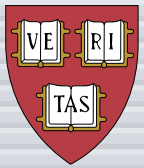
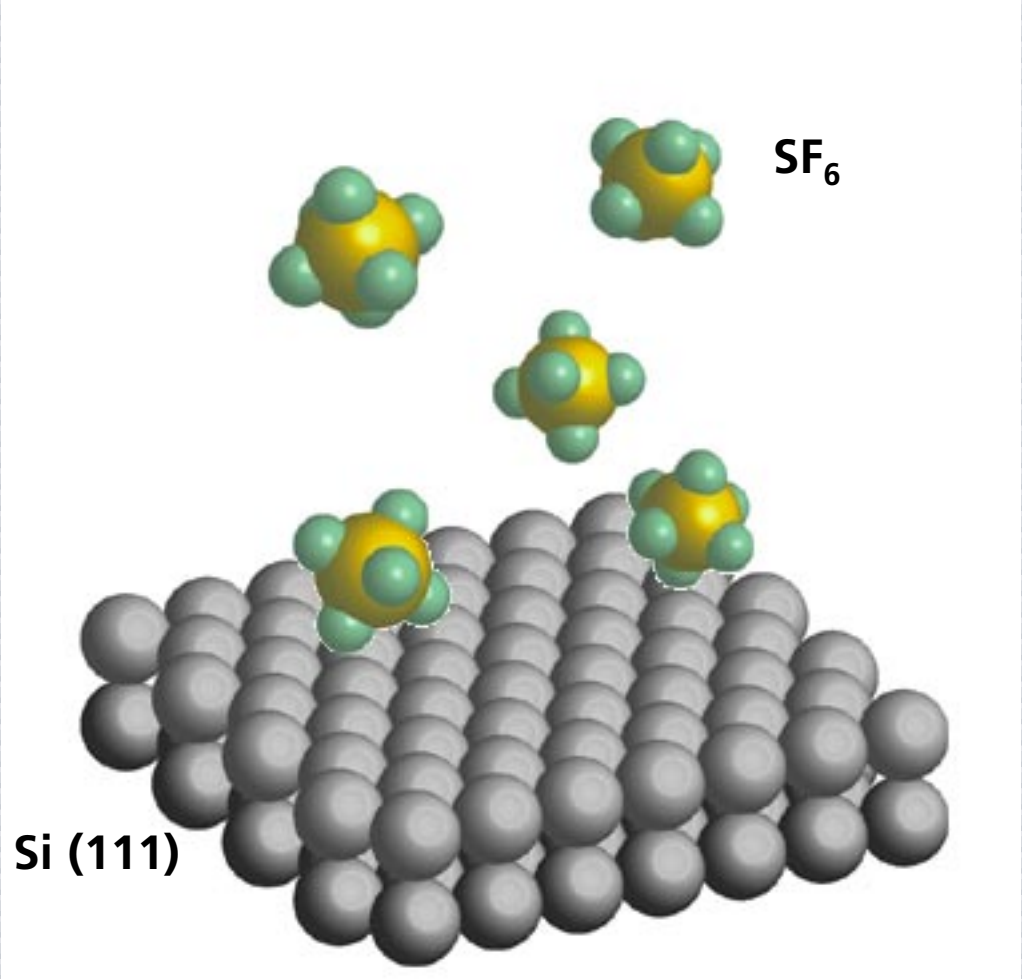
Femtosecond laser-assisted microstructuring of silicon surfaces for novel detector, sensing, and display technologies

Jim Carey
Tsing-Hua Her
Mike Sheehy
Claudia Wu
Rebecca Younkin
Catherine Crouch
Meng Yan Shen
Li Zhao

