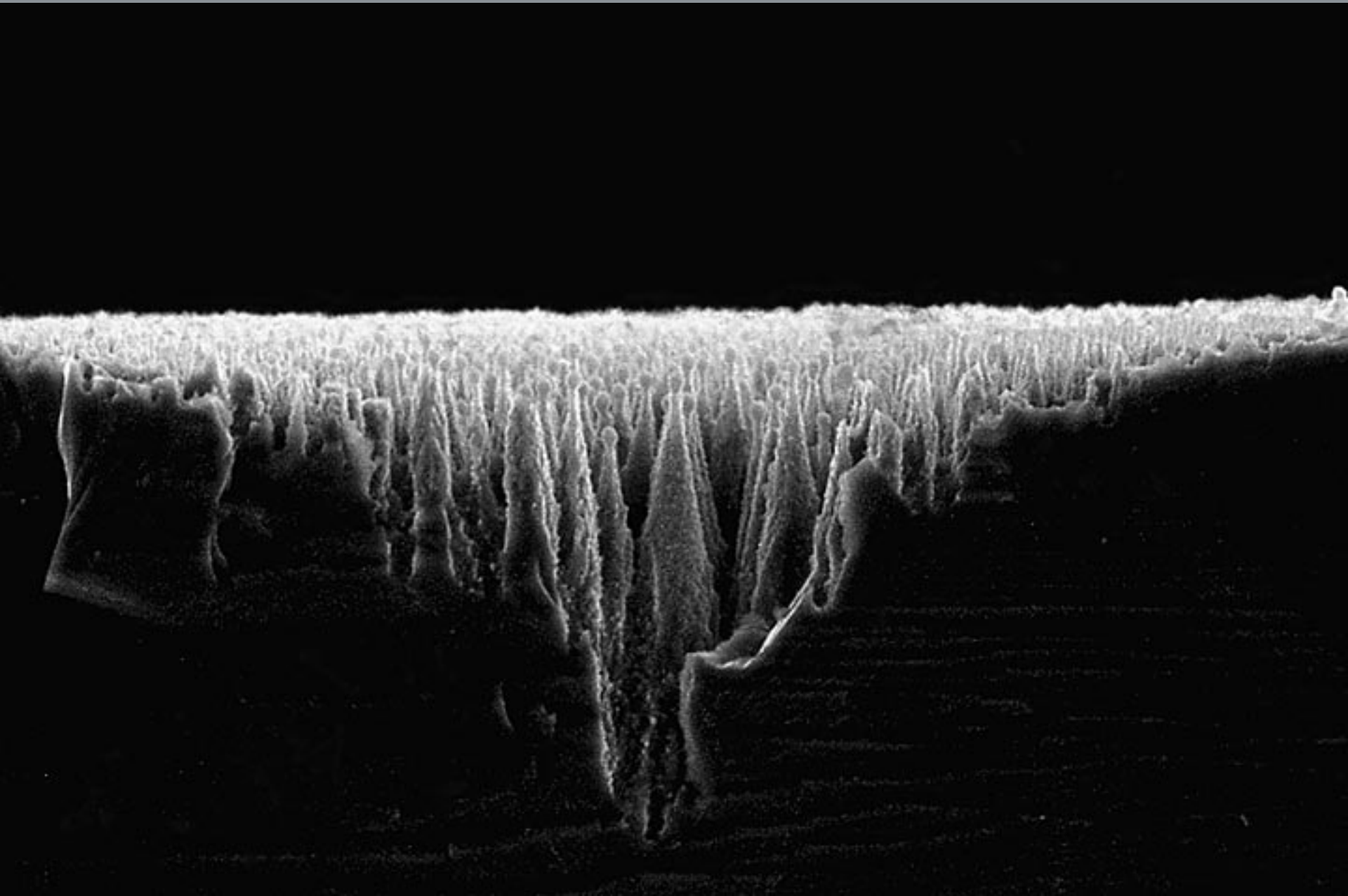

Introduction

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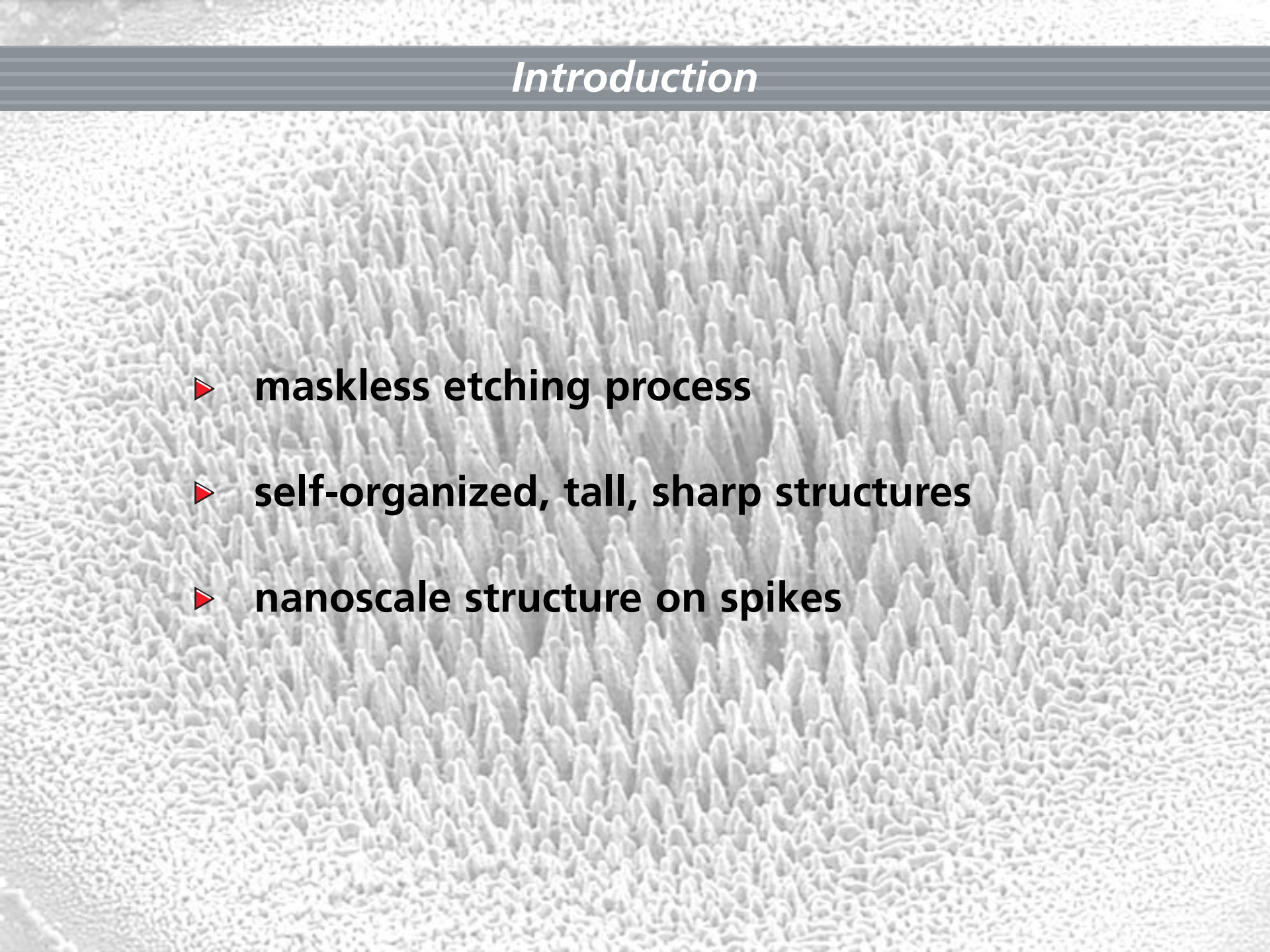
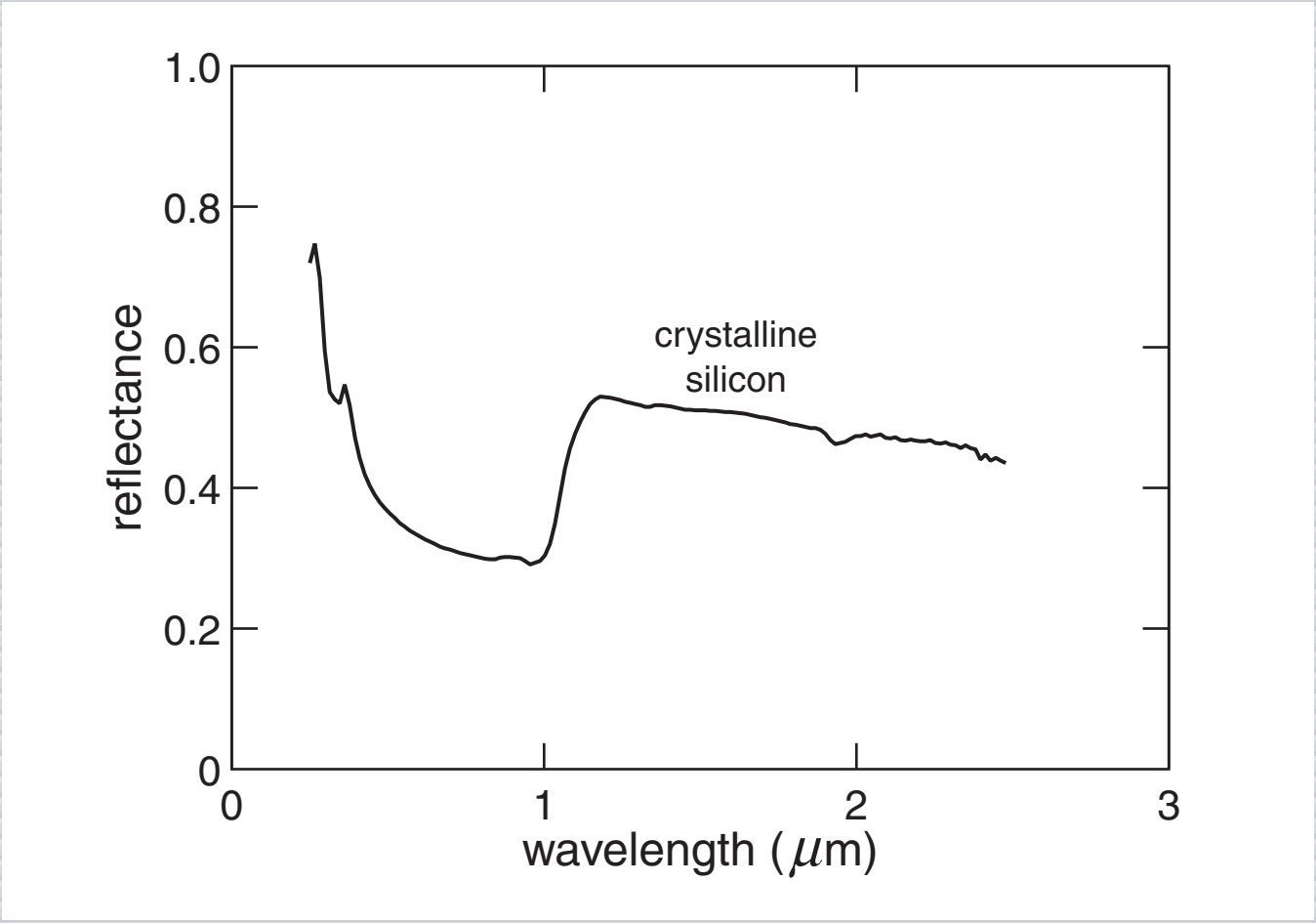


- **maskless etching process**
- **self-organized, tall, sharp structures**
- **nanoscale structure on spikes**

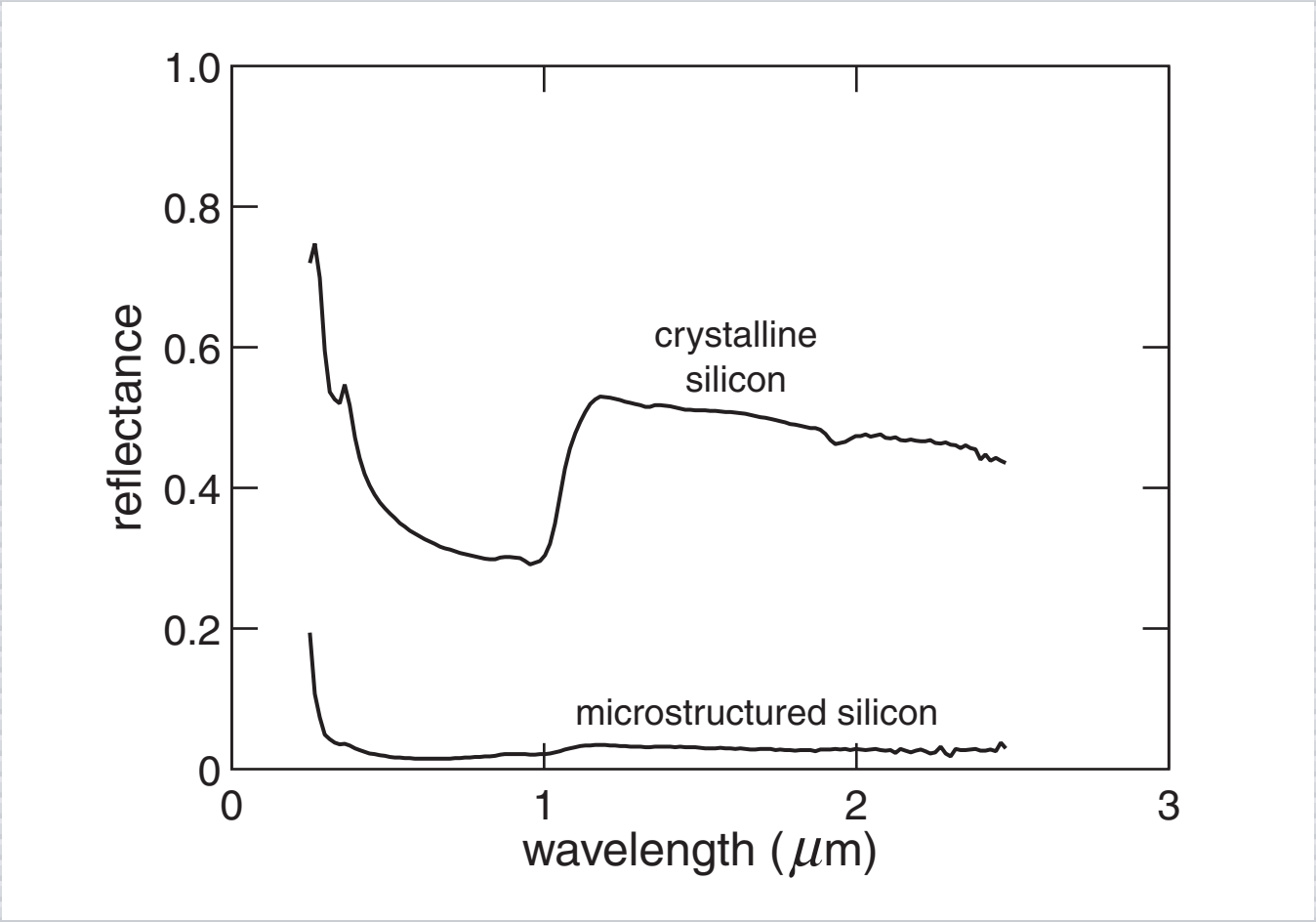
Outline

- Properties
- Structural and chemical analysis
- Outlook

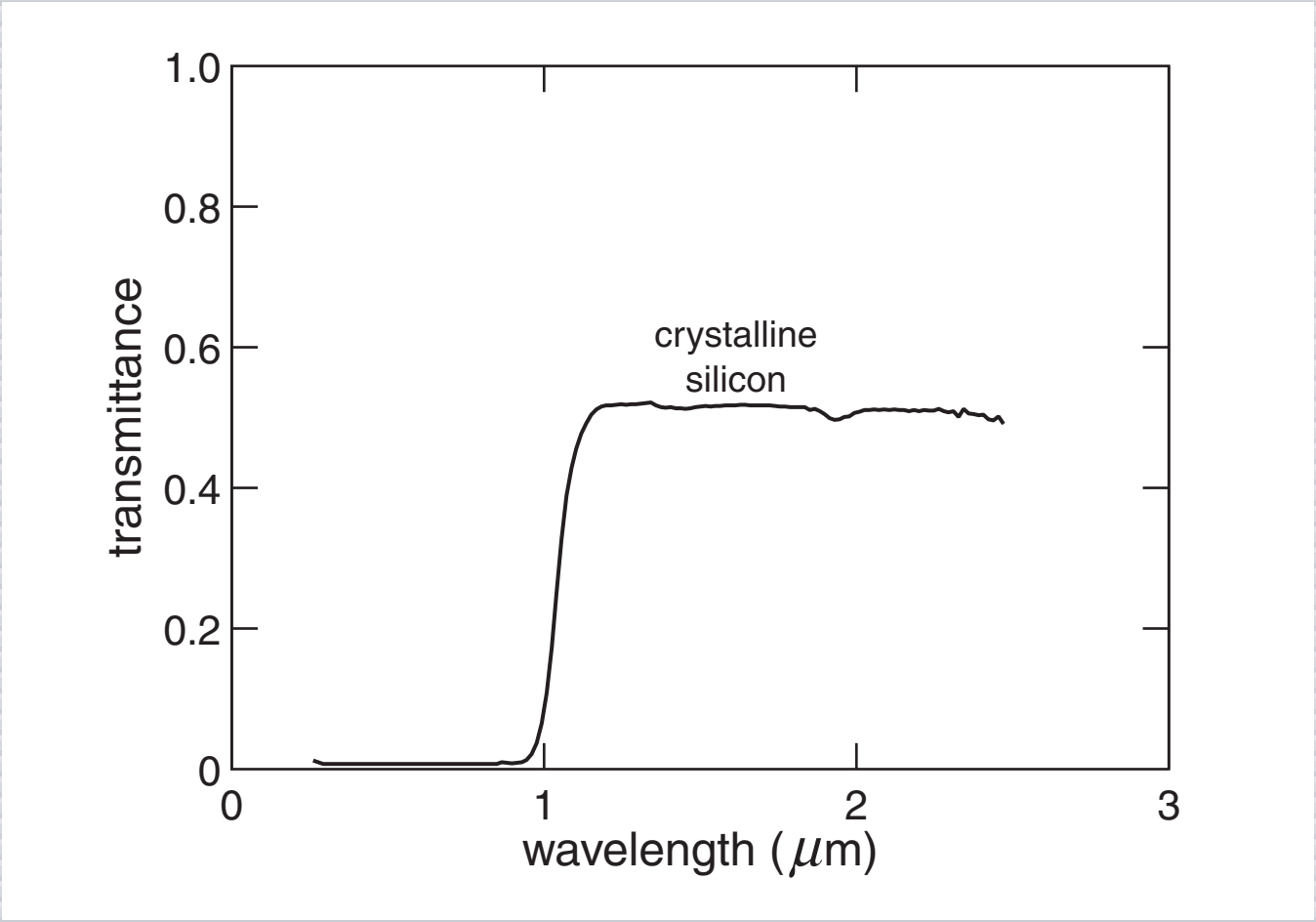
reflectance (integrating sphere)



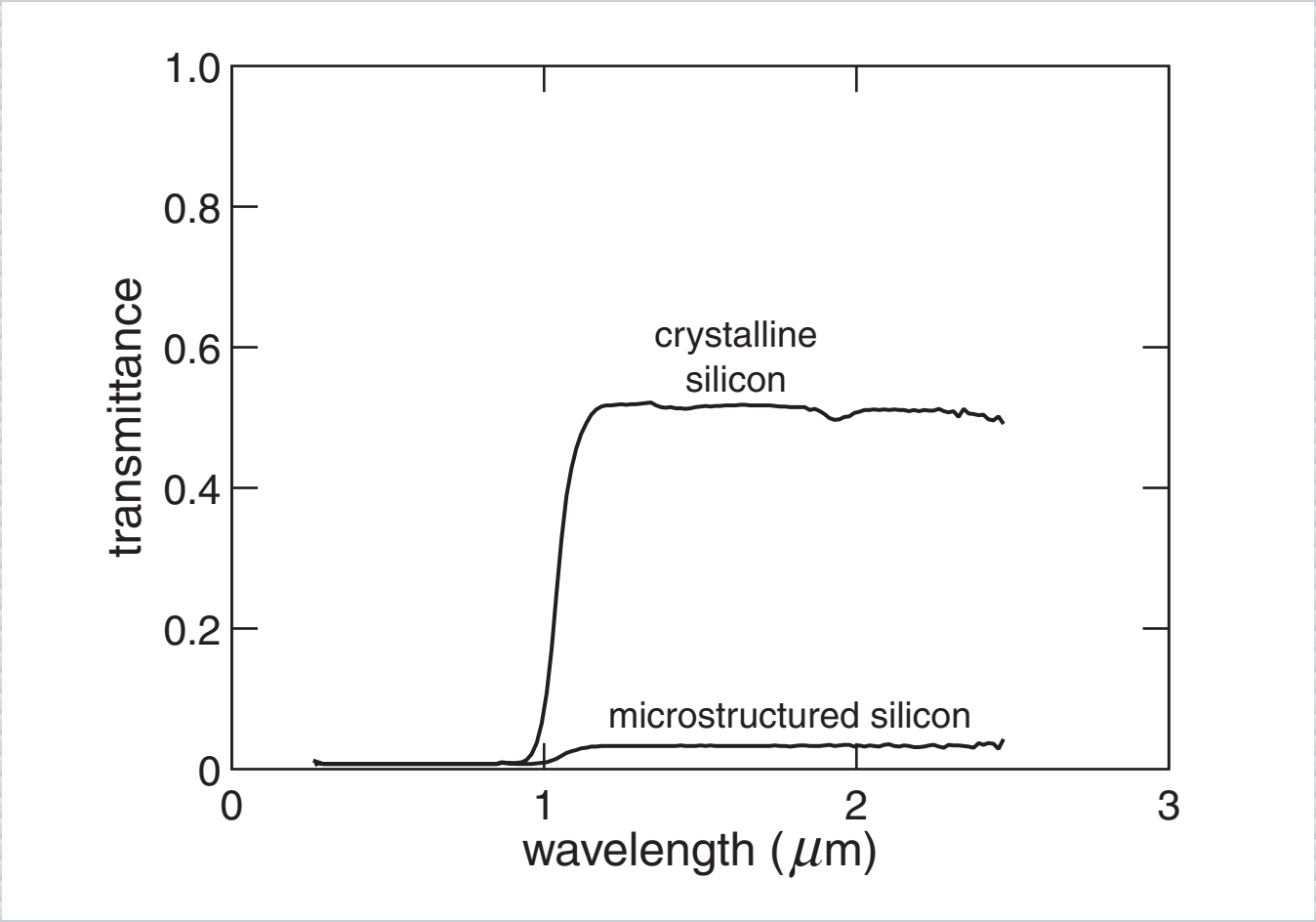
reflectance (integrating sphere)



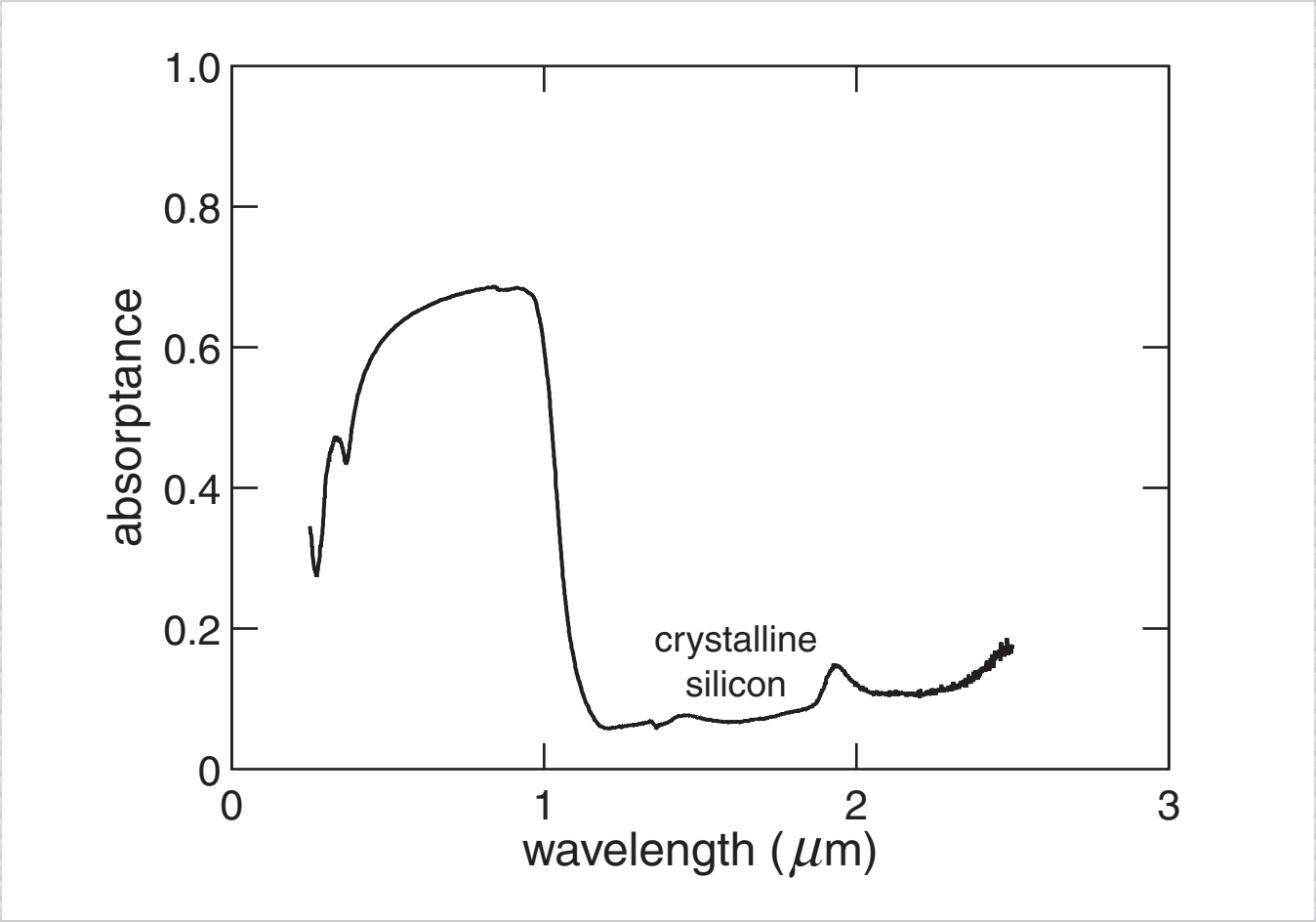
transmittance (integrating sphere)



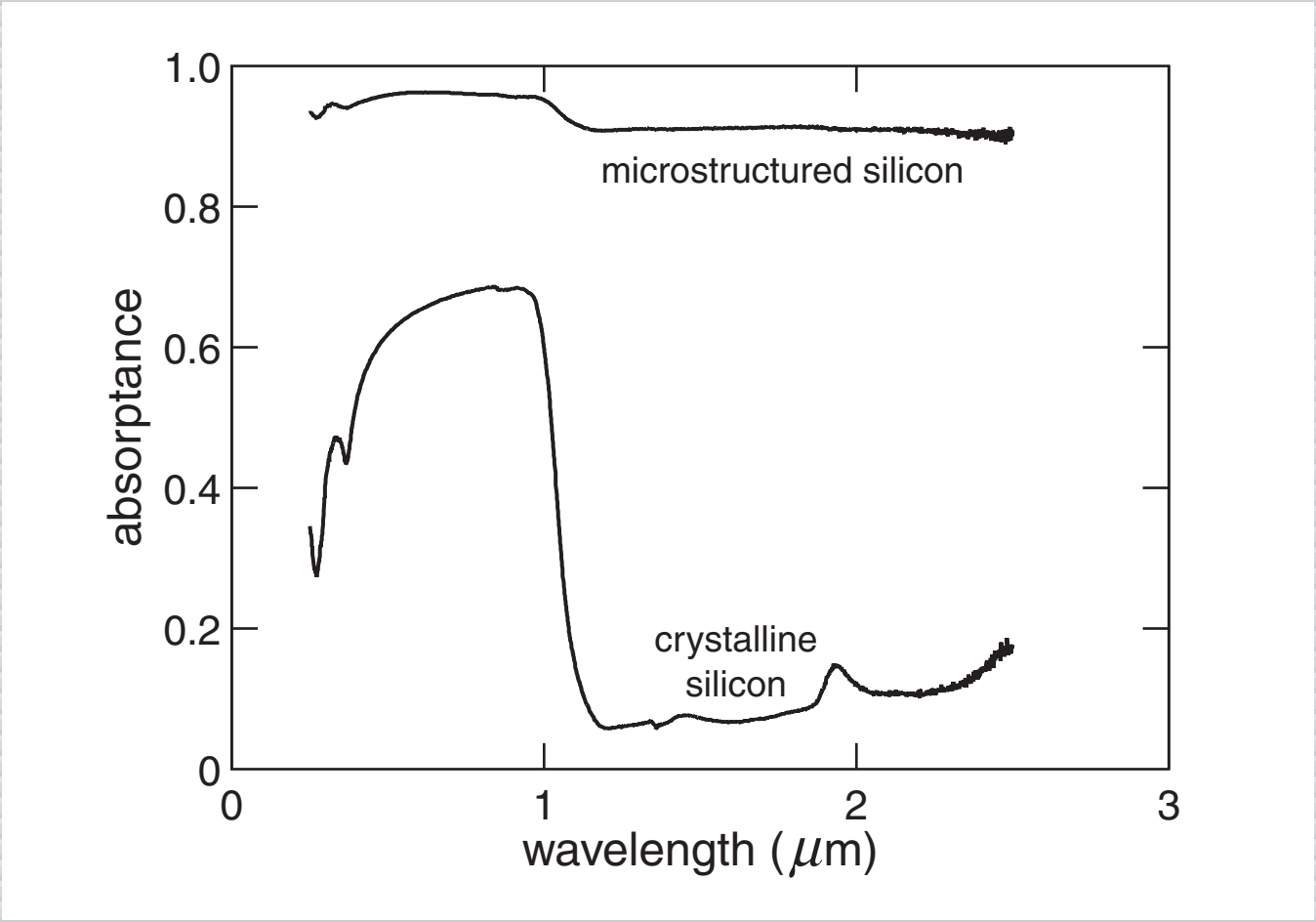
transmittance (integrating sphere)



absorptance (1 – *R* – *T*)



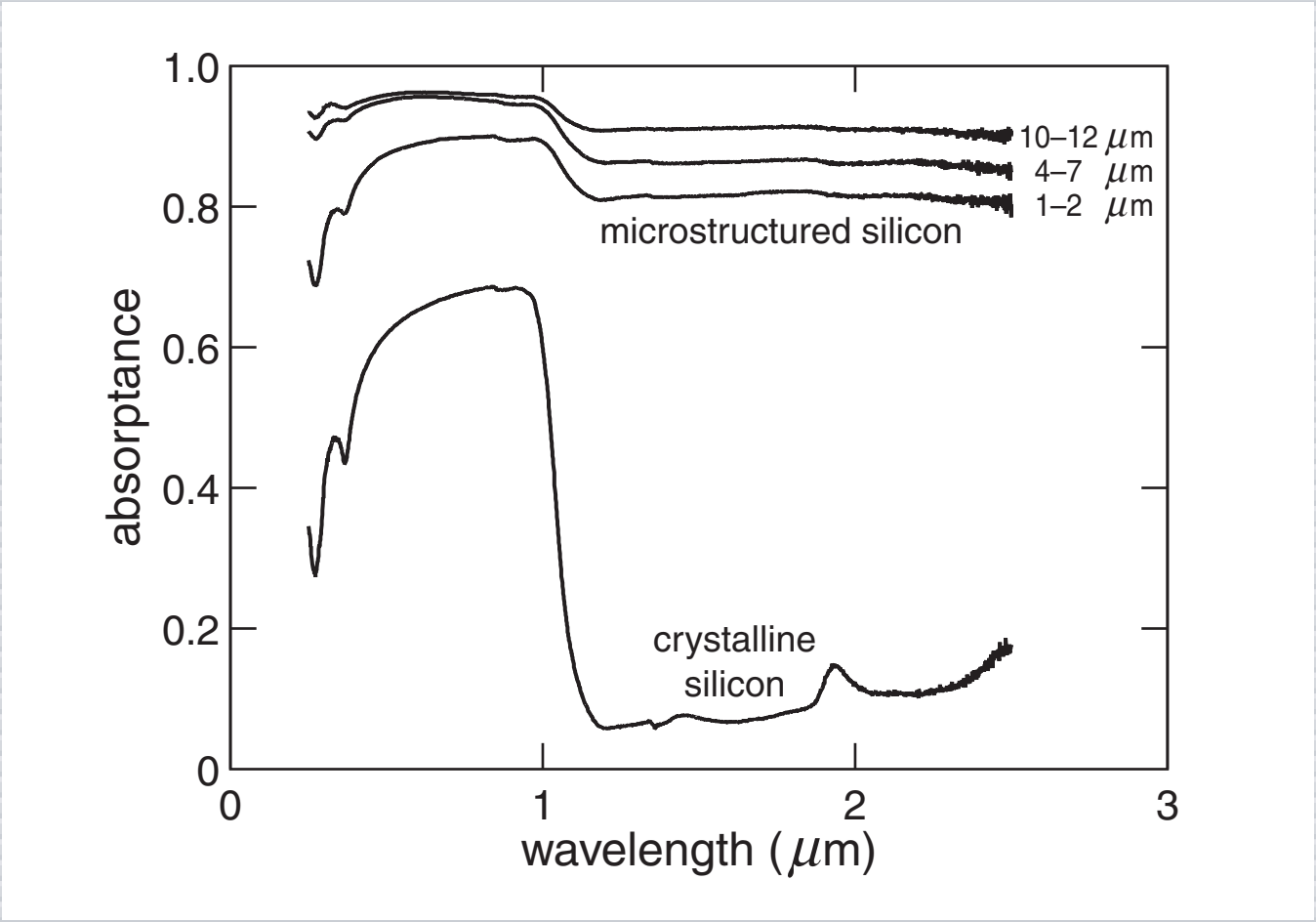
absorptance (1 – *R* – *T*)



Appl. Phys. Lett. **78, 1850 (2001)**

Properties

absorptance (1 – *R* – *T*)



Appl. Phys. Lett. **78, 1850 (2001)**

Properties

Points to keep in mind:

- **near unity absorption**
- **sub-band gap absorption**
- **IR photoelectron generation**

Properties

Points to keep in mind:

- **near unity absorption**
- **sub-band gap absorption**
- **IR photoelectron generation**

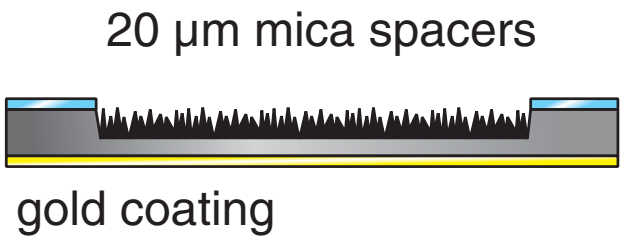
can spikes be used as field emitters?

field emission setup

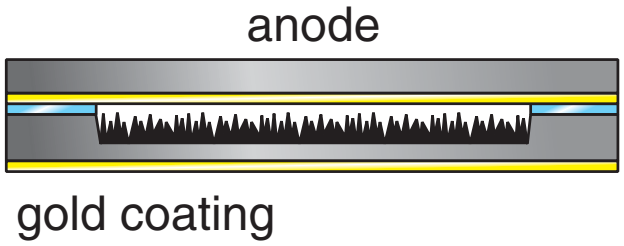
field emission setup

gold coating

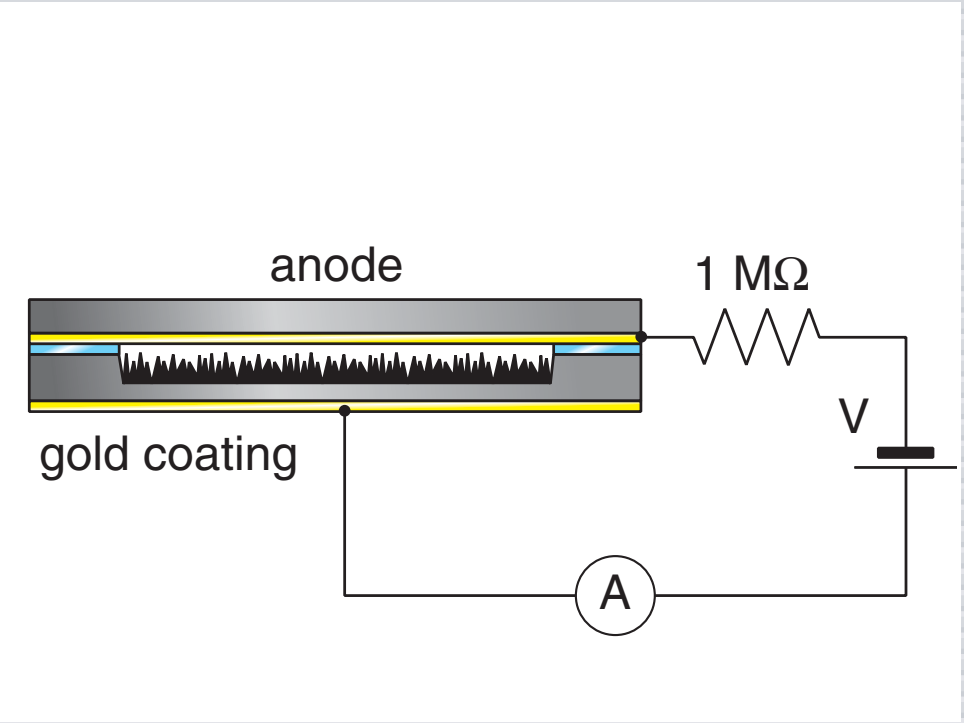
field emission setup



field emission setup



field emission setup



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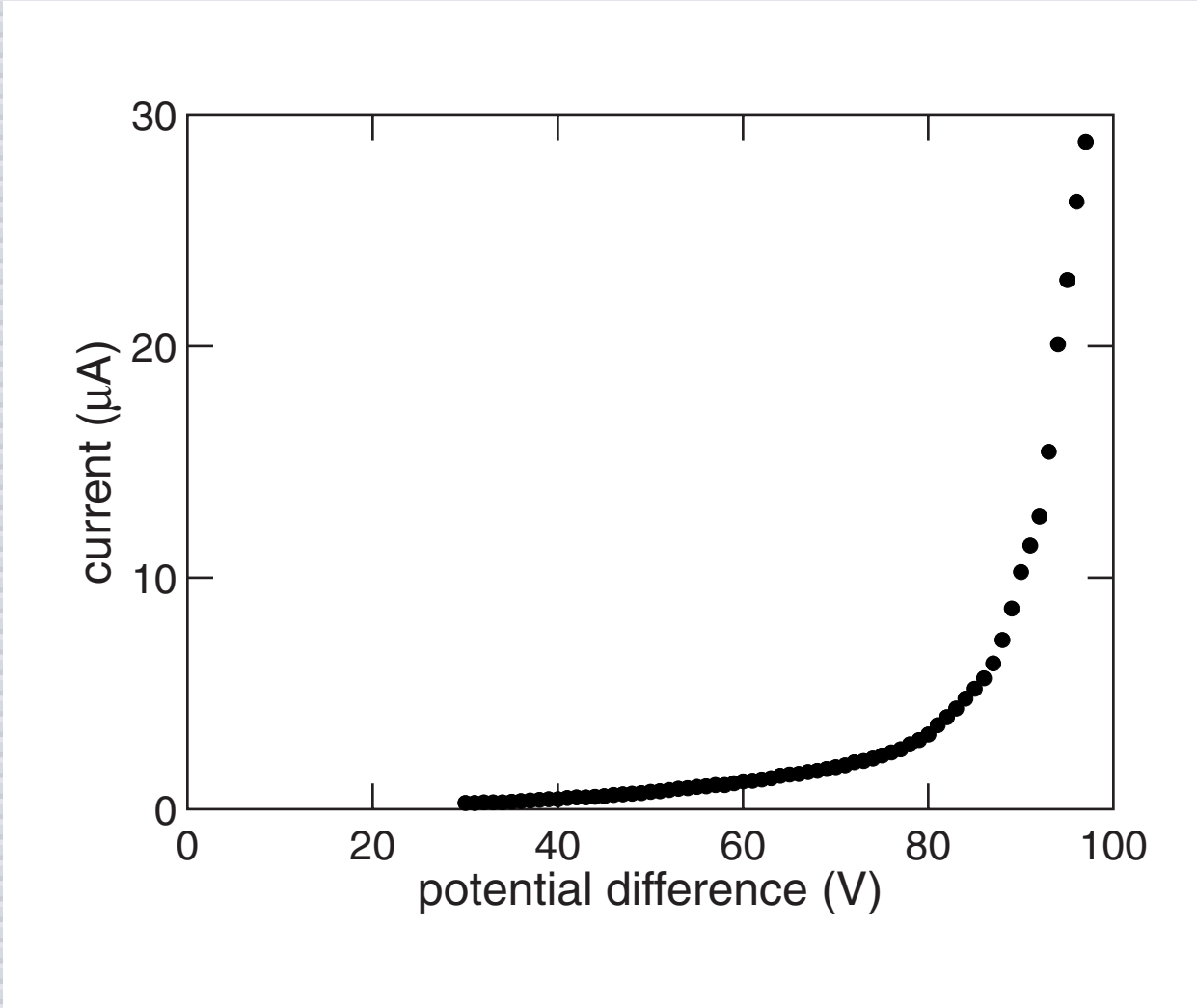

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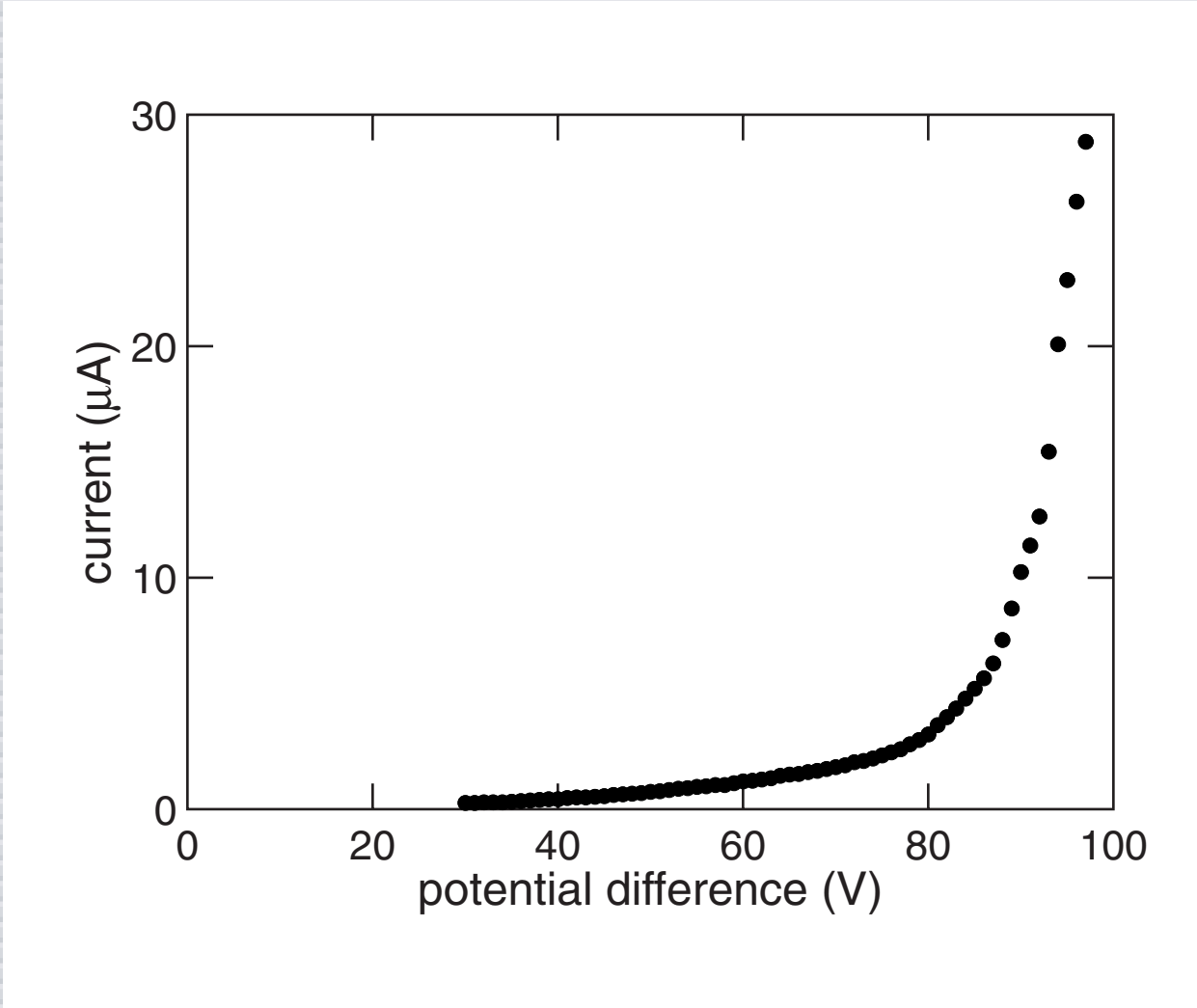
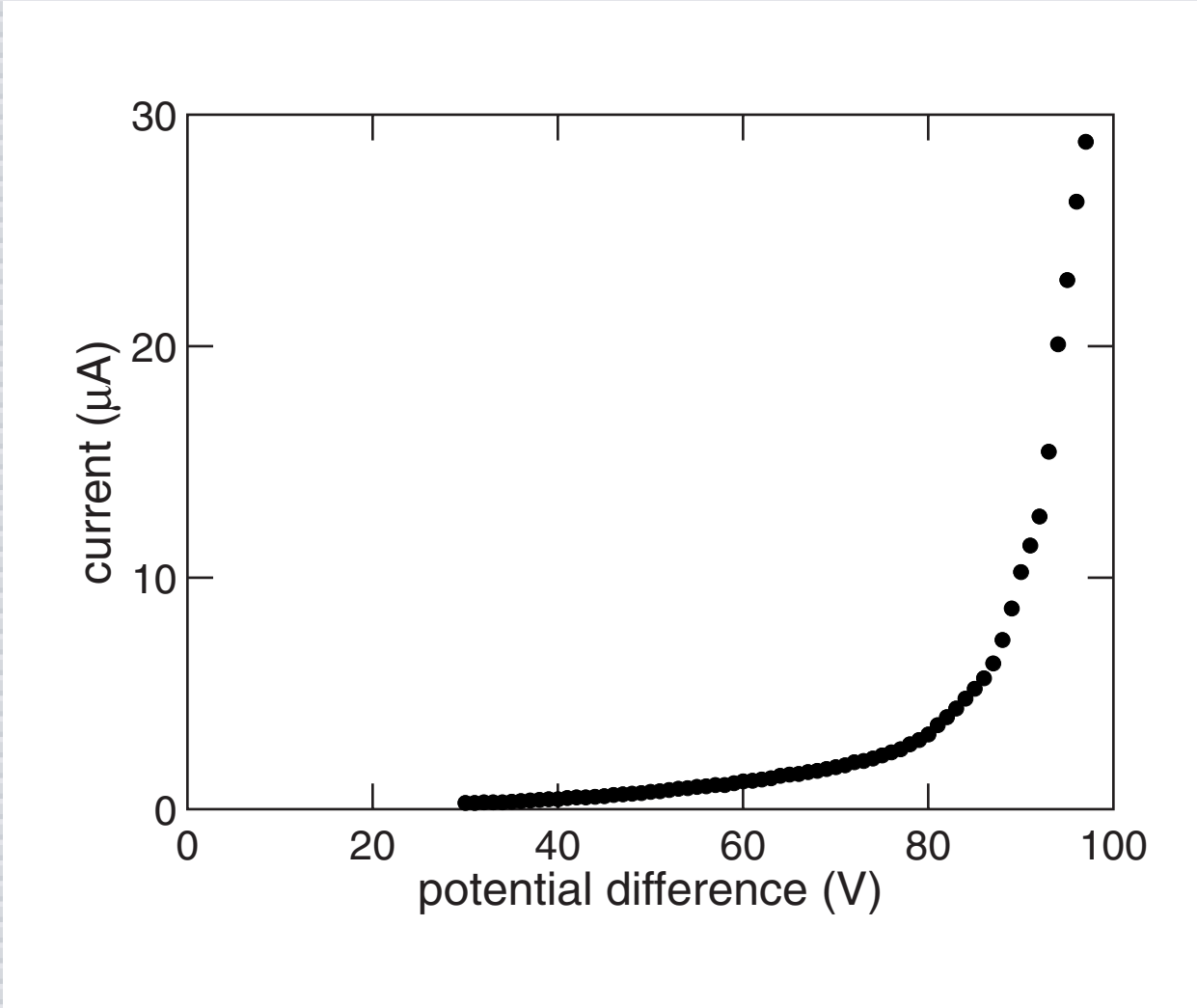