Zhejiang University
Hangzhou, China, 17 October 2002

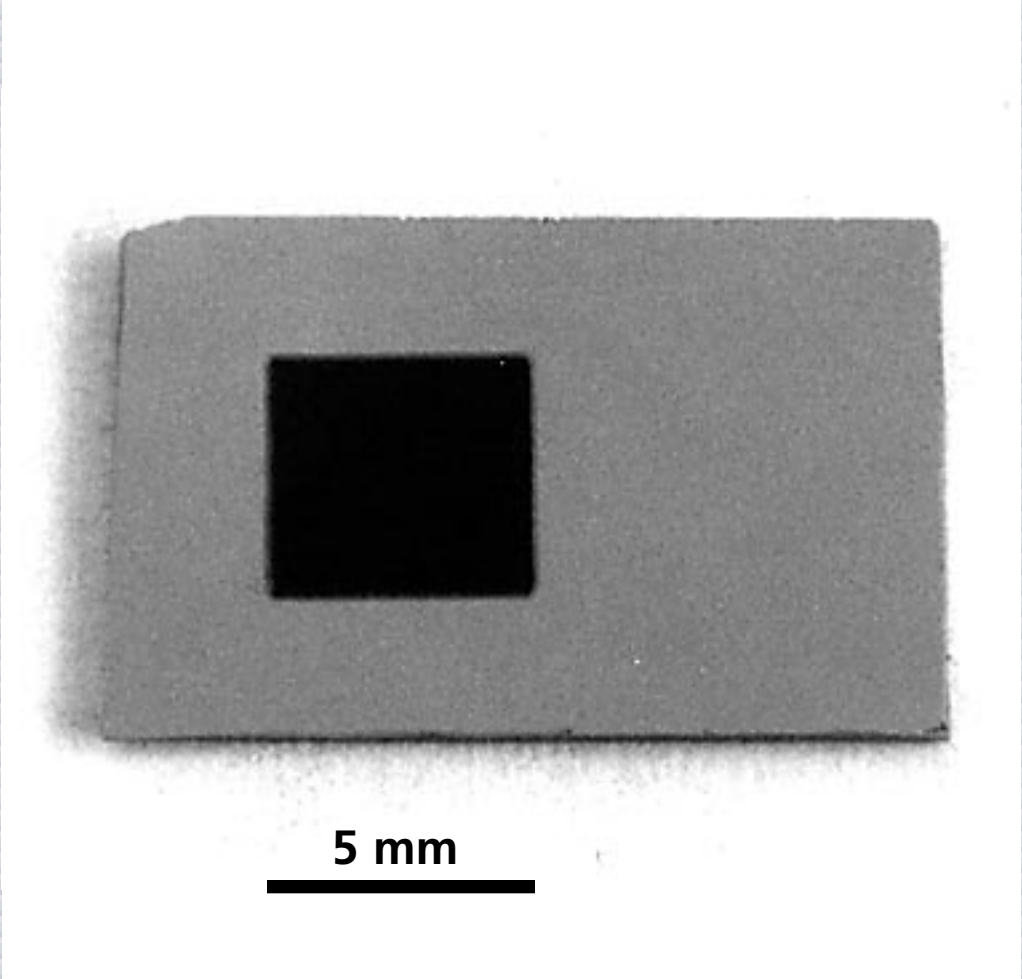


Introduction



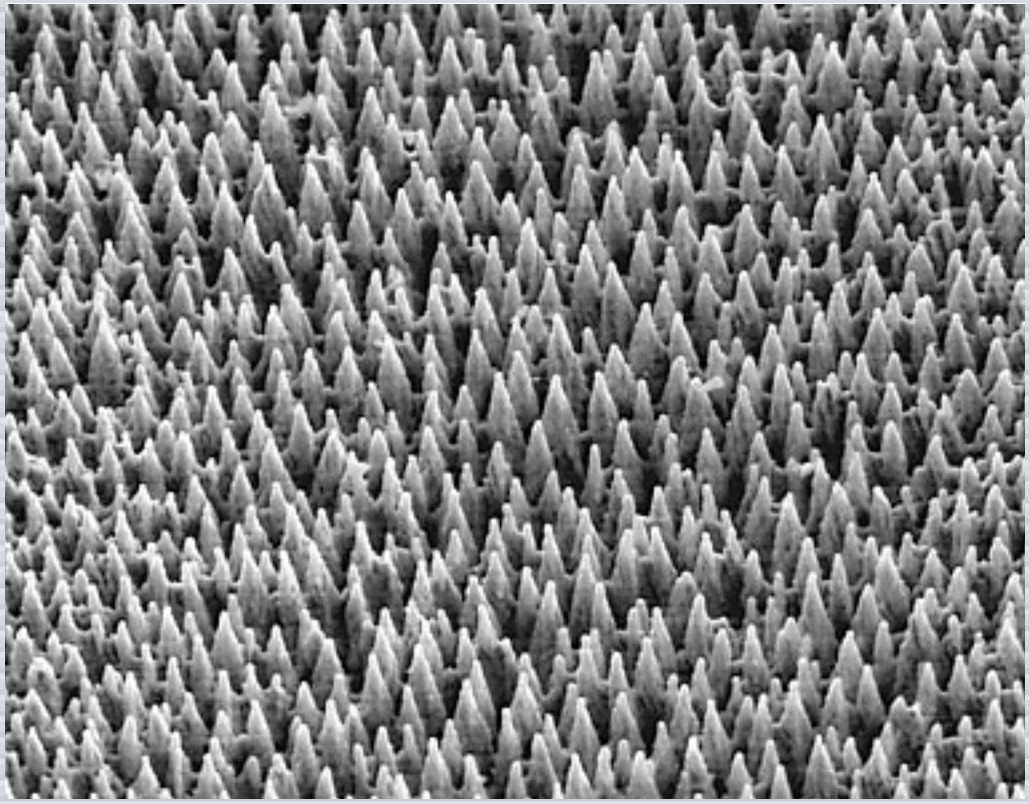
irradiate with 100-fs 10 kJ/m^2 pulses

Introduction



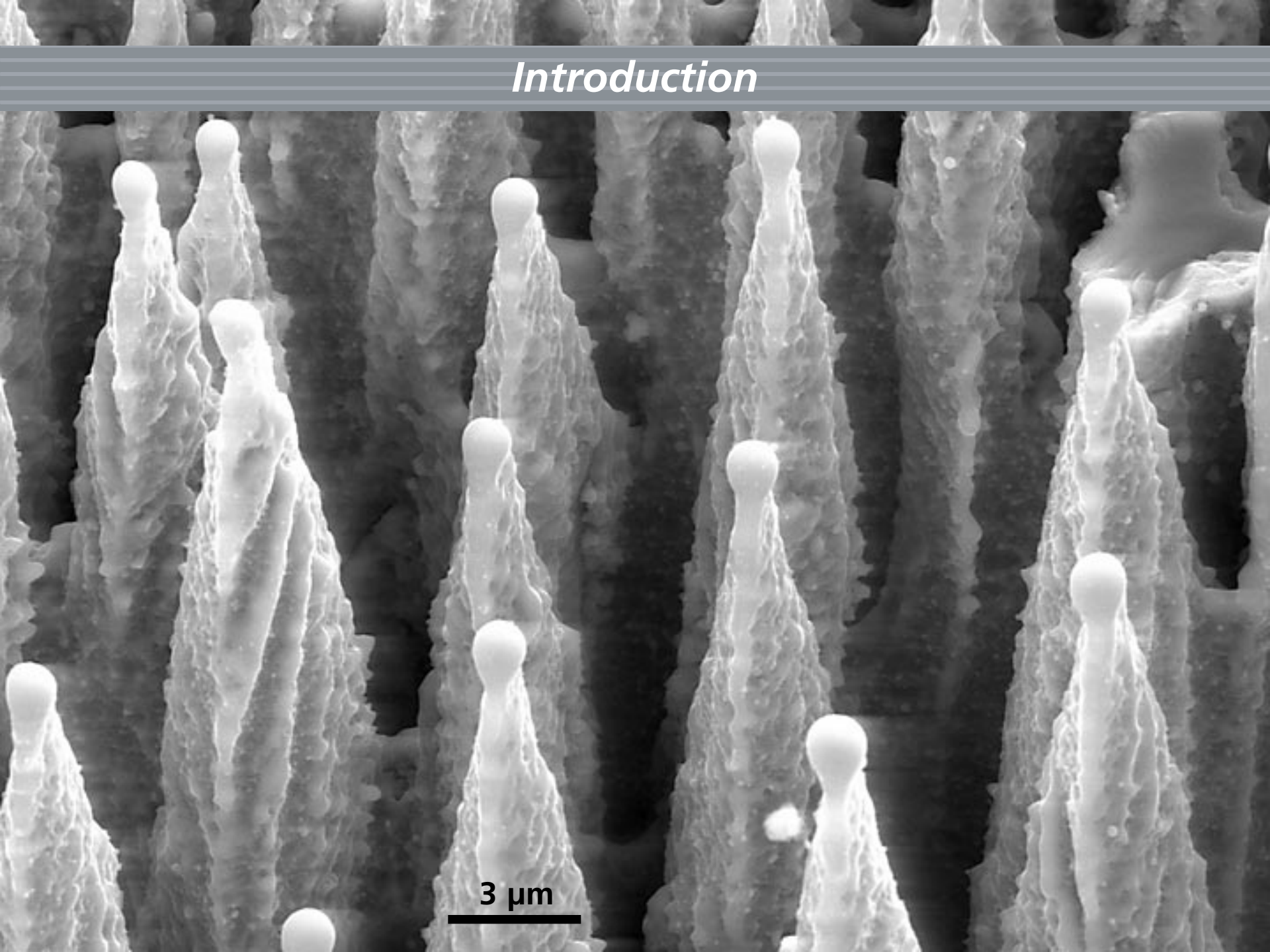
“black silicon”