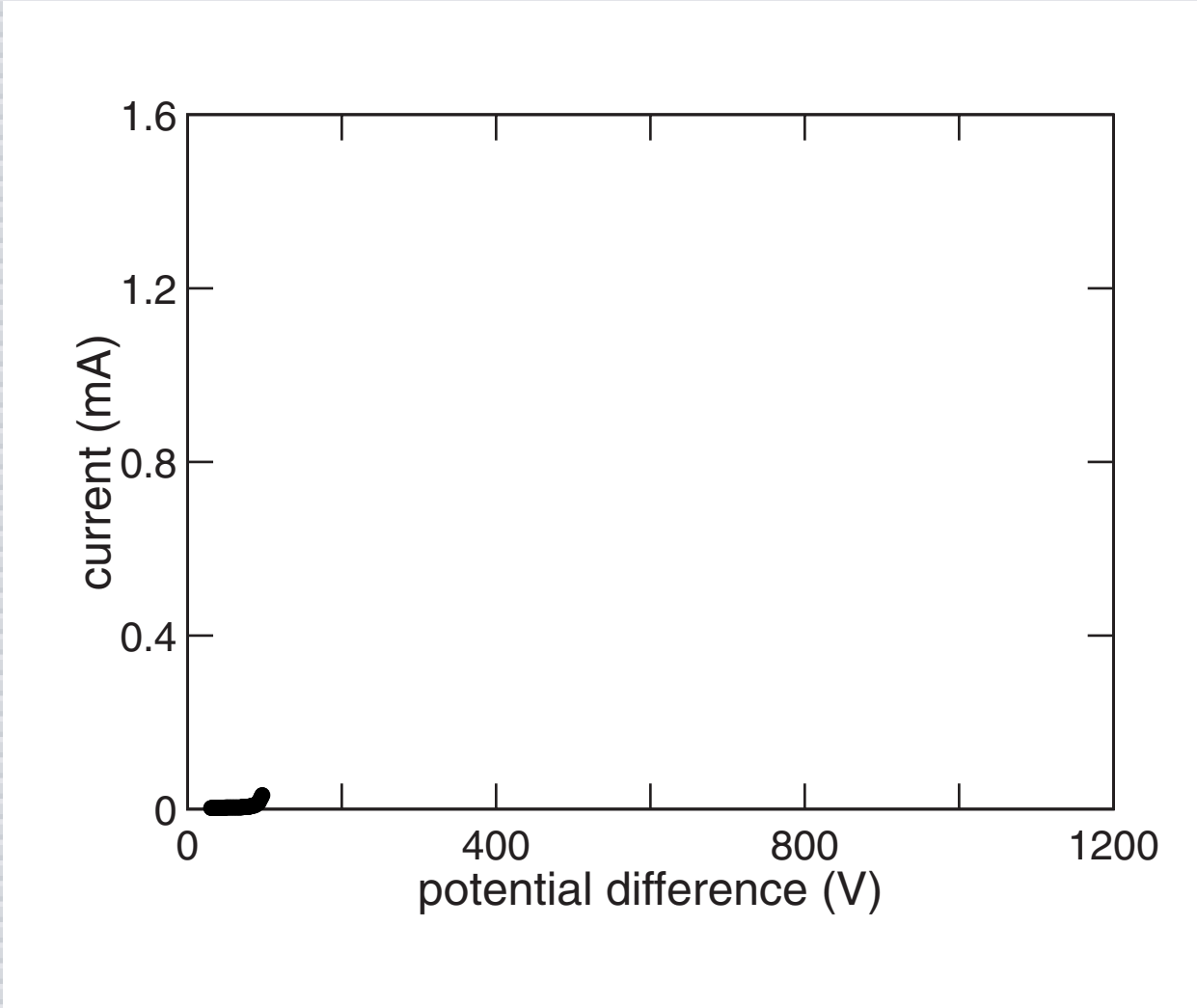
turn-on field (1 μA/cm^2): 1.2 V/μm

Properties



threshold field (10 μA/cm^2): 2.1 V/μm

Properties



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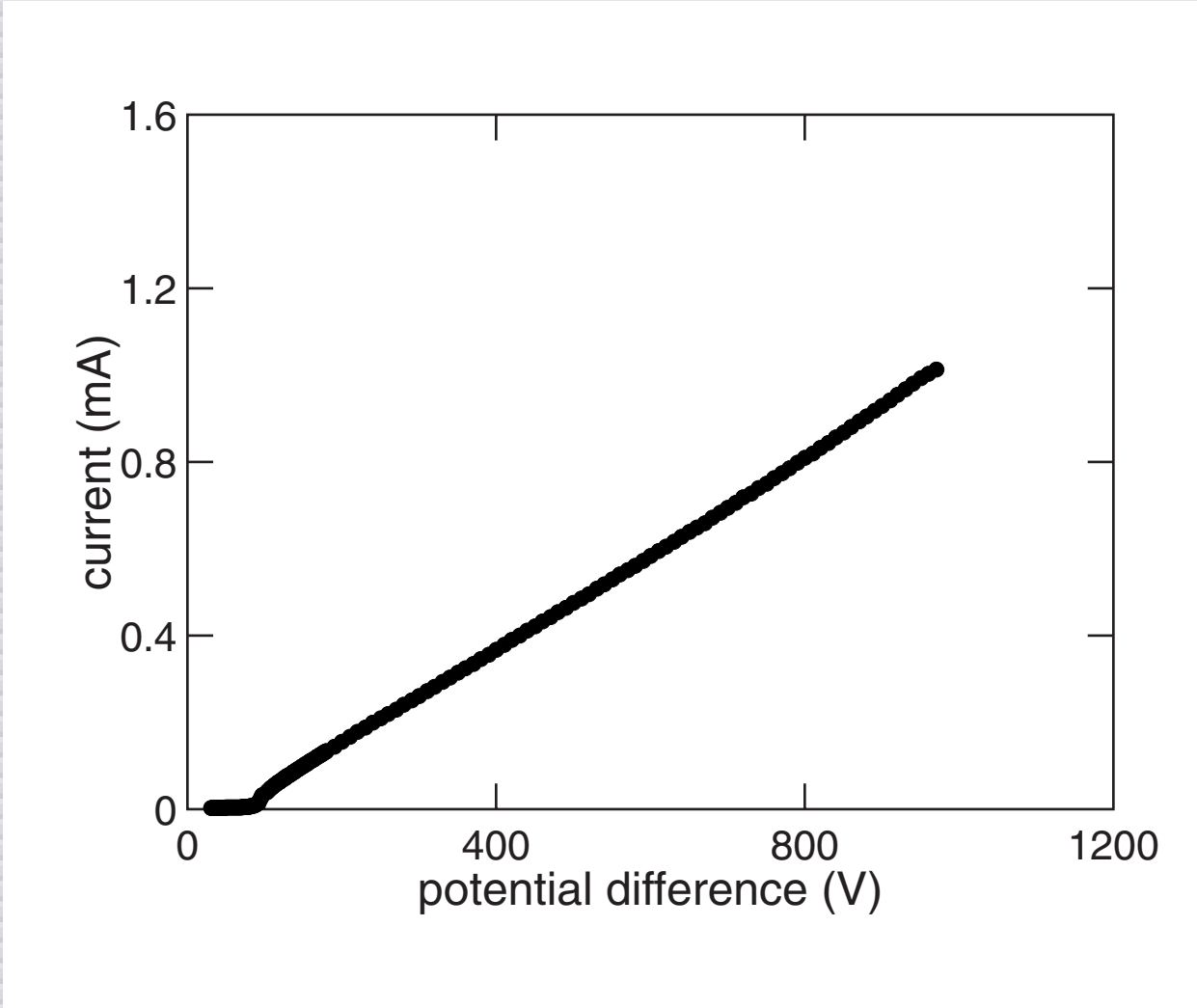

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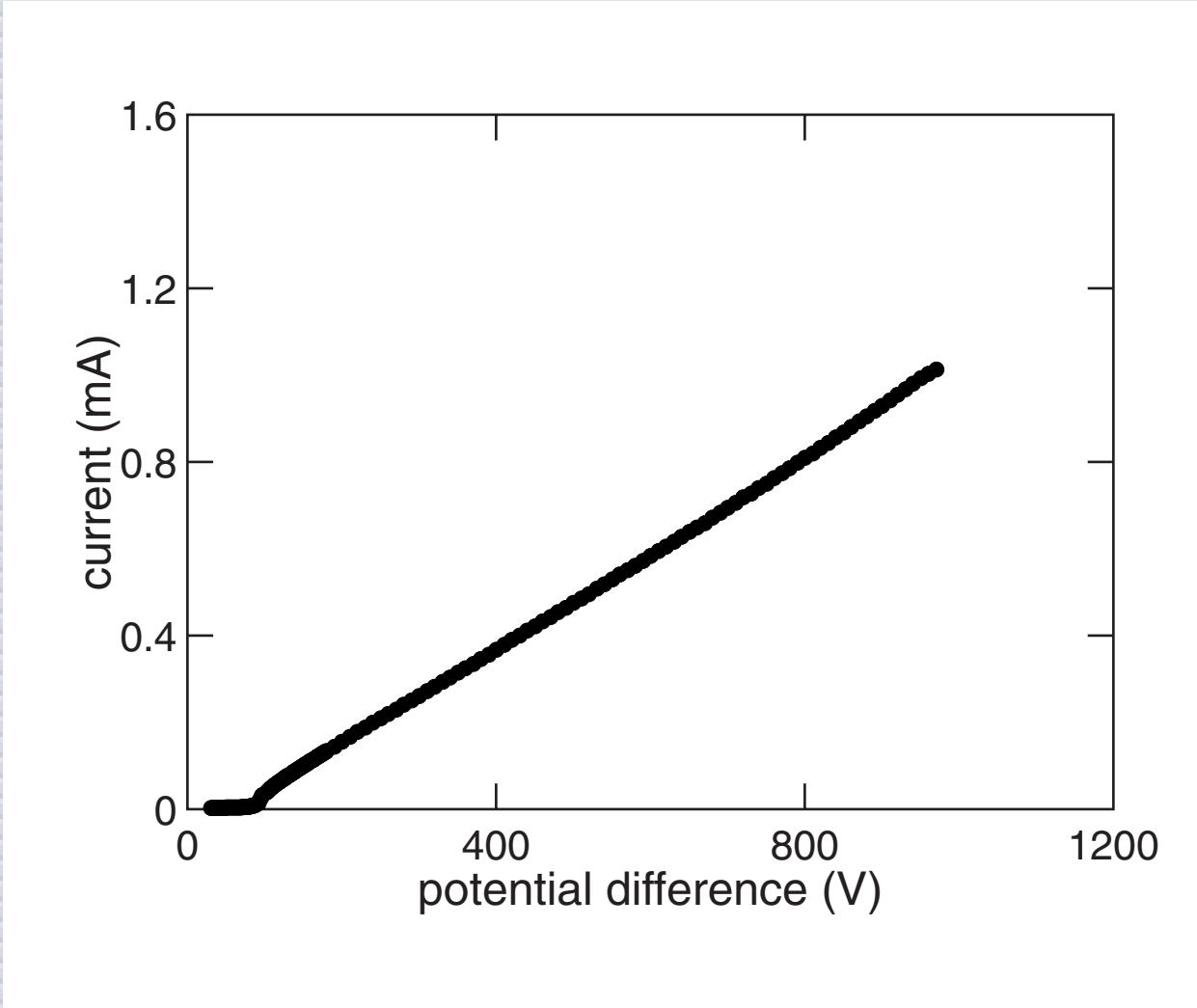
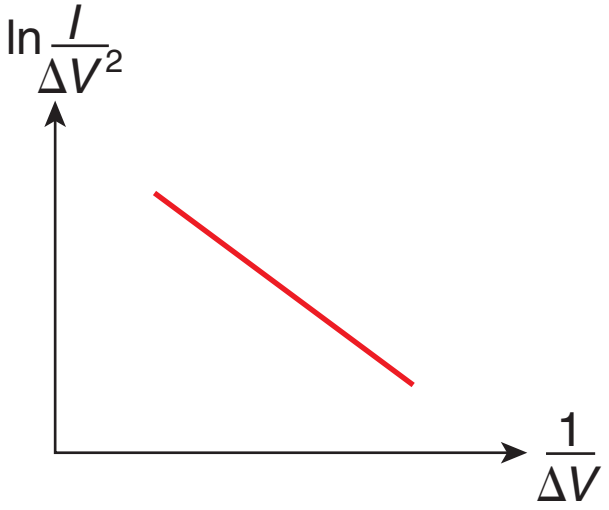


maximum current: 20 mA (4 mm^2 sample)

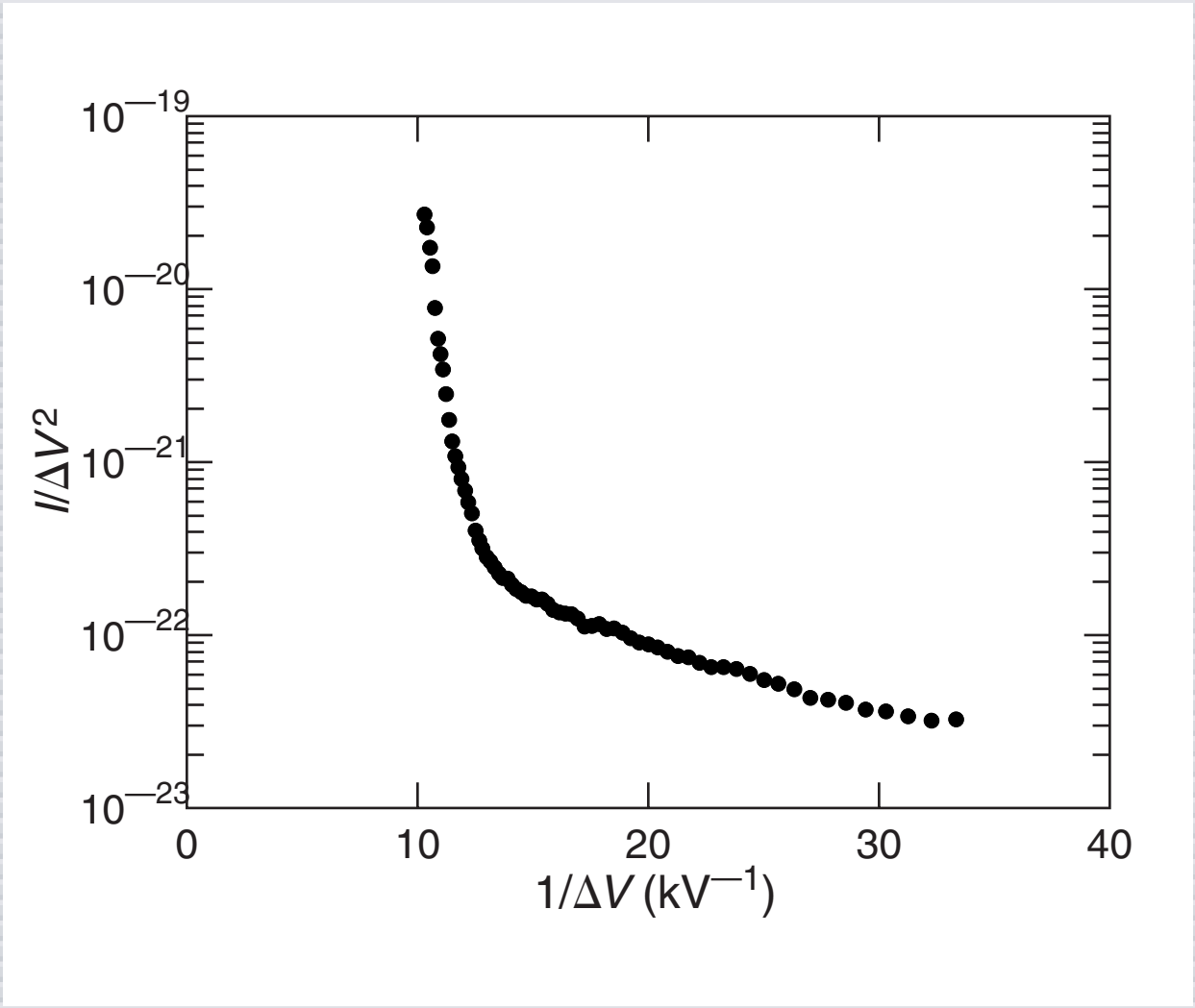
Properties

$$\ln \frac{I}{\Delta V^2} = \ln a - b\frac{1}{\Delta V}$$

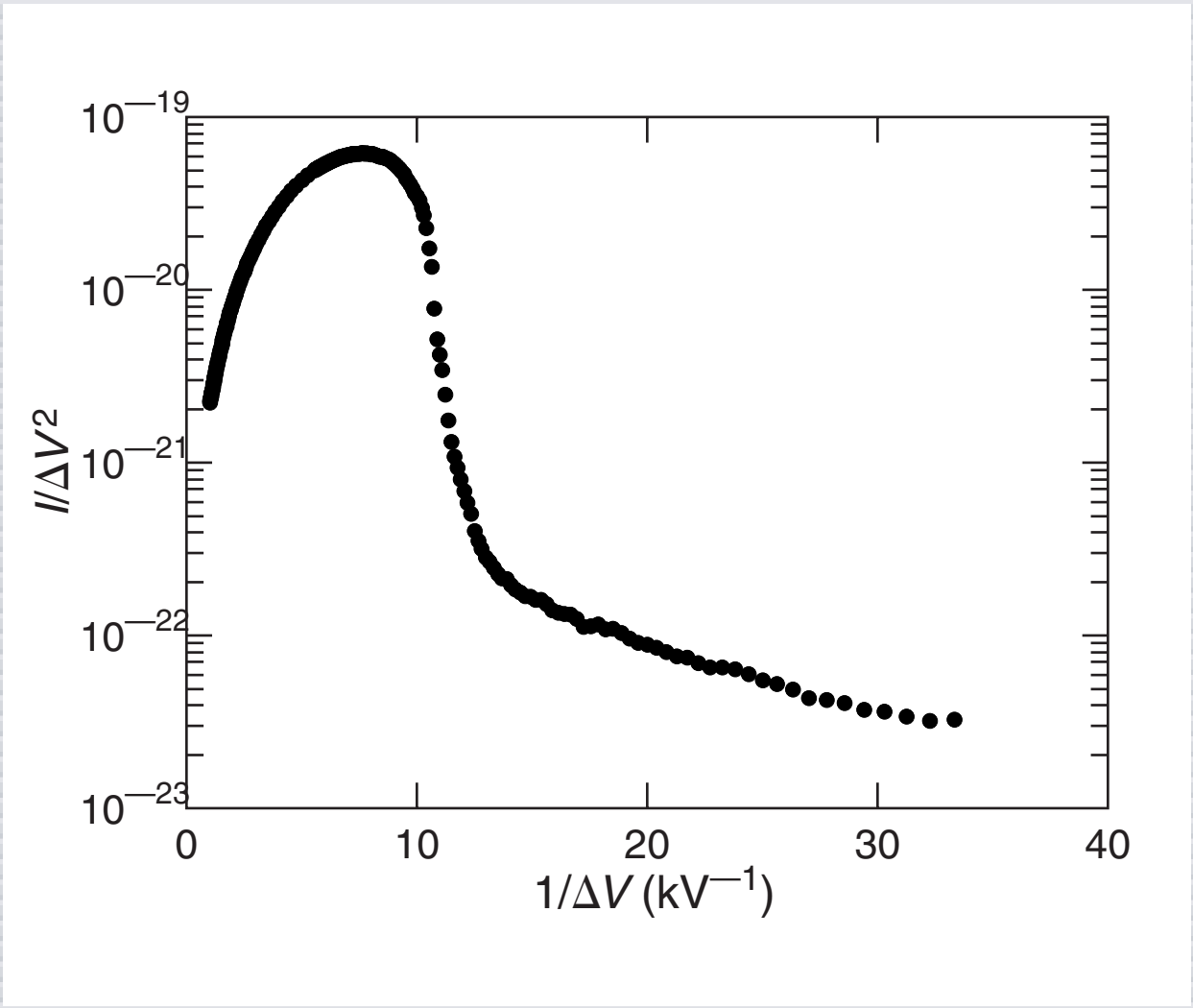


R.H. Fowler and L. Nordheim, *Proc. R. Soc. Lond. A* (1928)

Properties



Properties



Properties

Points to keep in mind:

- **near unity absorption**
- **sub-band gap absorption**
- **IR photoelectron generation**
- **high field emission at low fields**

Outline

- Properties
- **Structural and chemical analysis**
- Outlook

Structural and chemical analysis

- **What causes these properties?**
- **Other gases?**

Structural and chemical analysis

Ion channeling and electron backscattering:

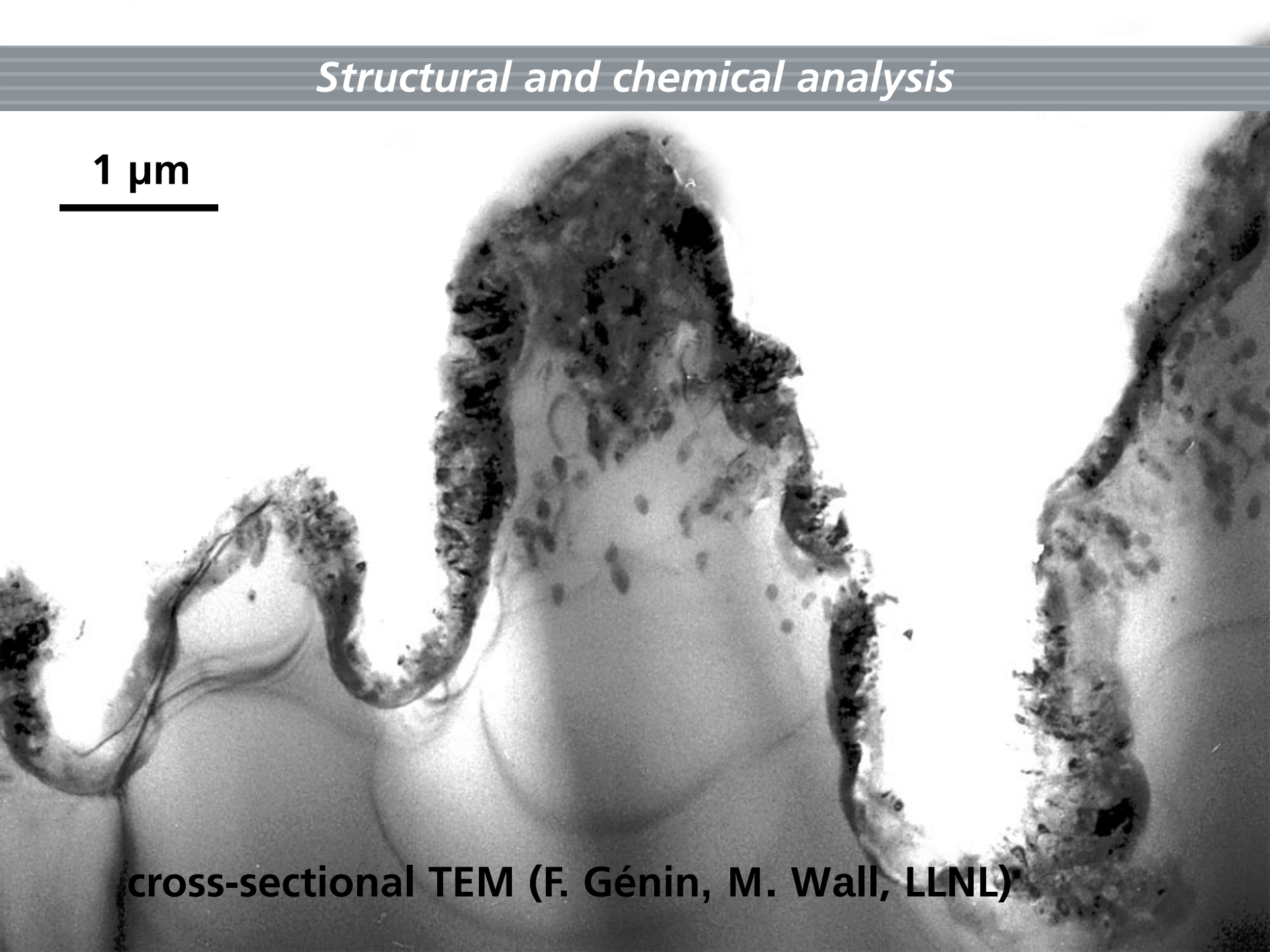
- **spikes retain crystalline order**
- **high density of defects**

Structural and chemical analysis

Secondary ion mass spectrometry:

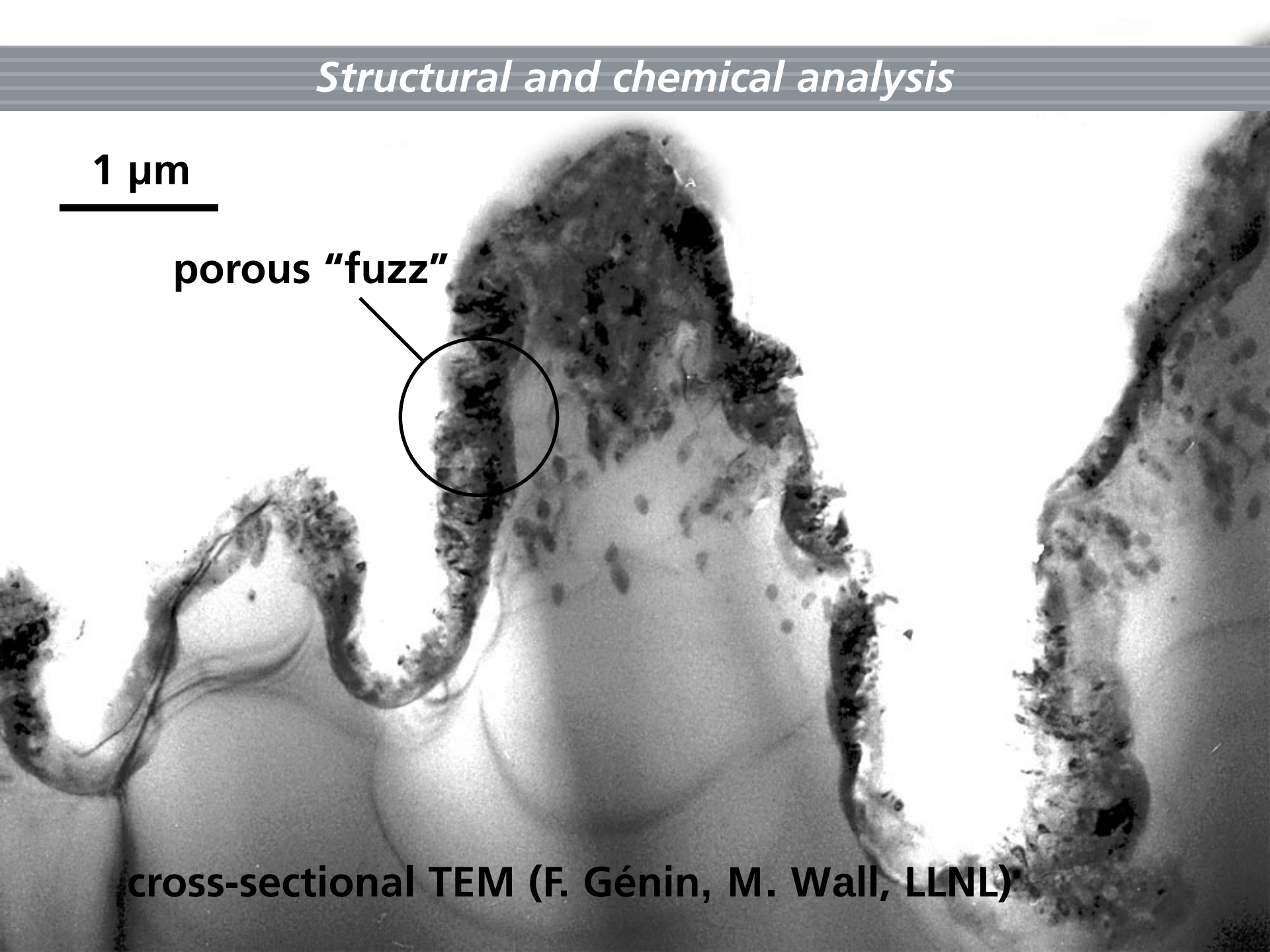
- **10^{20} cm^{-3} sulfur**
- **10^{17} cm^{-3} fluorine**

Structural and chemical analysis



cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



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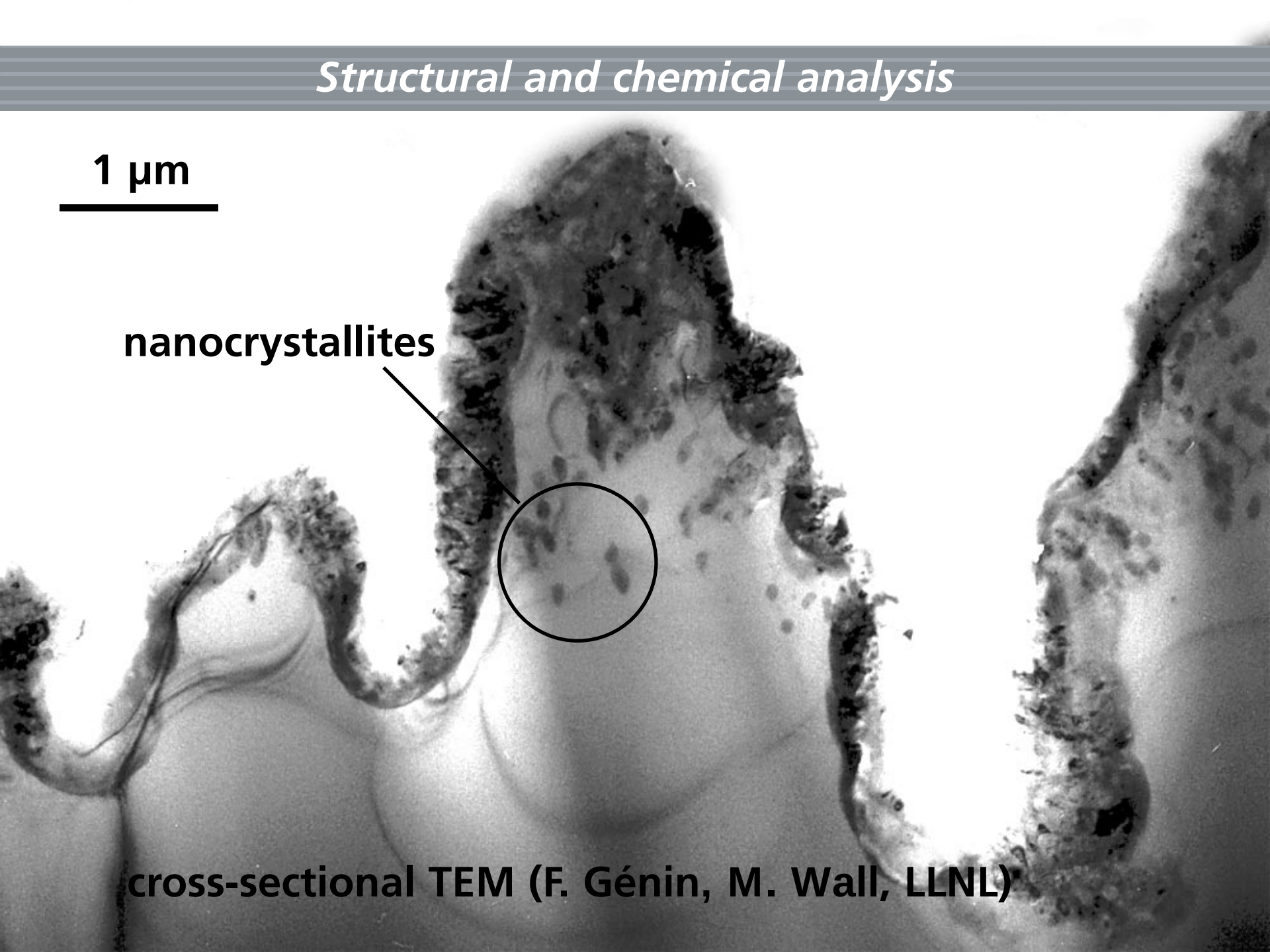
Structural and chemical analysis



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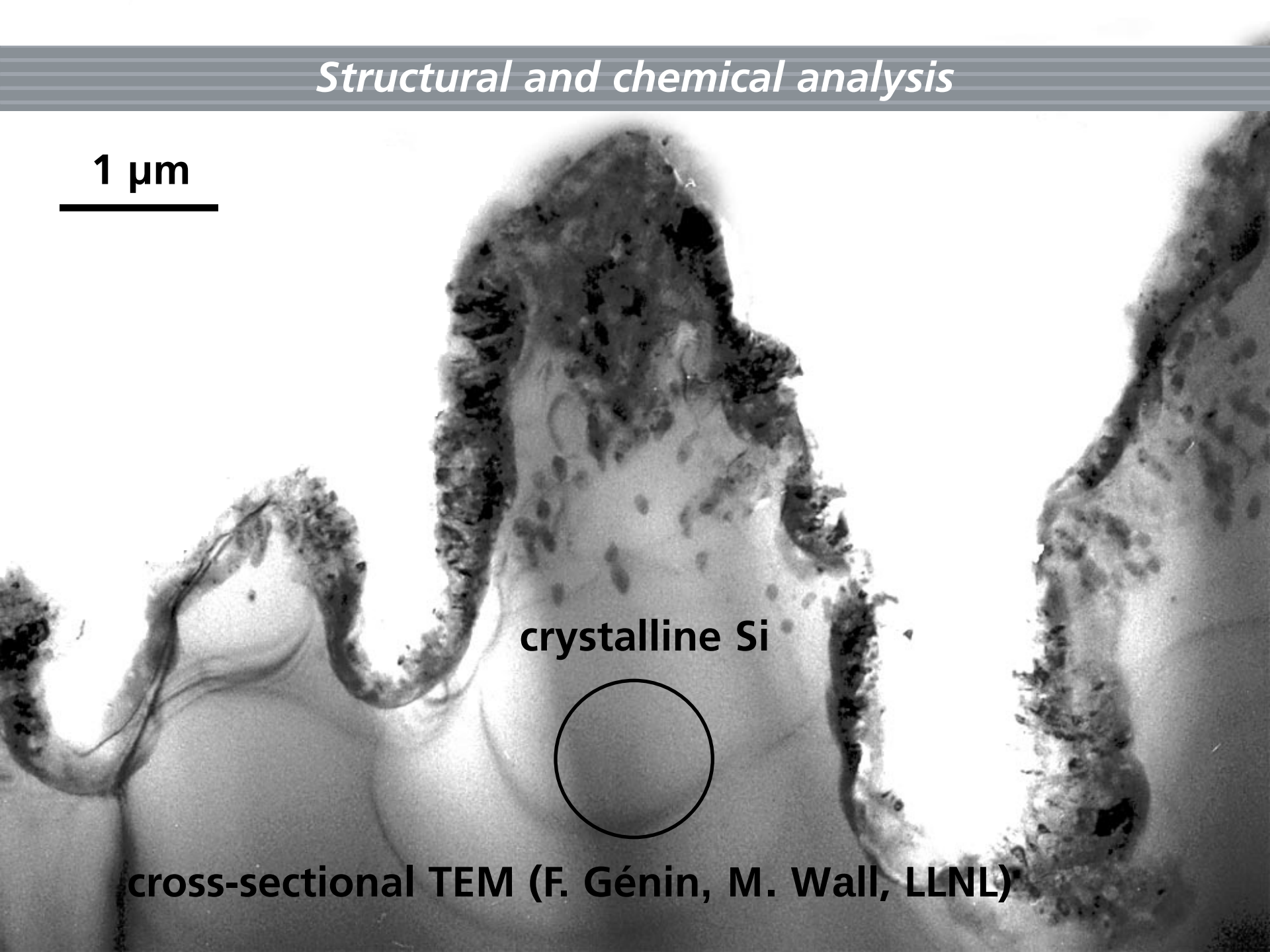

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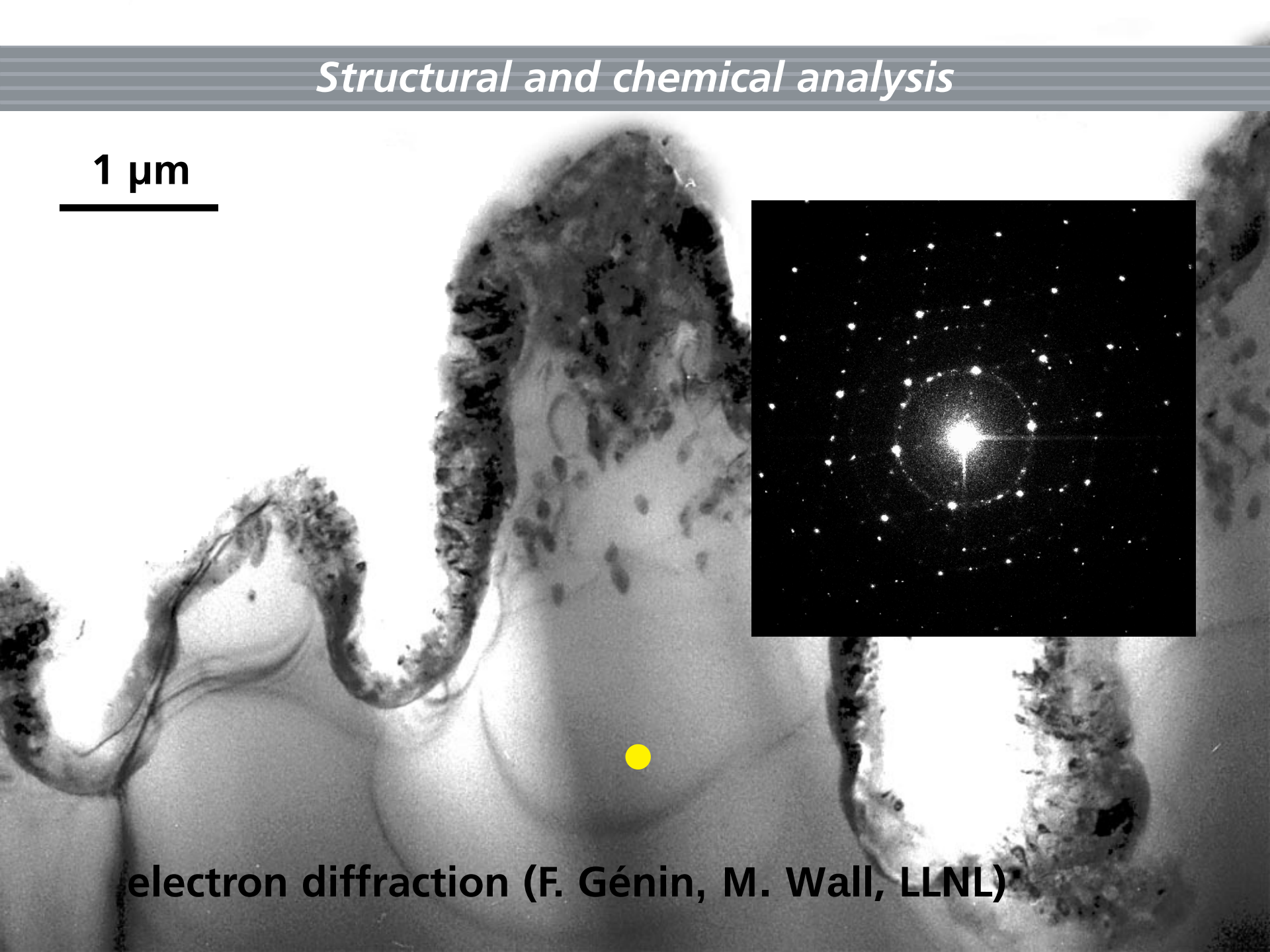
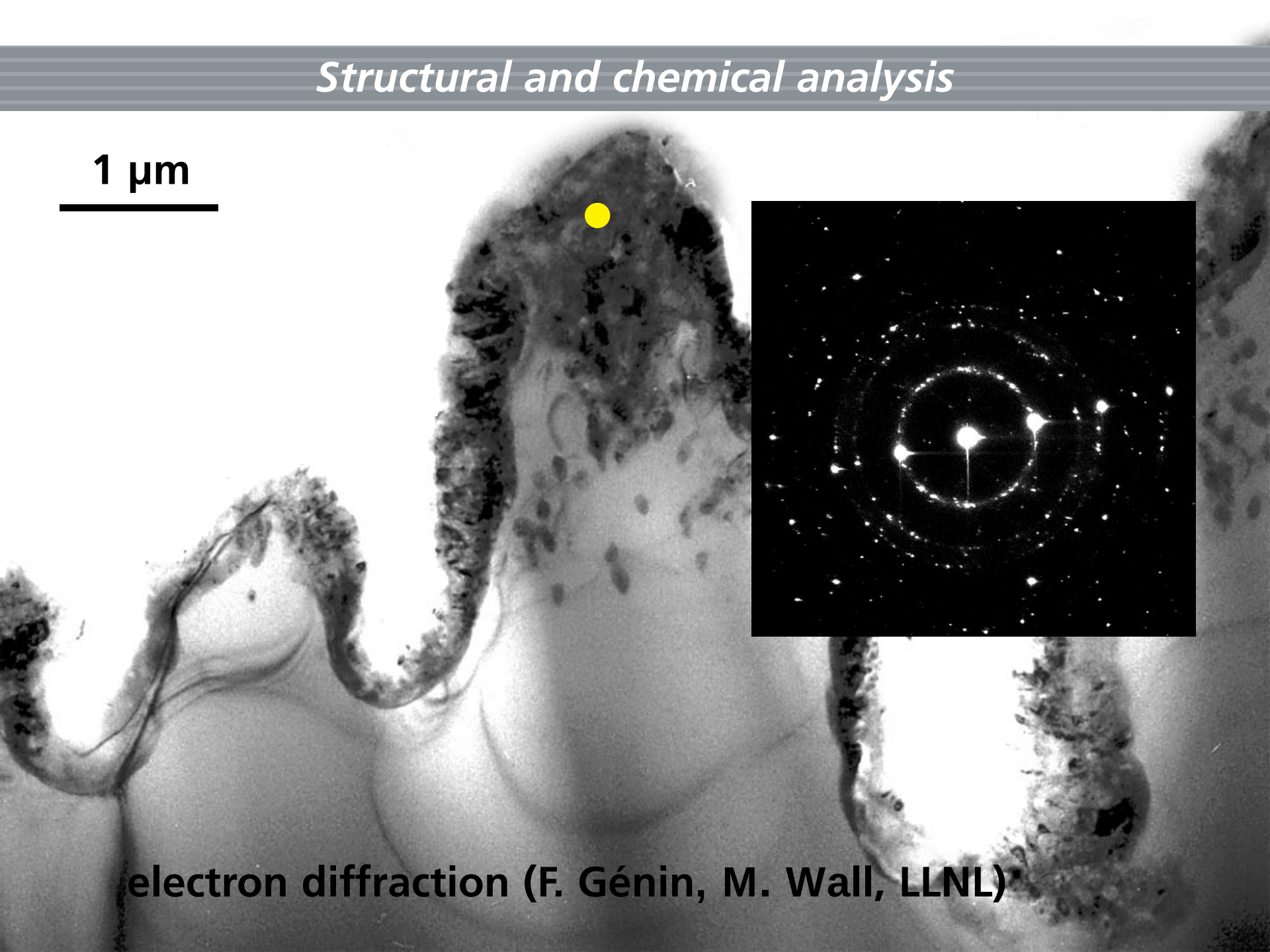
Structural and chemical analysis



electron diffraction (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



electron diffraction (F. Génin, M. Wall, LLNL)

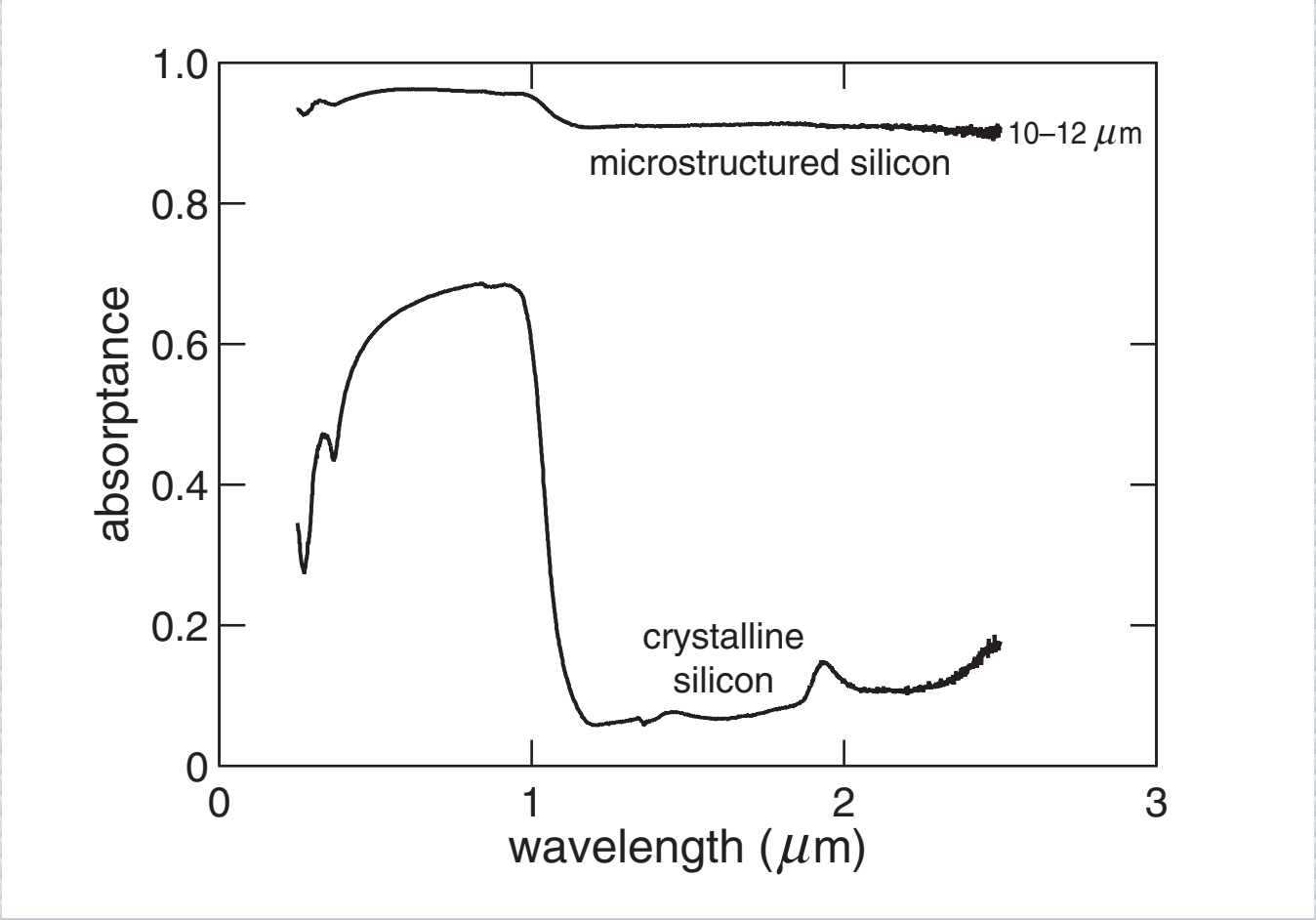
Structural and chemical analysis

cross-sectional TEM:

- **core of spikes: undisturbed Si**
- **surface layer: disordered Si, impurities, nanocrystallites and pores**

Structural and chemical analysis

anneal 4 hours at 1200 K



***Appl. Phys. Lett*. 78, 1850 (2001)**

Structural and chemical analysis

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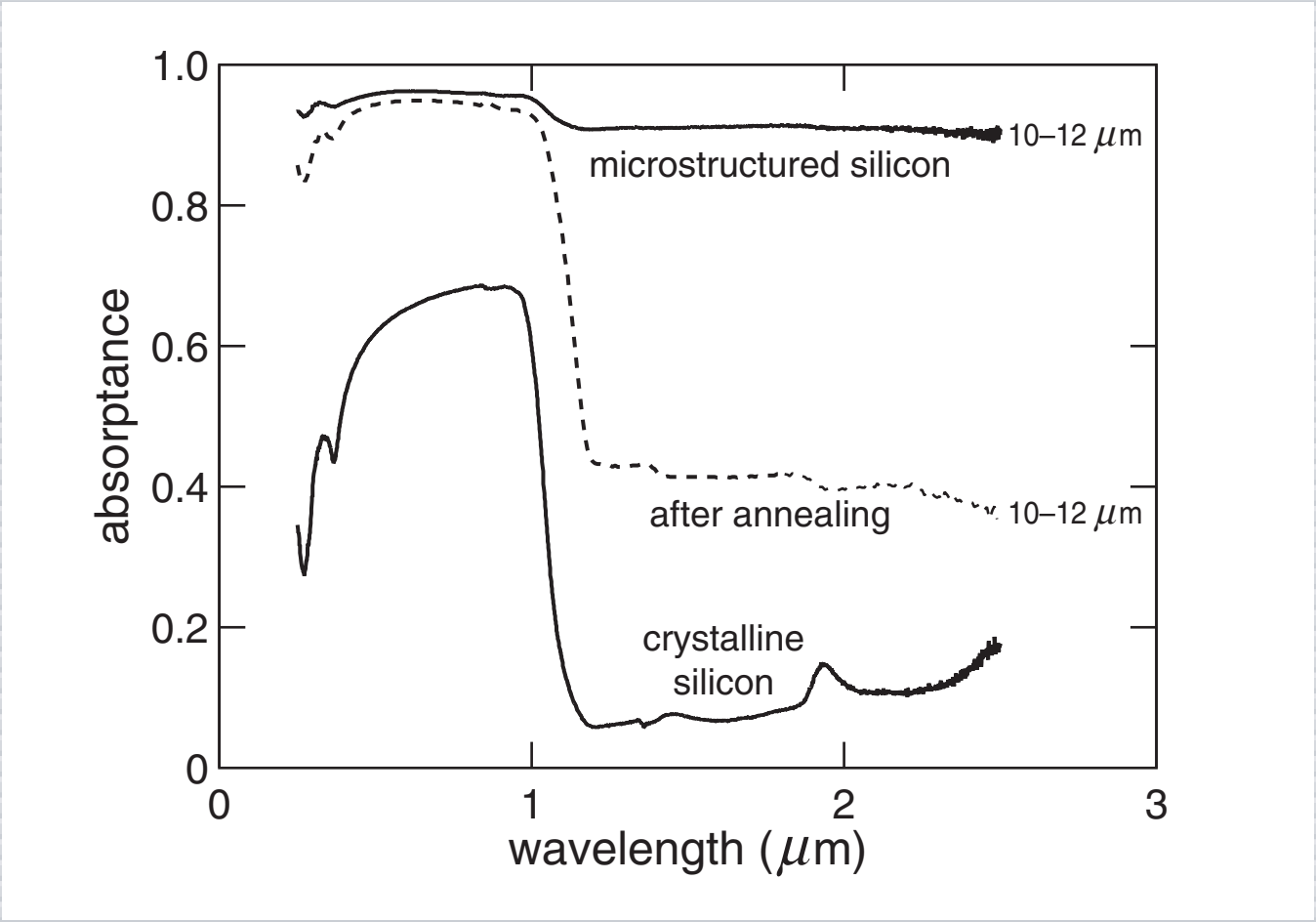

Appl. Phys. Lett. **78, 1850 (2001)**

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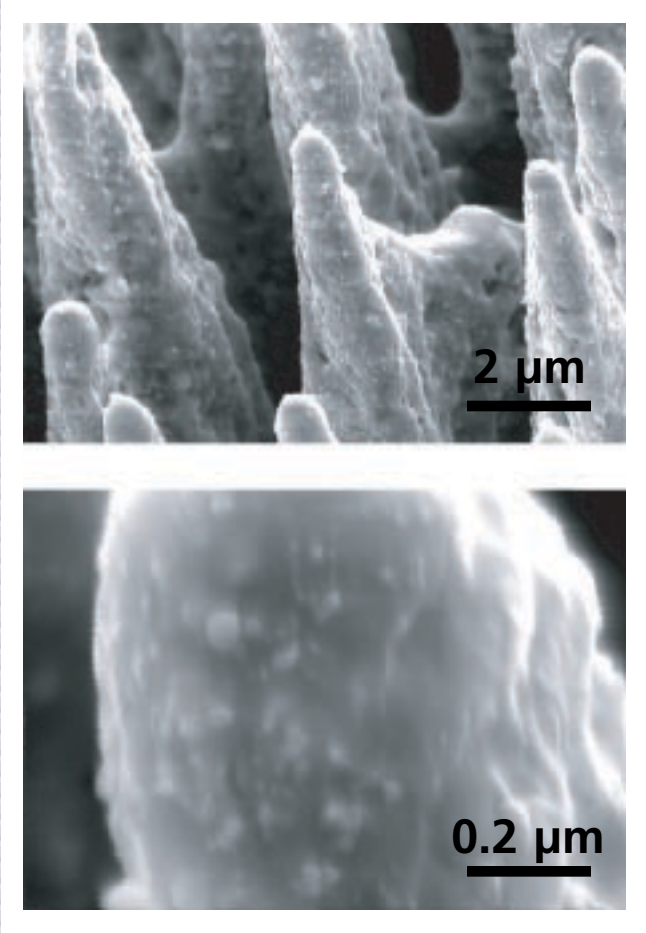

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Structural and chemical analysis

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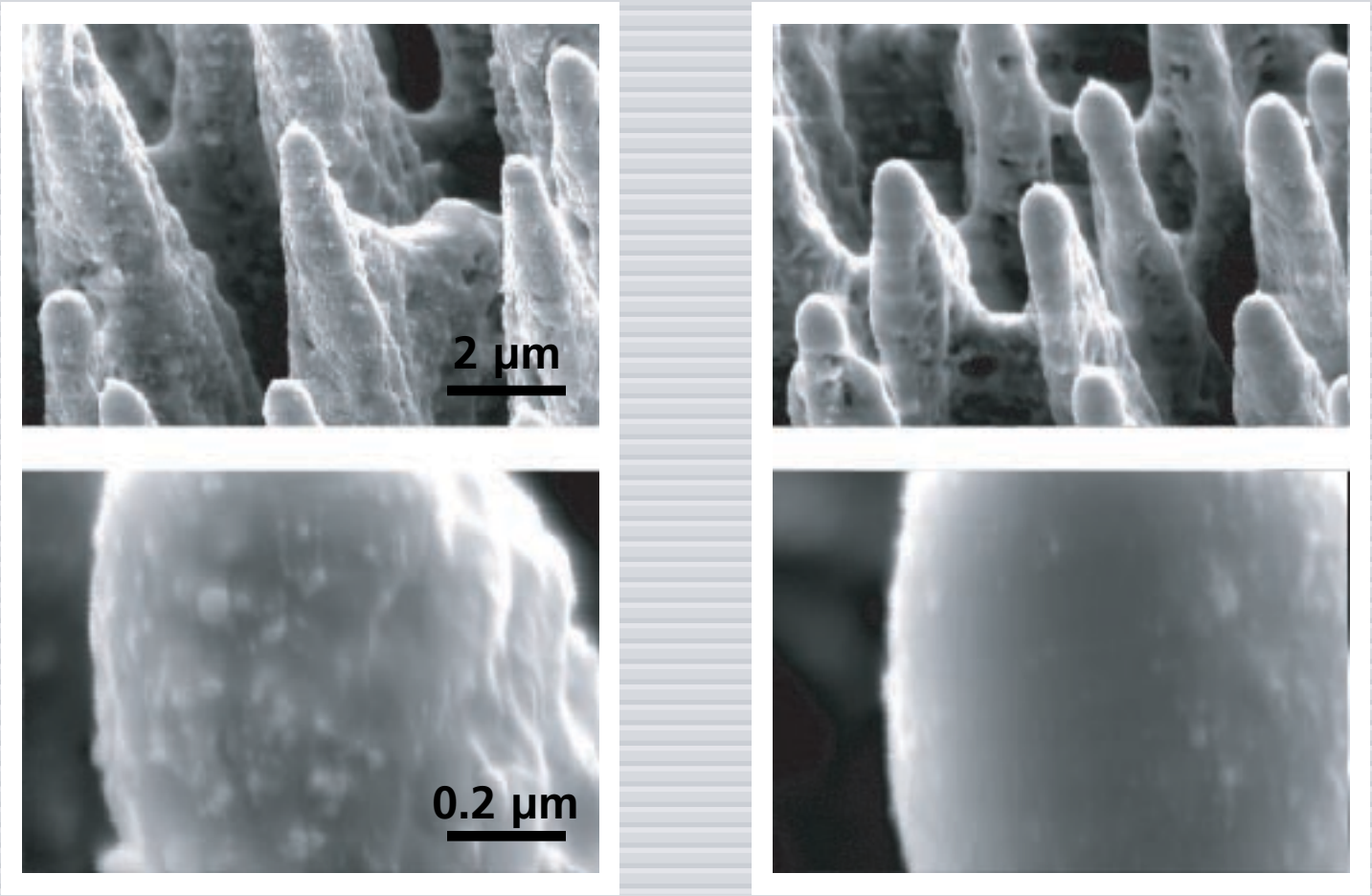


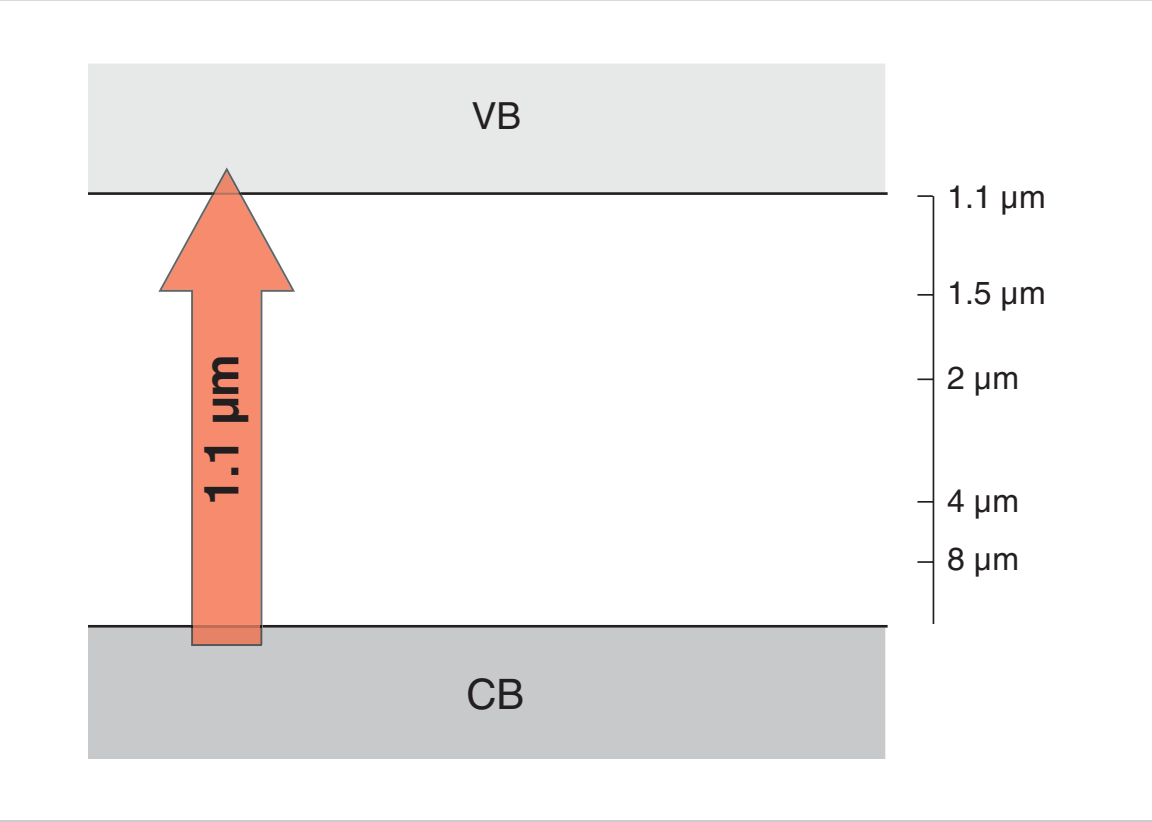
Appl. Phys. Lett. **78,** 1850 (2001)

Structural and chemical analysis

Effects of annealing:

- **IR absorption: reduced twofold**
- **SEM: fewer surface nanostructures**
- **SIMS: sulfur content reduced twofold**

sulfur introduces states in the gap



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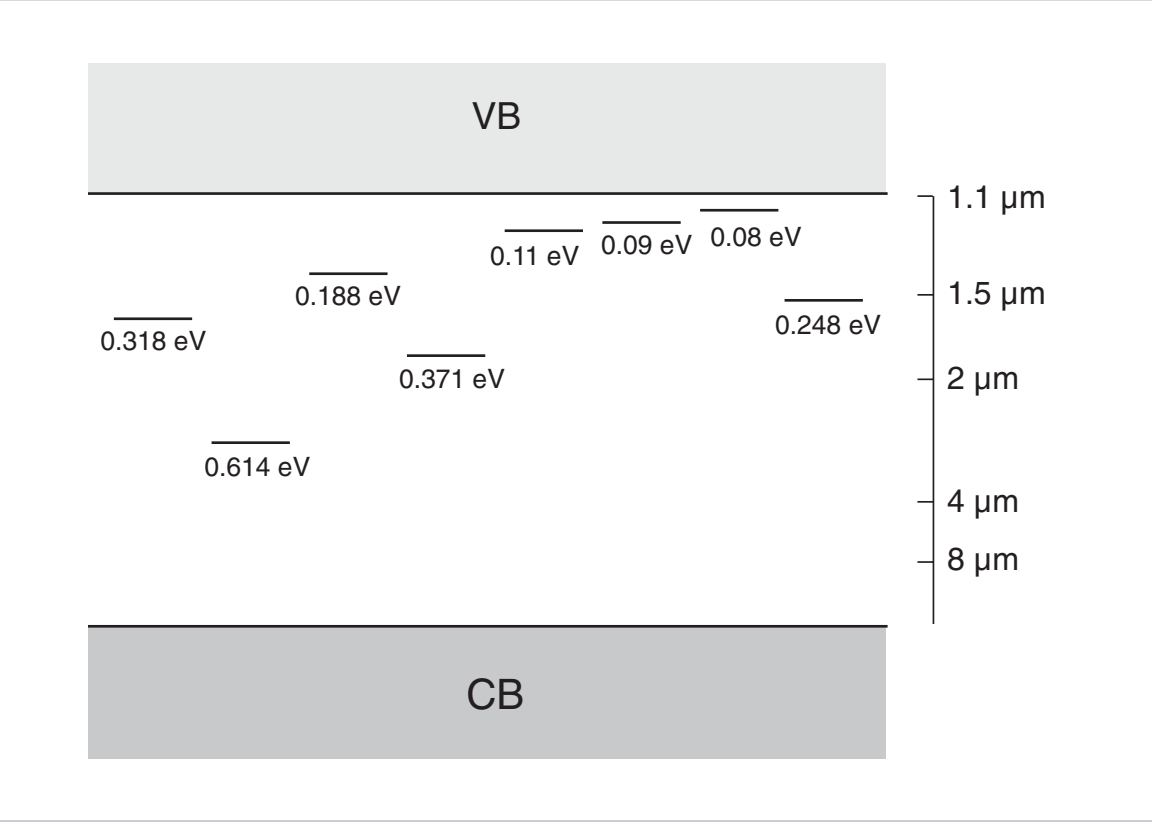
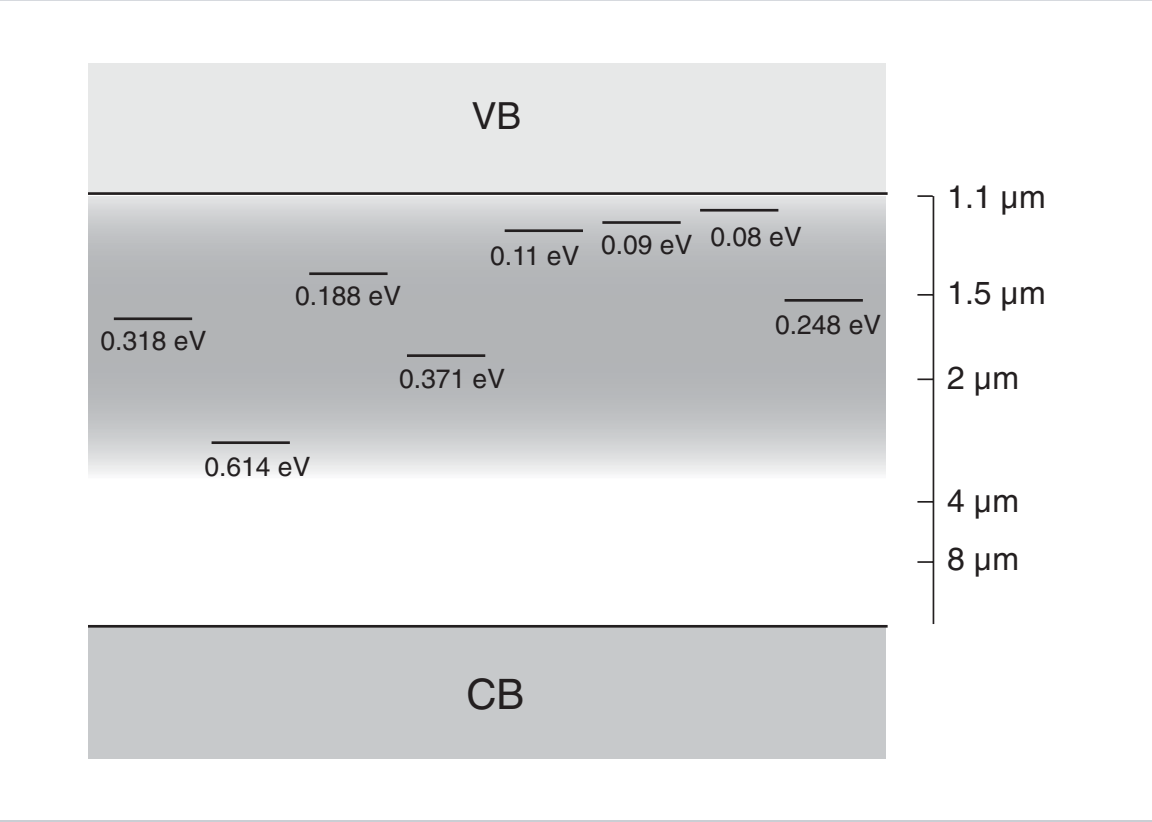
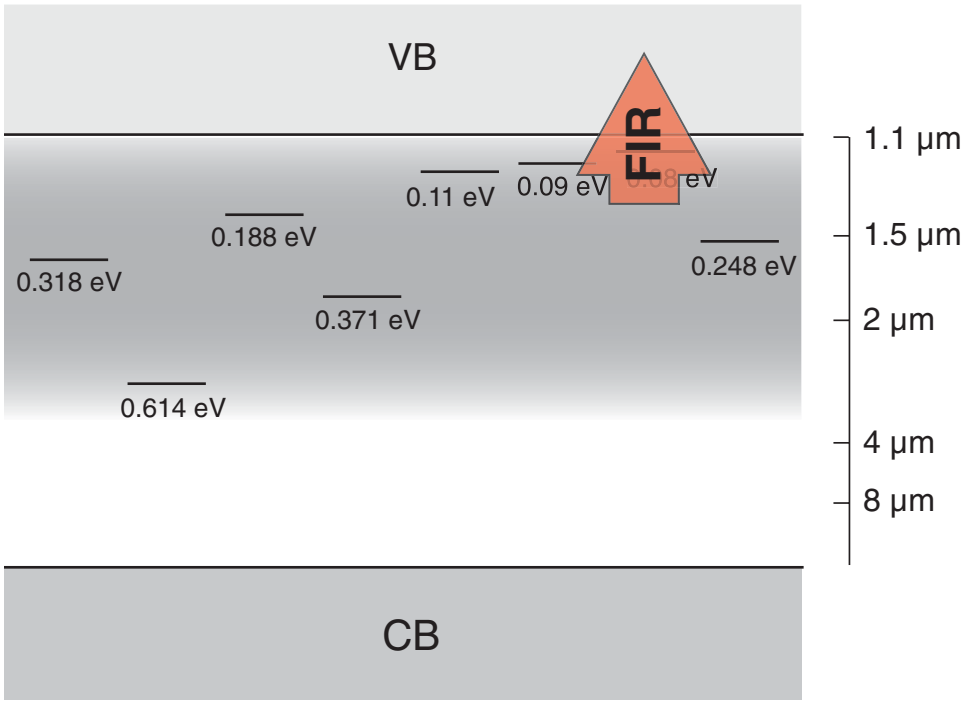


Janzén, *et al.*, *Phys. Rev. B* **29**,1907 (1984)

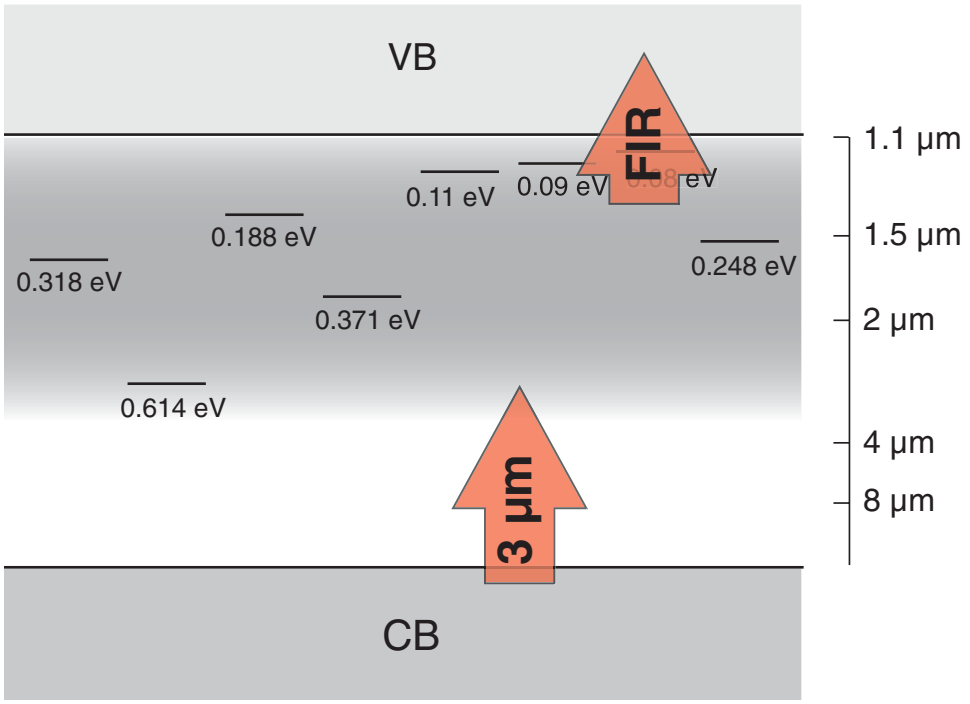
states broaden into a band



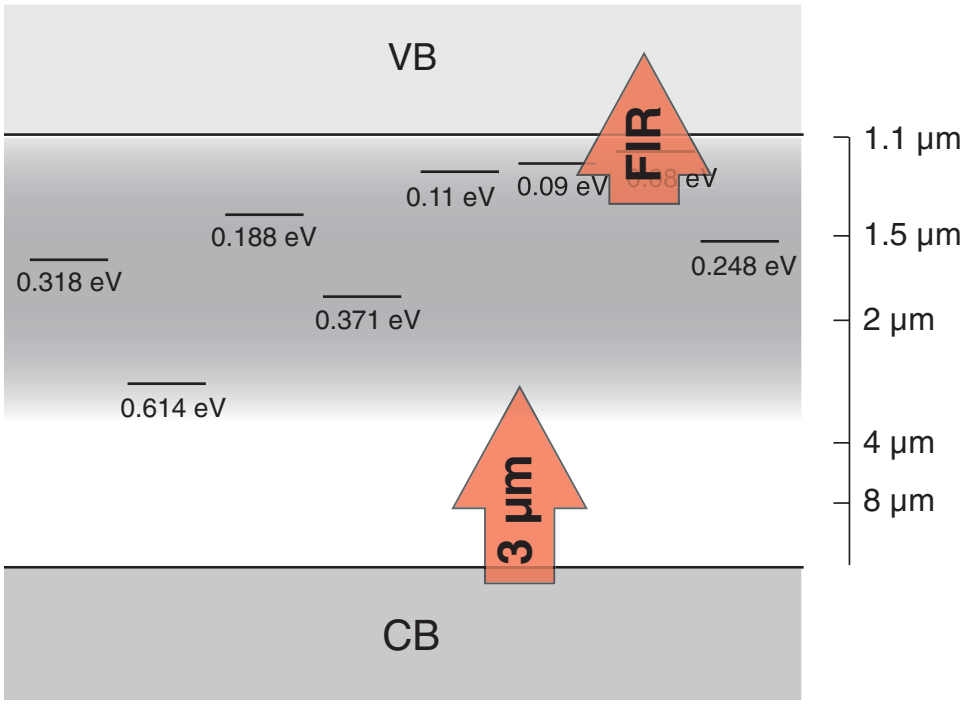
donor: metal-like behavior



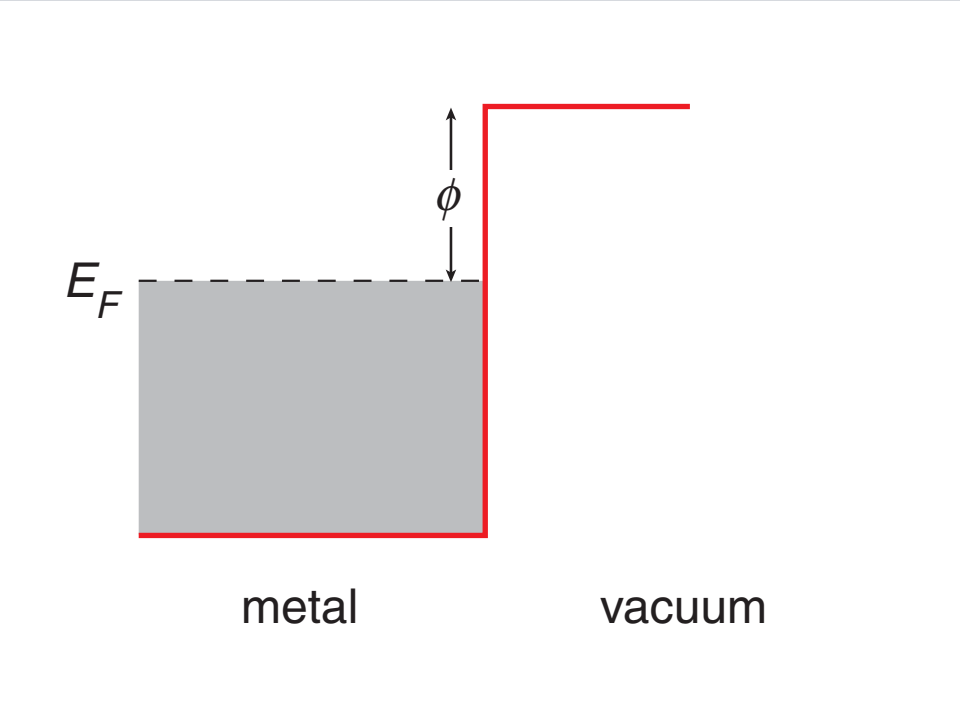
acceptor: absorption until 3 µm

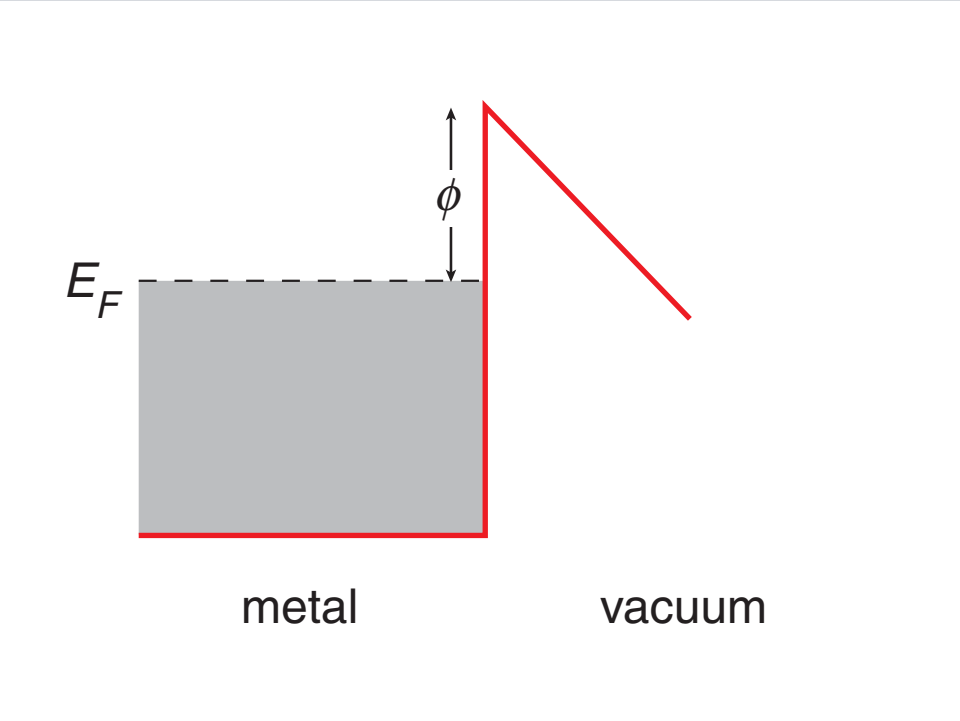


acceptor: absorption out to 3 μm

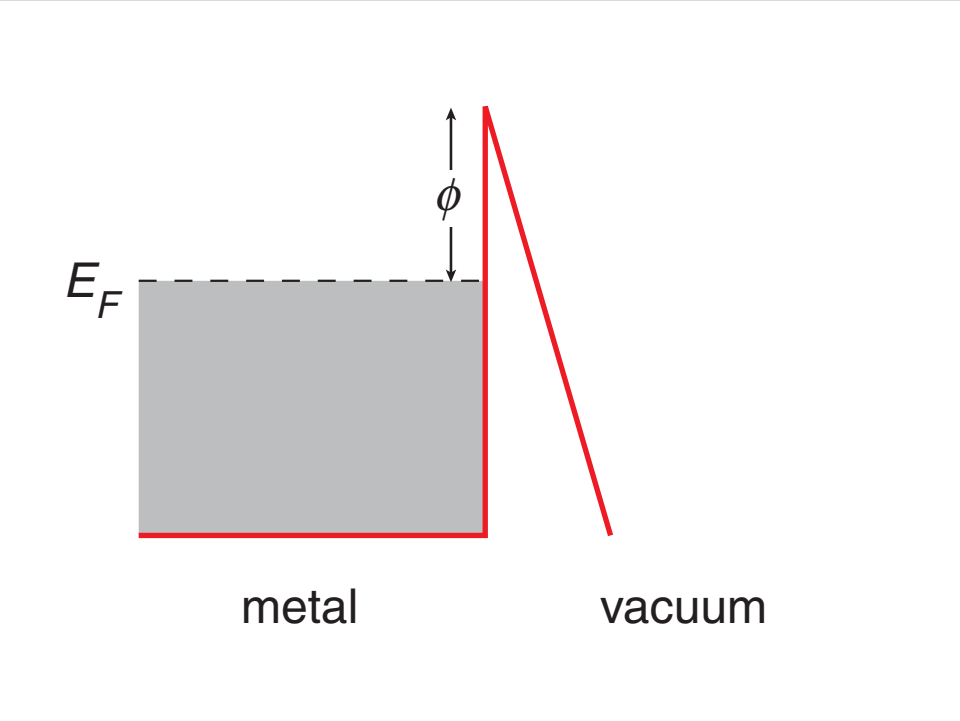


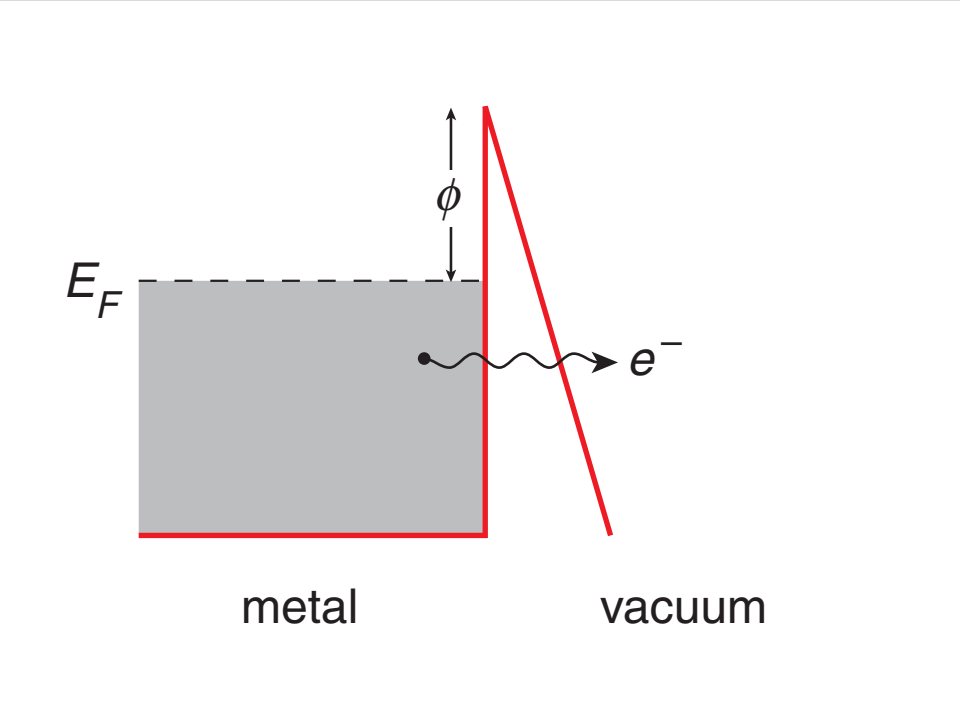
near-IR transmittance rises around 3 μm

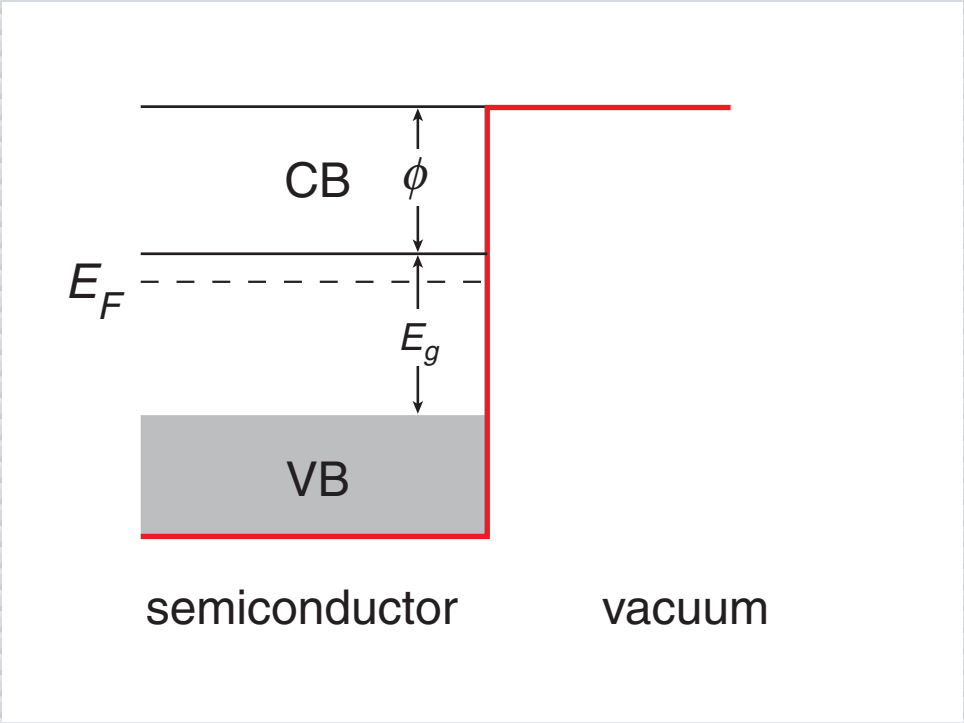

ϕ
E_F
metal
vacuum

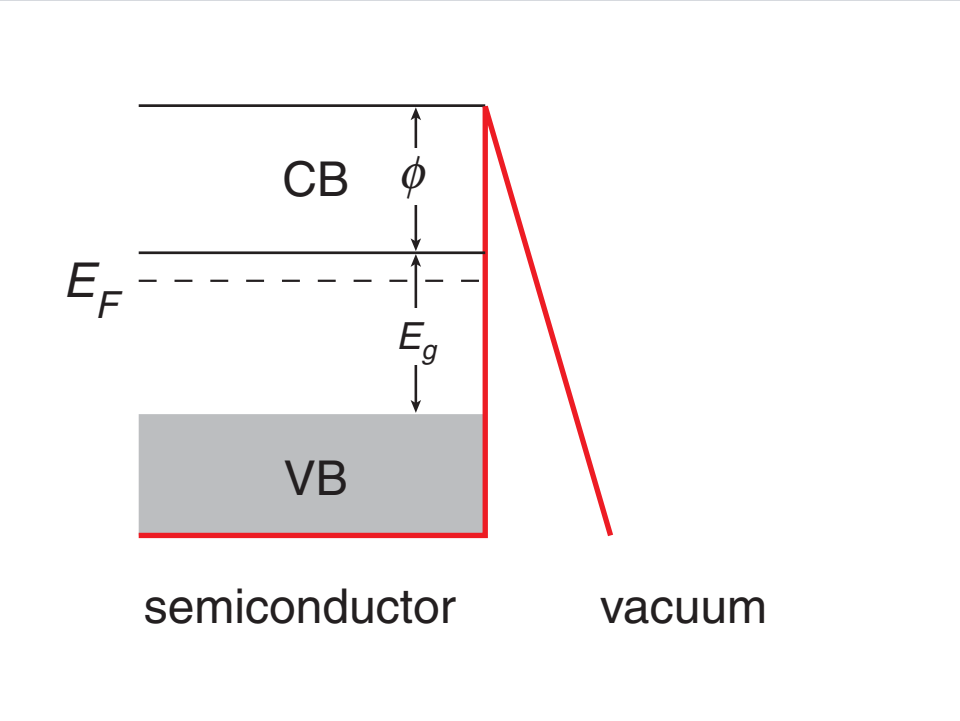

ϕ
E_F
metal
vacuum

Structural and chemical analysis




ϕ
E_F
e^-
metal
vacuum


CB
ϕ
E_F
E_g
VB
semiconductor
vacuum


CB
ϕ
E_F
E_g
VB
semiconductor
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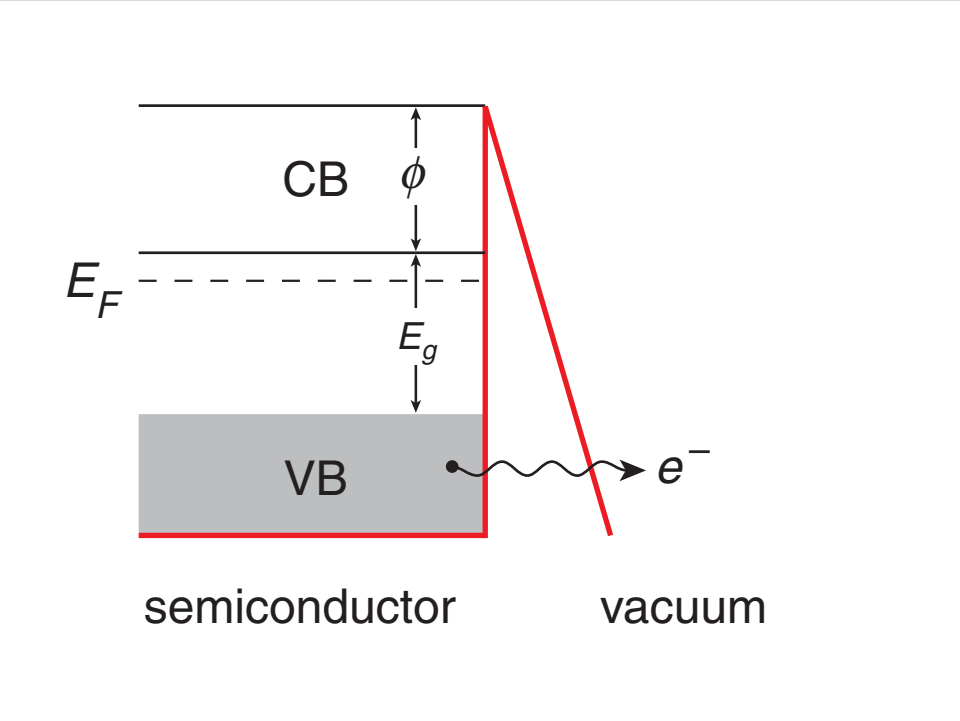
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ϕ
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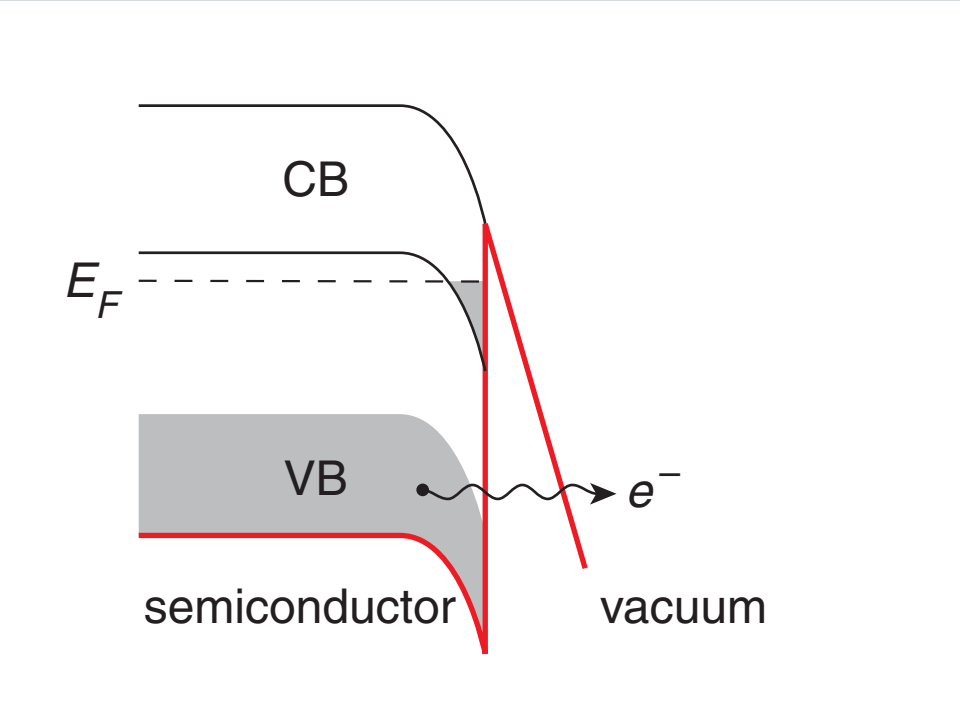
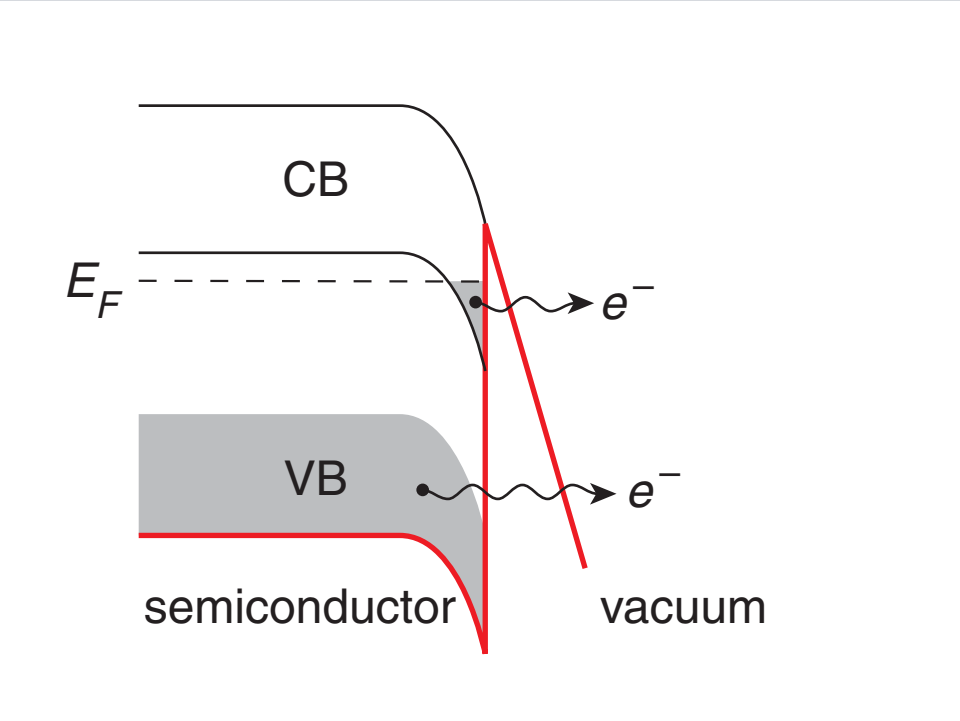
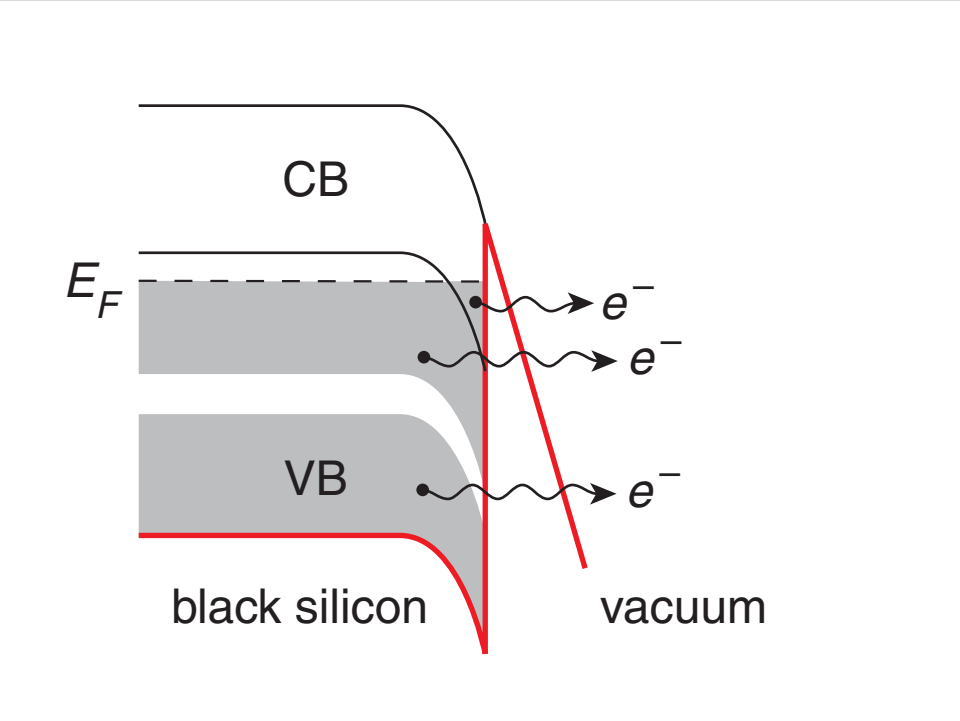
vacuum

Structural and chemical analysis

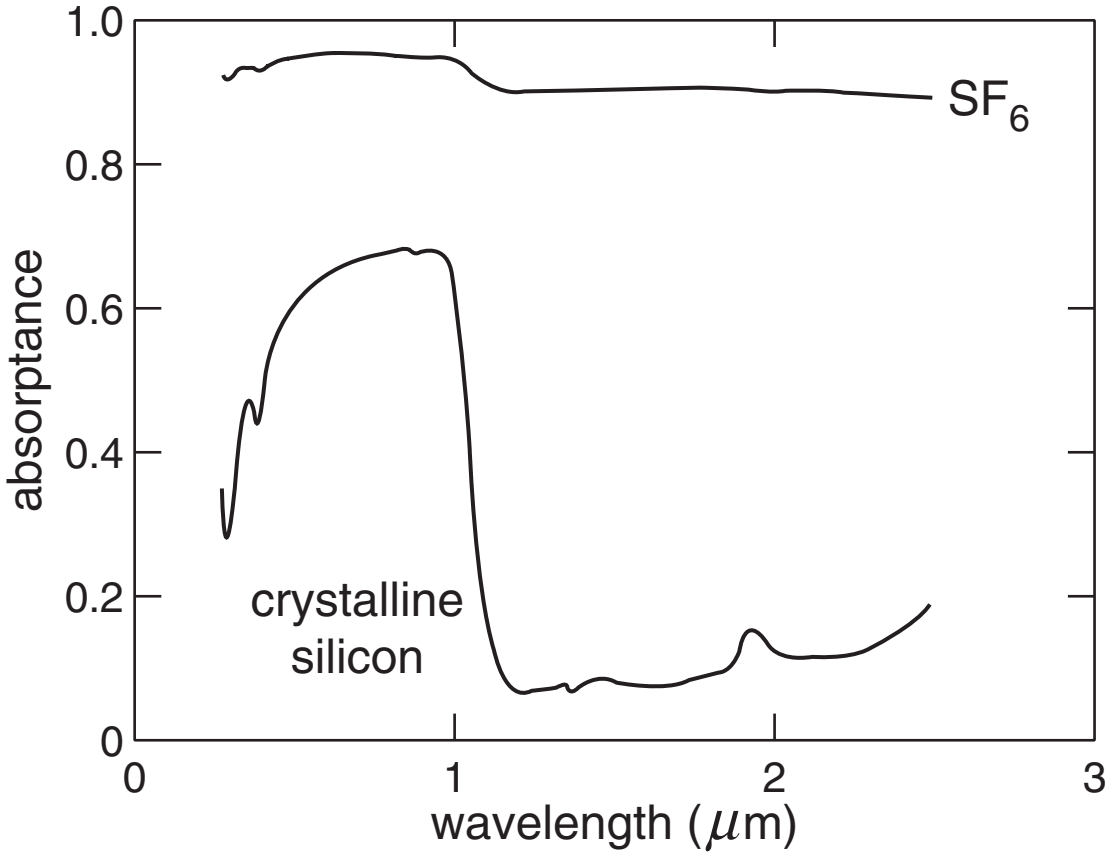



CB
E_F
e^-
VB
e^-
semiconductor
vacuum

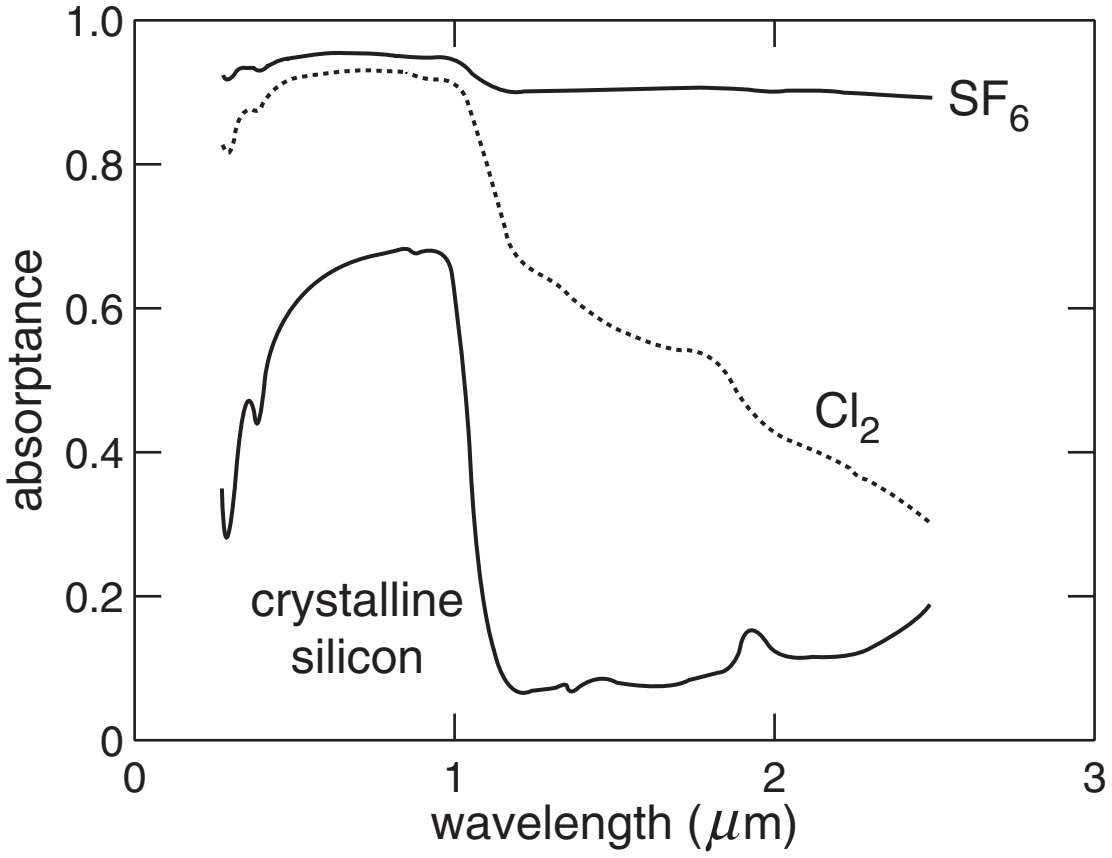
sulfur band provides additional electrons