Introduction



20 µm

Introduction



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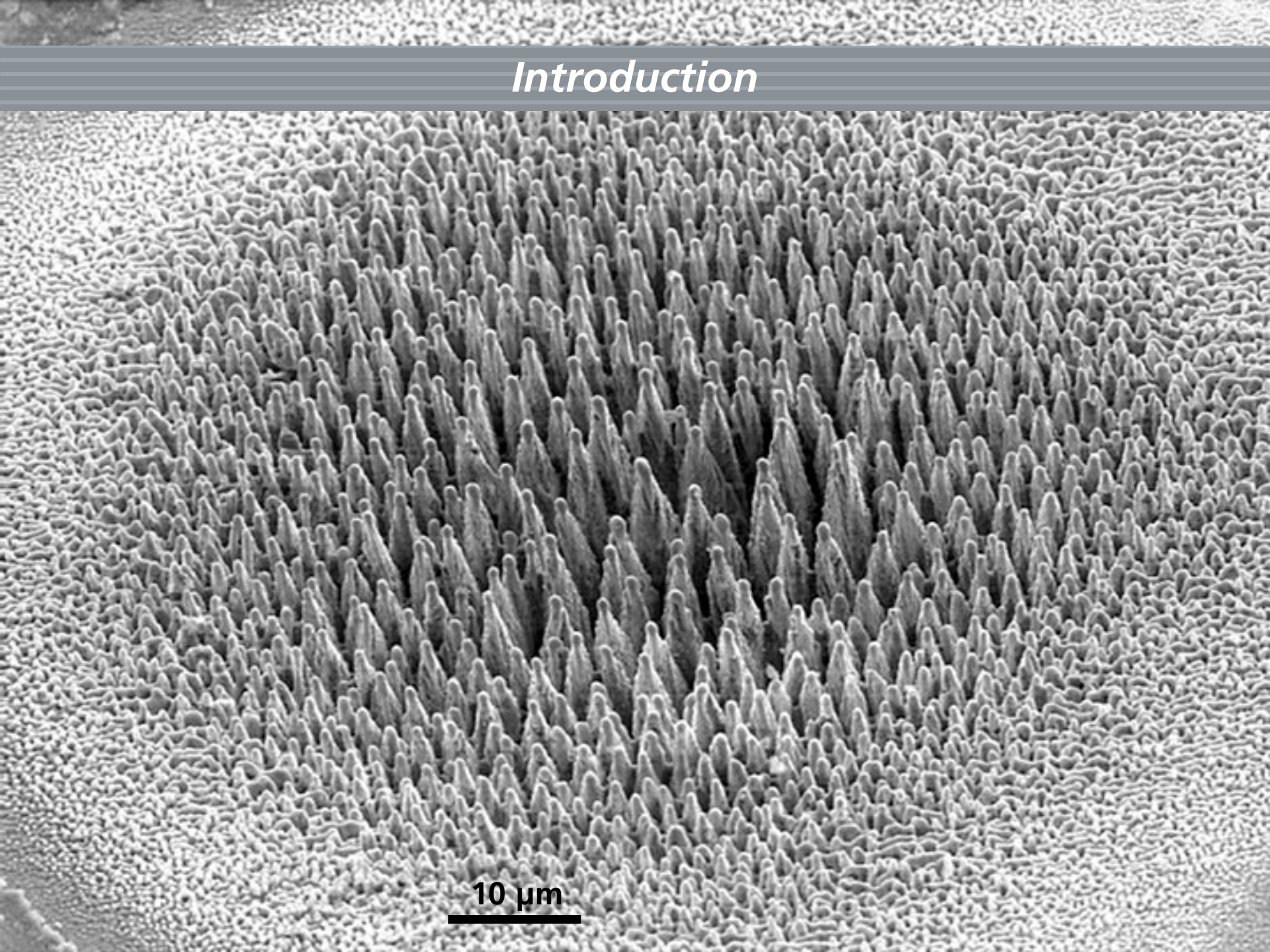