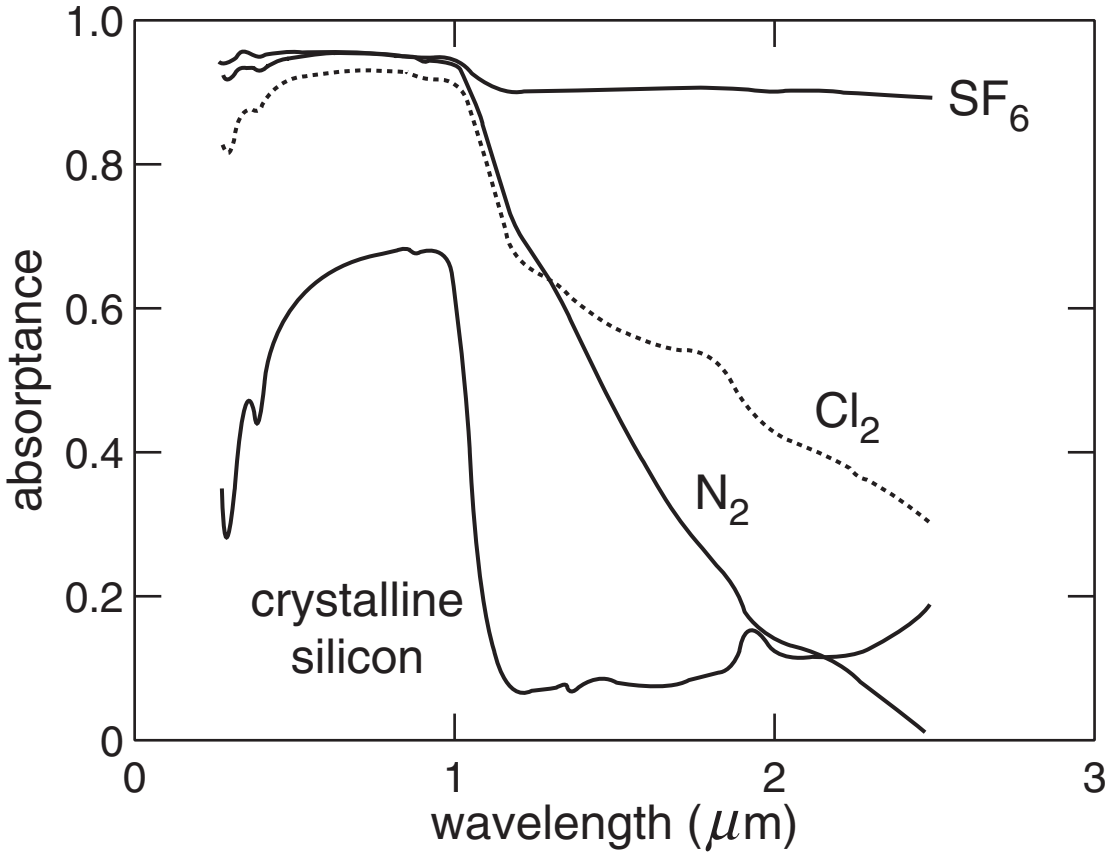
effect of ambient gas on absorptance



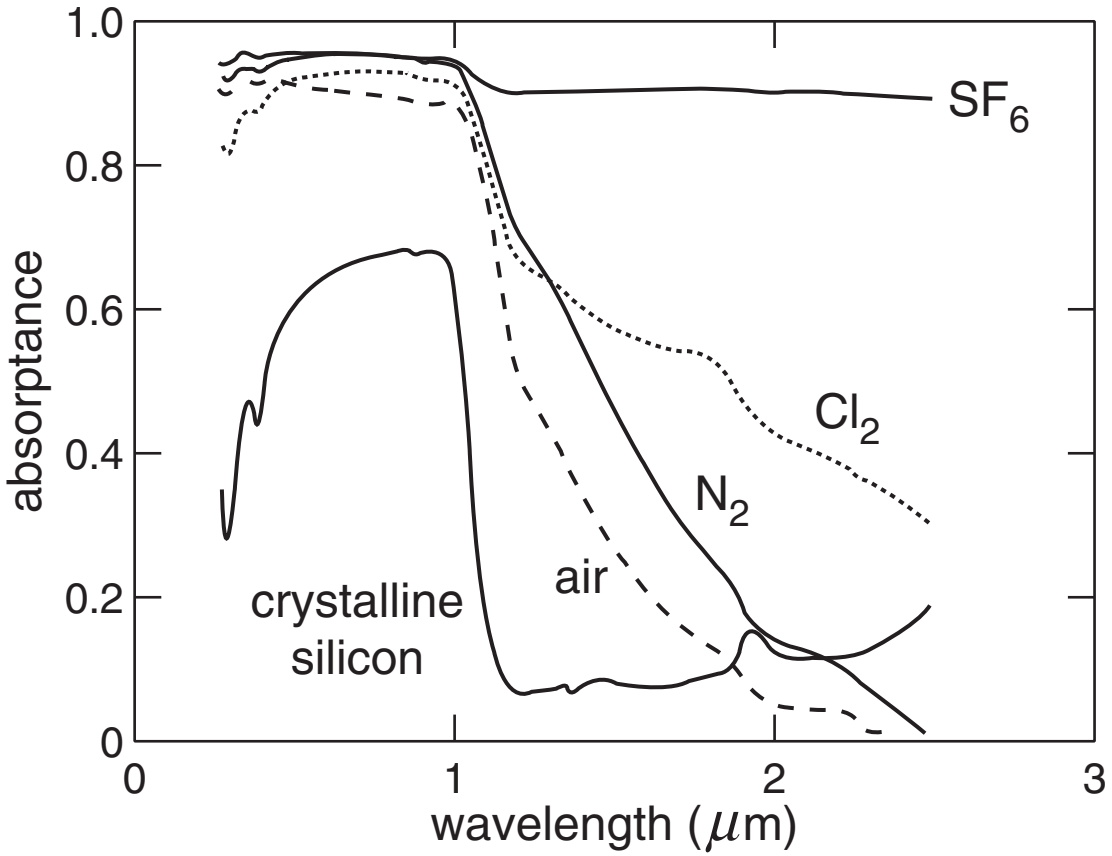
effect of ambient gas on absorptance



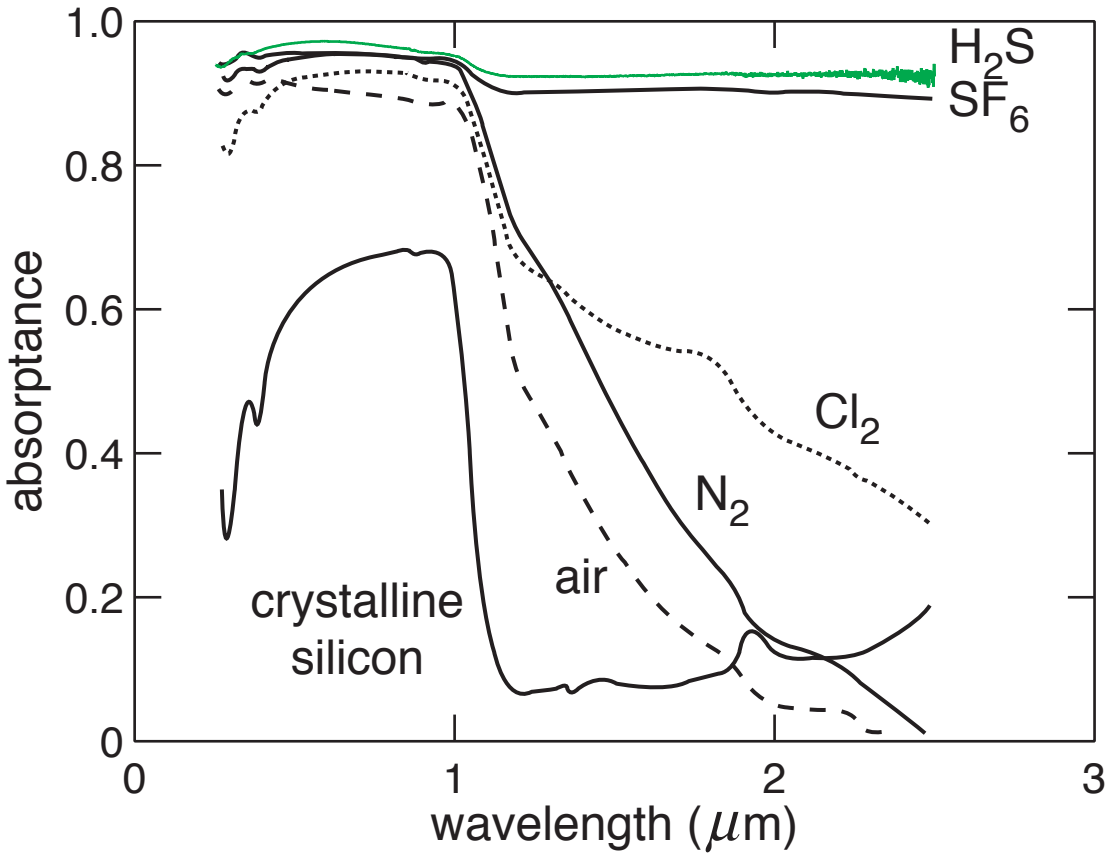
effect of ambient gas on absorptance



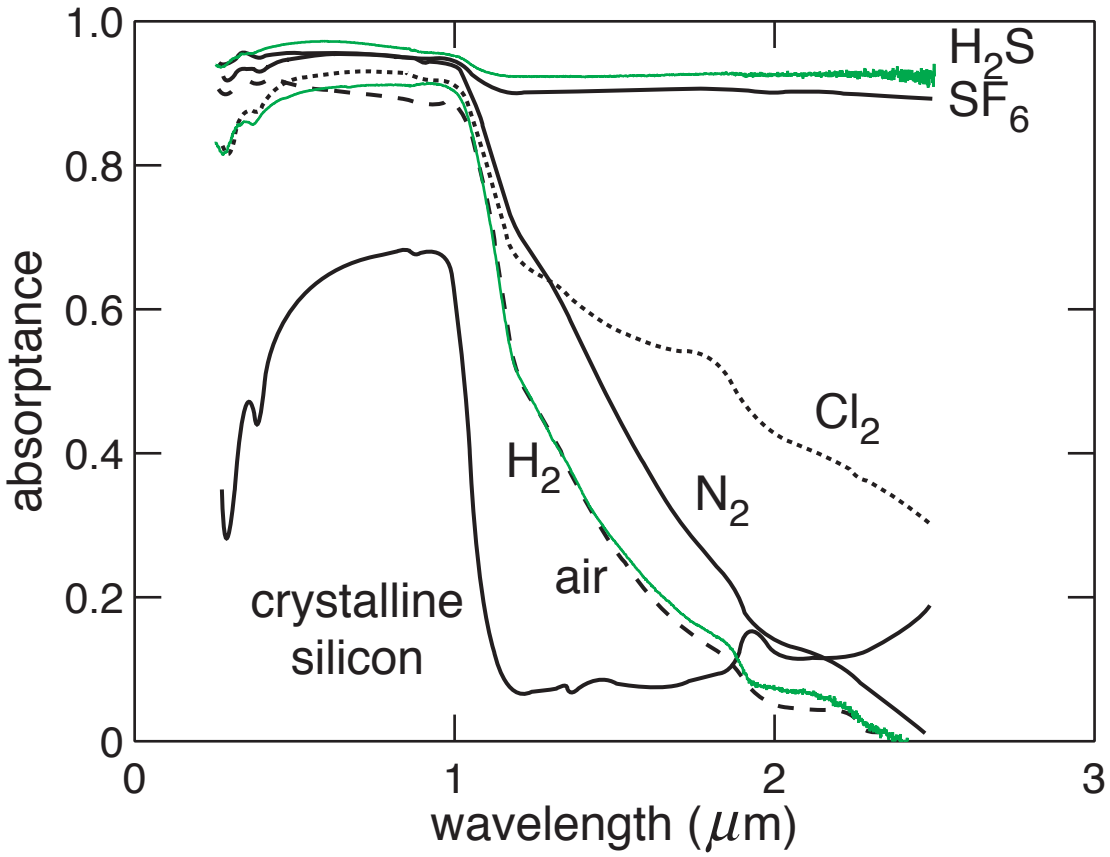
effect of ambient gas on absorptance



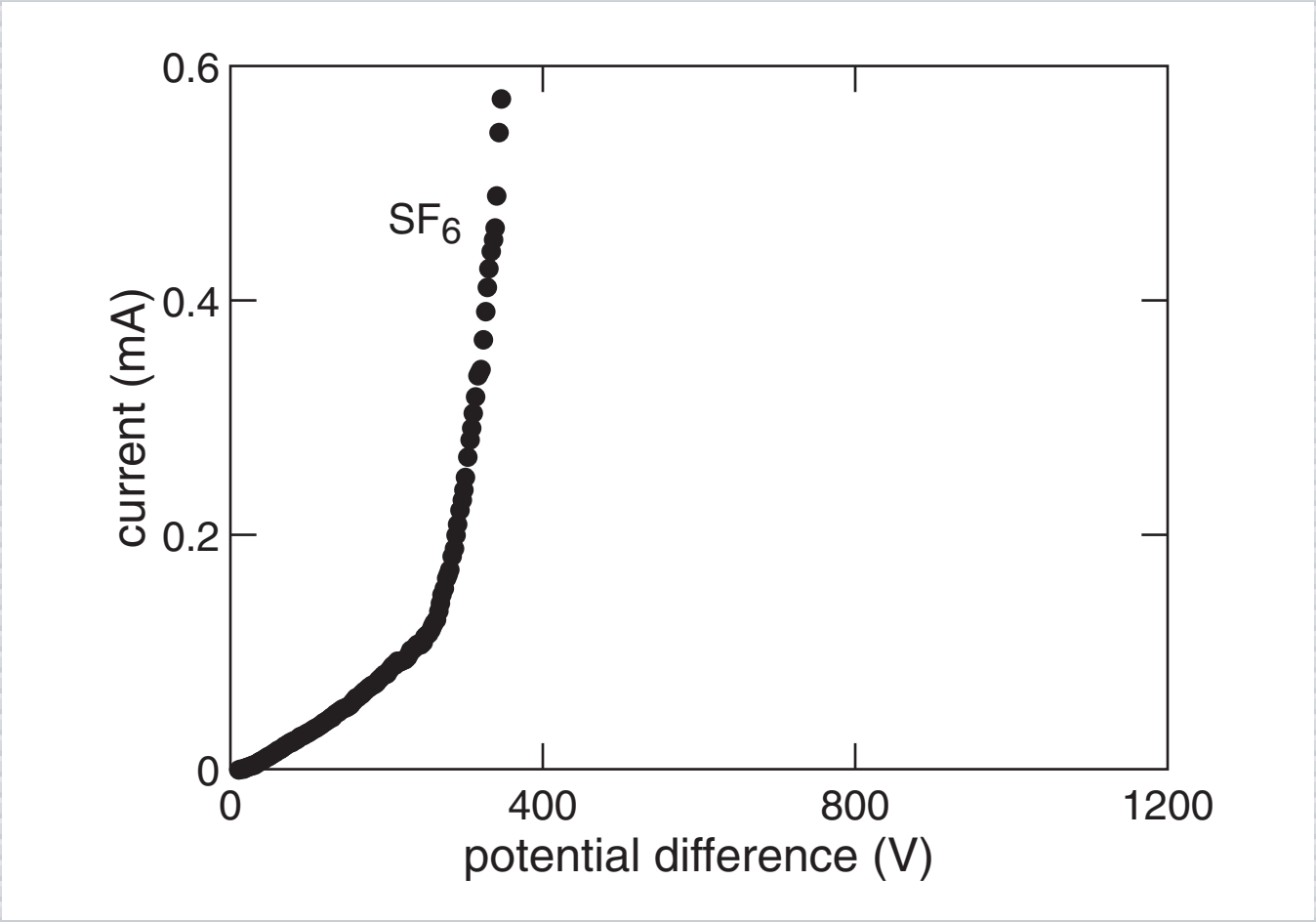
effect of ambient gas on absorptance



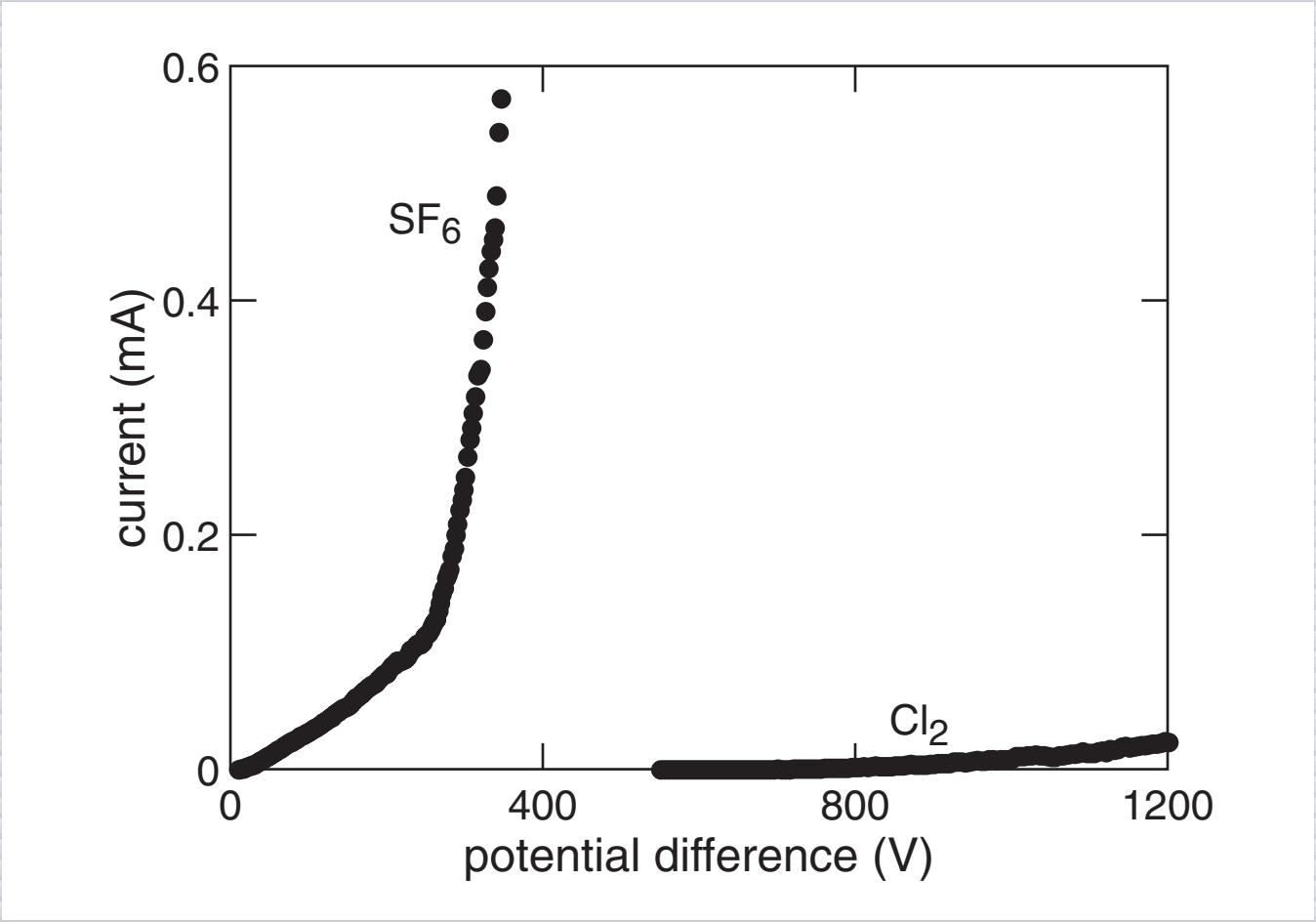
effect of ambient gas on absorptance



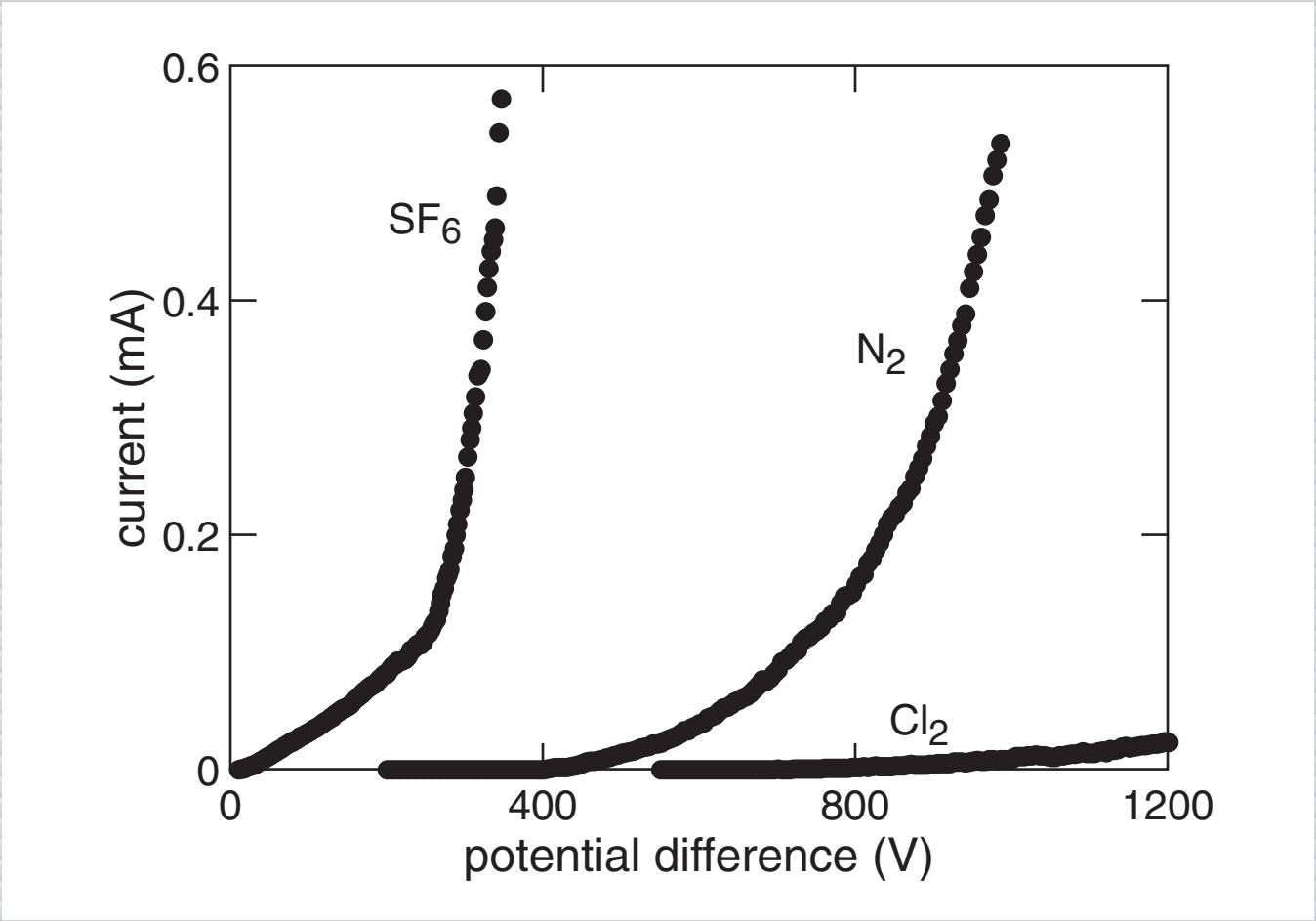
effect of ambient gas on field emission



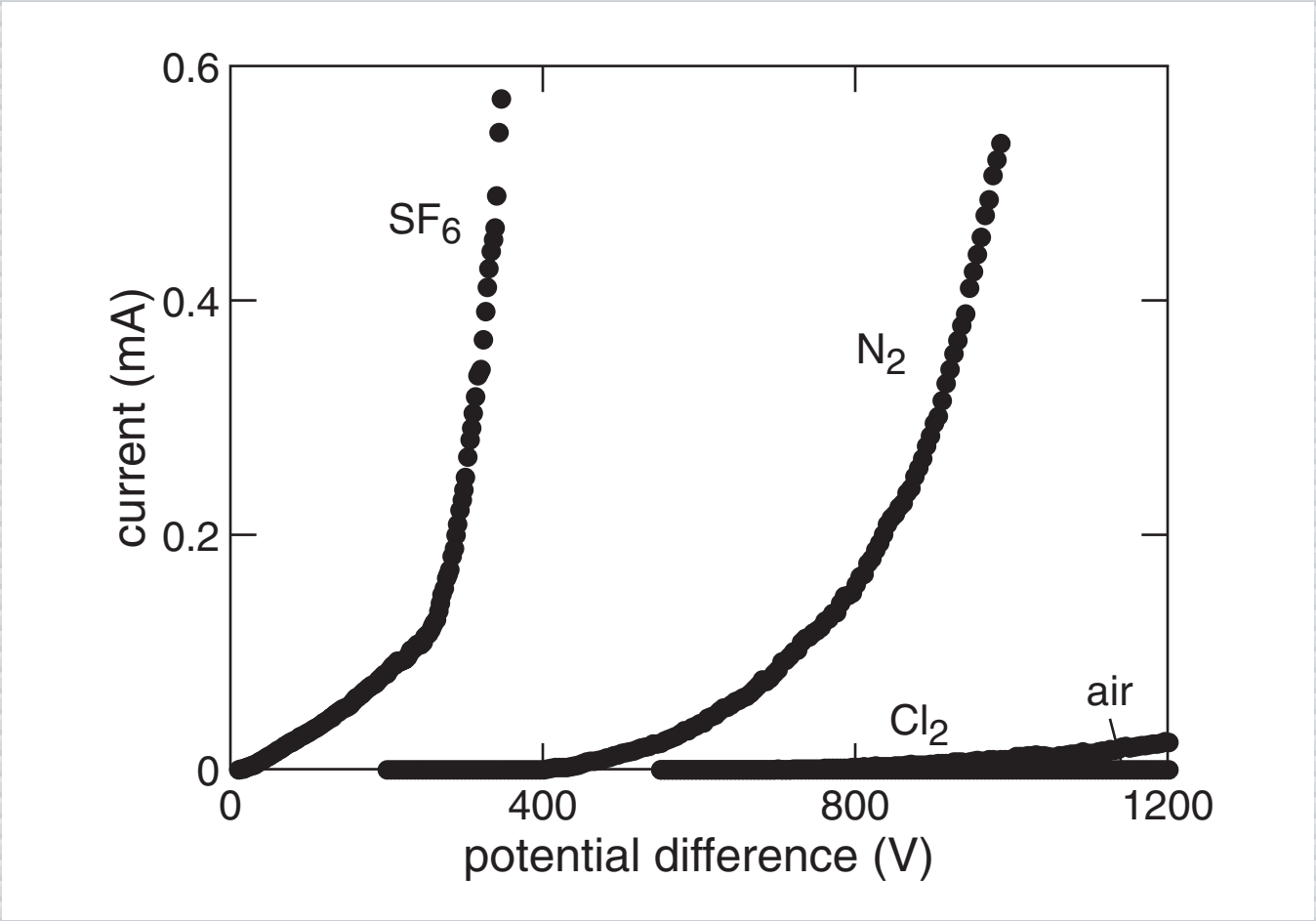
effect of ambient gas on field emission

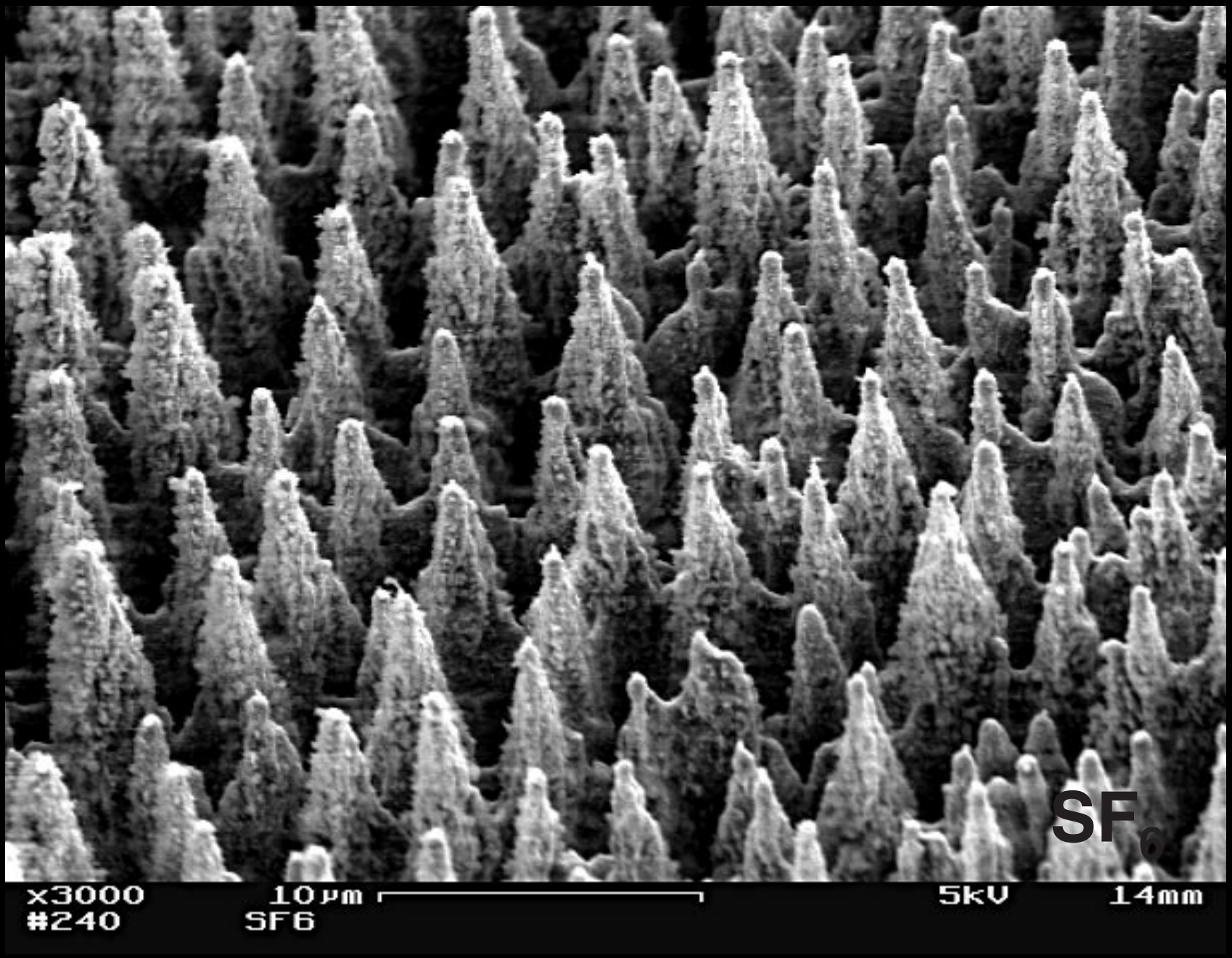


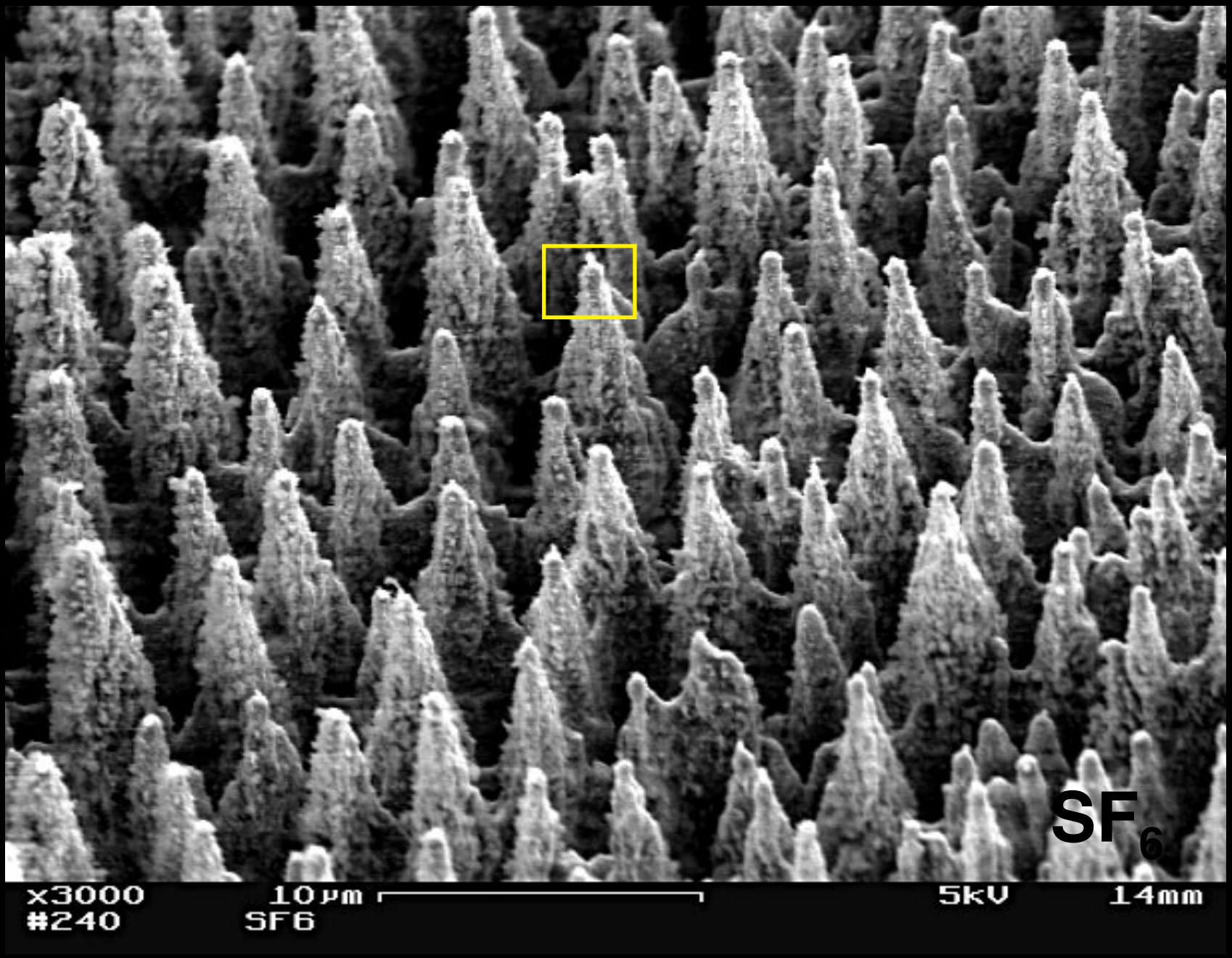
effect of ambient gas on field emission

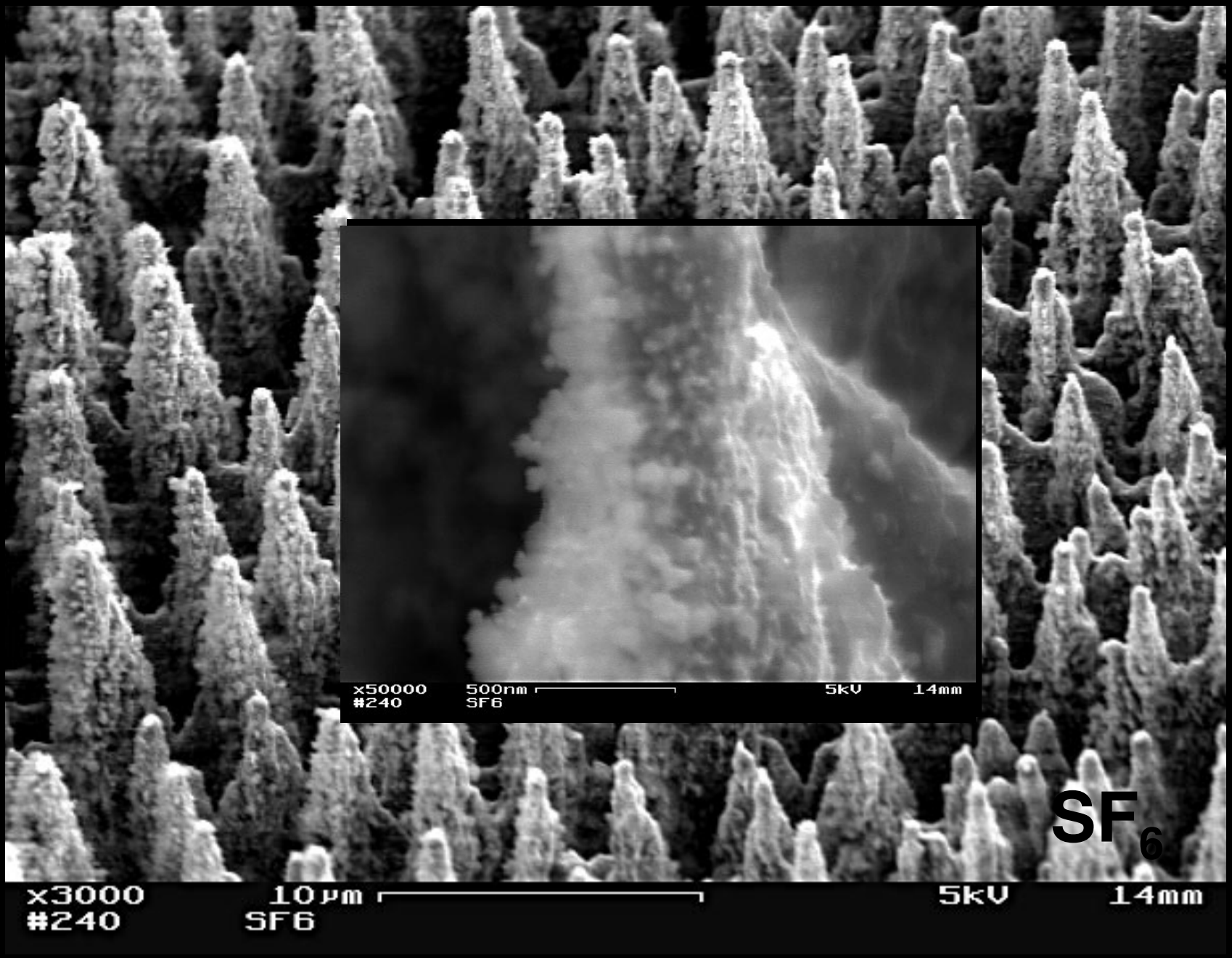


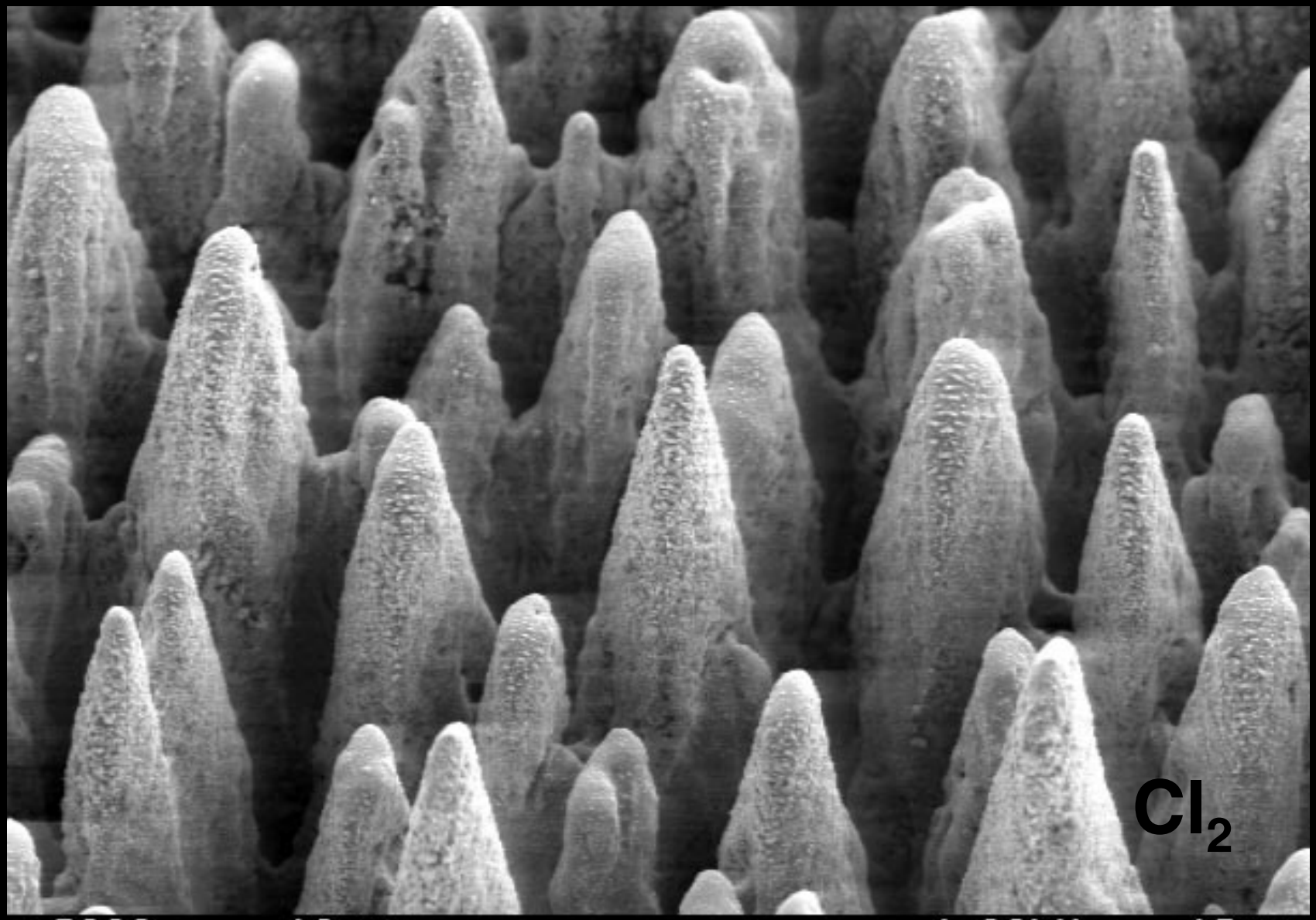
effect of ambient gas on field emission

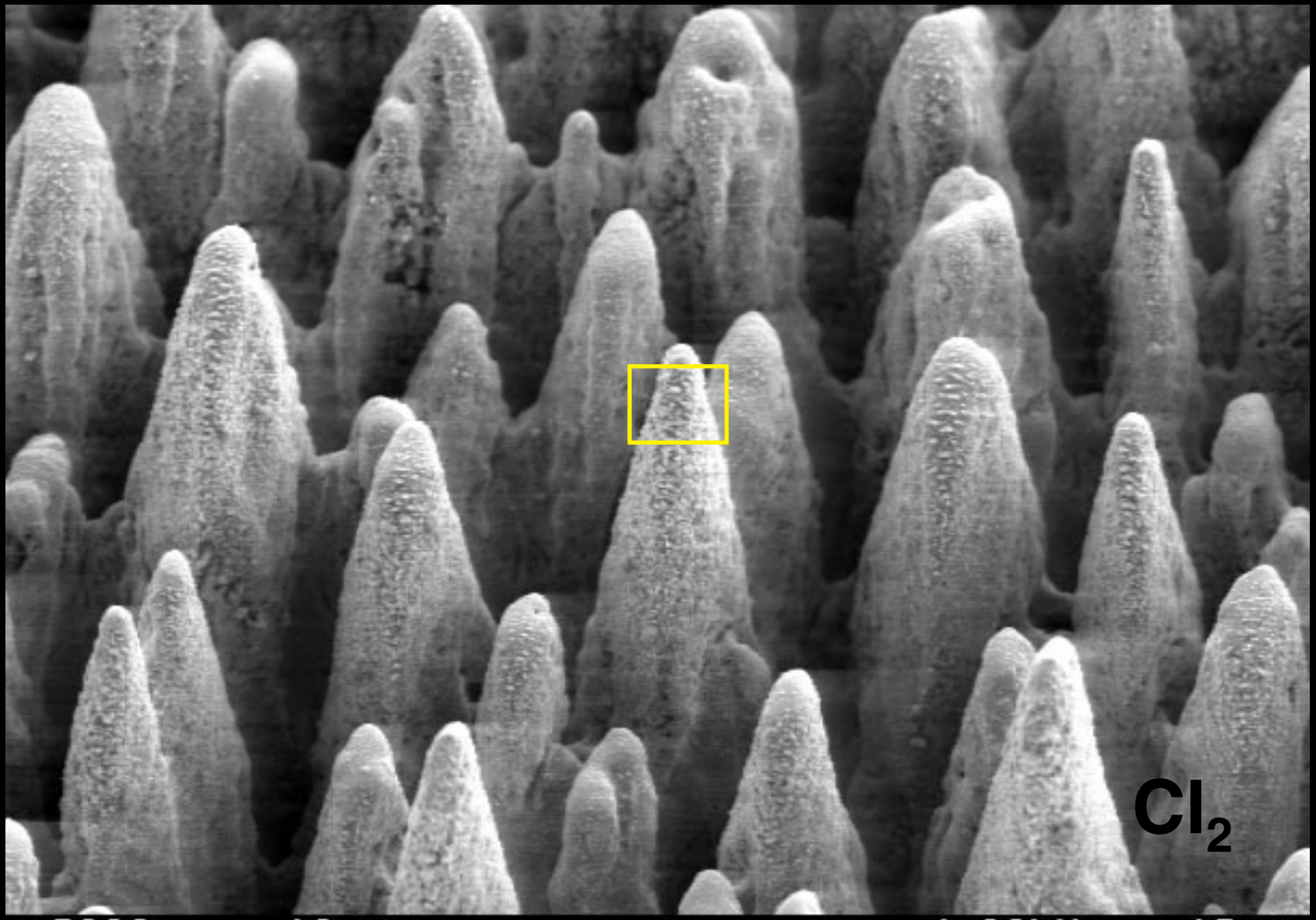


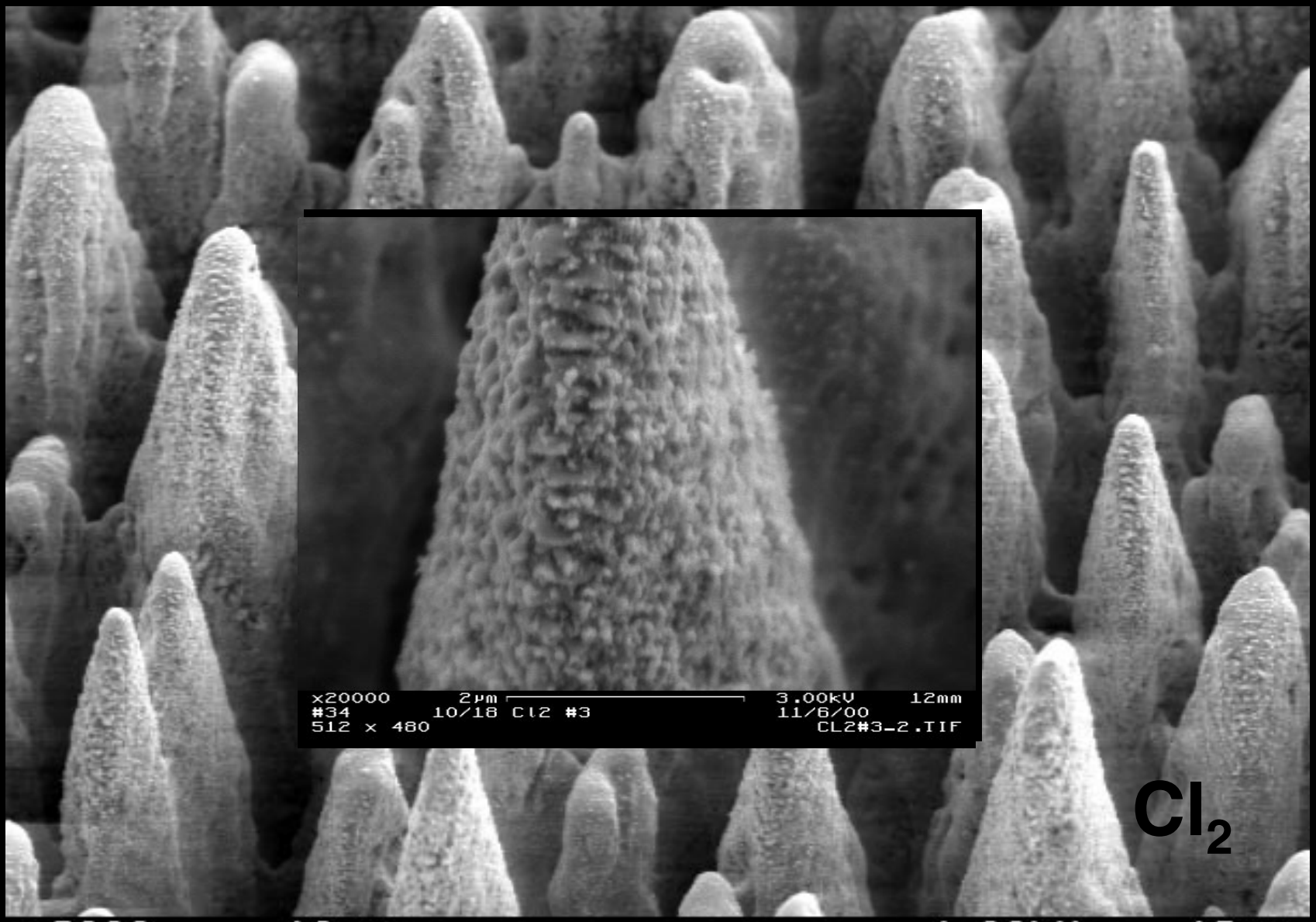

SF6
x3000
#240
10µm
SF6
5kV
14mm

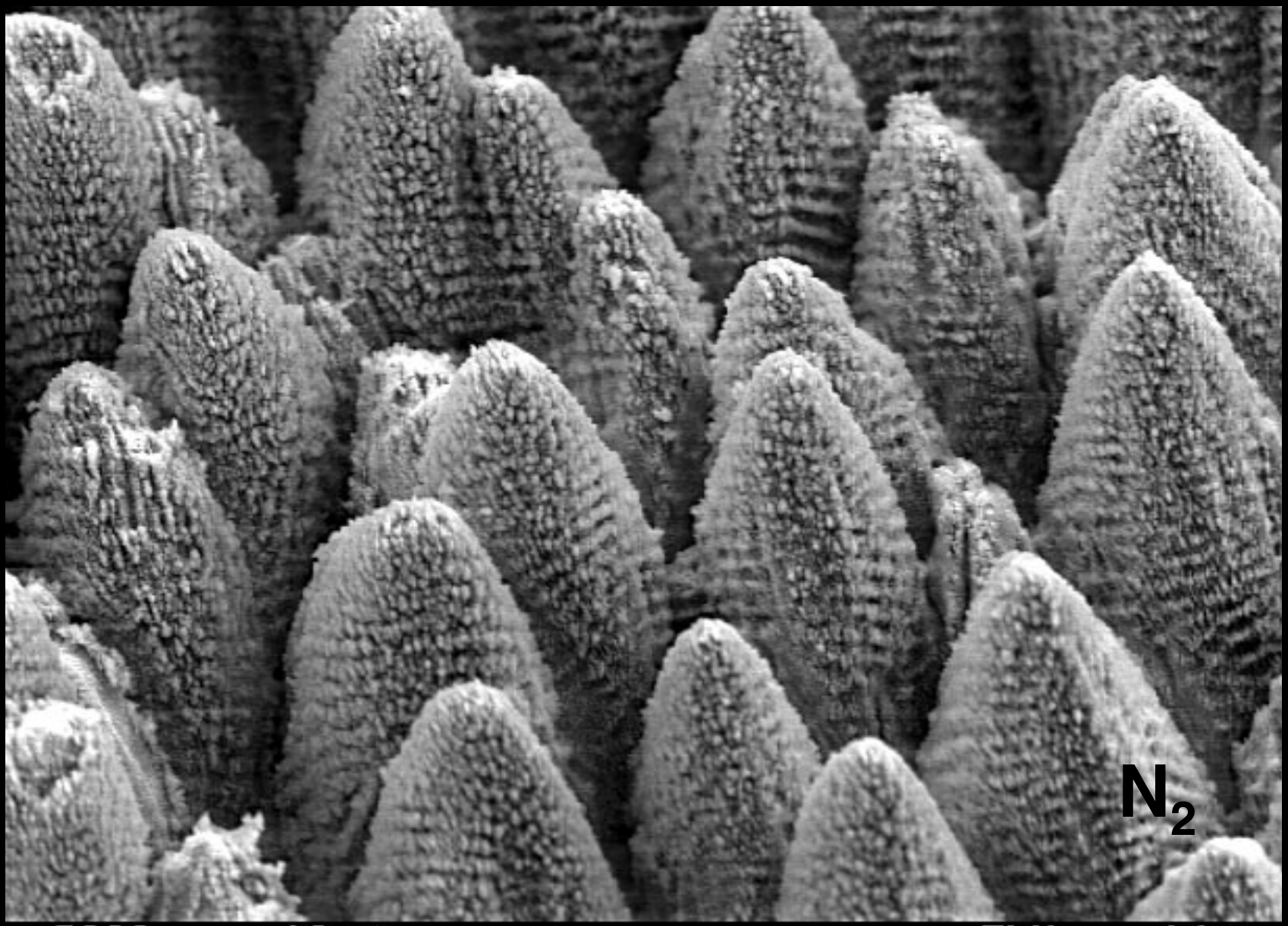

SF6
x3000
#240
10µm
SF6
5kV
14mm

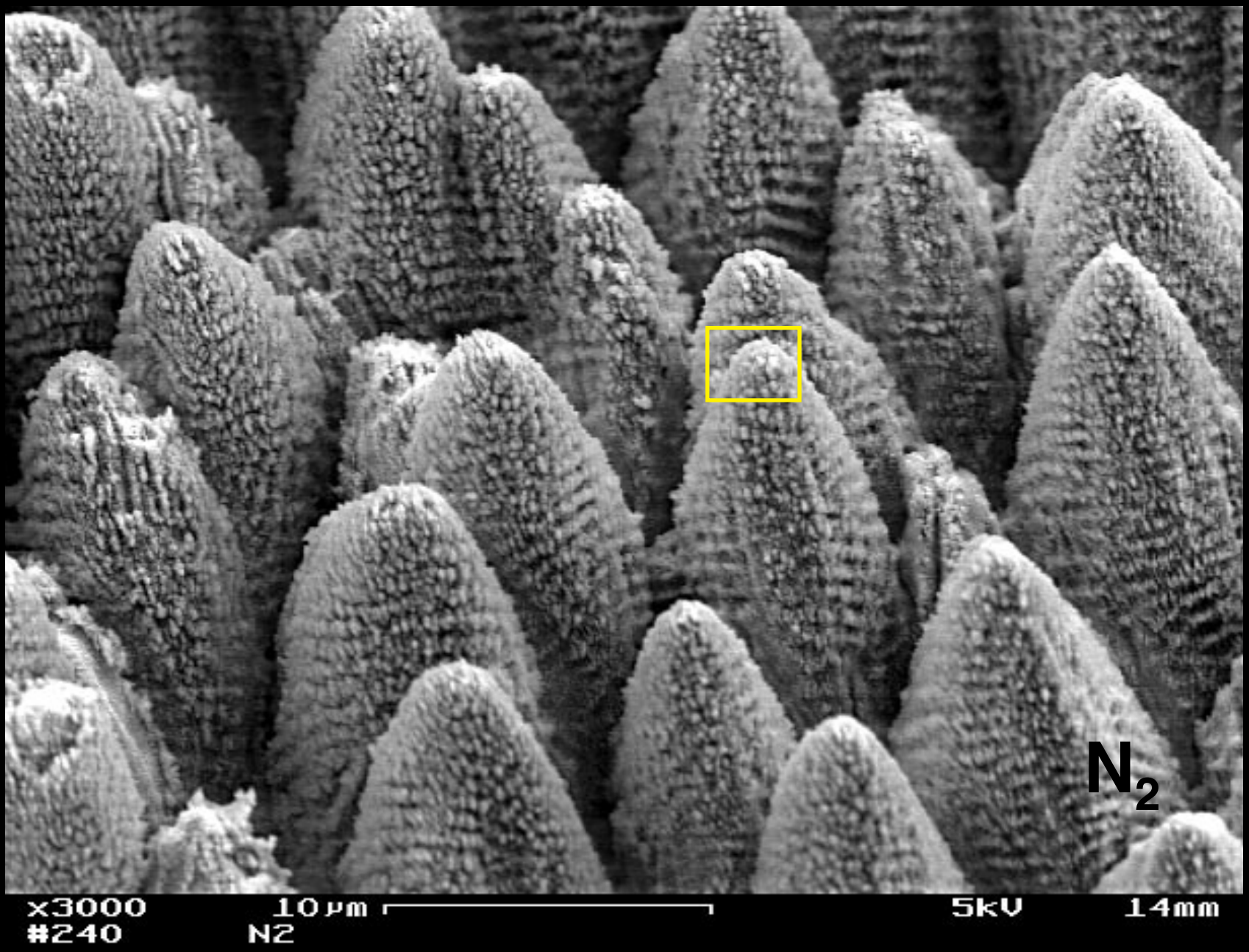

x50000
#240
500nm
SF6
5kV
14mm
SF6
x3000
#240
10µm
SF6
5kV
14mm

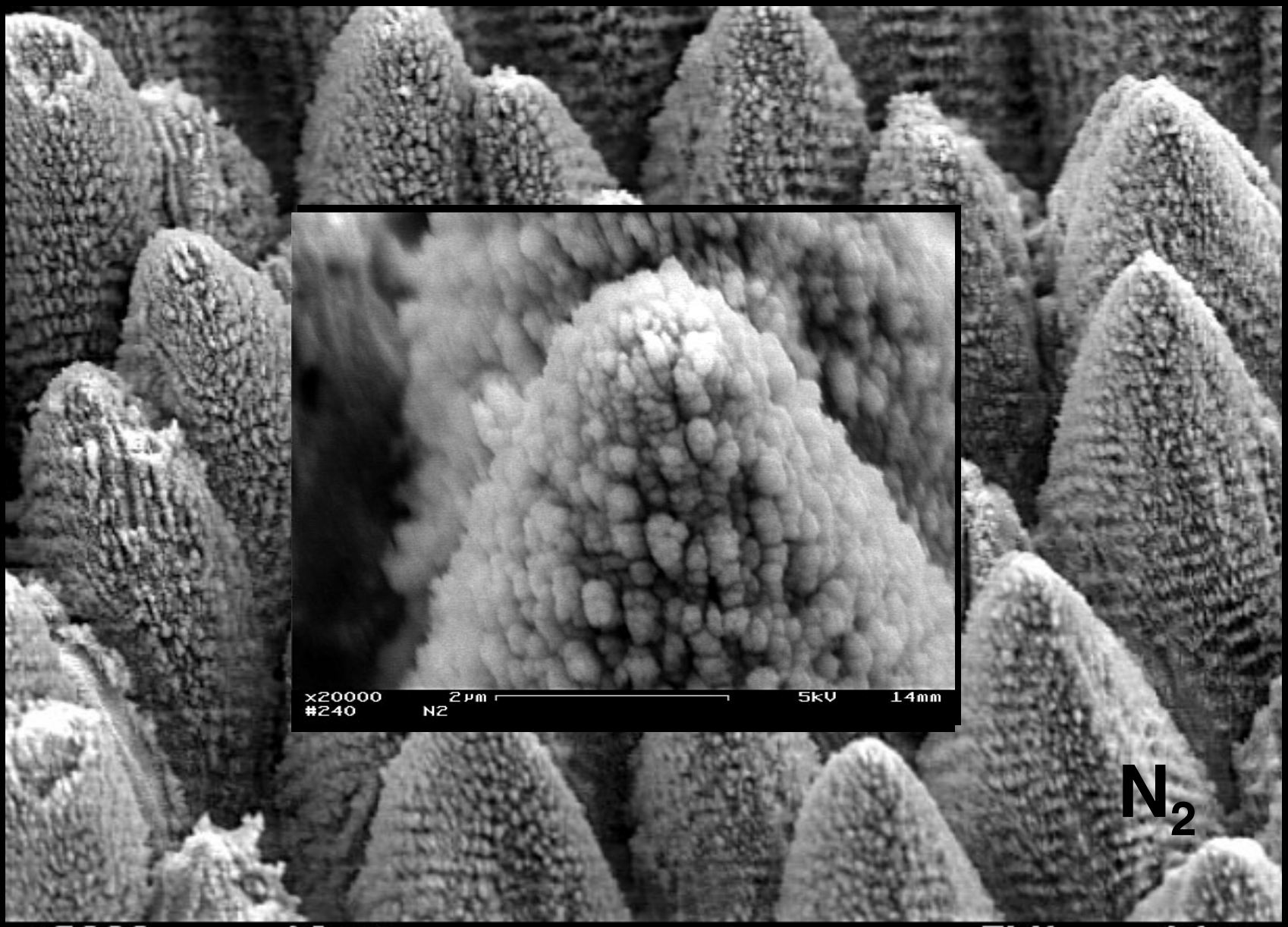

Cl_2
x3000 10μm
#34 10/18 Cl2 #3
512 x 480
4.00kV 12mm
11/6/00
CL2#3-1.TIF

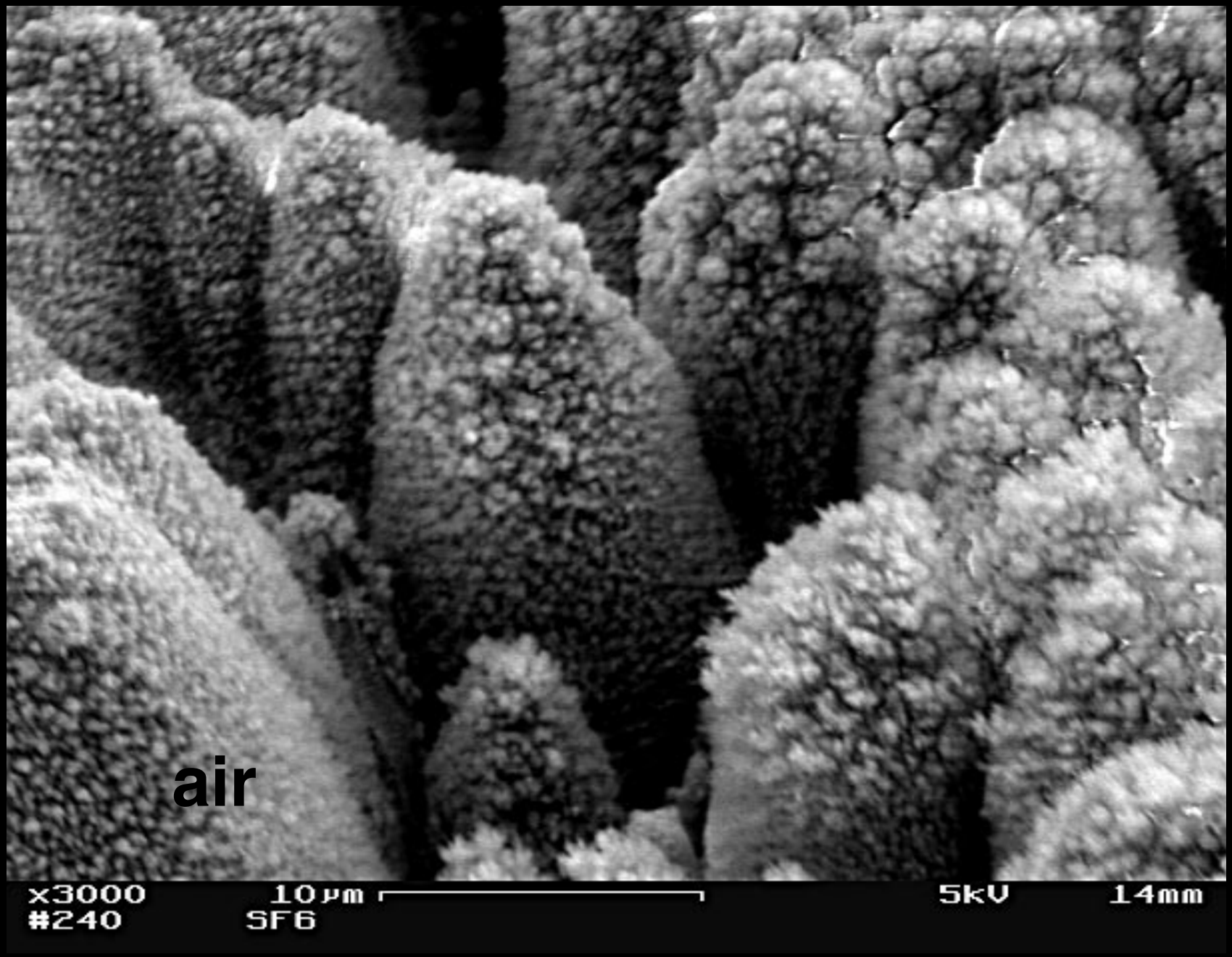

Cl_2
x3000 10μm 4.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3_1.TIF

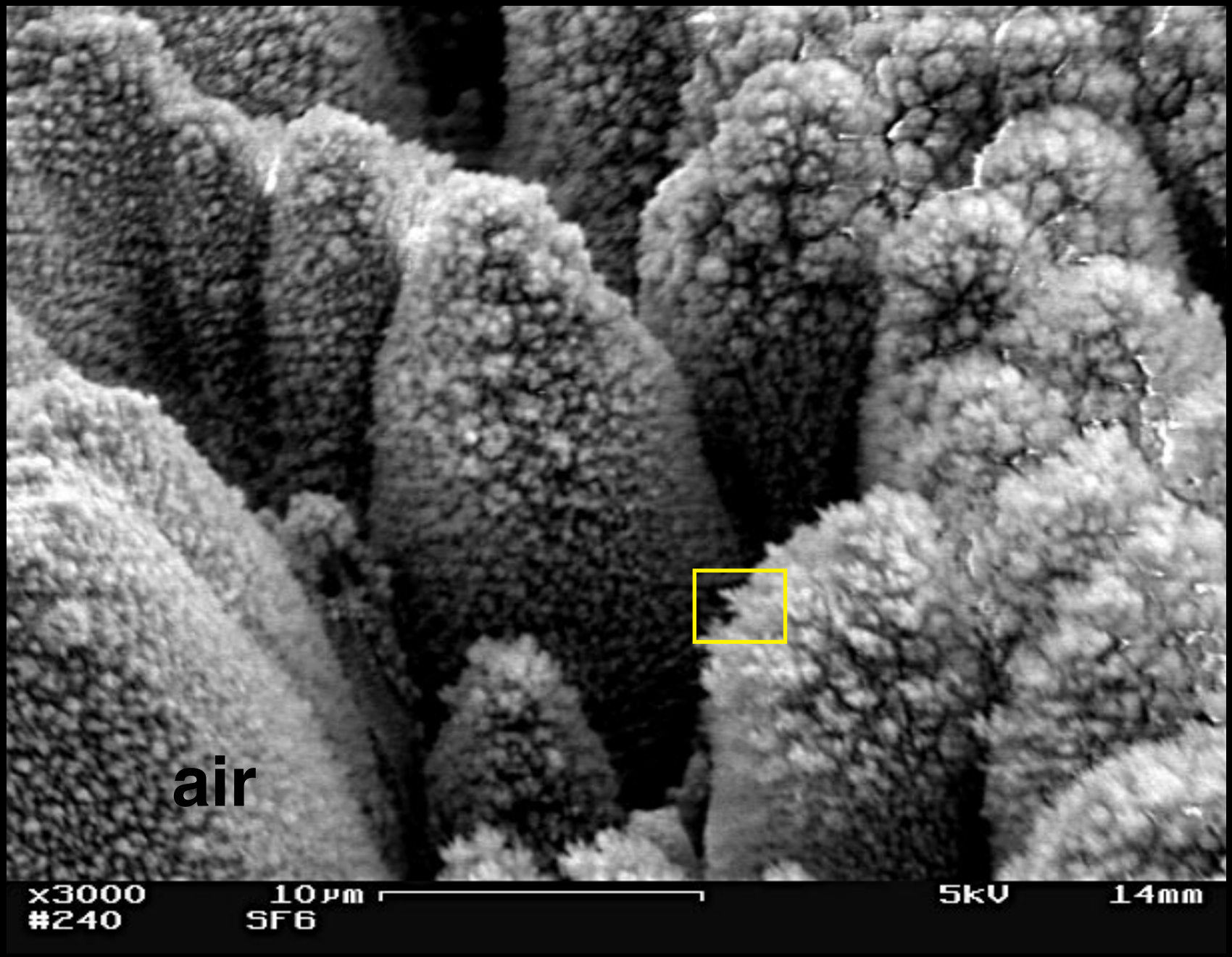

x20000 2µm 3.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3_2.TIF
Cl_2
x3000 10µm 4.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3_1.TIF

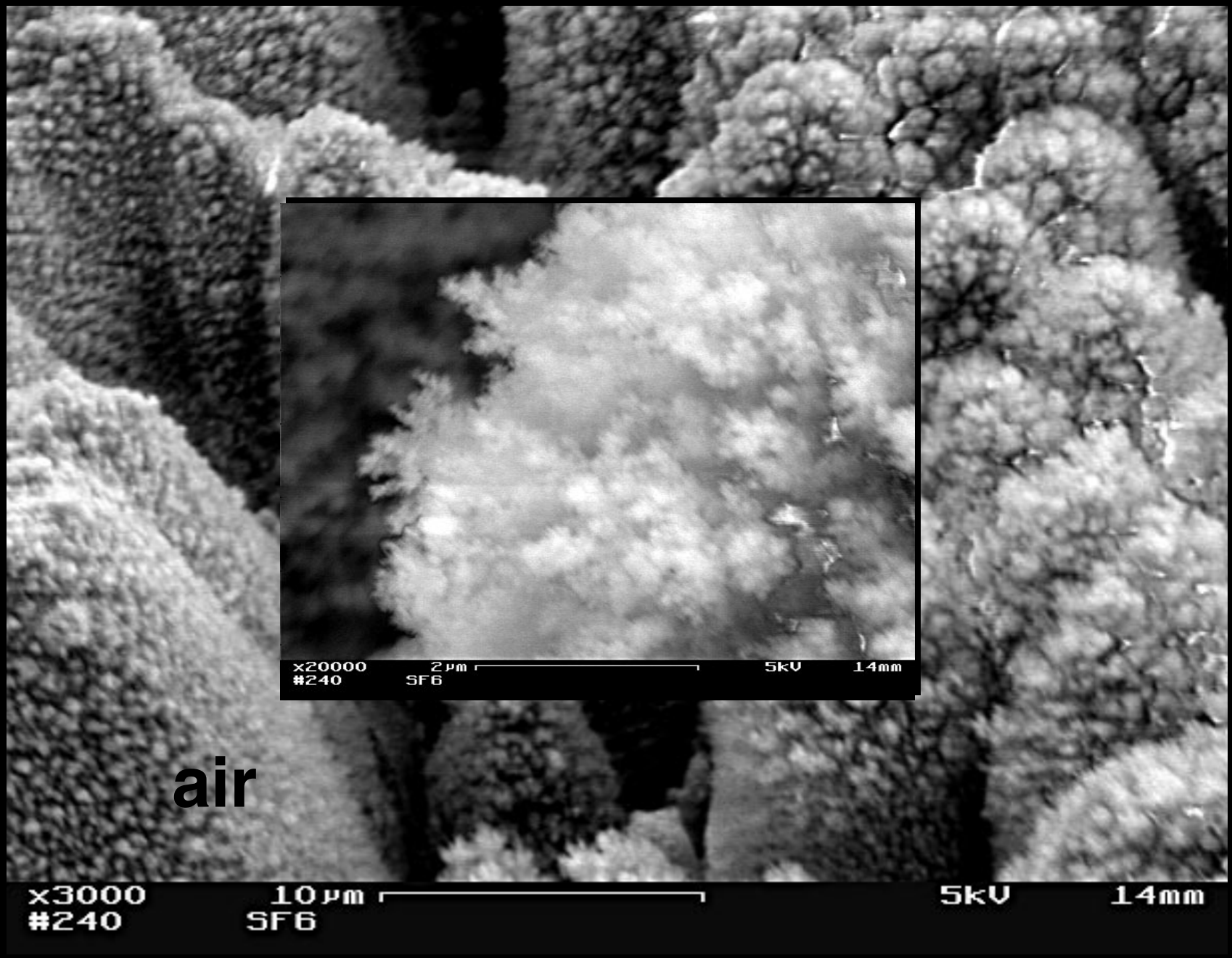

N_2
x3000
#240
10 µm
N2
5kV
14mm


N_2
x3000
#240
10 µm
N2
5kV
14mm

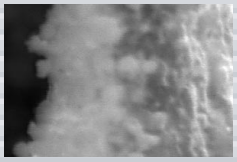
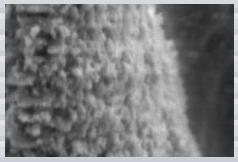
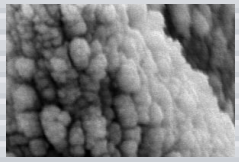

x20000 2µm 5kV 14mm
#240 N2
N_2