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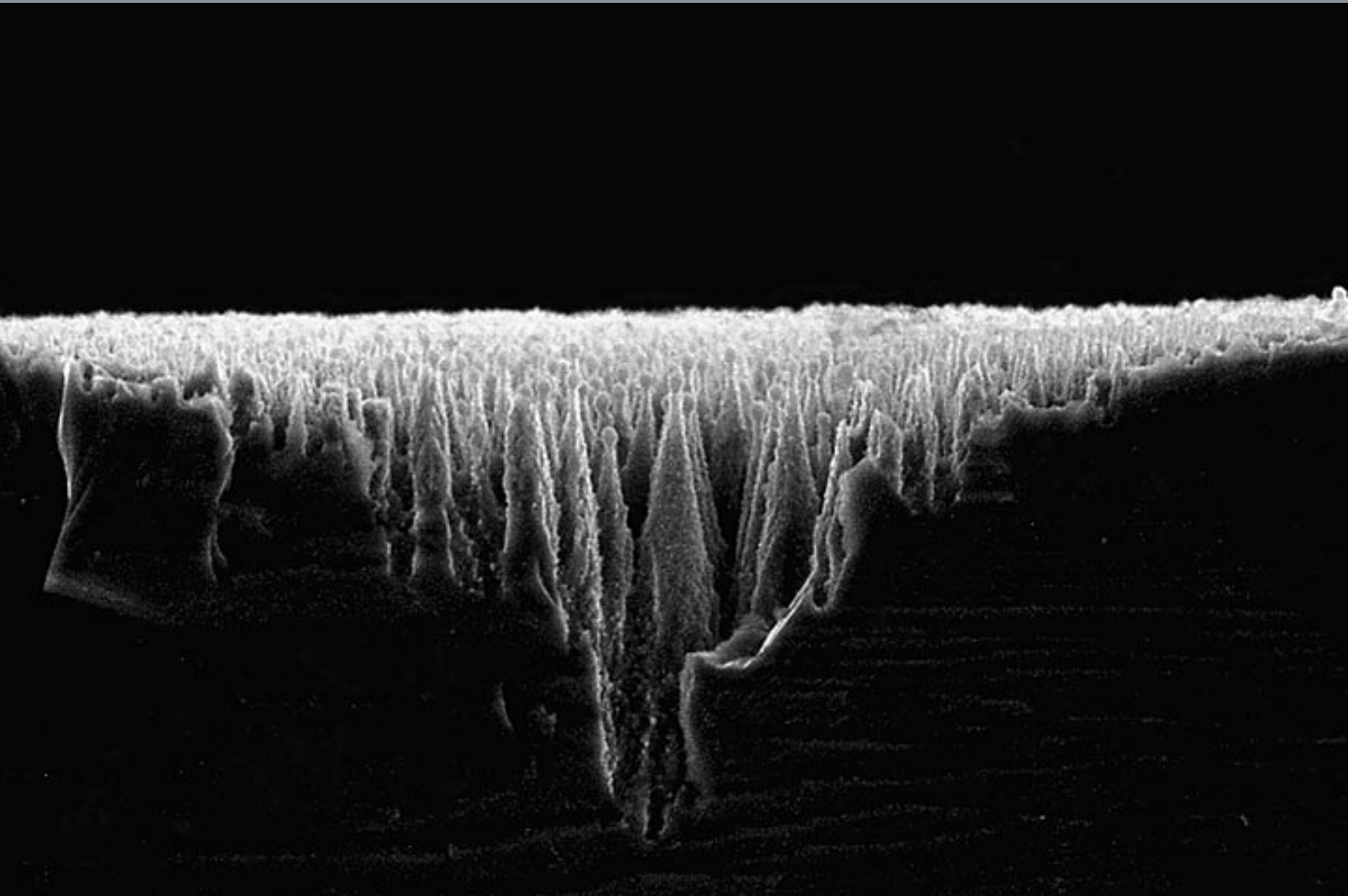

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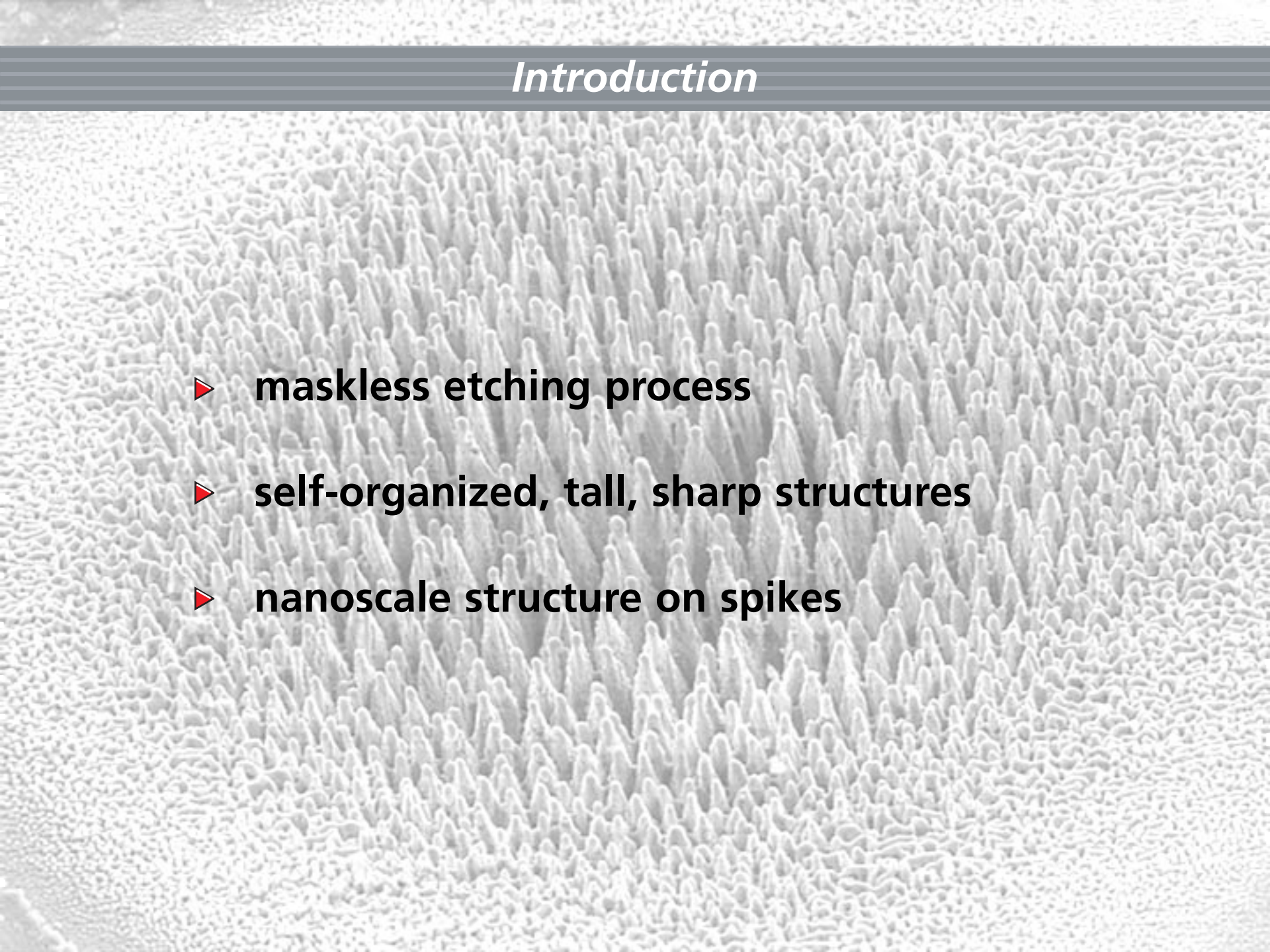
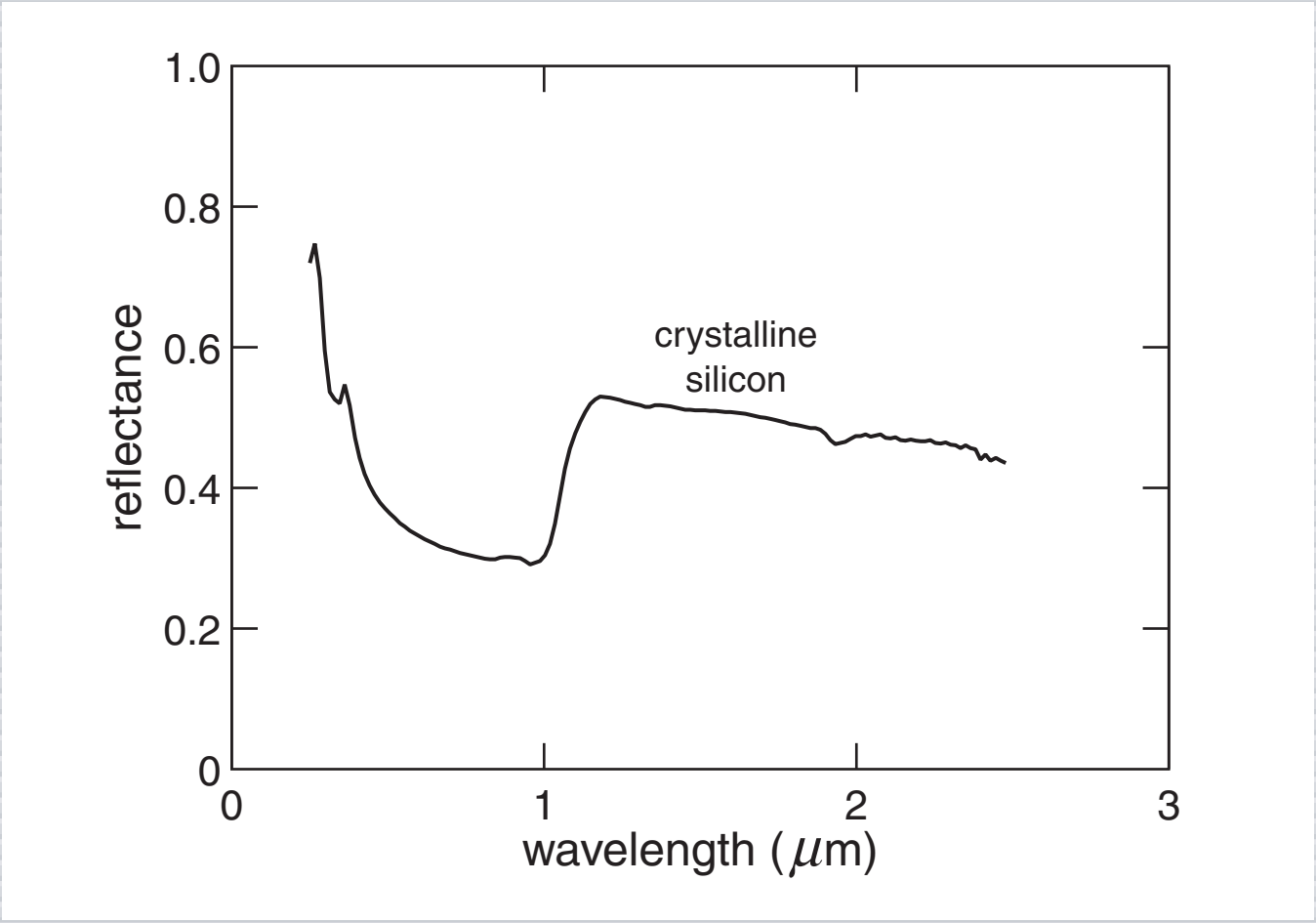