x3000 10µm 5kV 14mm
#240 N2


air
x3000
#240
10µm
SF6
5kV
14mm


air
x3000
#240
10μm
SF6
5kV
14mm


x20000 2µm 5kV 14mm
#240 SF6
air
x3000 10µm 5kV 14mm
#240 SF6

Structural and chemical analysis

	SF_6	Cl_2	N_2	air
IR absorption	high	medium	low	low
field emission	high	low	medium	low
SIMS	high S	?	?	high O
nanostructure				

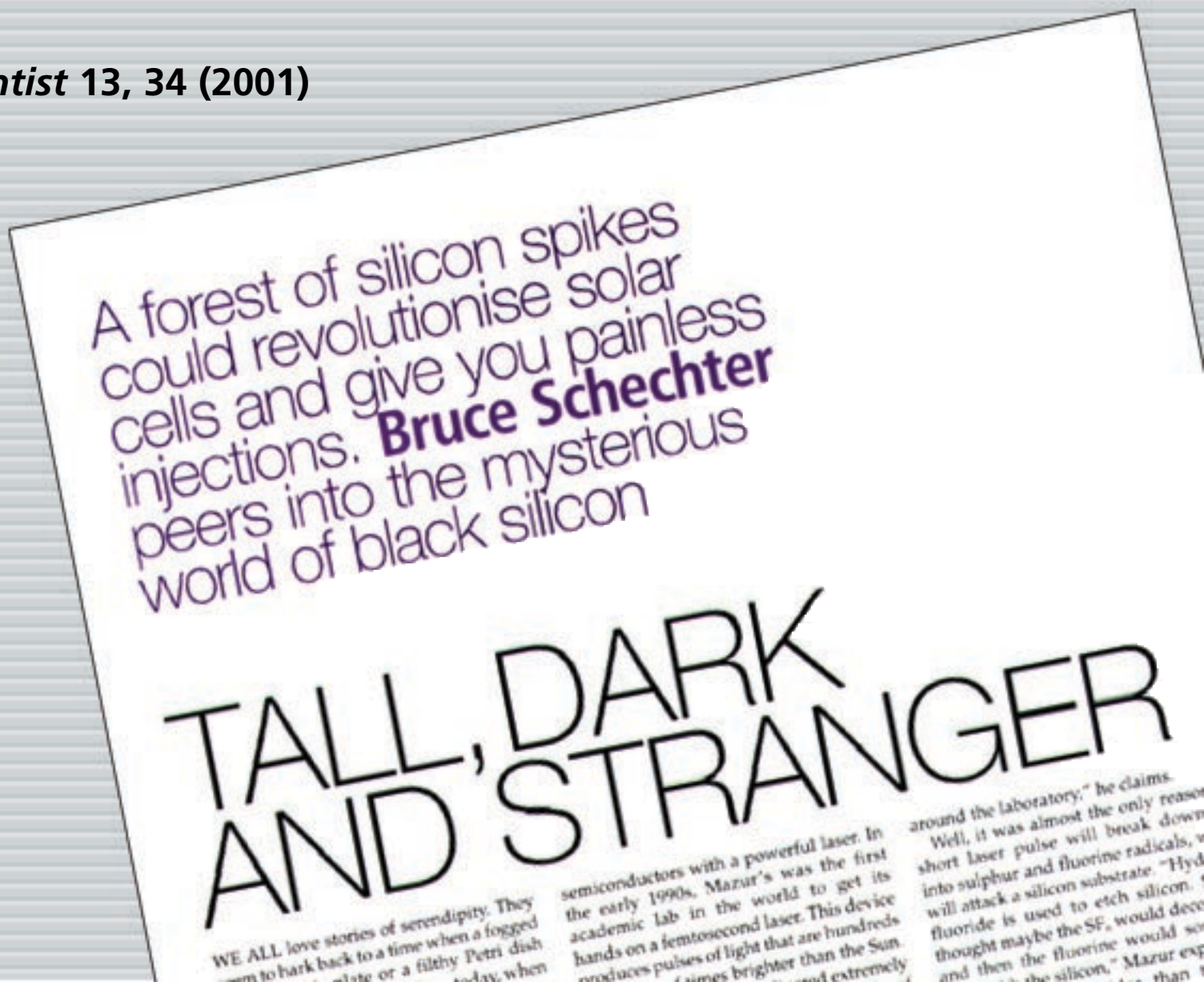
Structural and chemical analysis

- significant incorporation of ambient species
- nanostructured surface layer
- sulfur content correlates with IR absorption

Outline

- Properties
- Structural and chemical analysis
- **Outlook**

New Scientist 13, 34 (2001)



A forest of silicon spikes could revolutionise solar cells and give you painless injections. **Bruce Schechter** peers into the mysterious world of black silicon

TALL, DARK AND STRANGER

WE ALL love stories of serendipity. They seem to hark back to a time when a fogged photographic plate or a filthy Petri dish

semiconductors with a powerful laser. In the early 1990s, Mazur's was the first academic lab in the world to get its hands on a femtosecond laser. This device produces pulses of light that are hundreds

around the laboratory," he claims.

Well, it was almost the only reason short laser pulse will break down into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrofluoride is used to etch silicon. thought maybe the SF_6 would decompose and then the fluorine would react with the silicon," Mazur explains

Outlook

- **detector technology**

Outlook

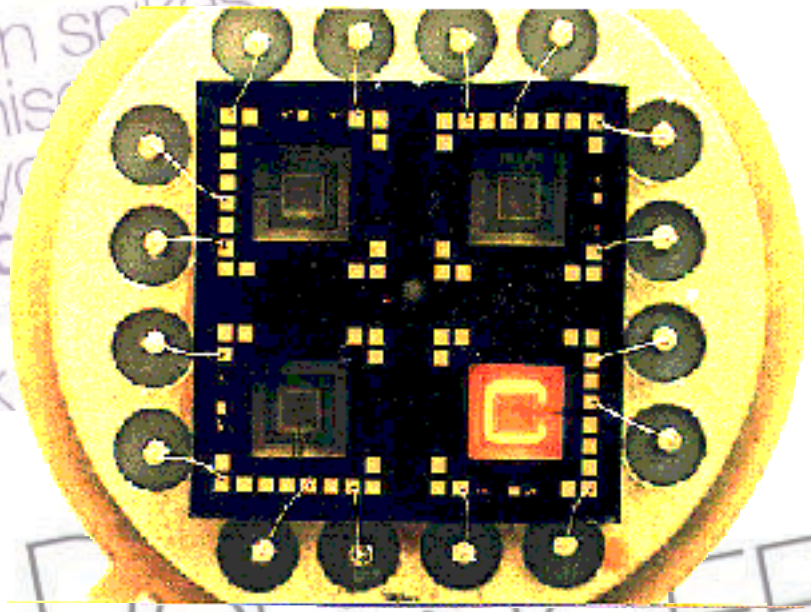
- **detector technology**
- **solar cells**

Outlook

- detector technology
- solar cells
- display technology

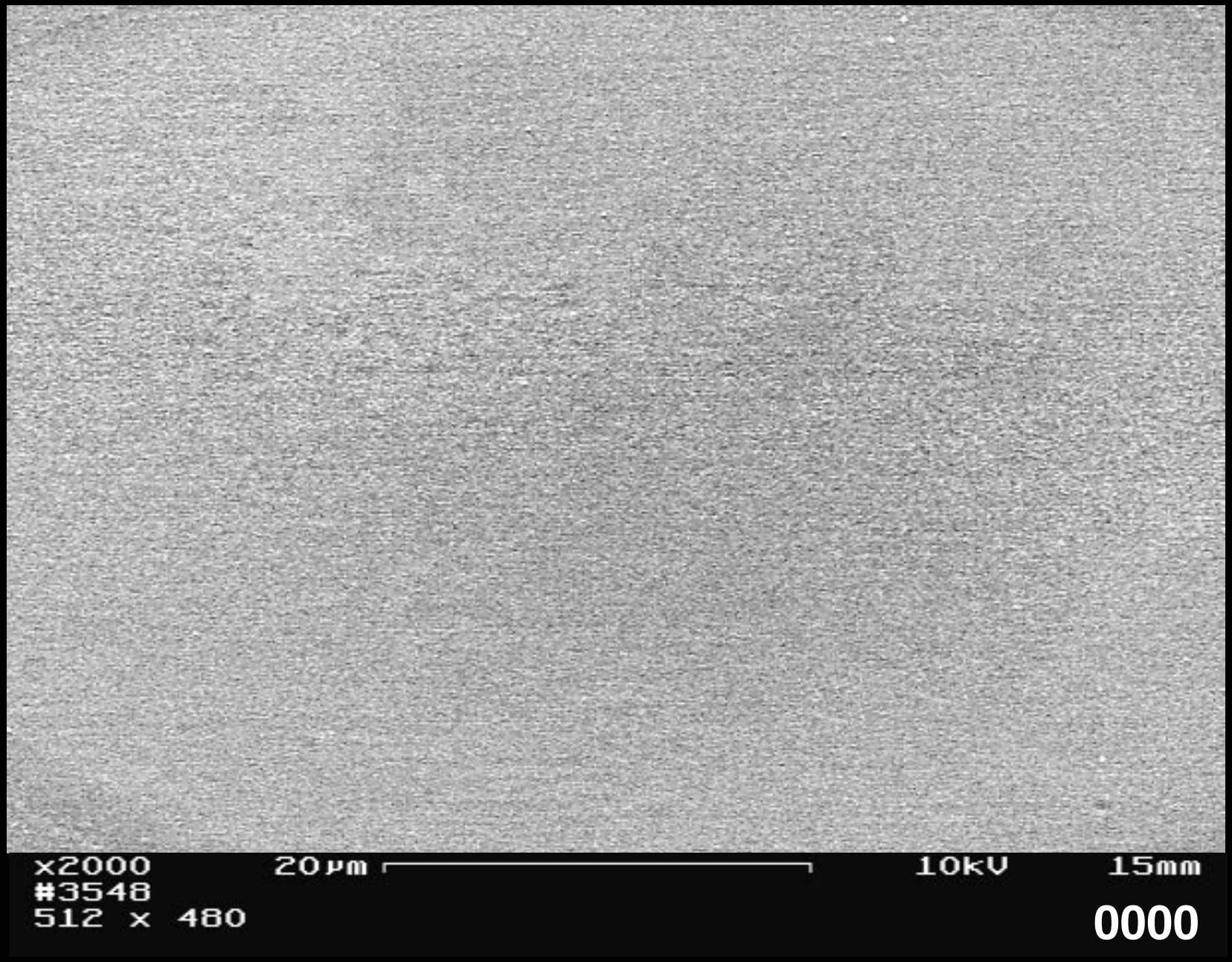
Outlook

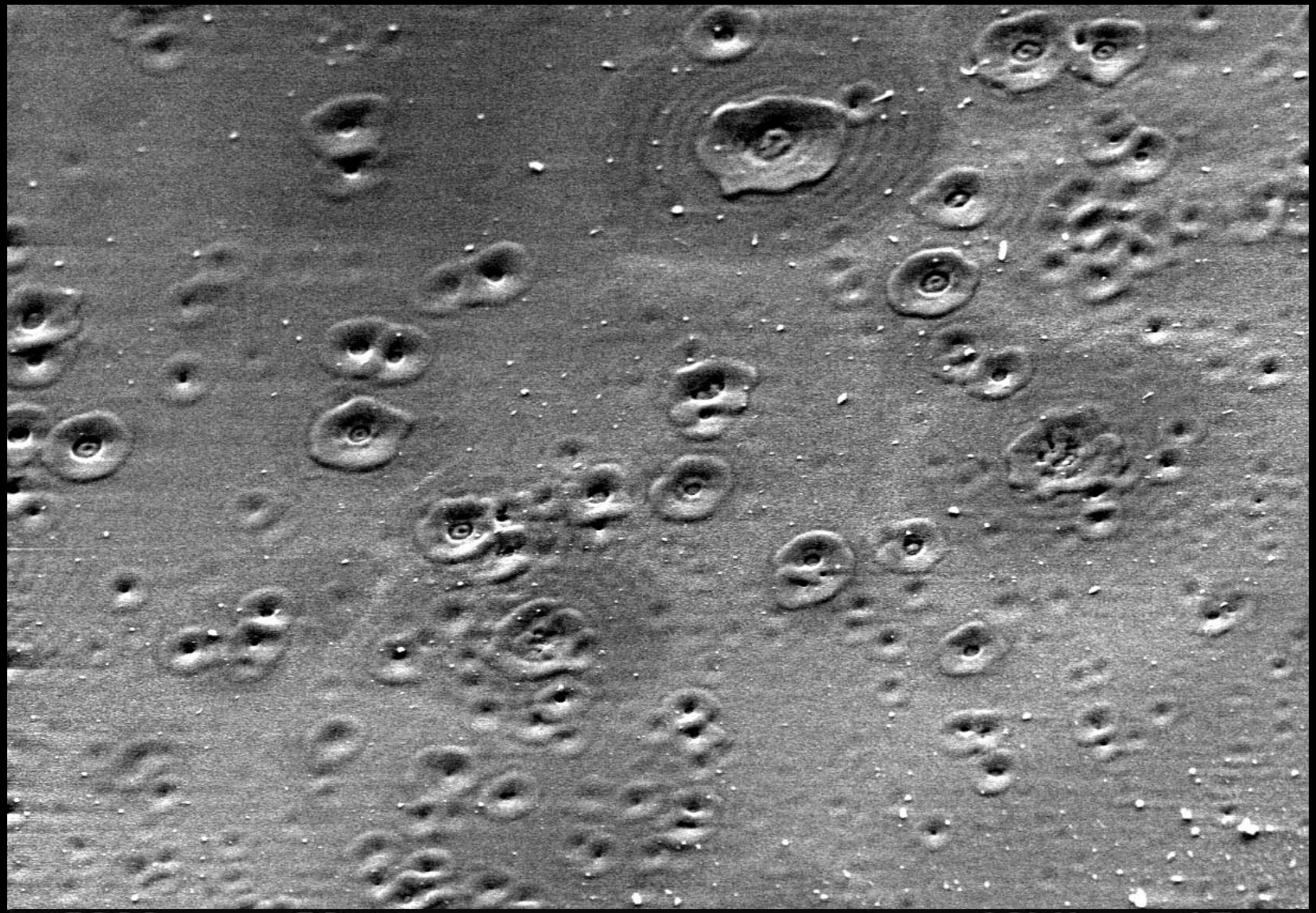
- detector technology
- solar cells
- display technology
- sensors



Outlook

- development of spikes
- spike formation through grids
- cell adhesion
- functionalization


x2000 20µm 10kV 15mm
#3548
512 x 480
0000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10kV
15mm
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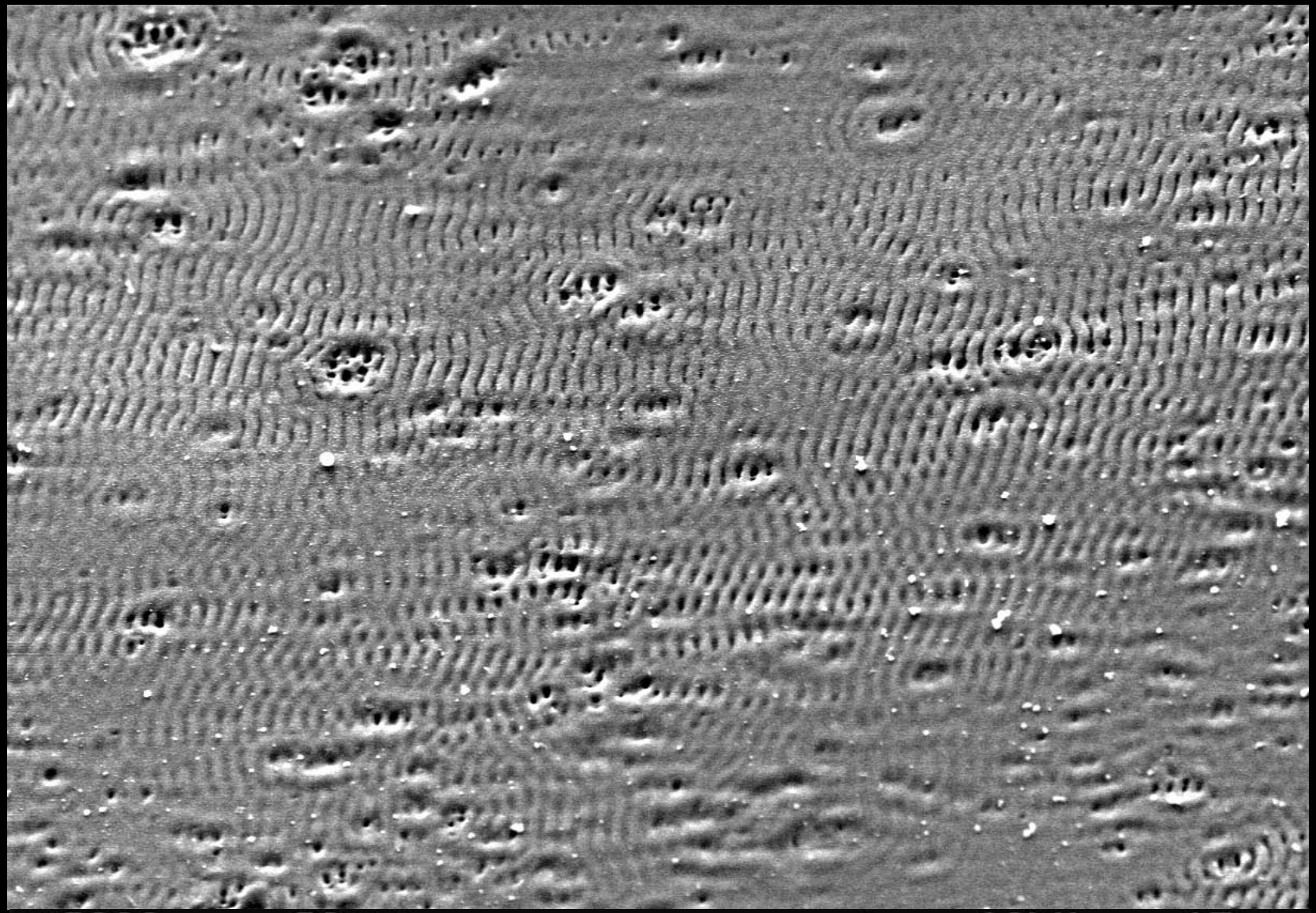
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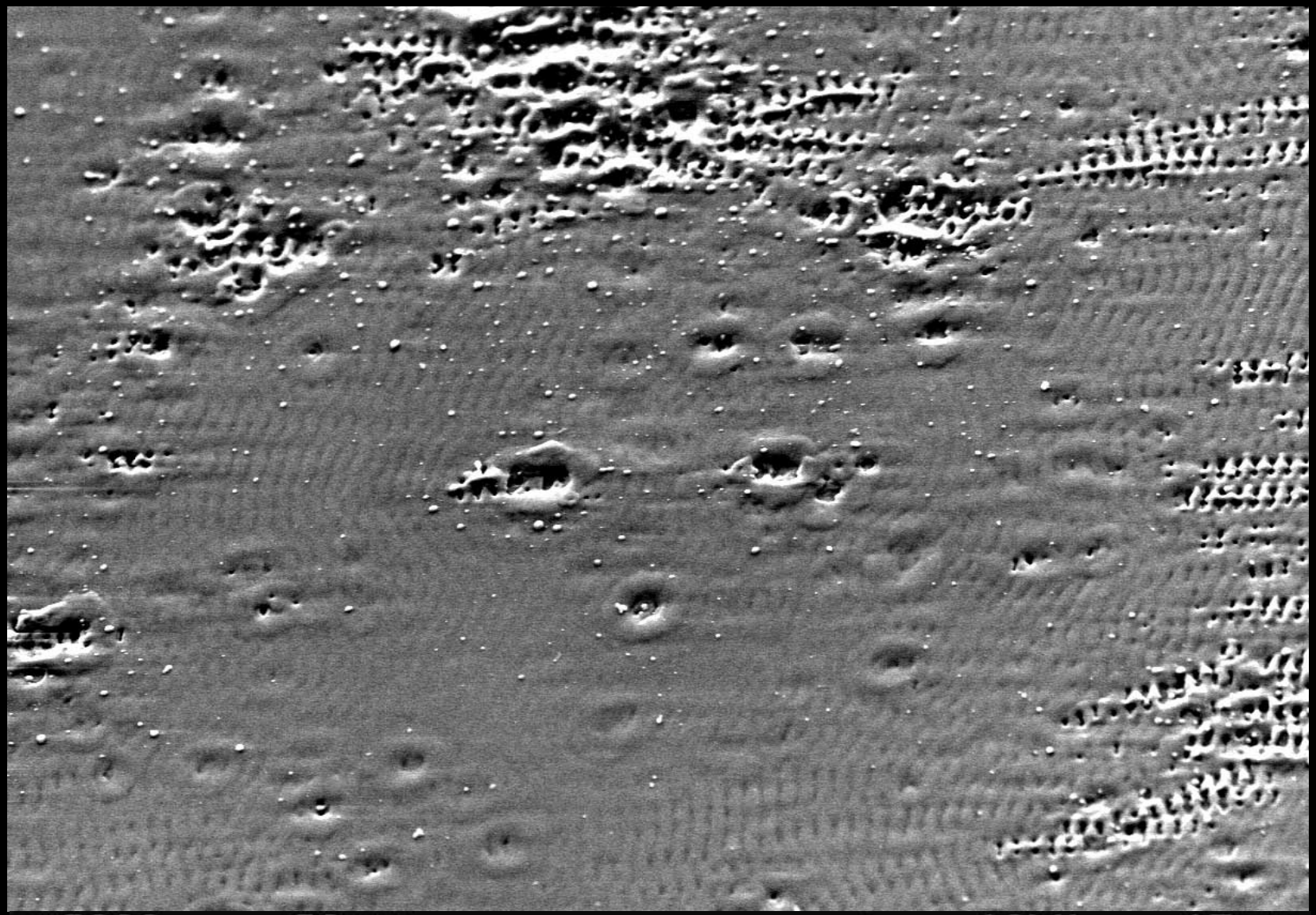
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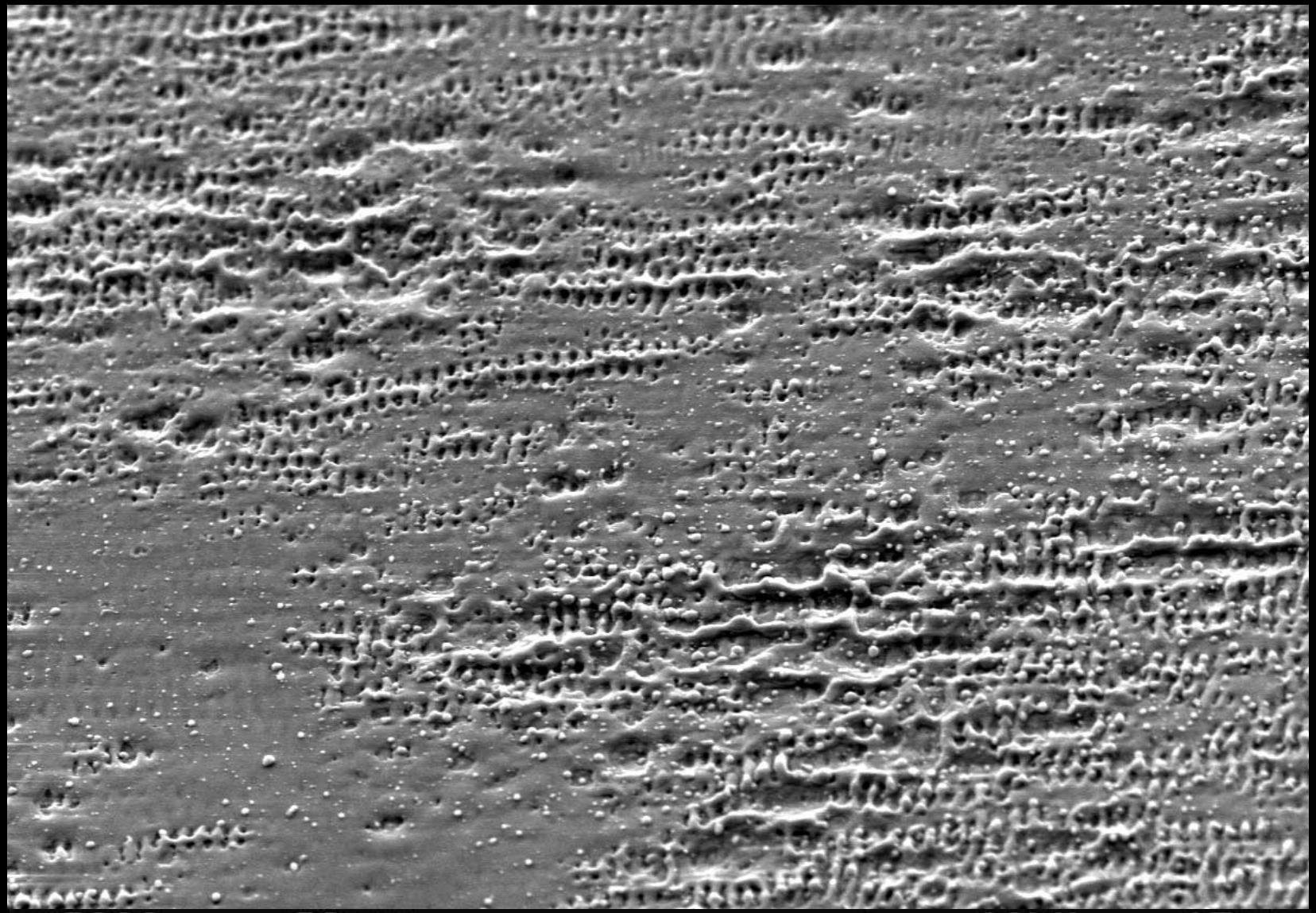
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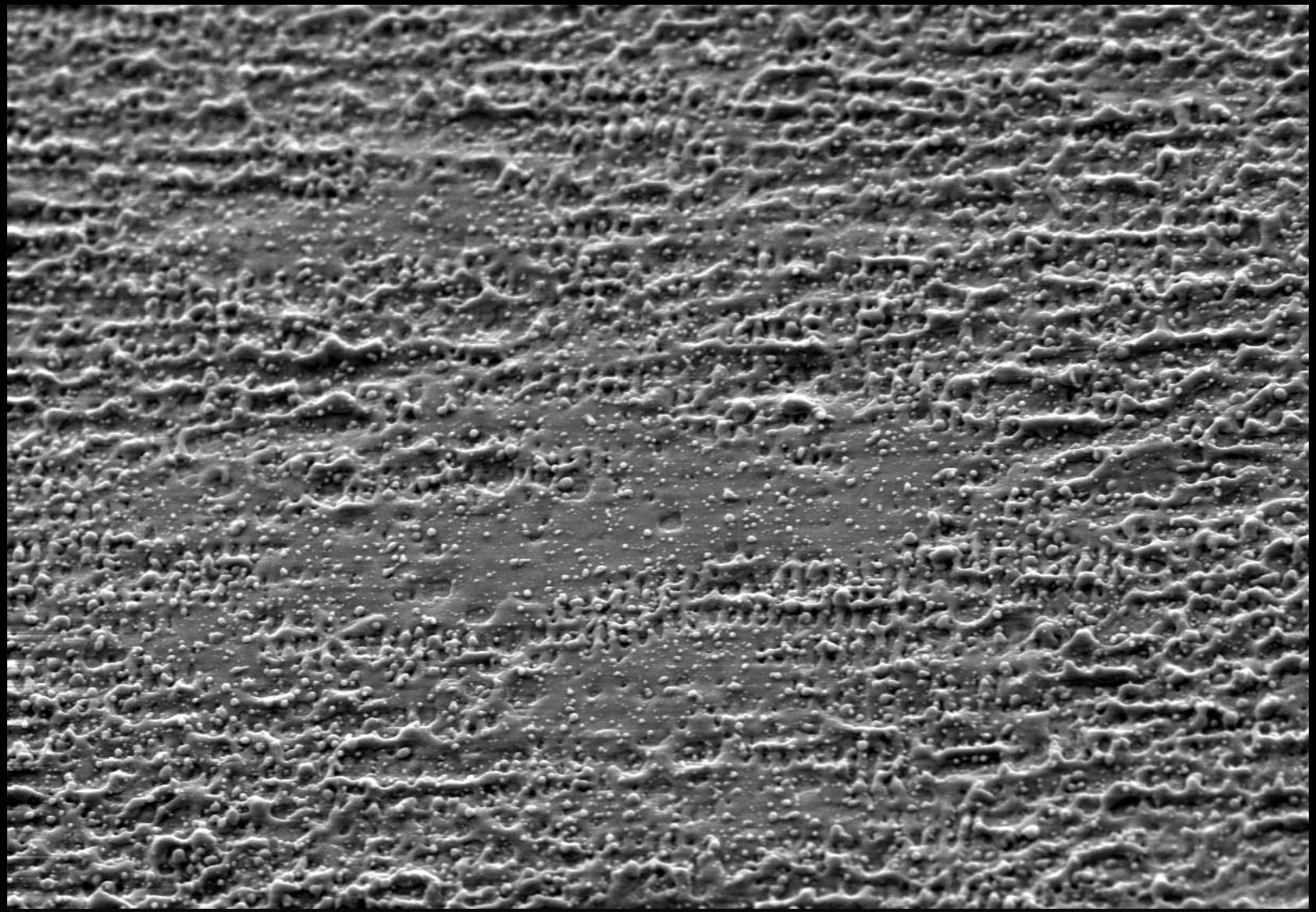
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10kV
15mm
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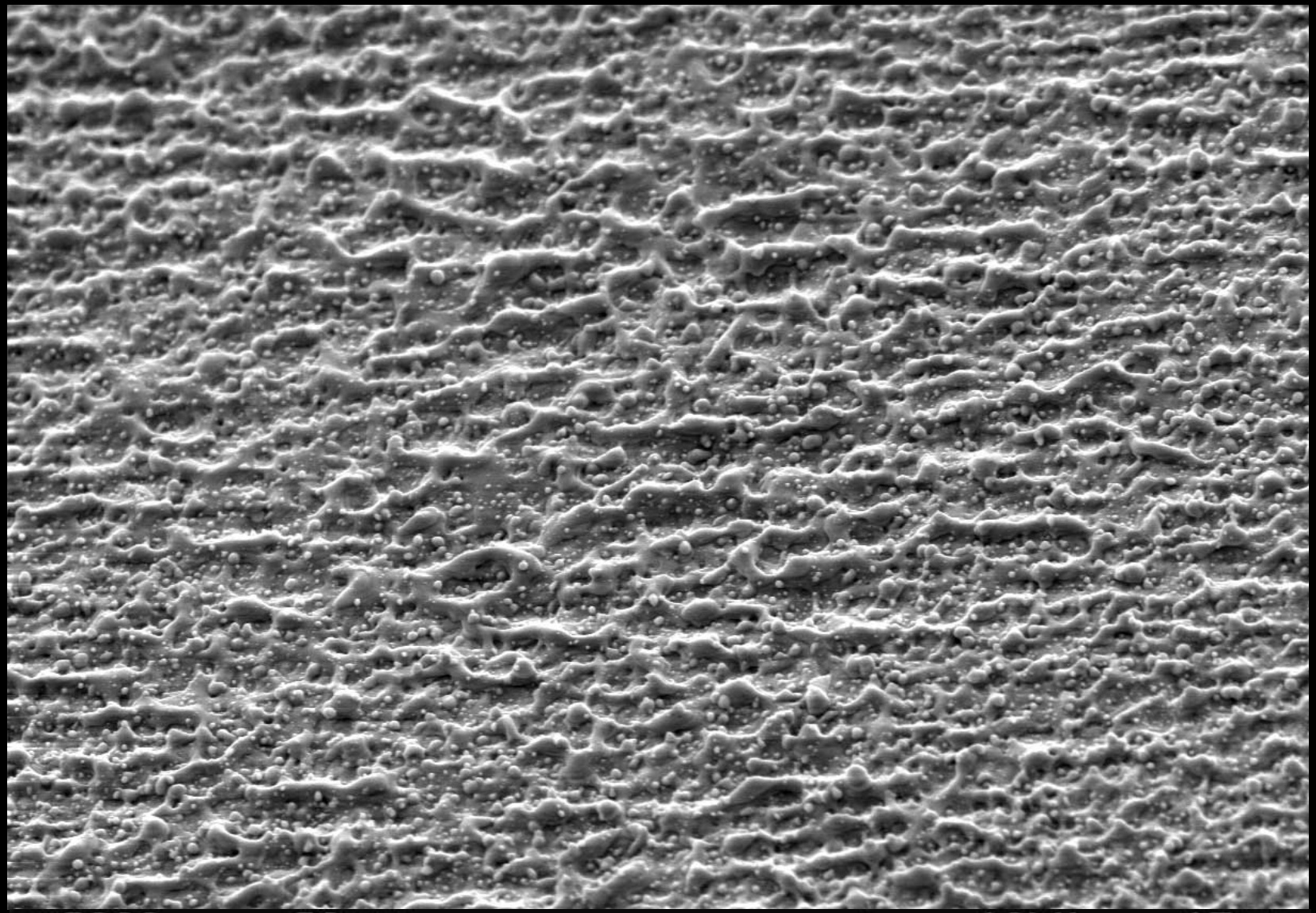
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512 x 480
20µm
10kV
15mm
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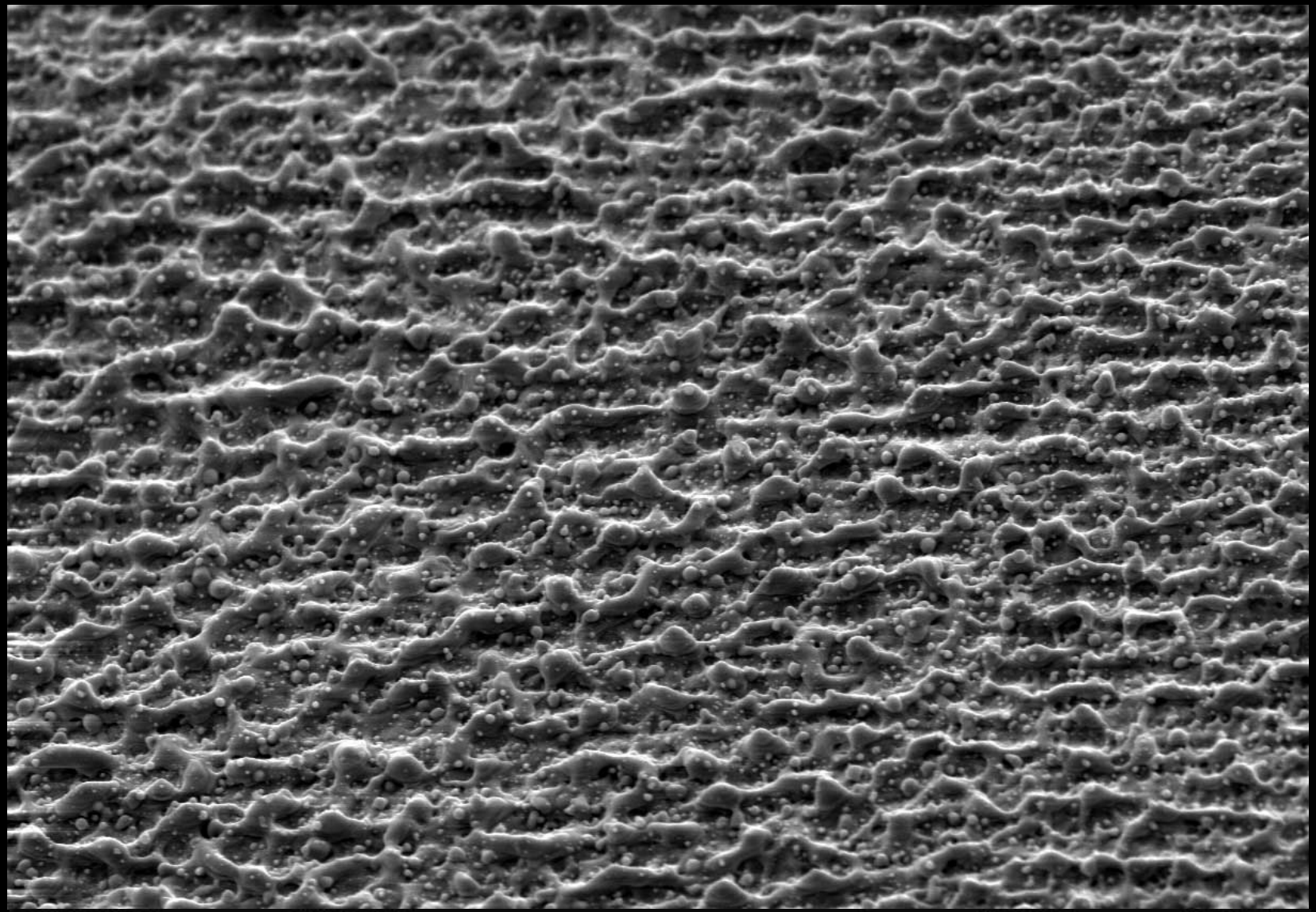
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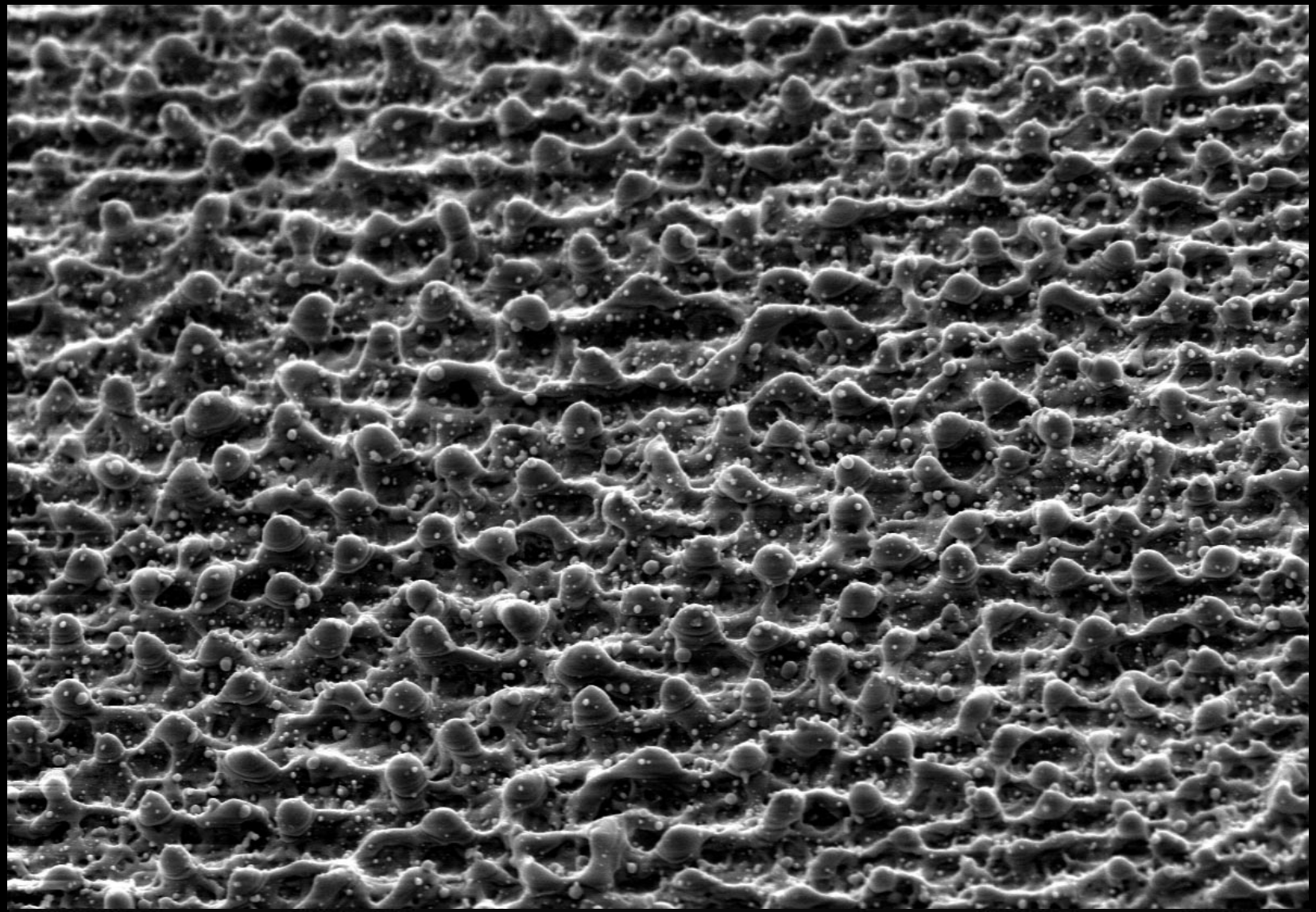
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15mm
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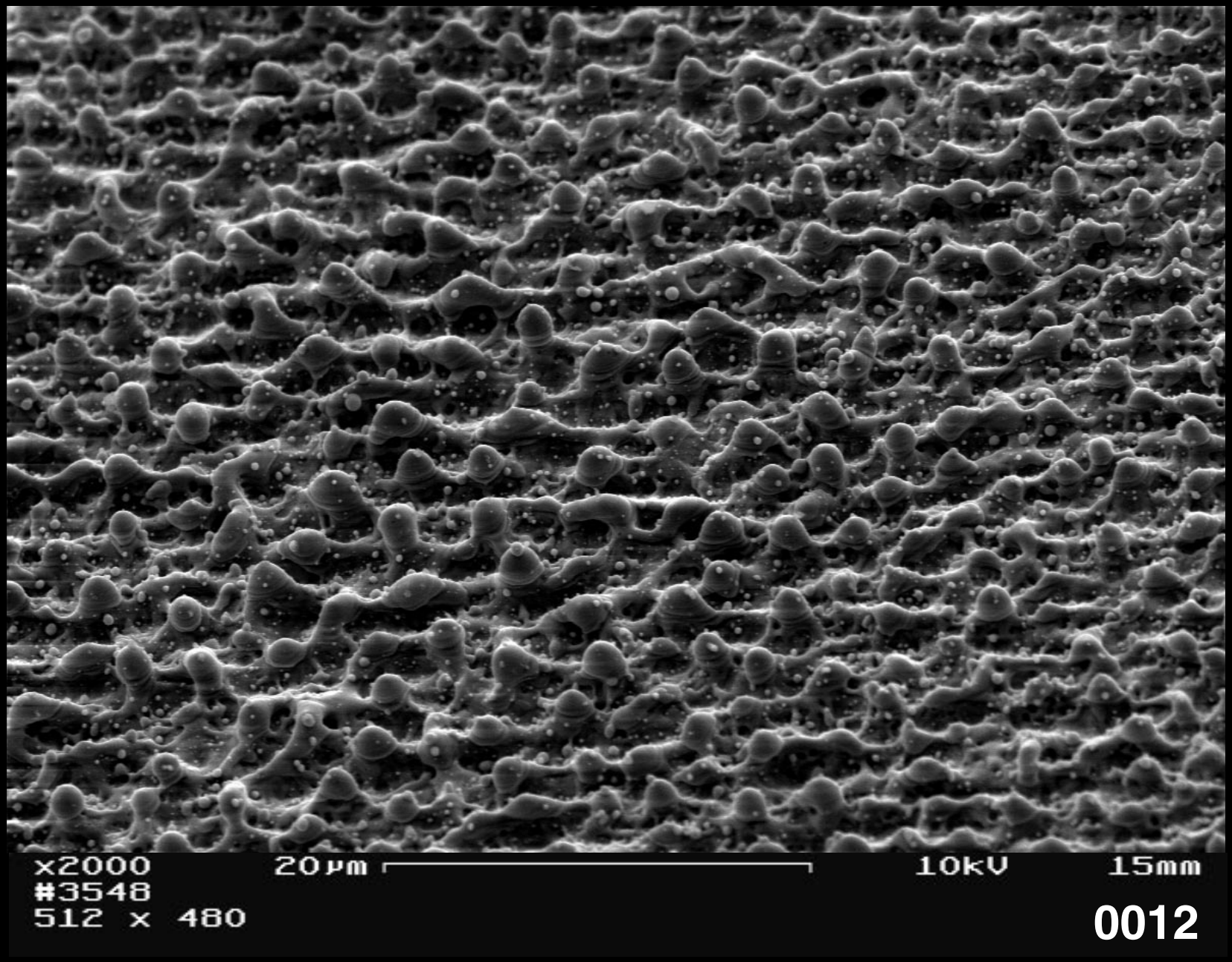
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15mm
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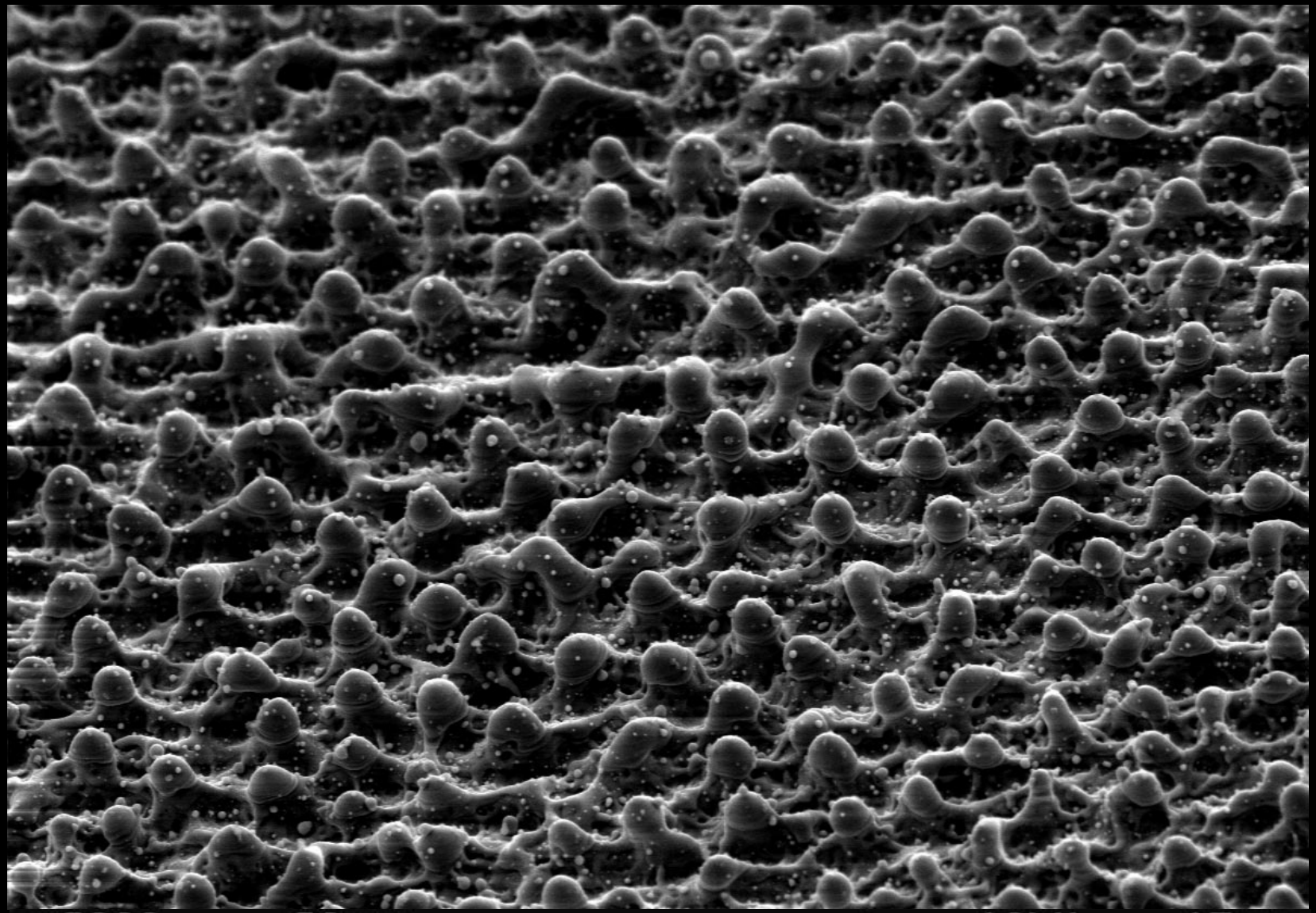
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15mm
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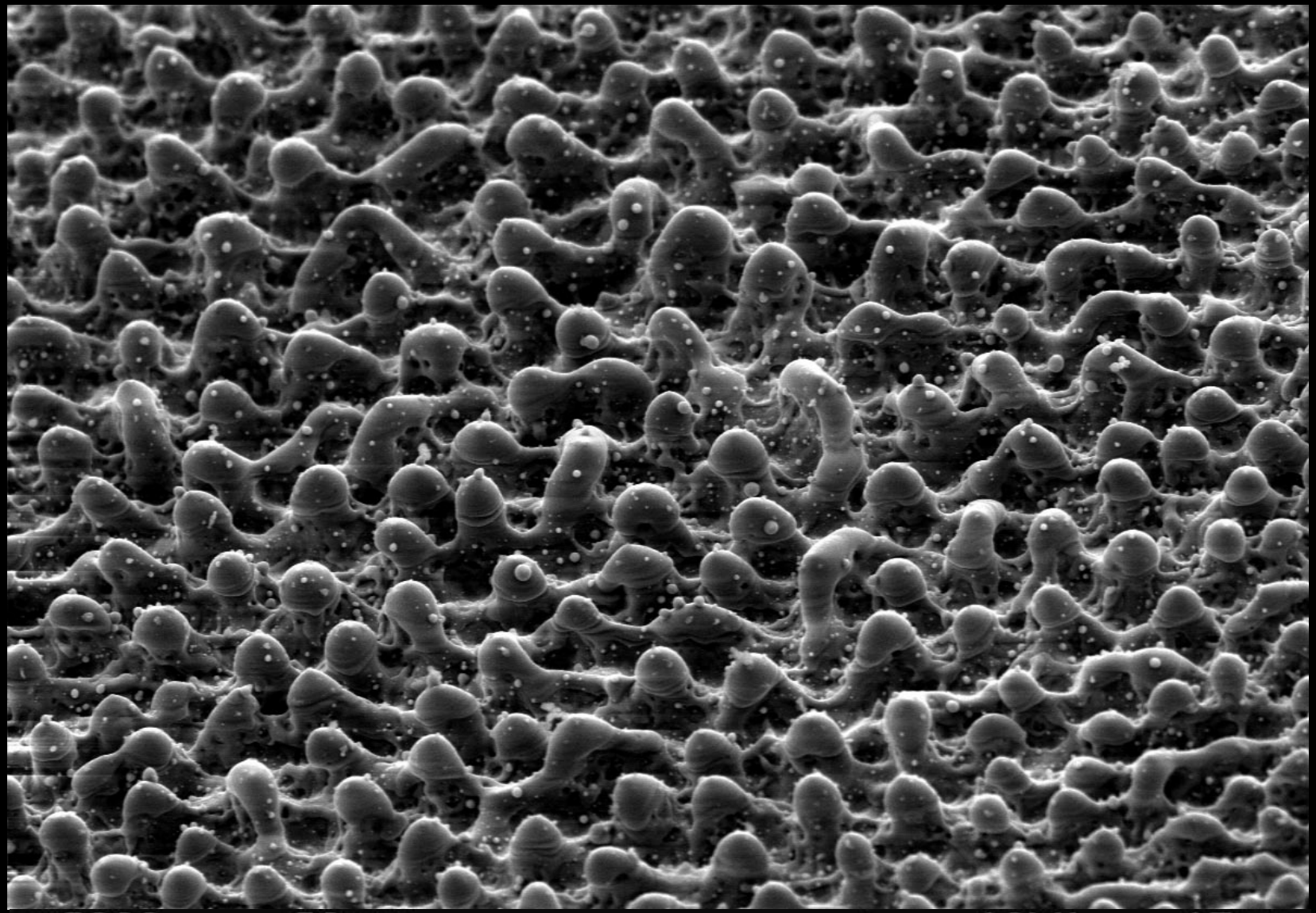
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10kV
15mm
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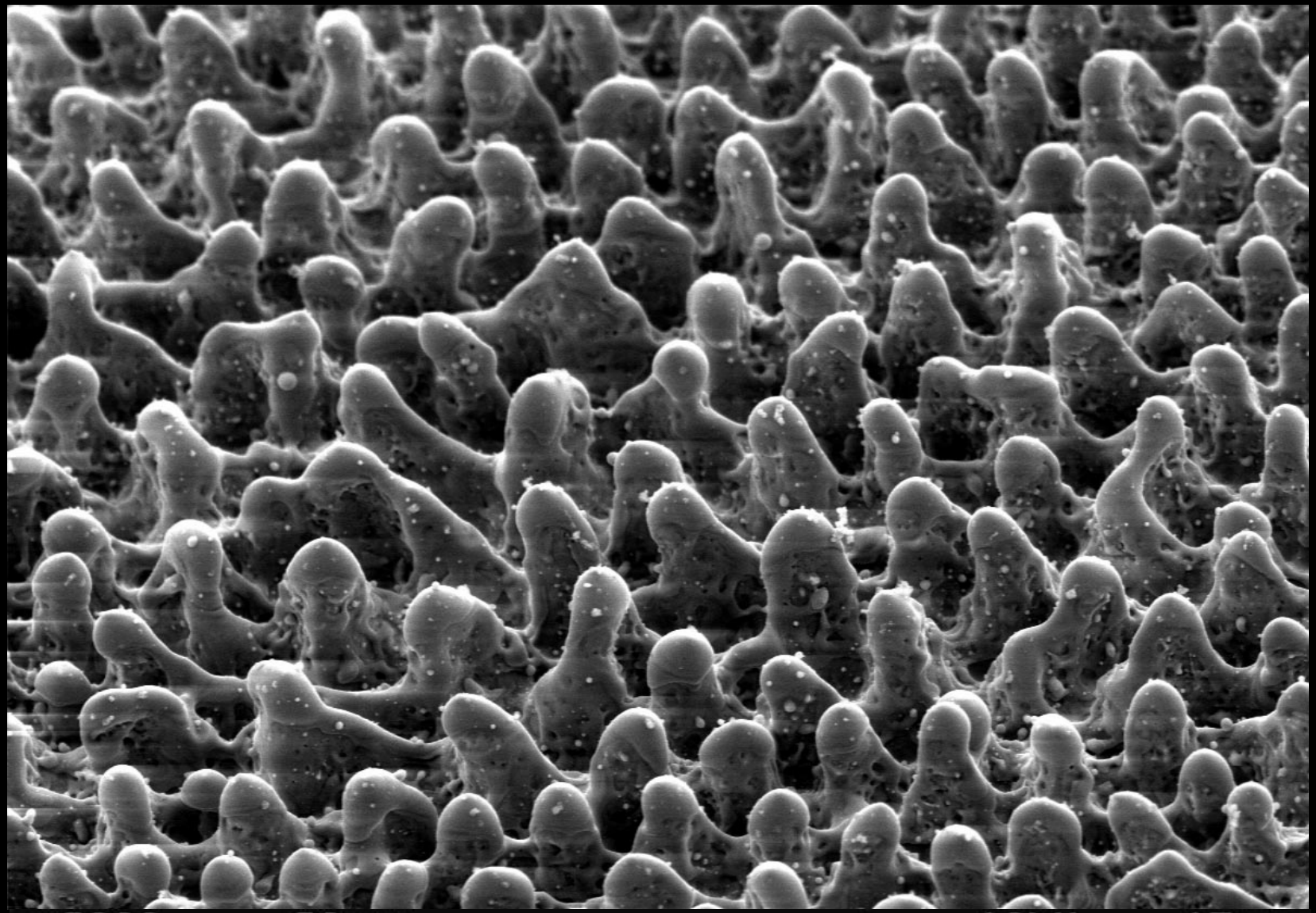
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10kV
15mm
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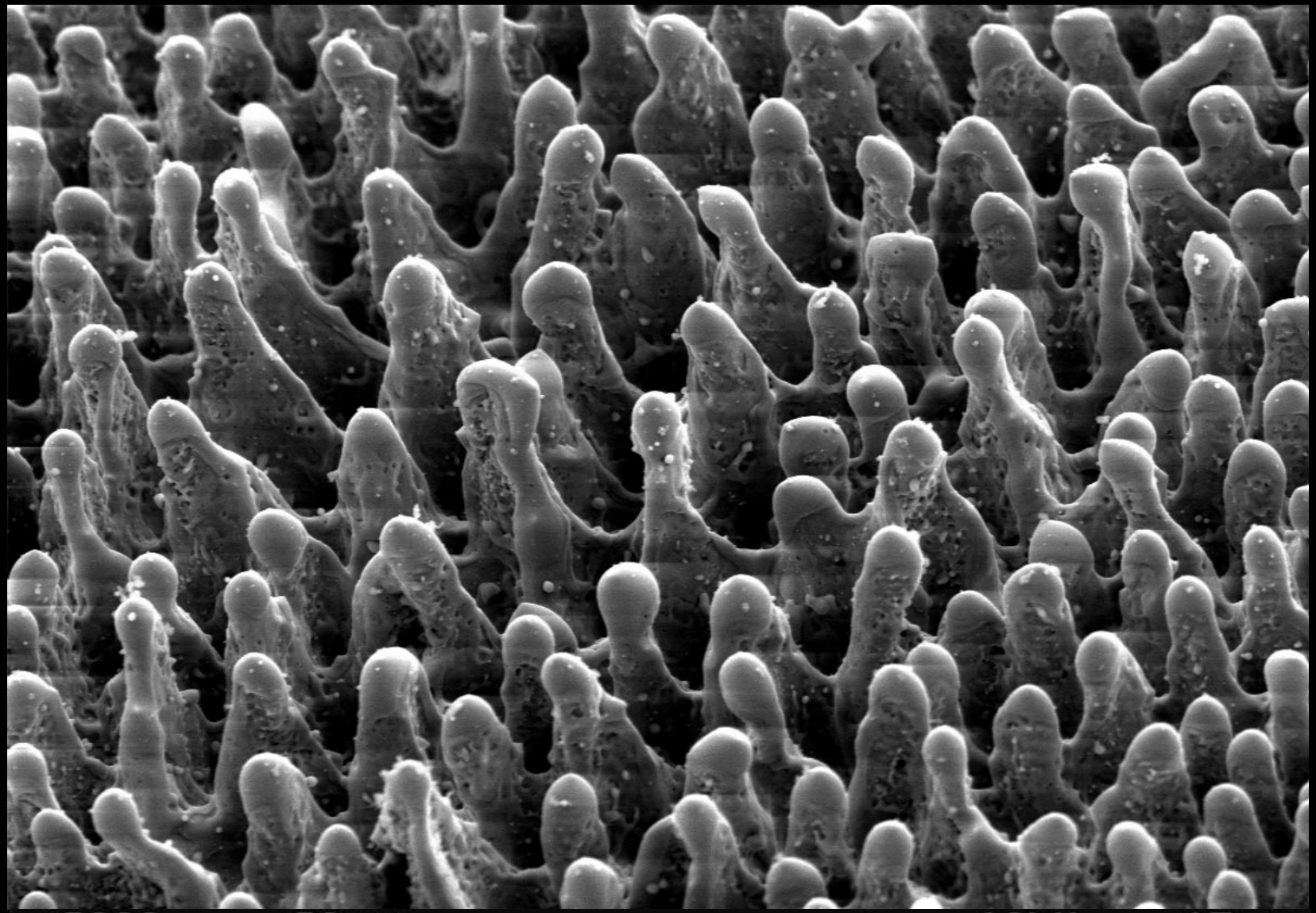
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#3548
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10kV
15mm
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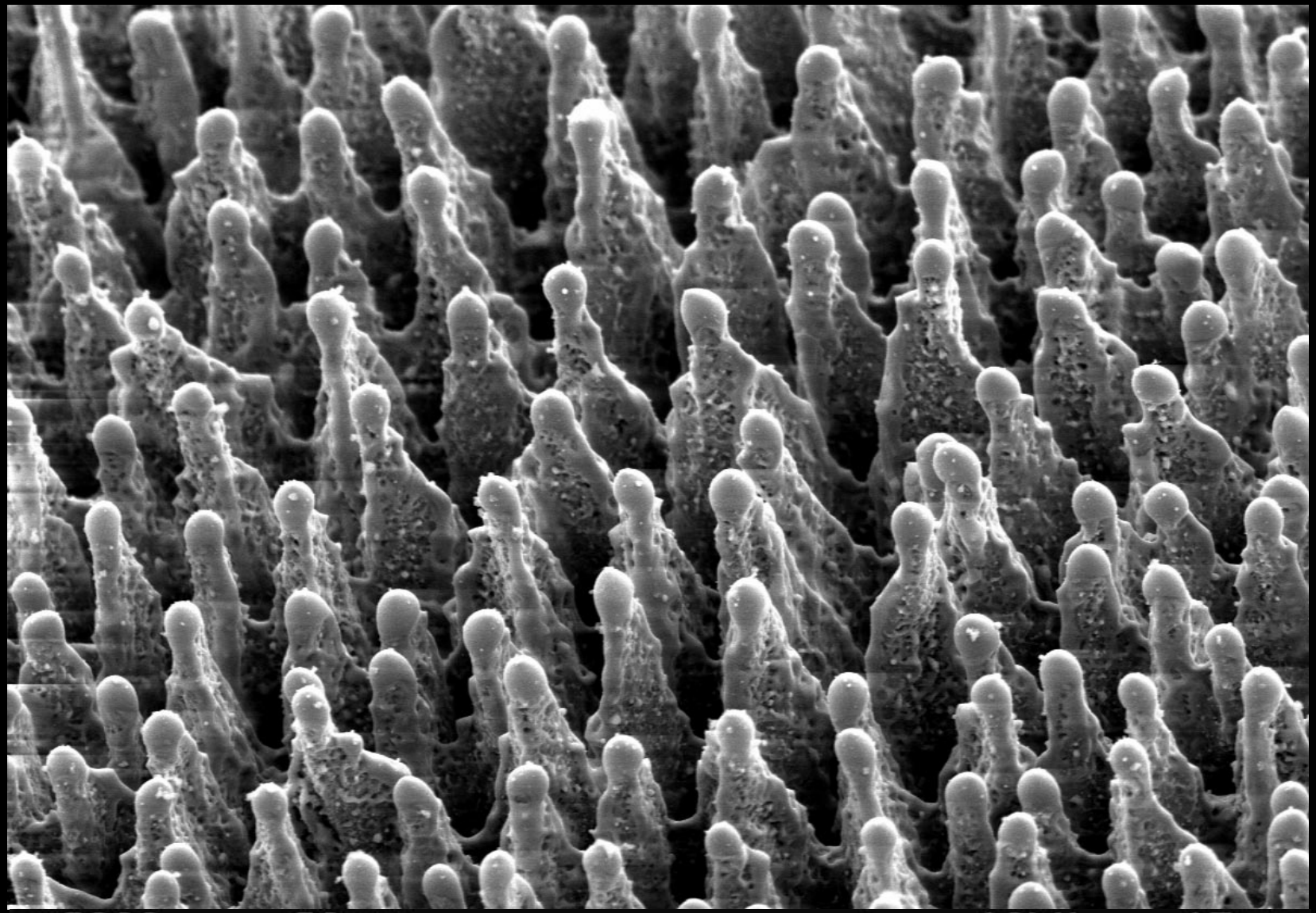
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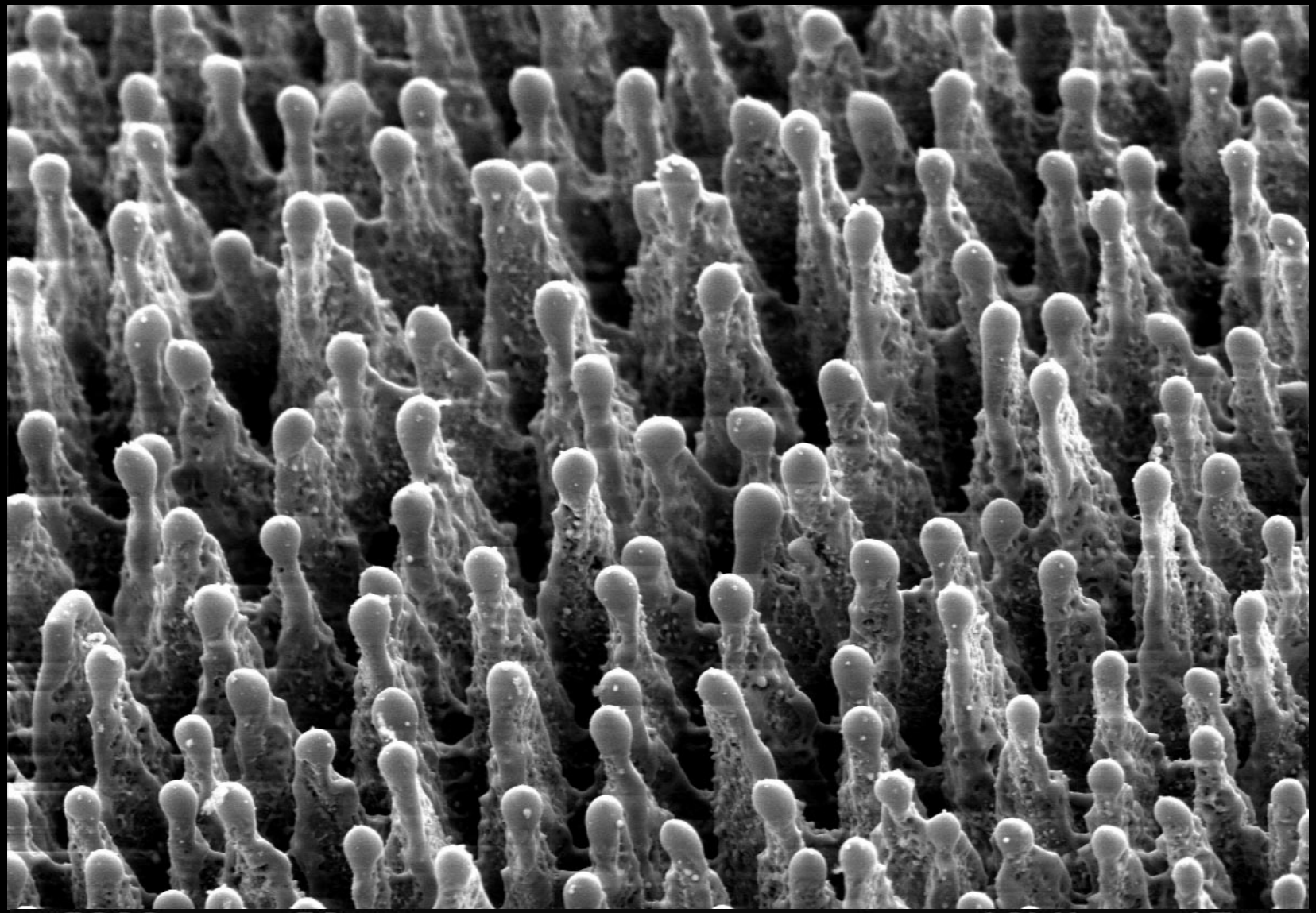
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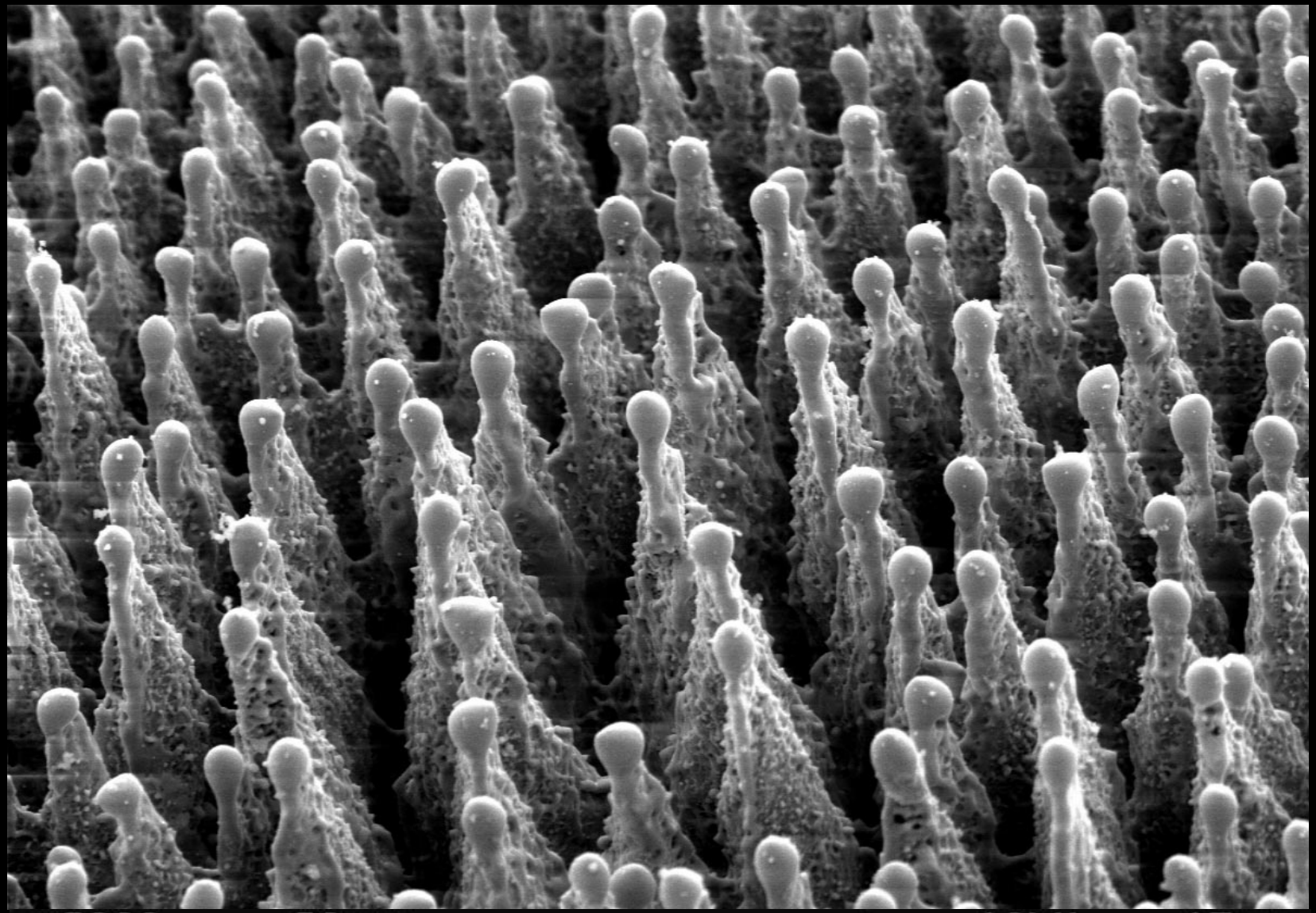
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20µm
10kV
15mm
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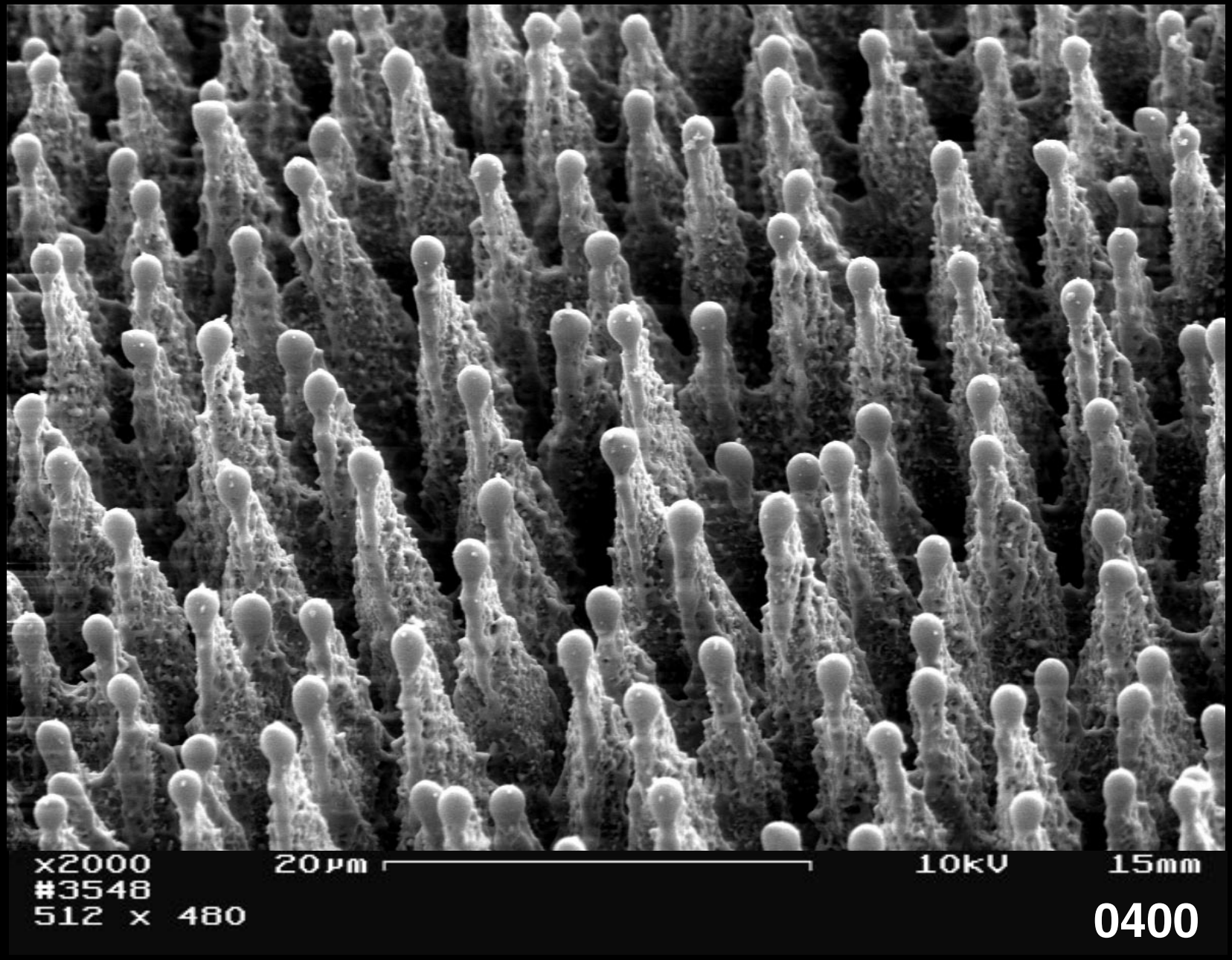
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10kV
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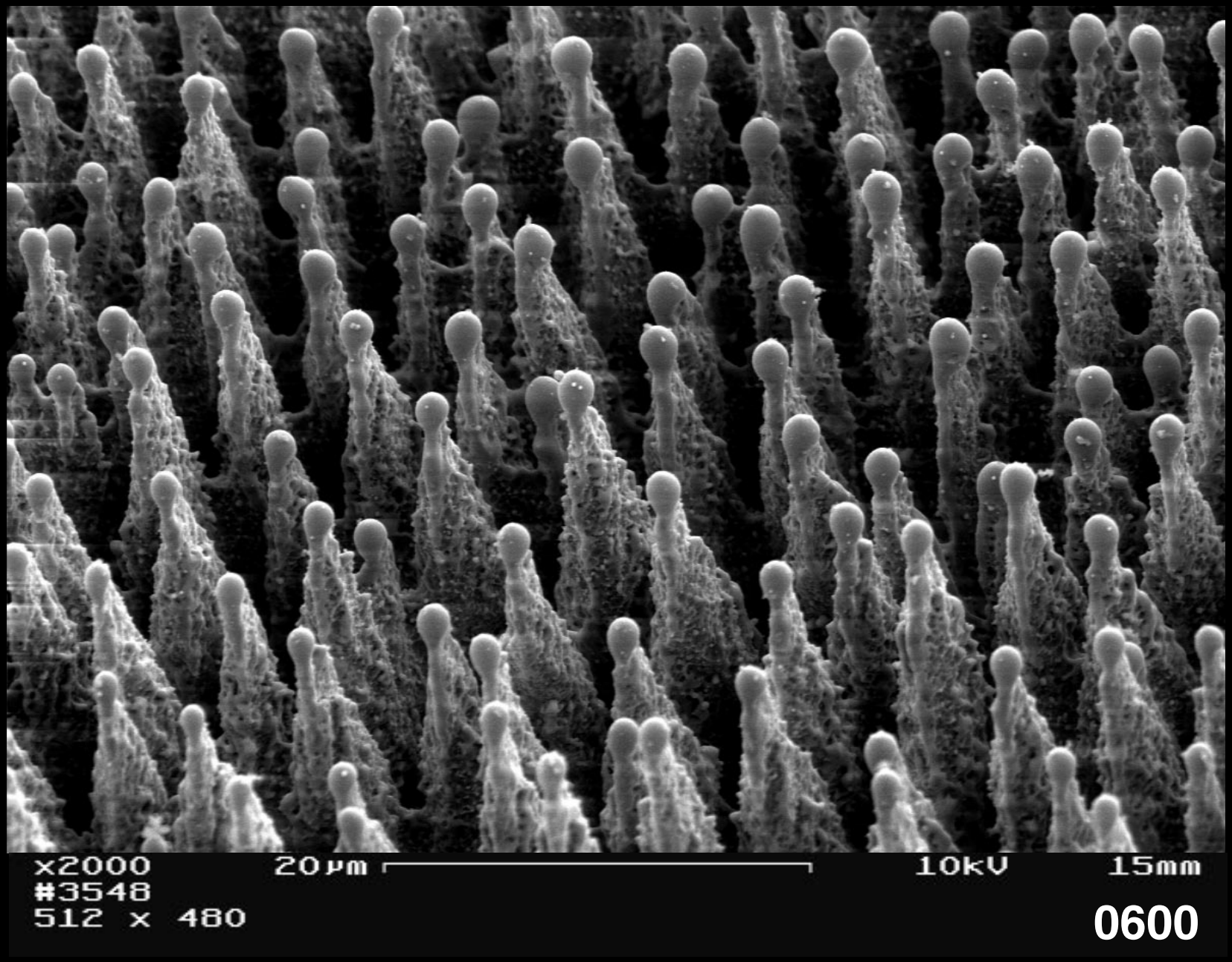
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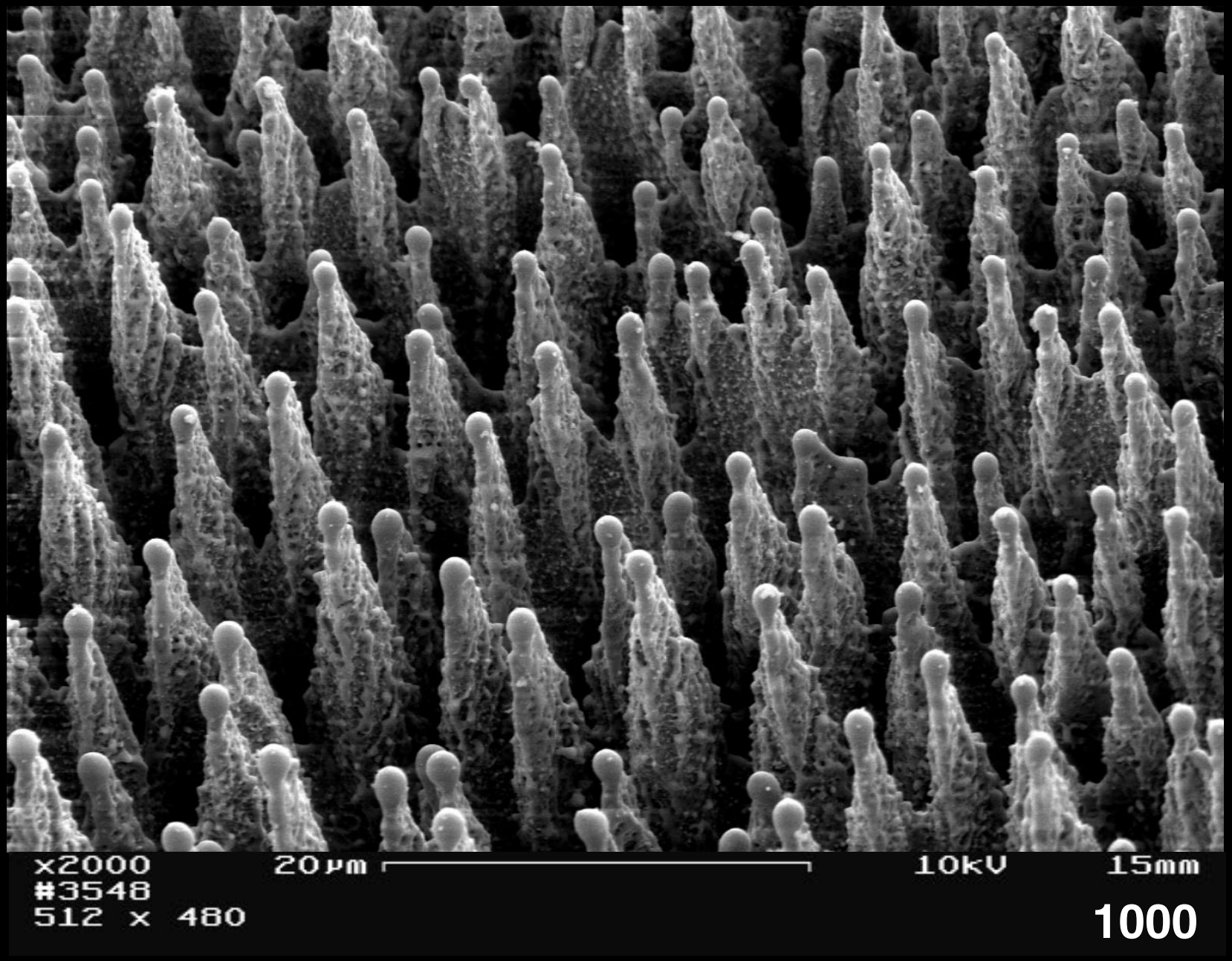
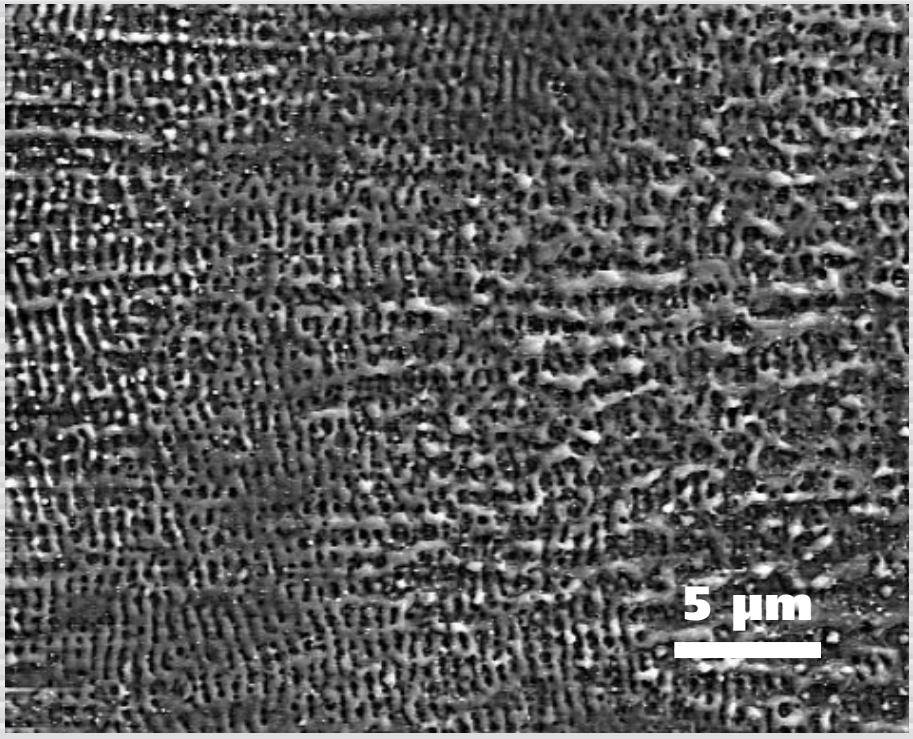
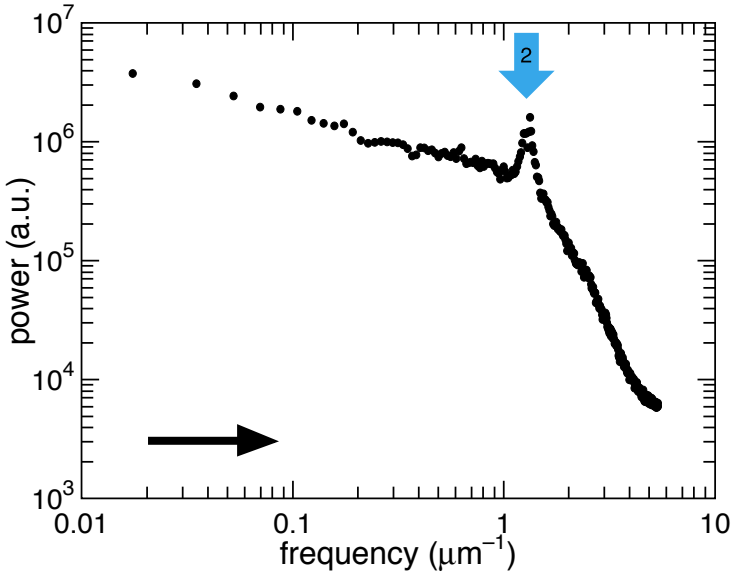