- **maskless etching process**
- **self-organized, tall, sharp structures**
- **nanoscale structure on spikes**

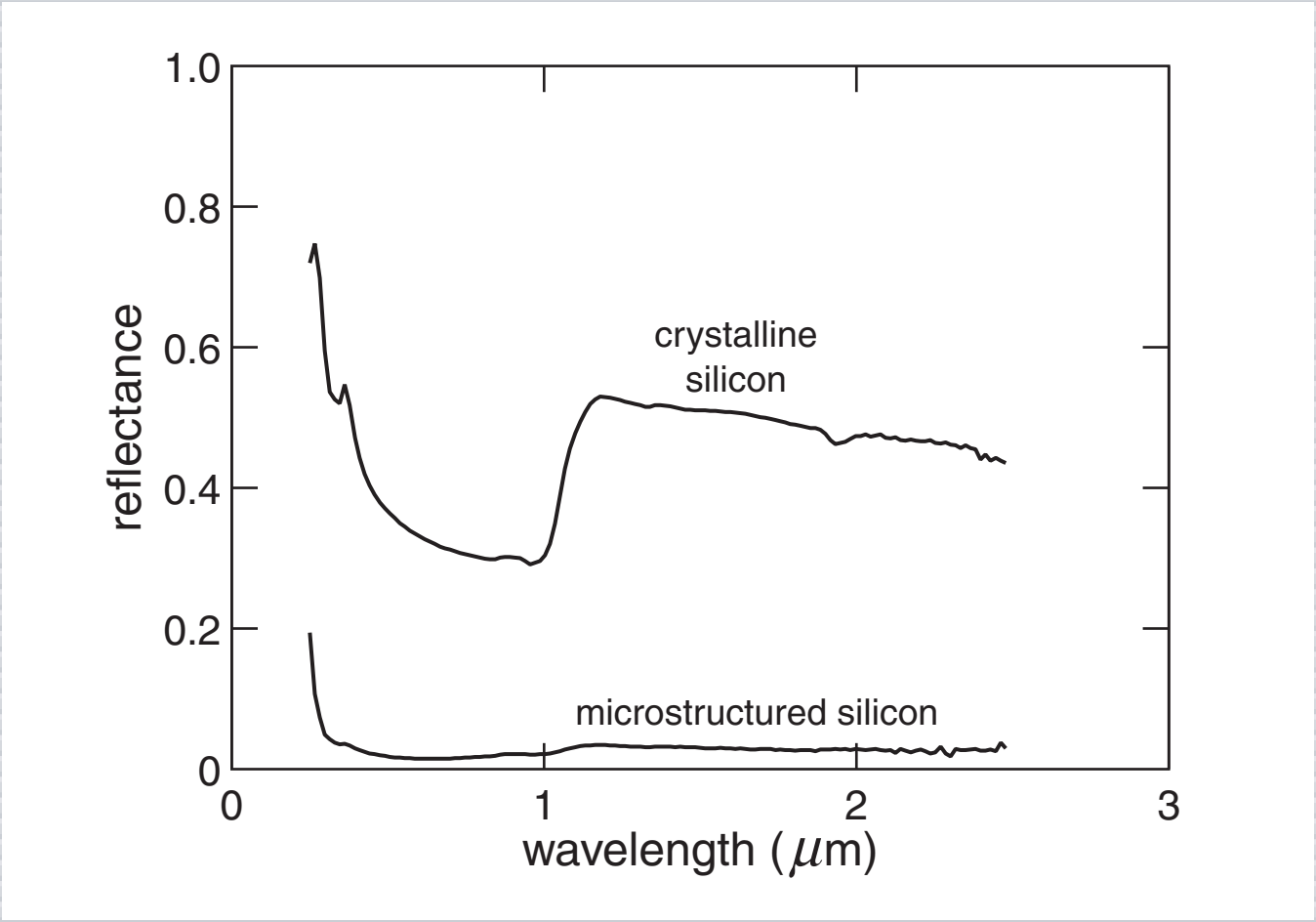
Outline

- Properties
- Structural and chemical analysis
- Outlook

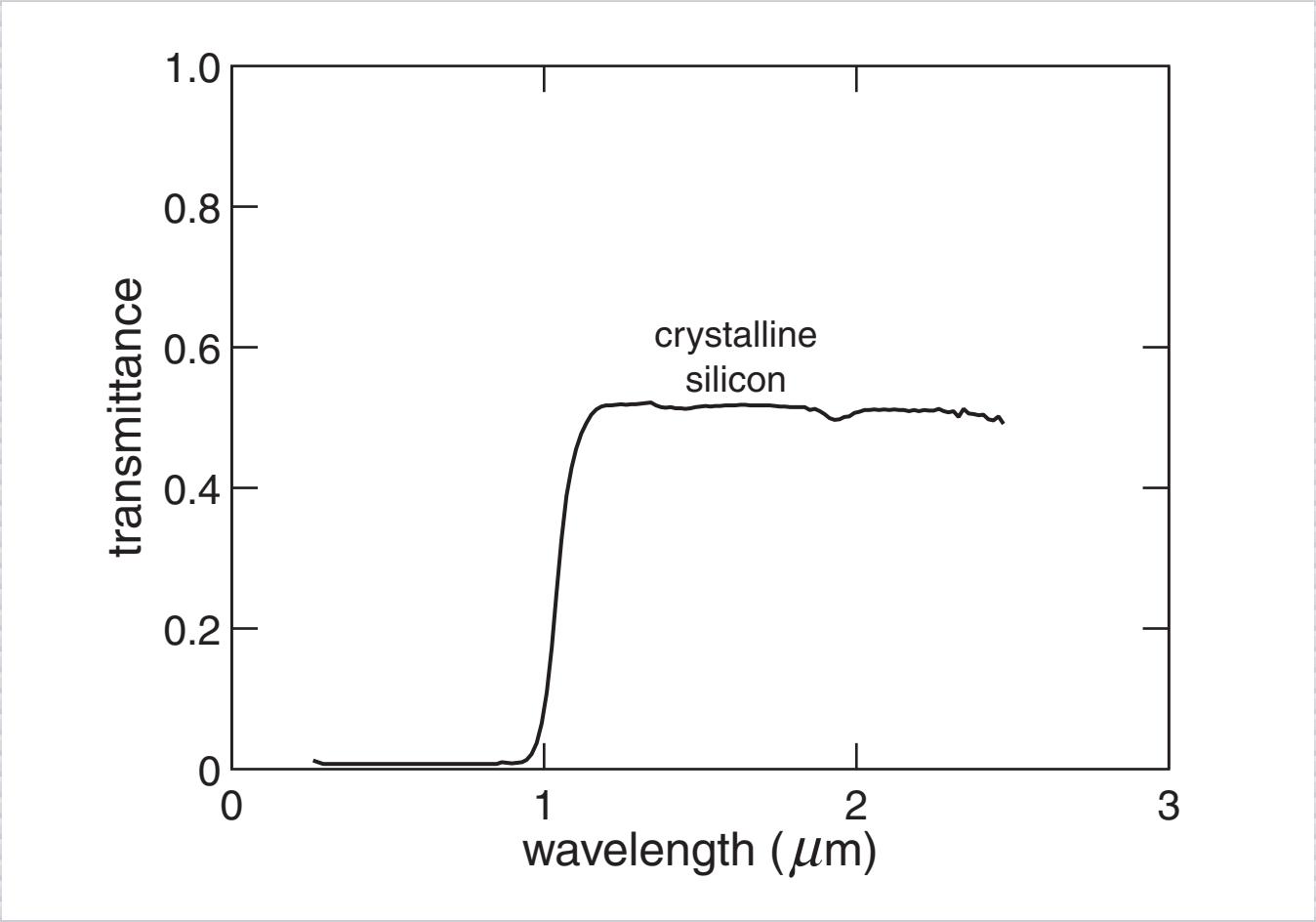
reflectance (integrating sphere)



reflectance (integrating sphere)



transmittance (integrating sphere)



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