x2000
#3548
512 x 480
20µm
10kV
15mm
1000

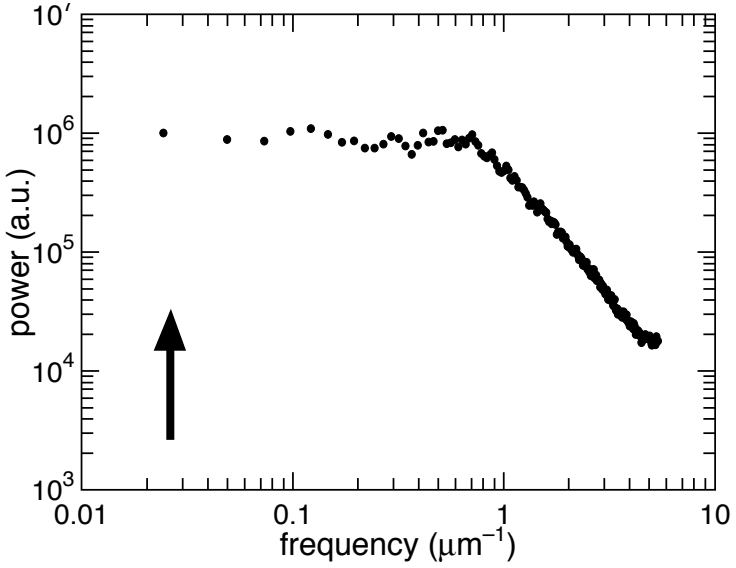
Formation

SF_6 2 pulses



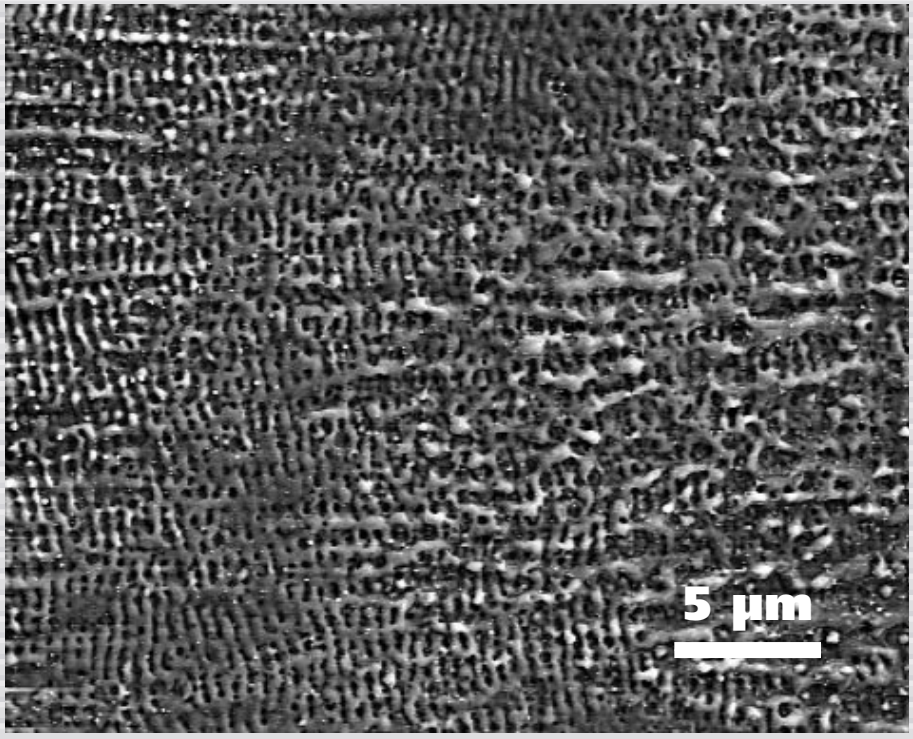
laser polarization →



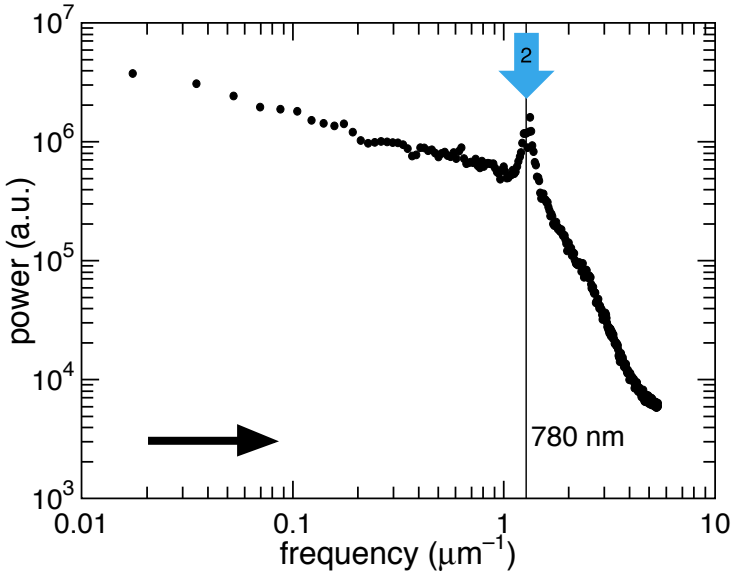


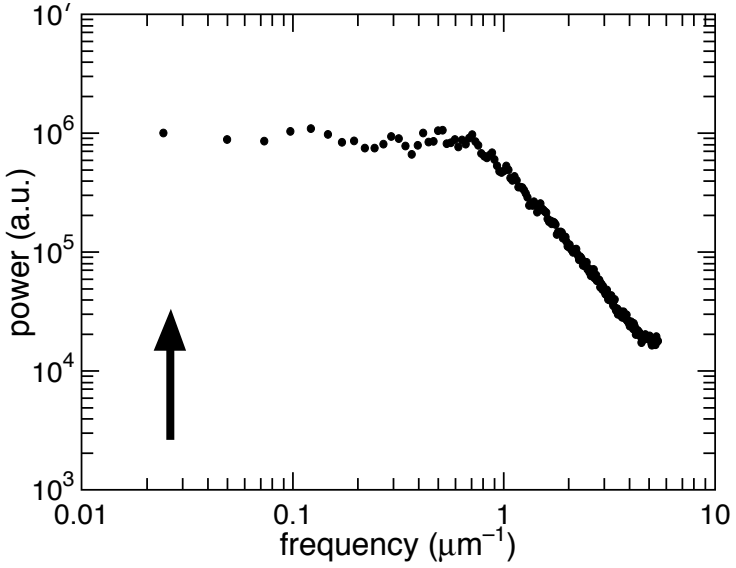
Formation

SF_6 2 pulses



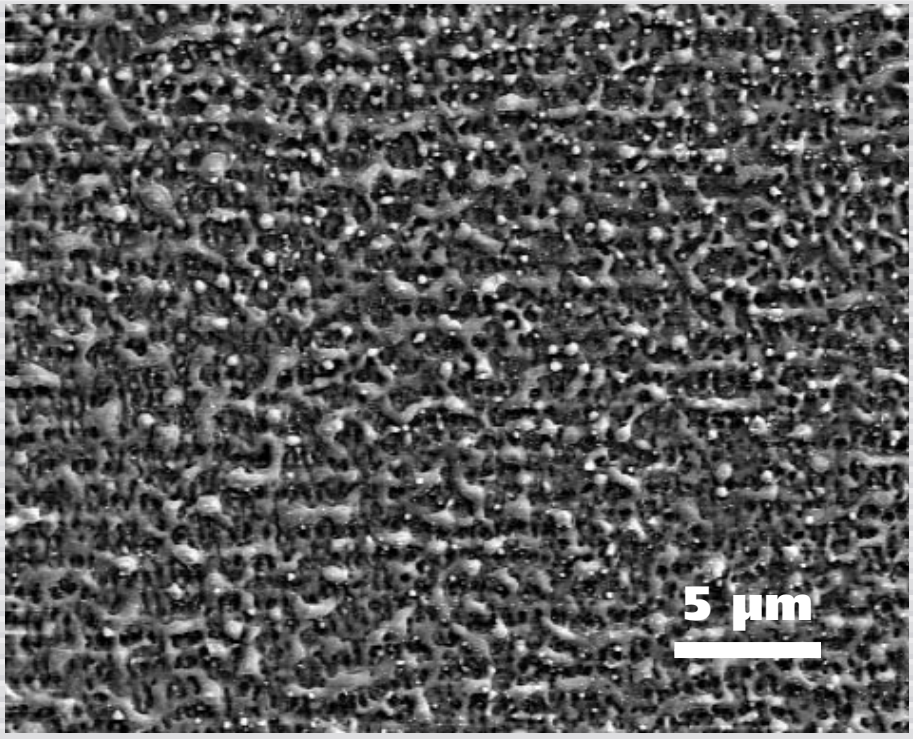
laser polarization



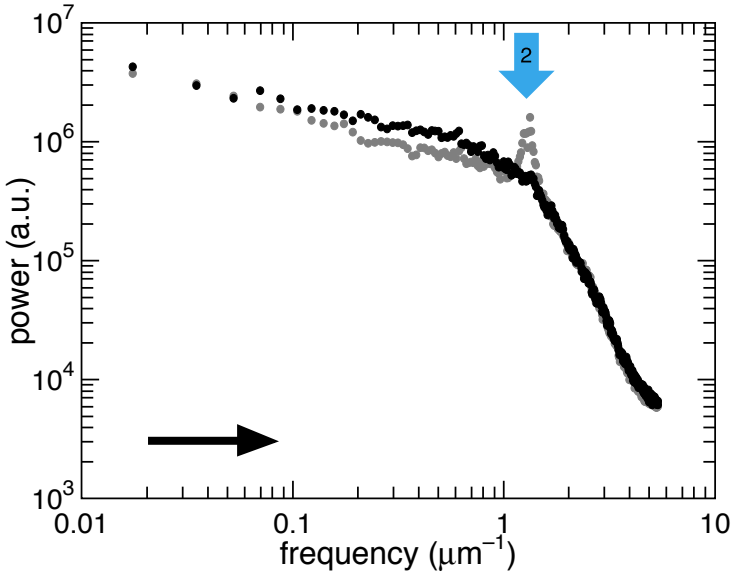


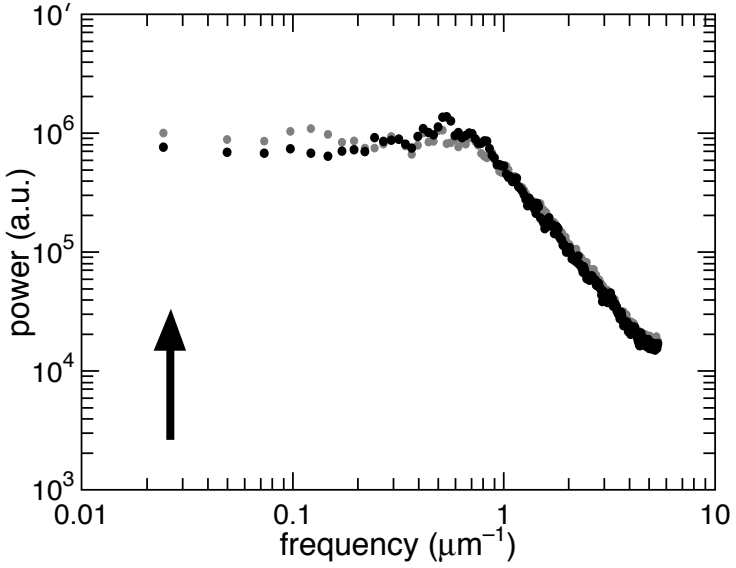
Formation

SF_6 3 pulses



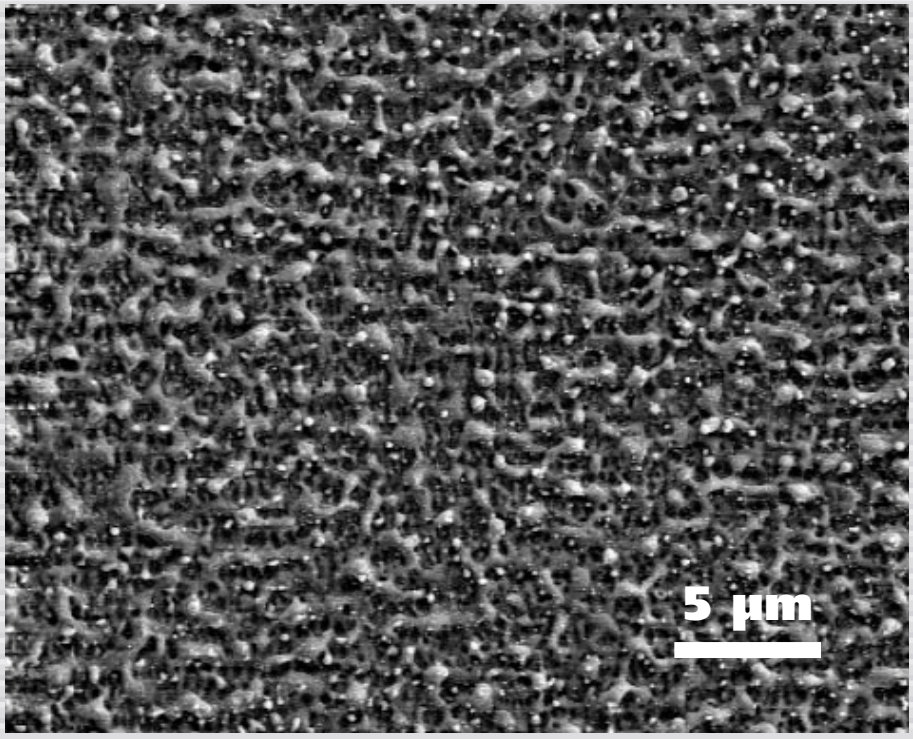
laser polarization



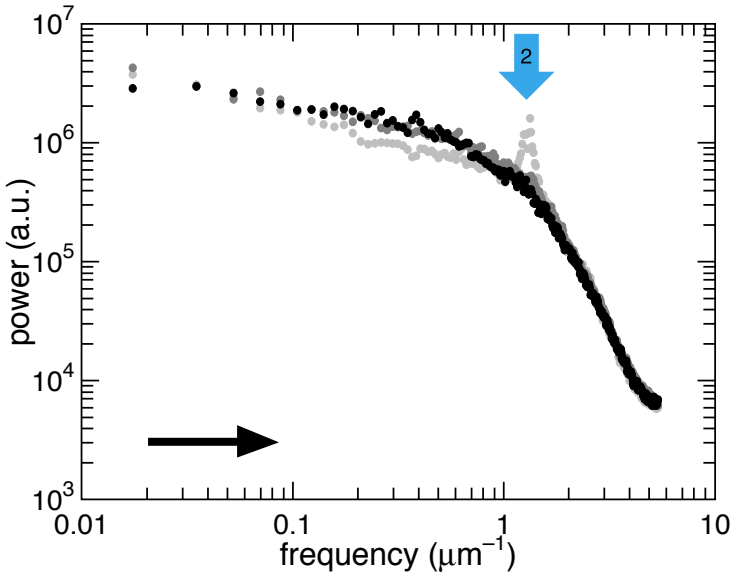


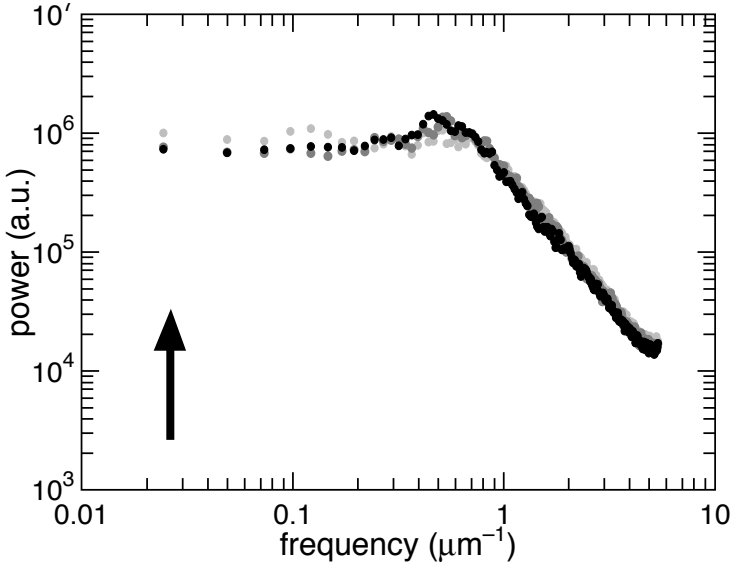
Formation

SF_6 4 pulses



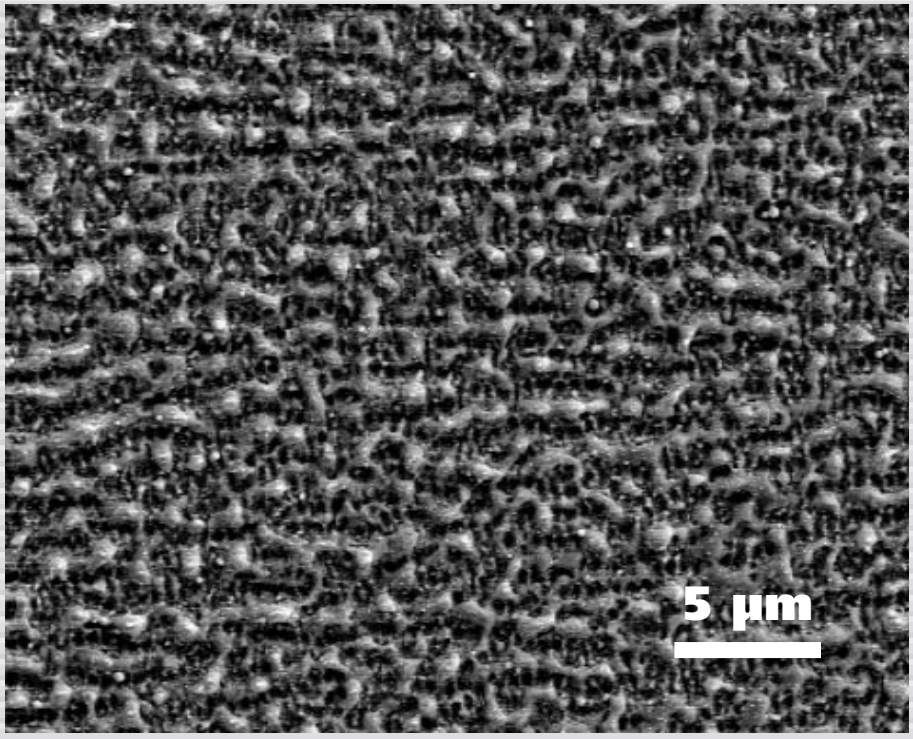
laser polarization



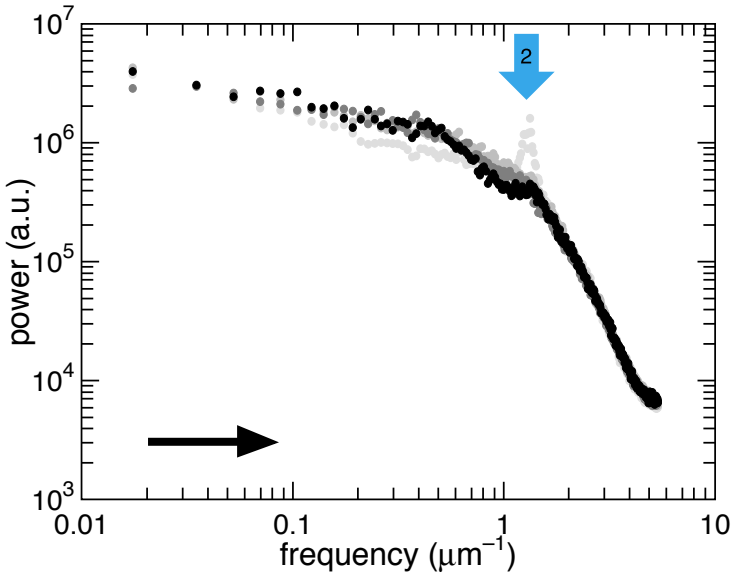


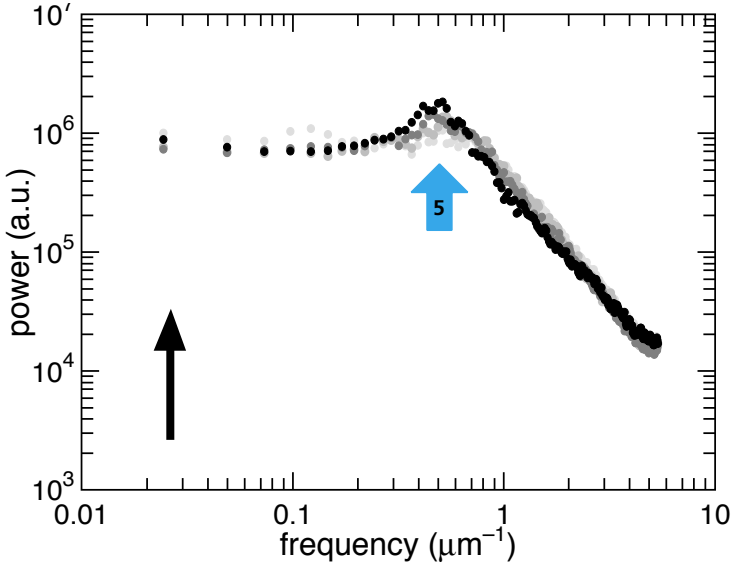
Formation

SF_6 5 pulses



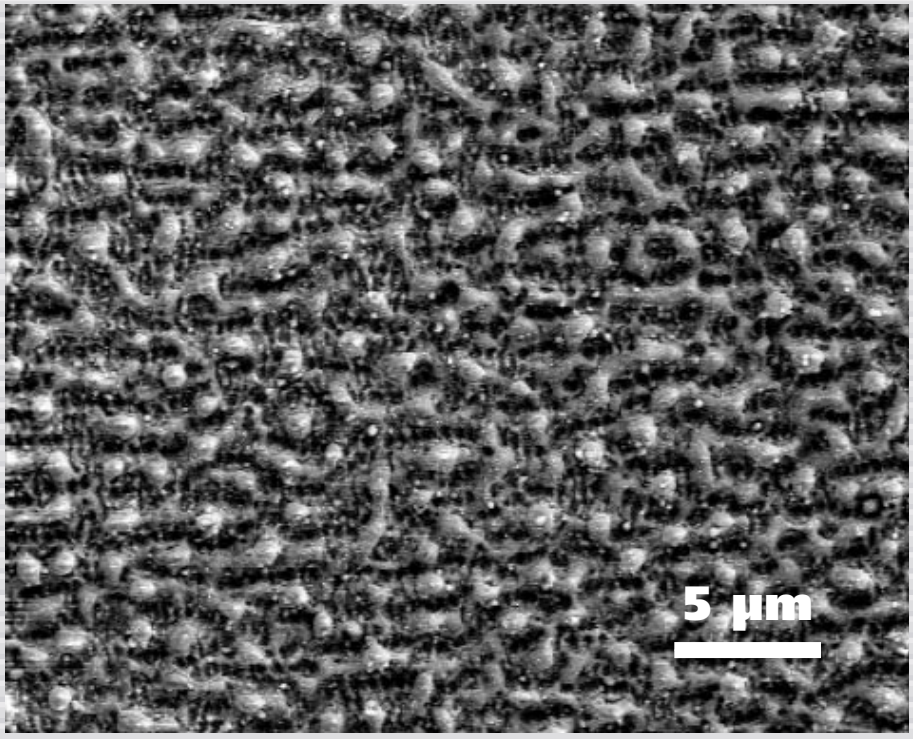
laser polarization



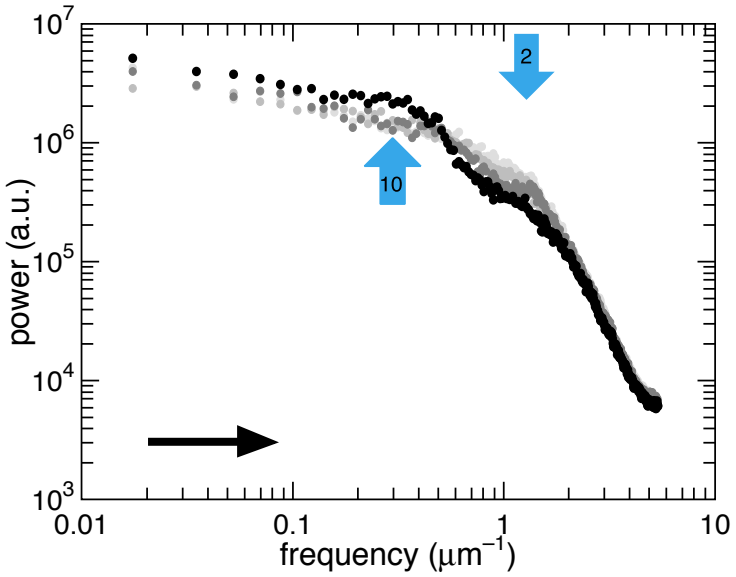


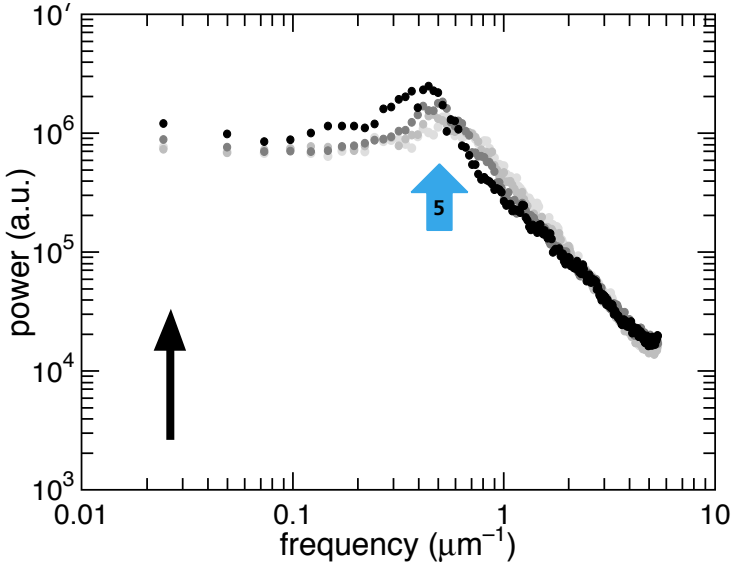
Formation

SF_6 10 pulses



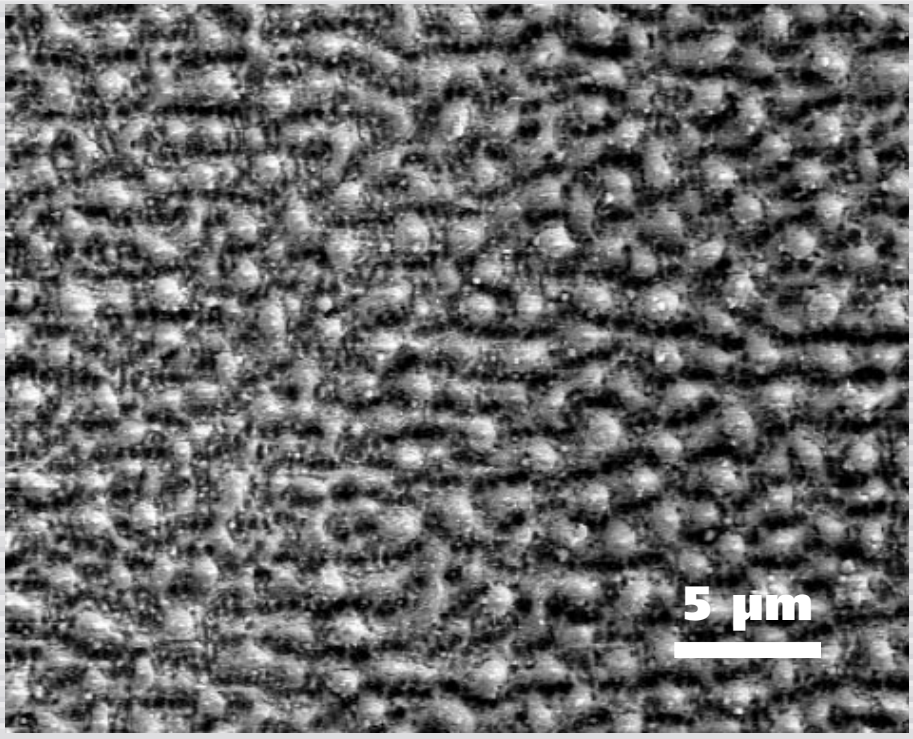
laser polarization



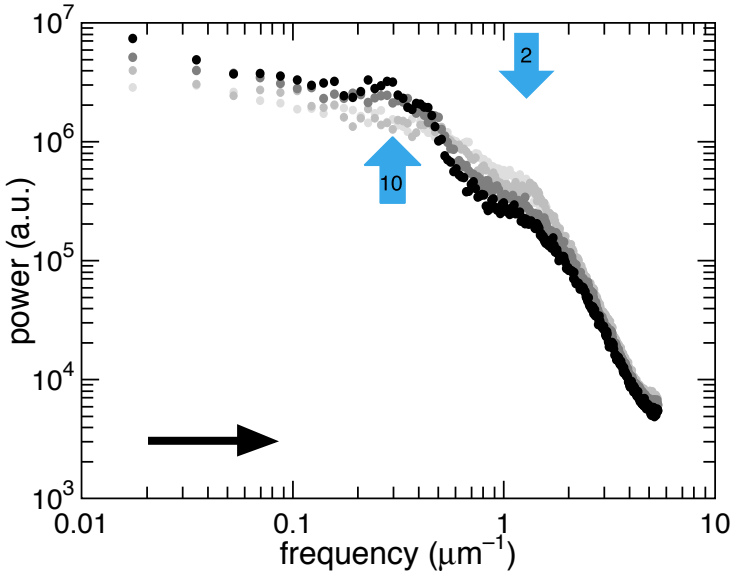


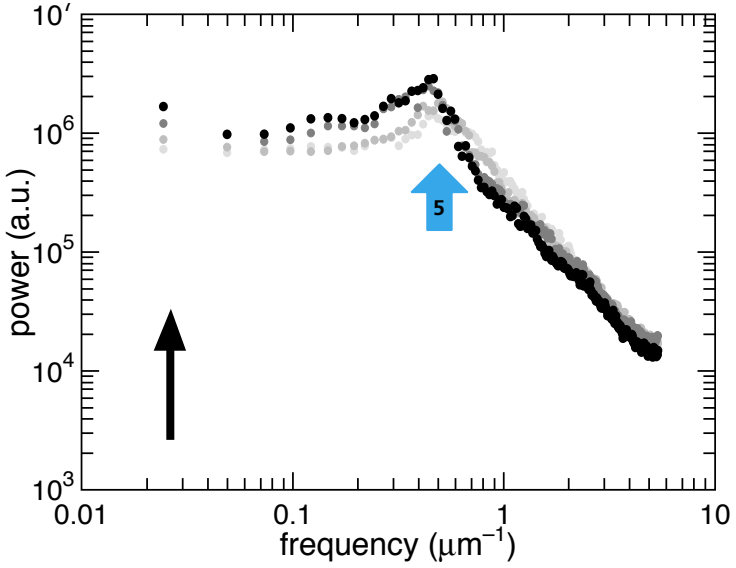
Formation

SF_6 15 pulses



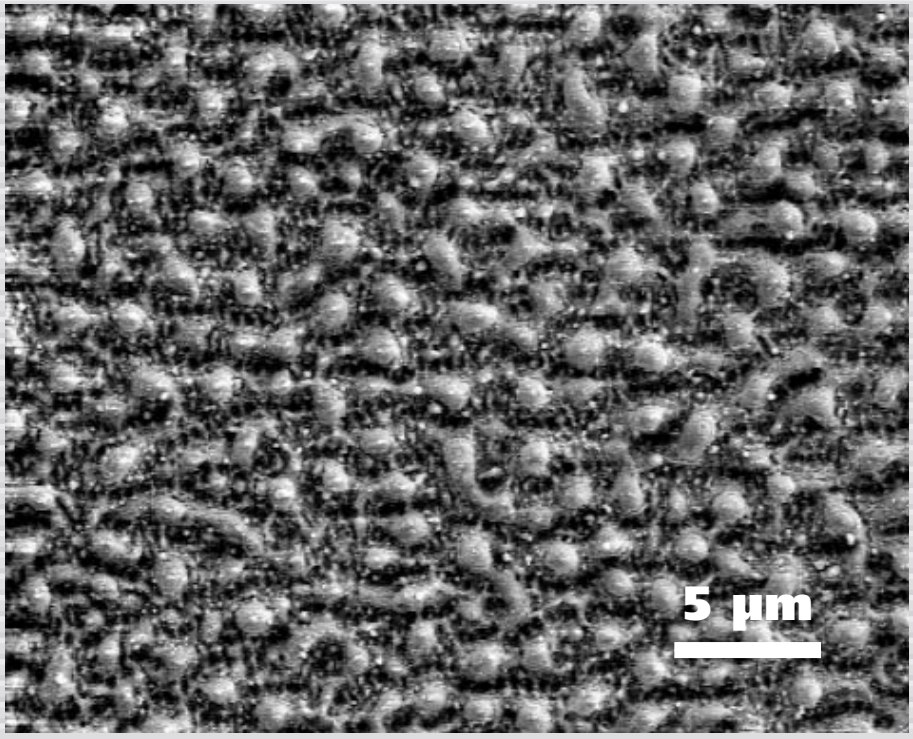
laser polarization



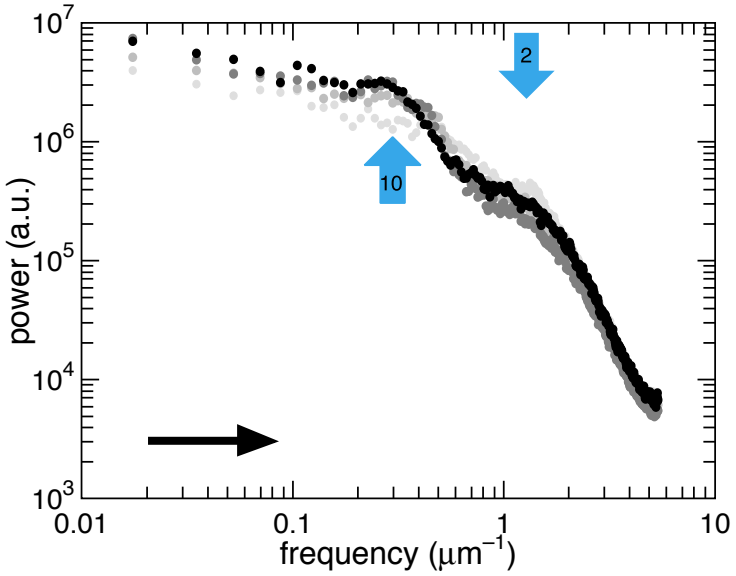


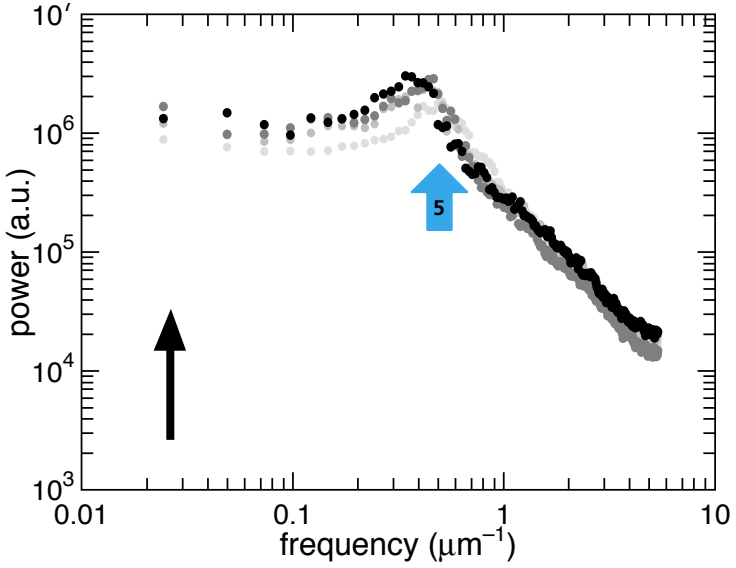
Formation

SF_6 20 pulses



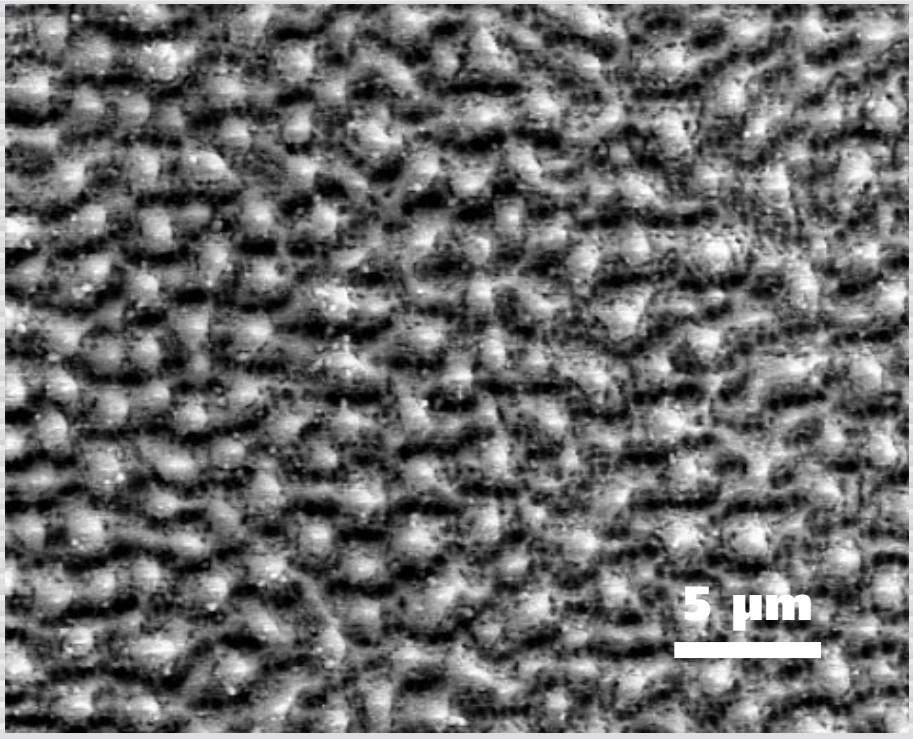
laser polarization →



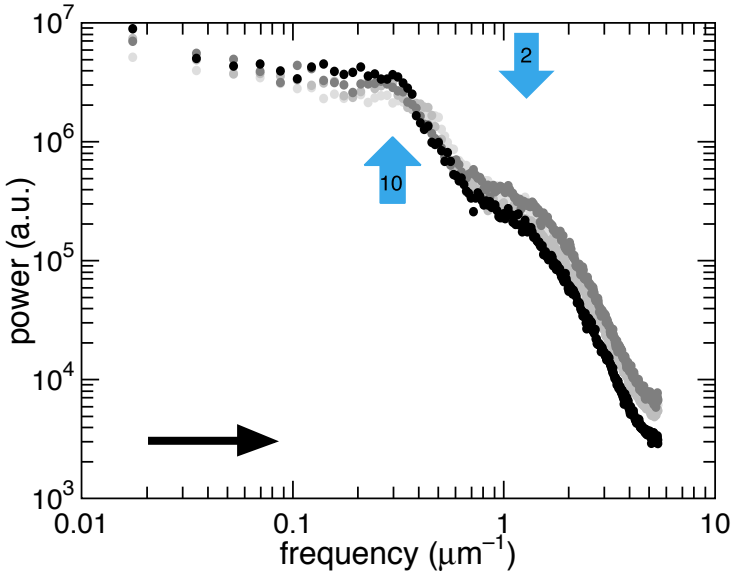


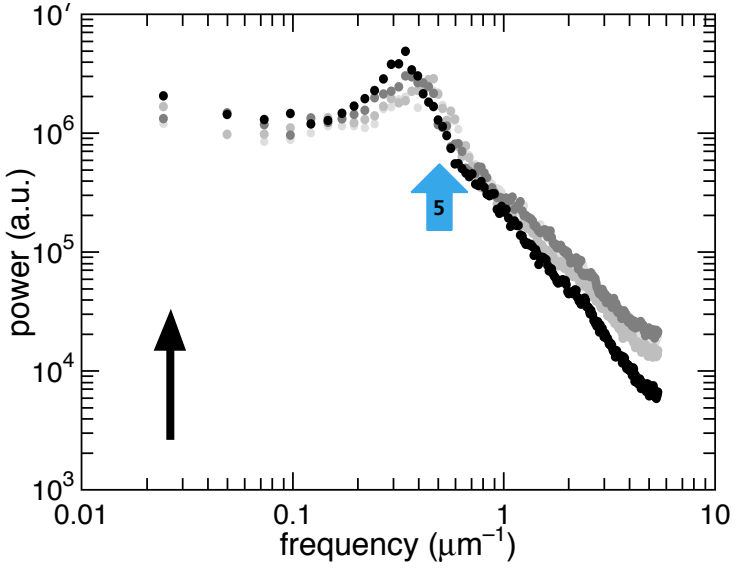
Formation

SF_6 50 pulses



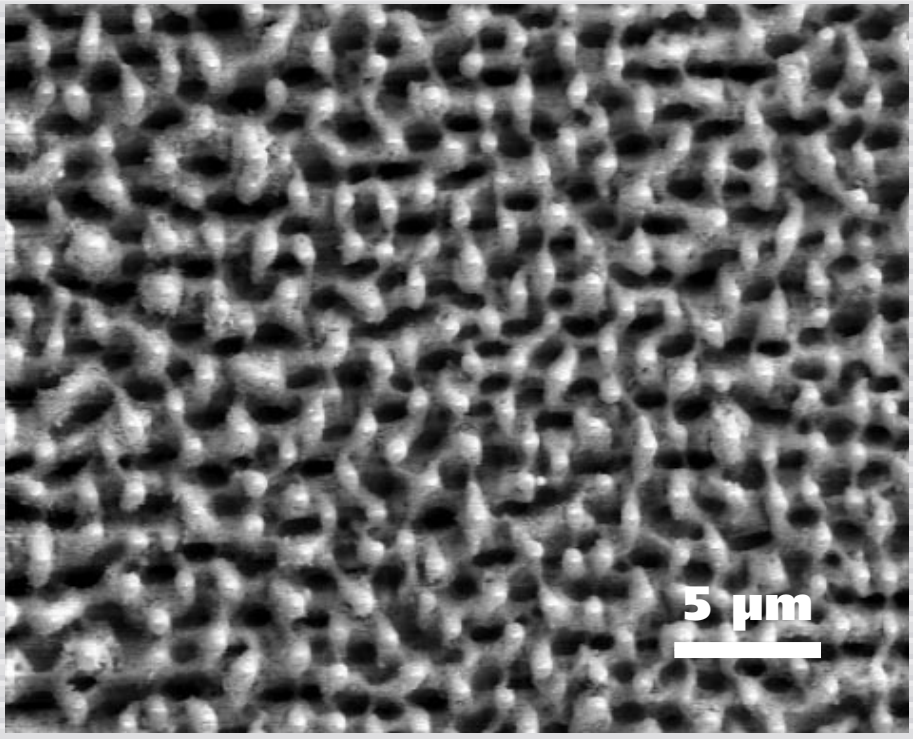
laser polarization



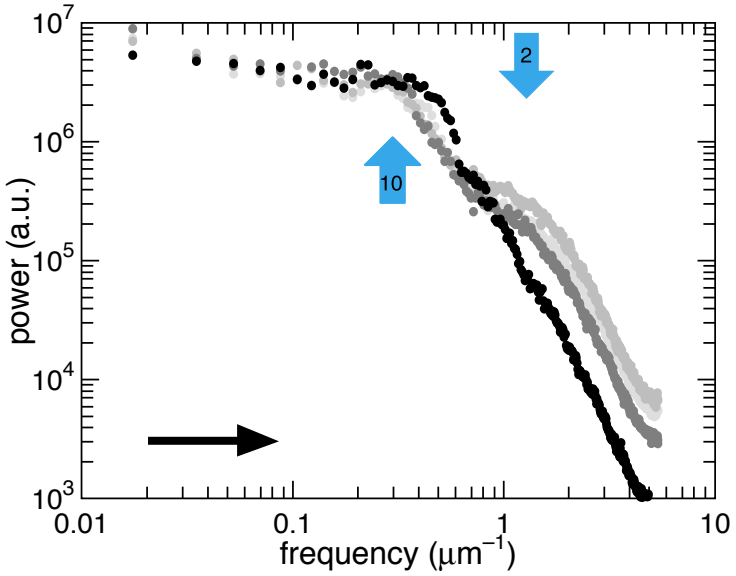


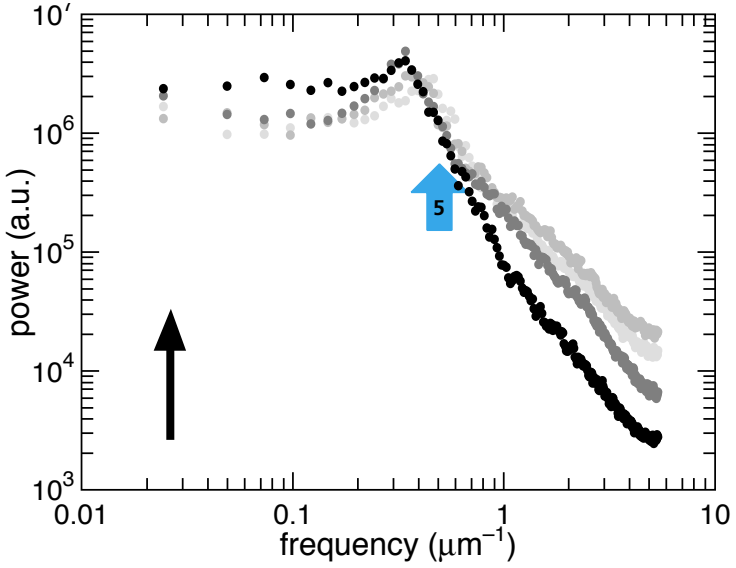
Formation

SF_6 200 pulses



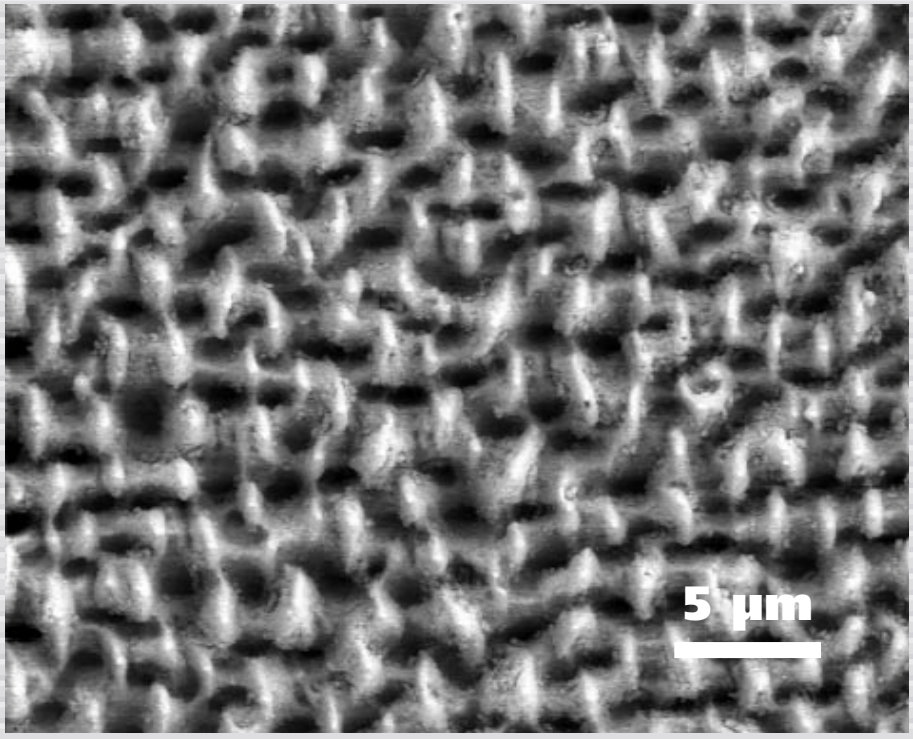
laser polarization



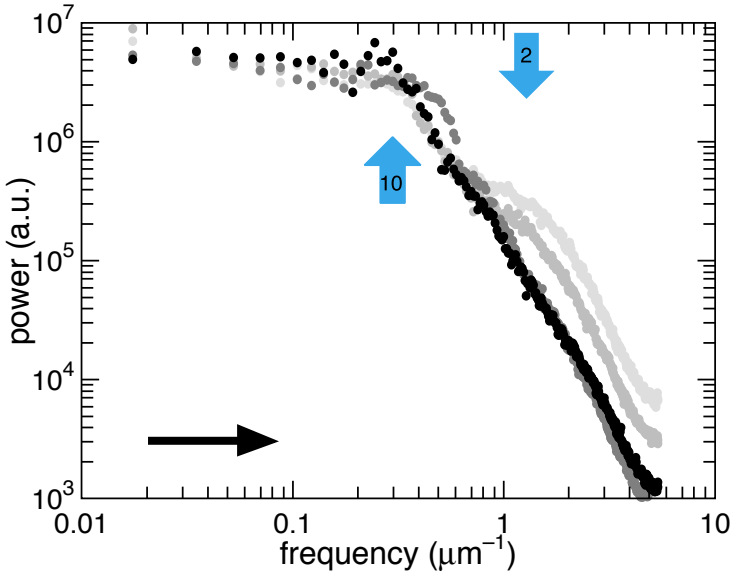


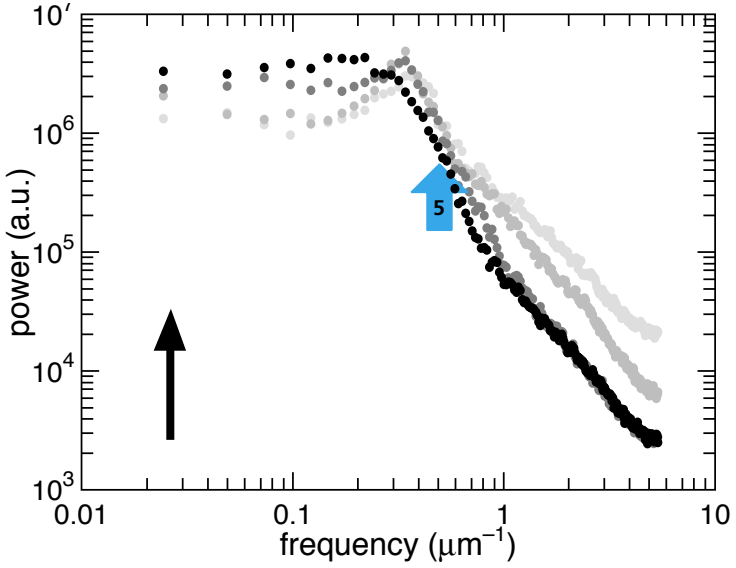
Formation

SF_6 500 pulses



laser polarization

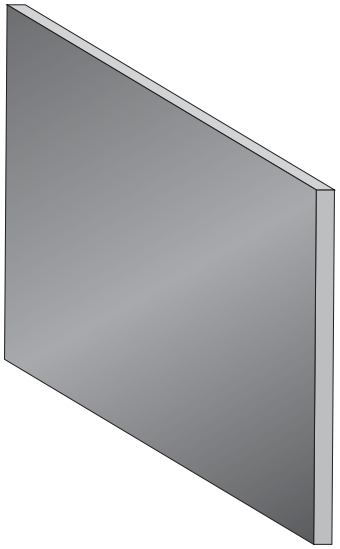




Outlook

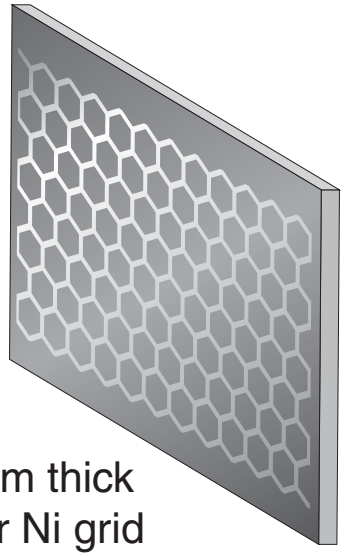
can ordering of spikes be improved by using a grid?

Outlook



Si or Ti substrate

place grid in front of substrate

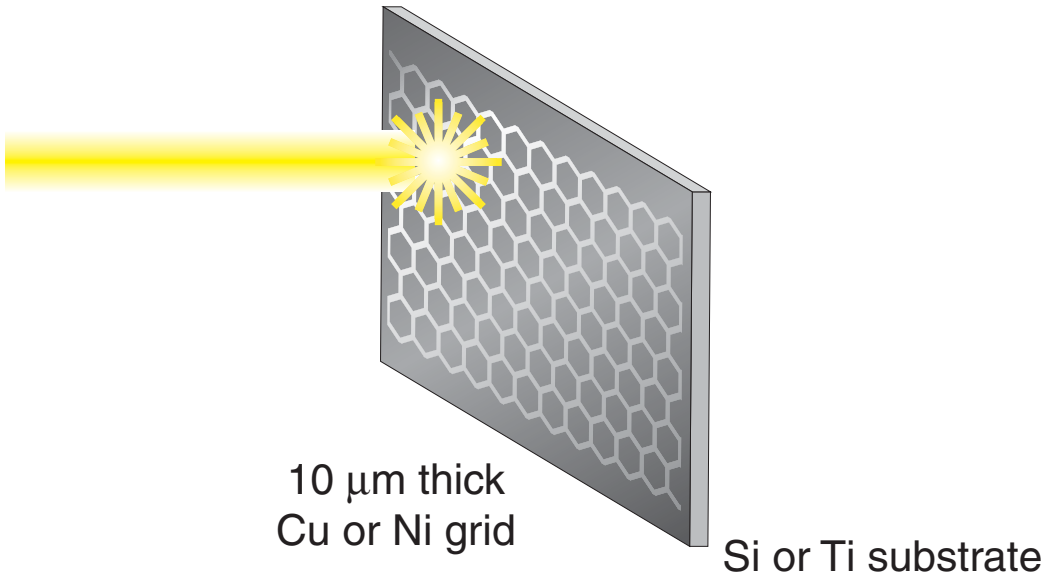


10 μm thick
Cu or Ni grid

Si or Ti substrate

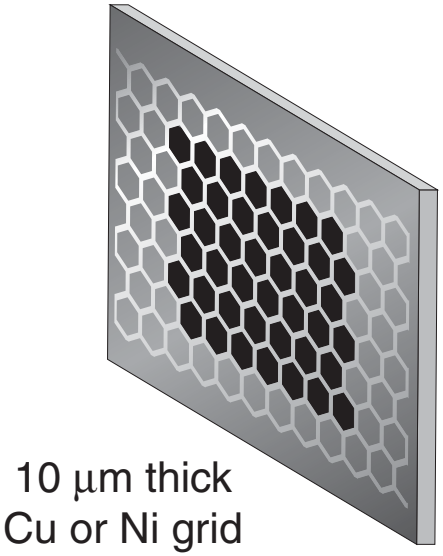
Outlook

scan laser beam



Outlook

scan laser beam

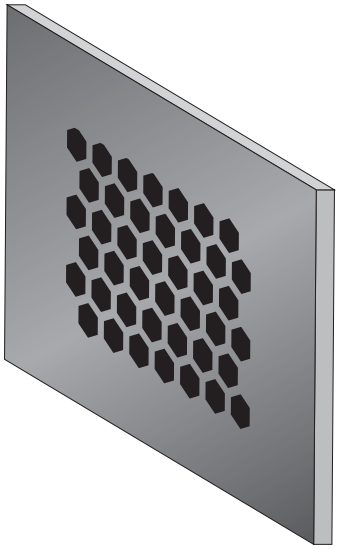


10 μm thick
Cu or Ni grid

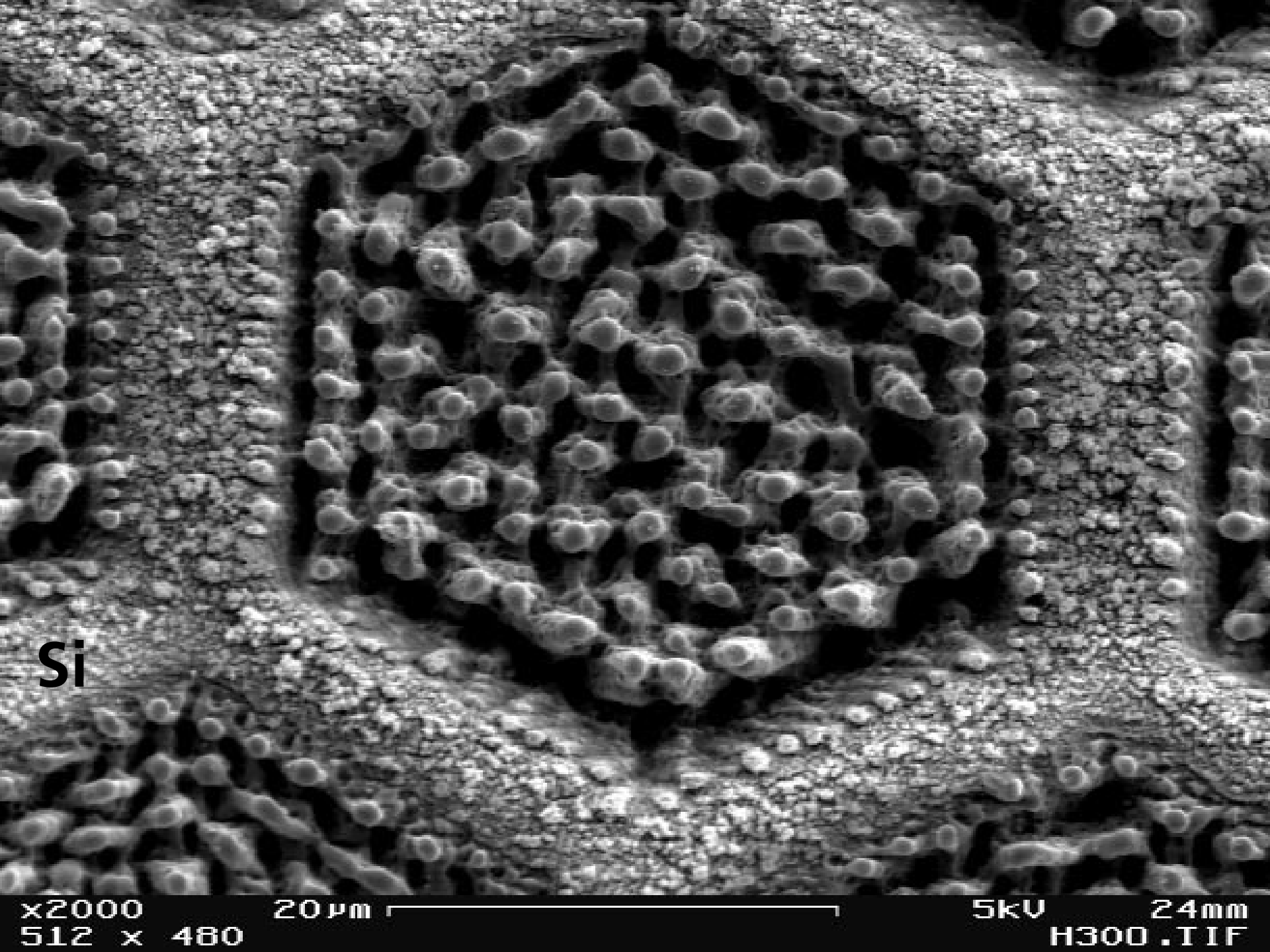
Si or Ti substrate

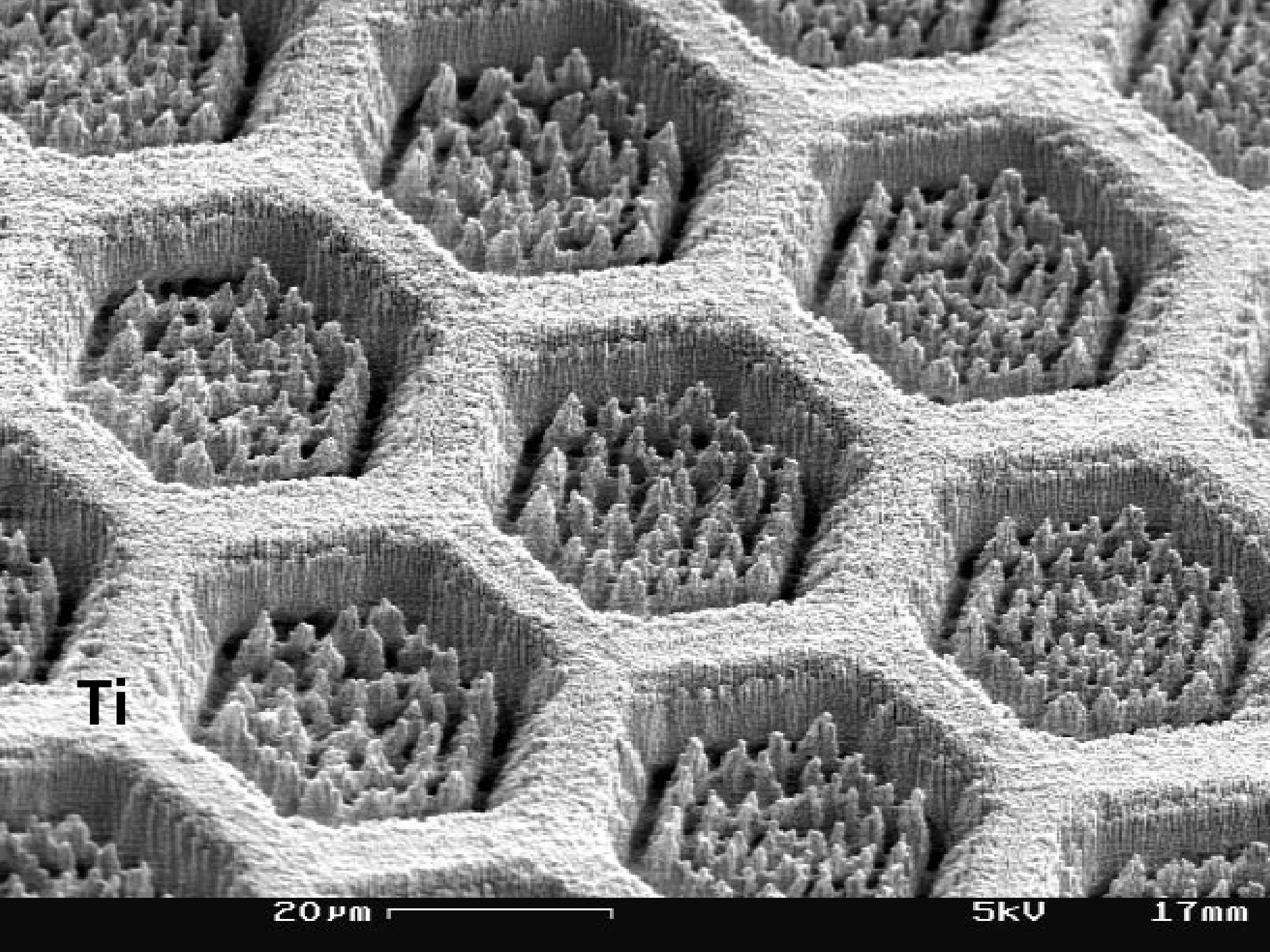
Outlook

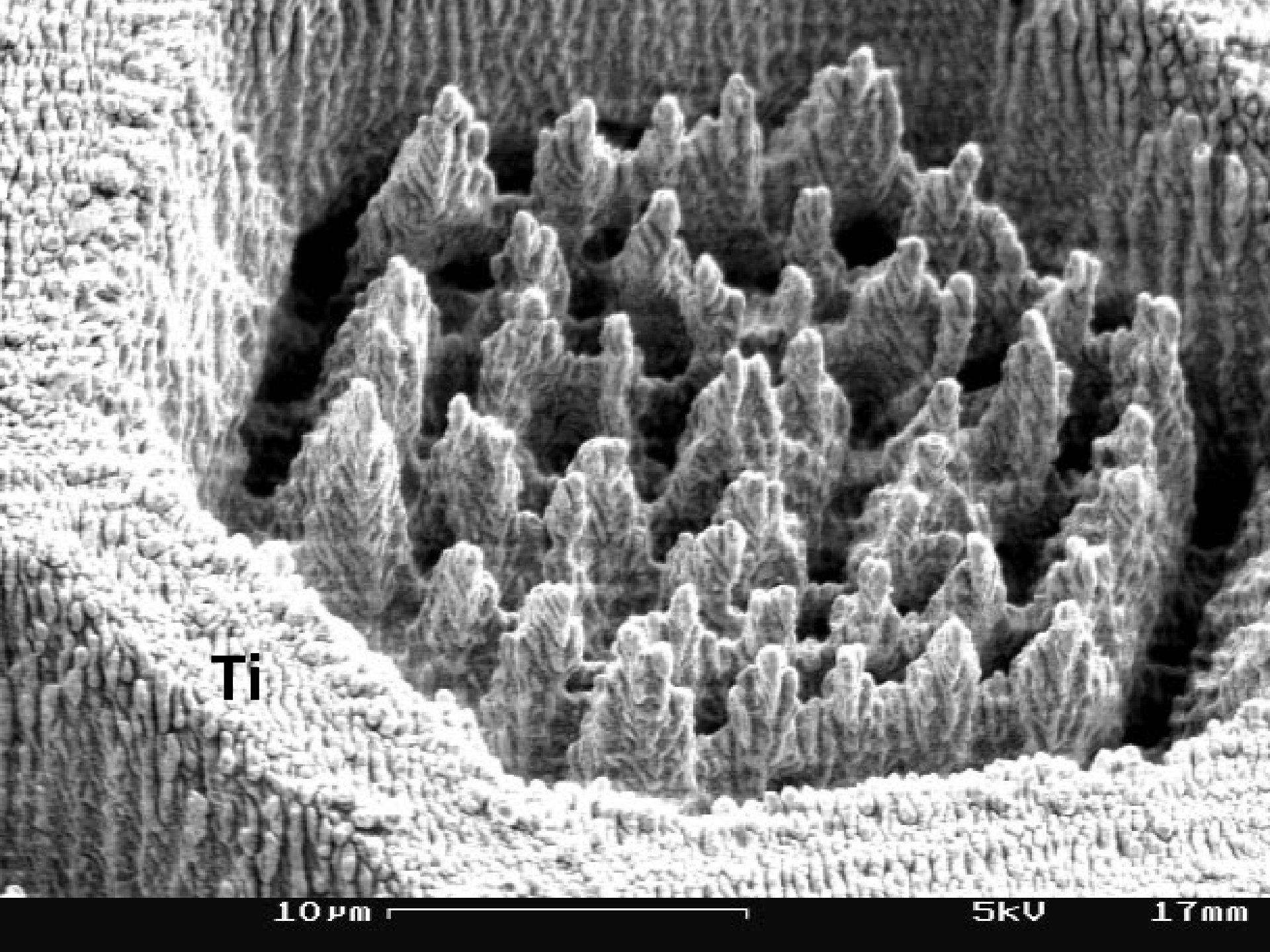
remove grid



Si or Ti substrate


Si
x2000 20µm 5kV 24mm
512 x 480 H300.TIF


Ti
20µm
5kV
17mm


Ti
10µm
5kV
17mm

Outlook

Summary

Microstructured silicon

- **fabricated by simple, maskless process**

Summary

Microstructured silicon

- **fabricated by simple, maskless process**
- **can be integrated with microelectronics**


GORDON McKAY
LABORATORY OF
APPLIED SCIENCE

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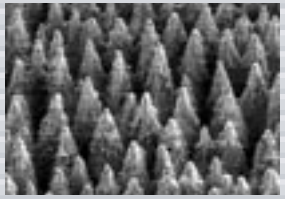
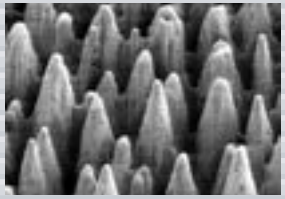
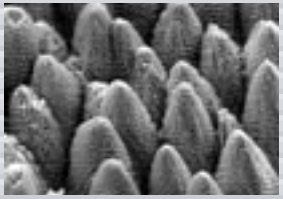
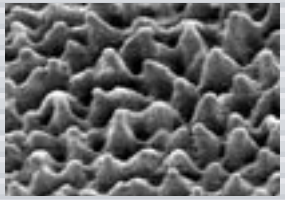
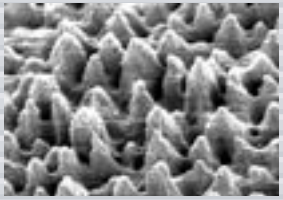
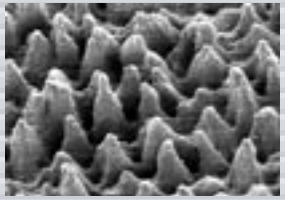
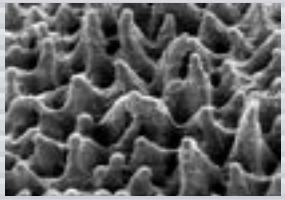
Dr. John Chervinsky (Harvard University)
Prof. Mike Aziz (Harvard University)

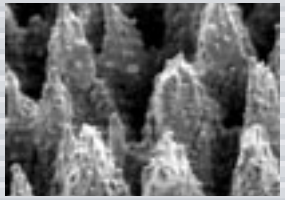
For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu

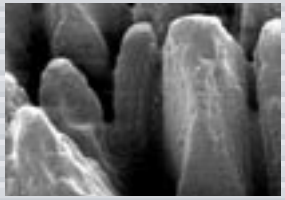
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti		reacts			

Only in SF_6:



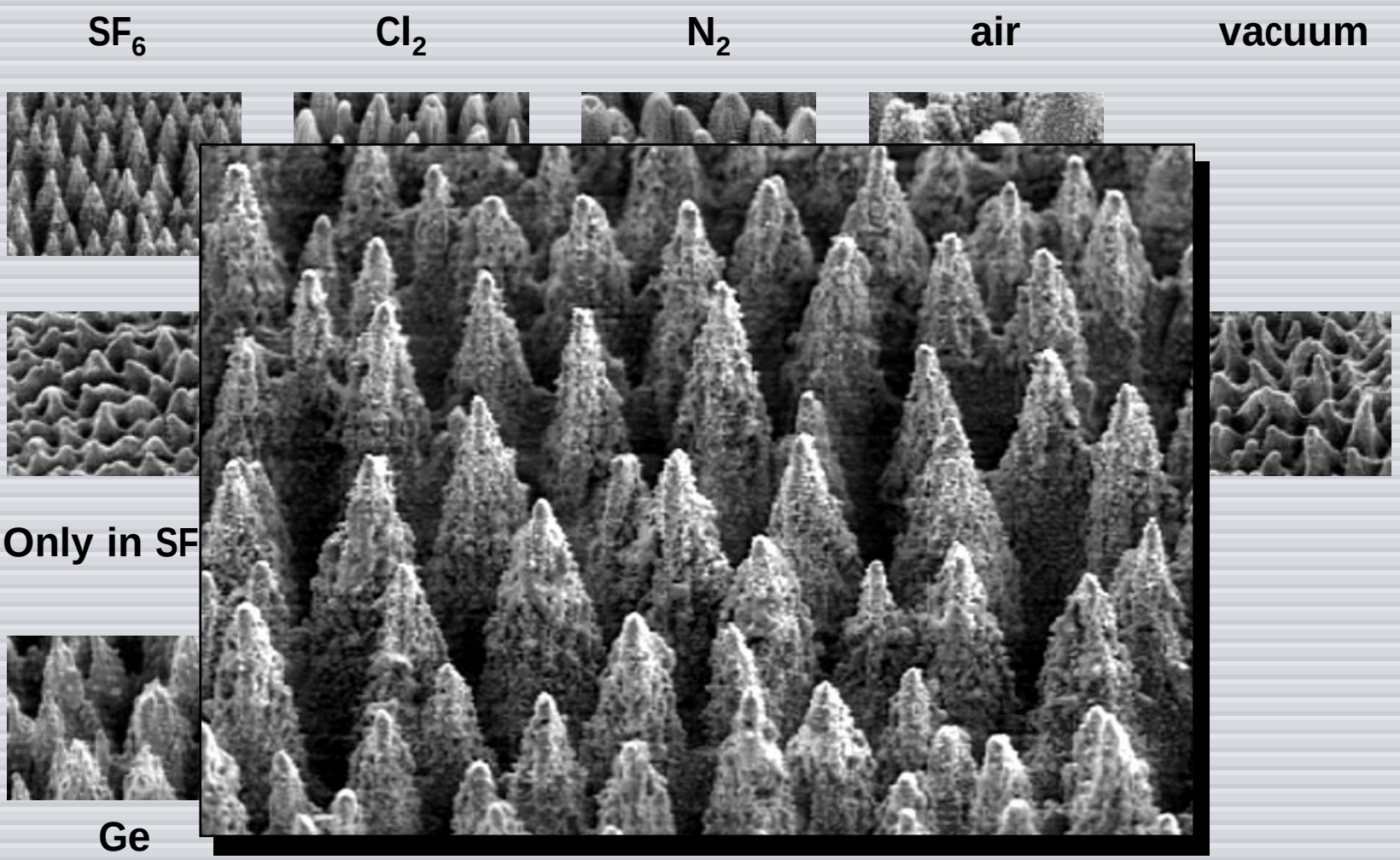
Ge



InP

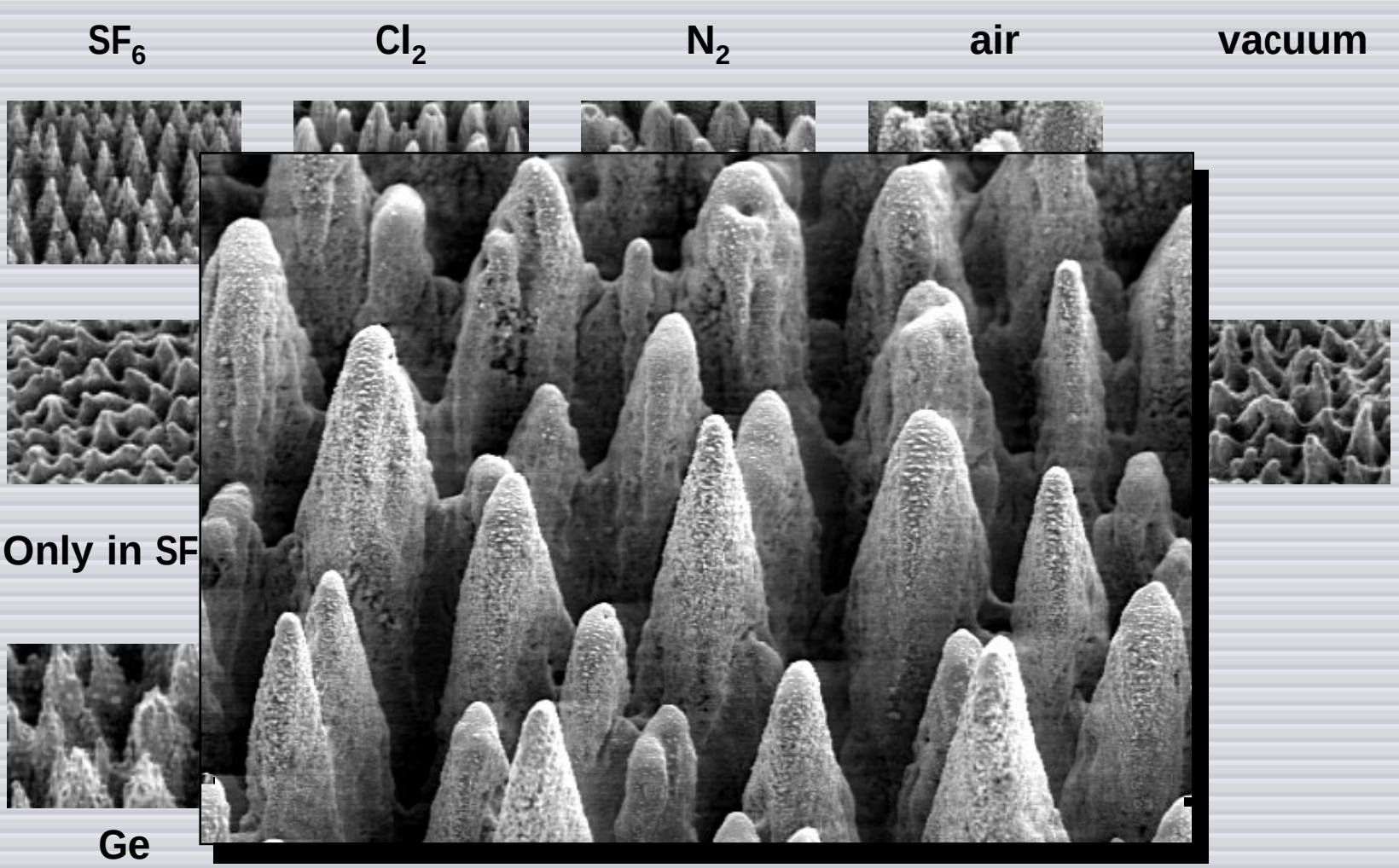
No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials



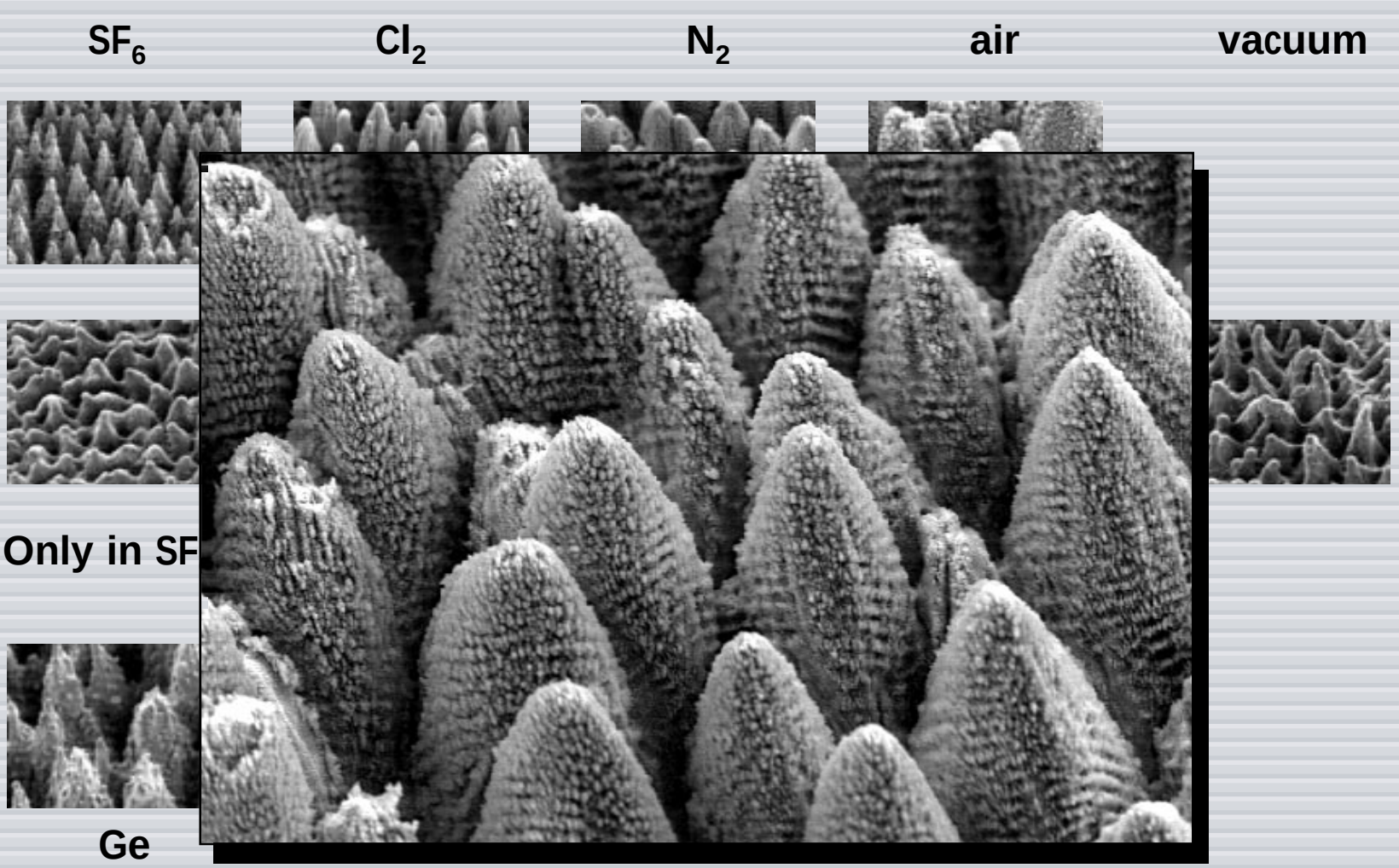
No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials



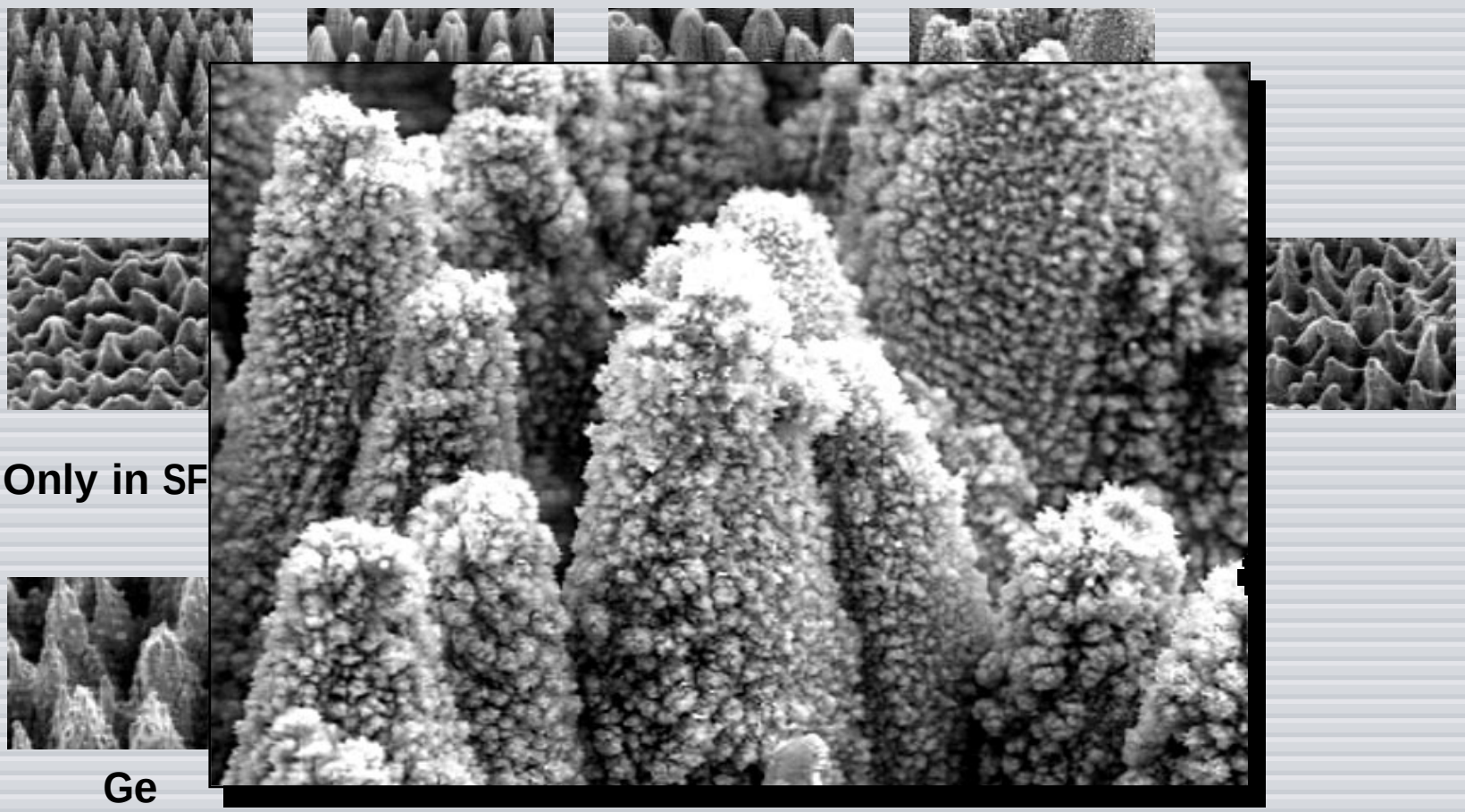
No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials



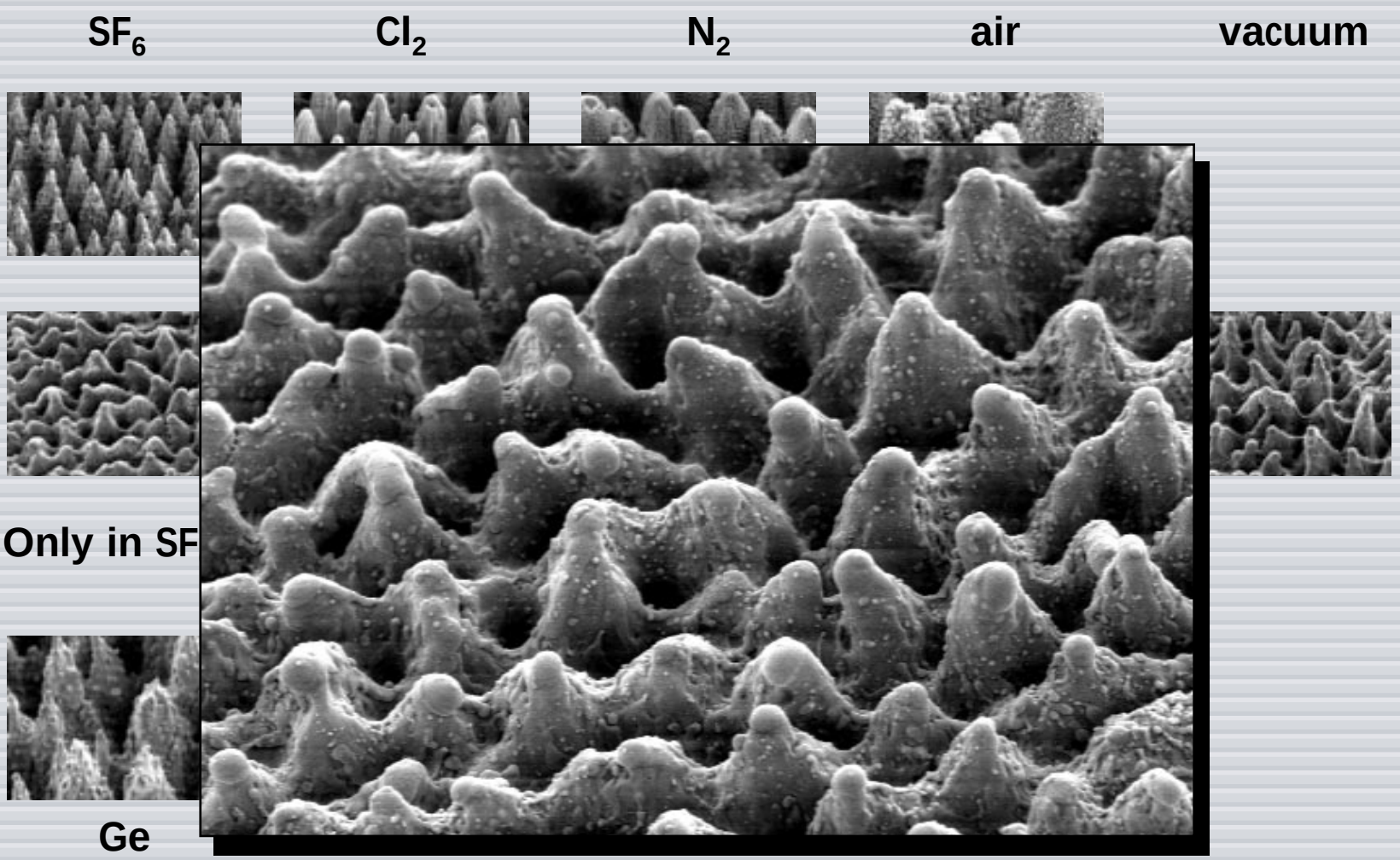
No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials



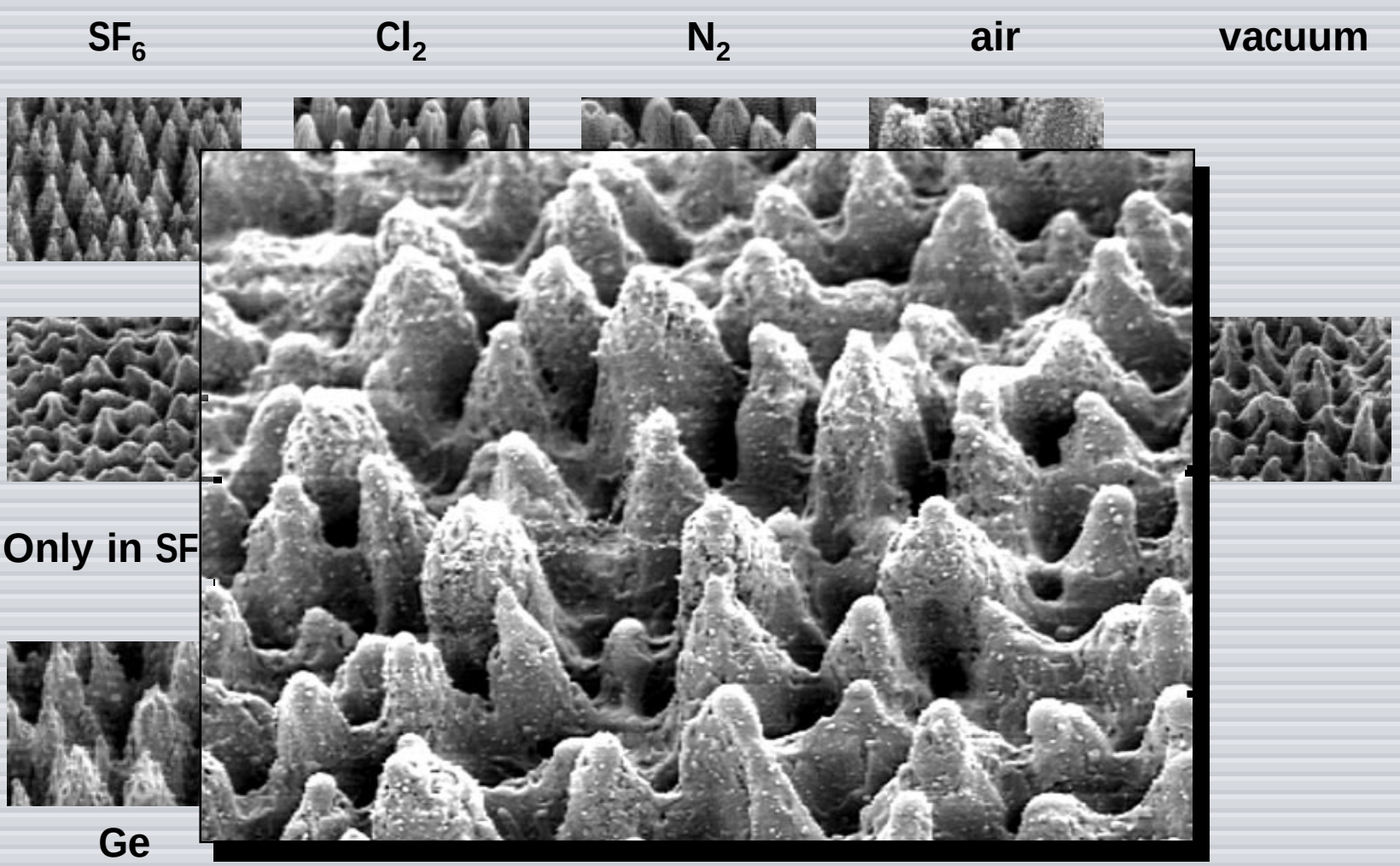
No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials



No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

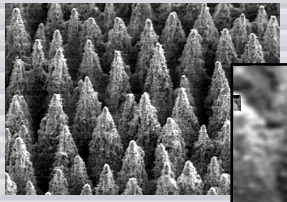


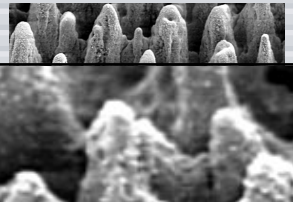
No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

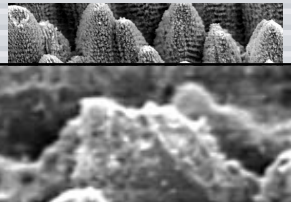
Materials

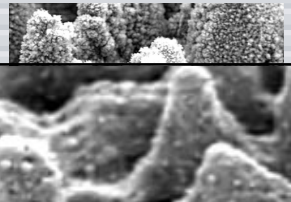
SF_6 Cl_2 N_2 air vacuum

Si

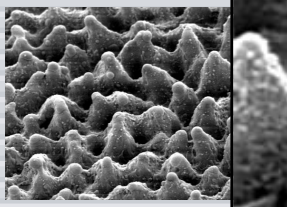


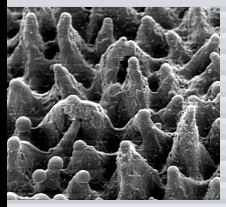




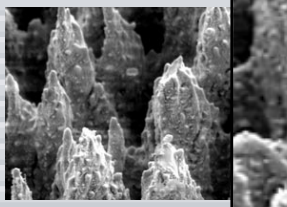


Ti





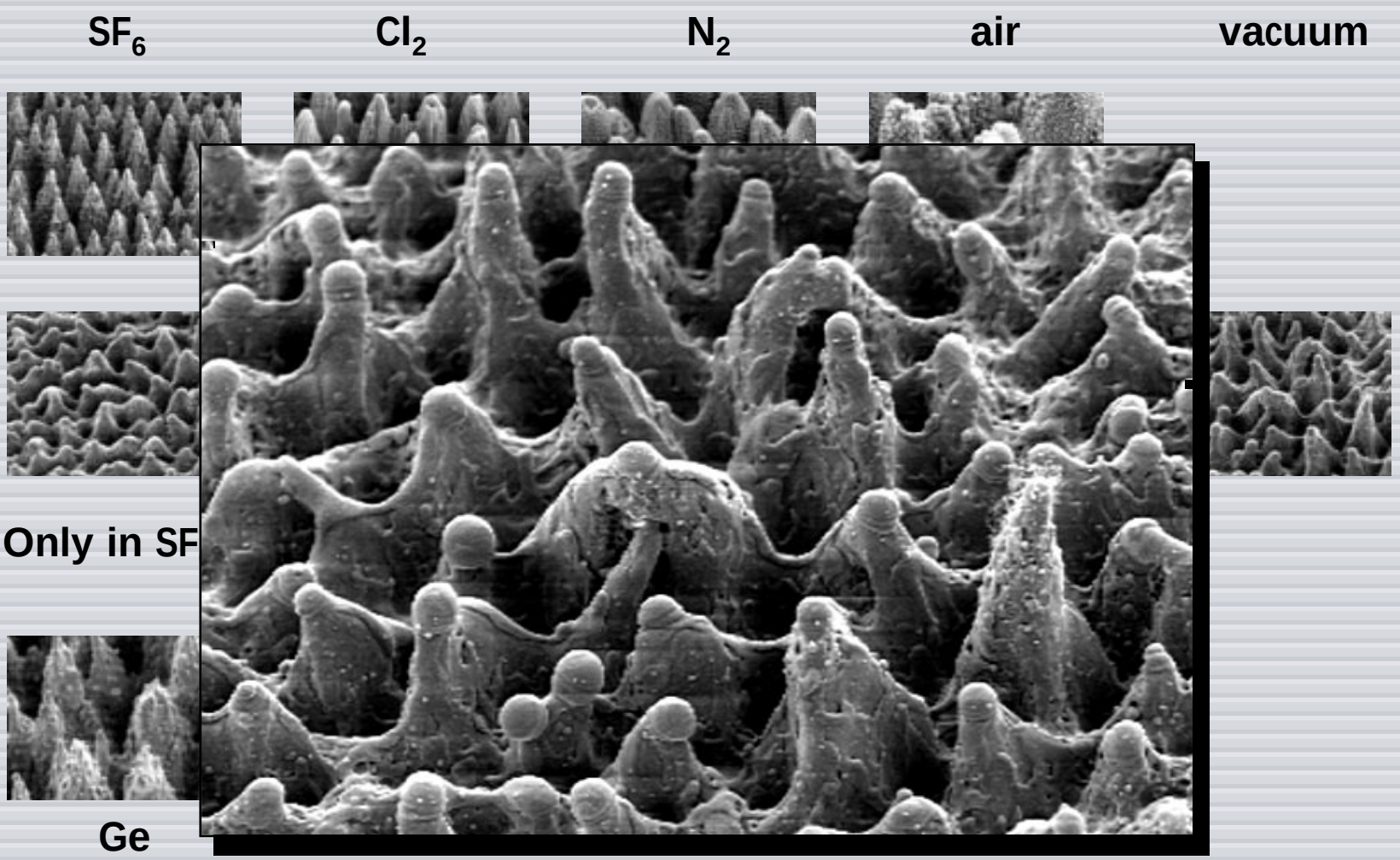
Only in SF



Ge

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

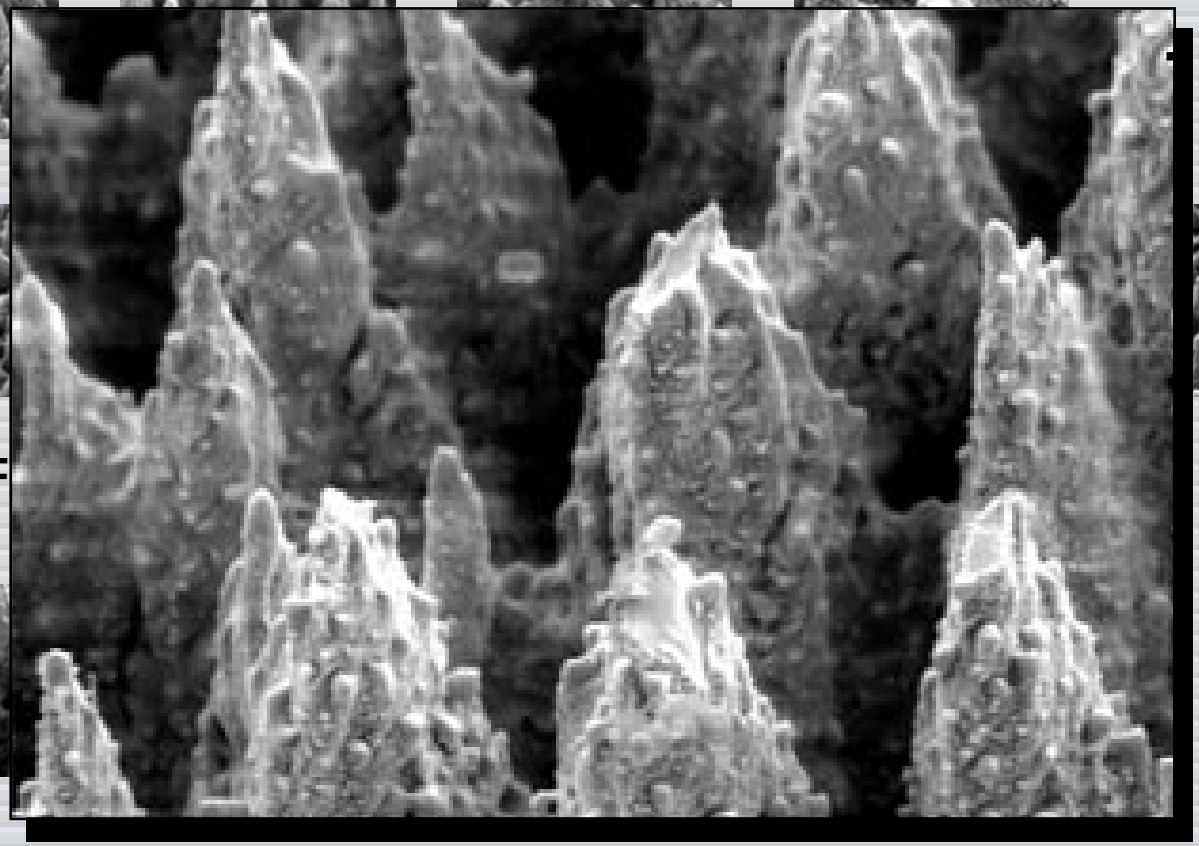
Materials



No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

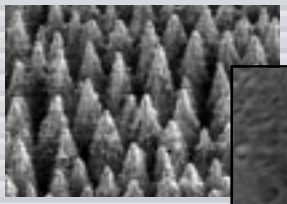
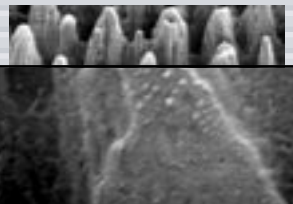
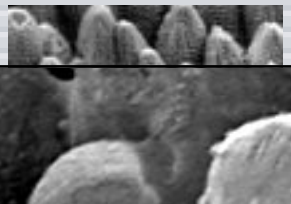
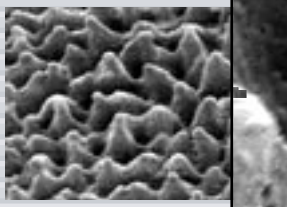
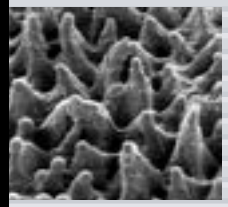
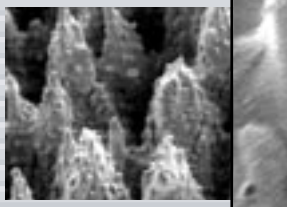
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					



Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Only in SF					
Ge					

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs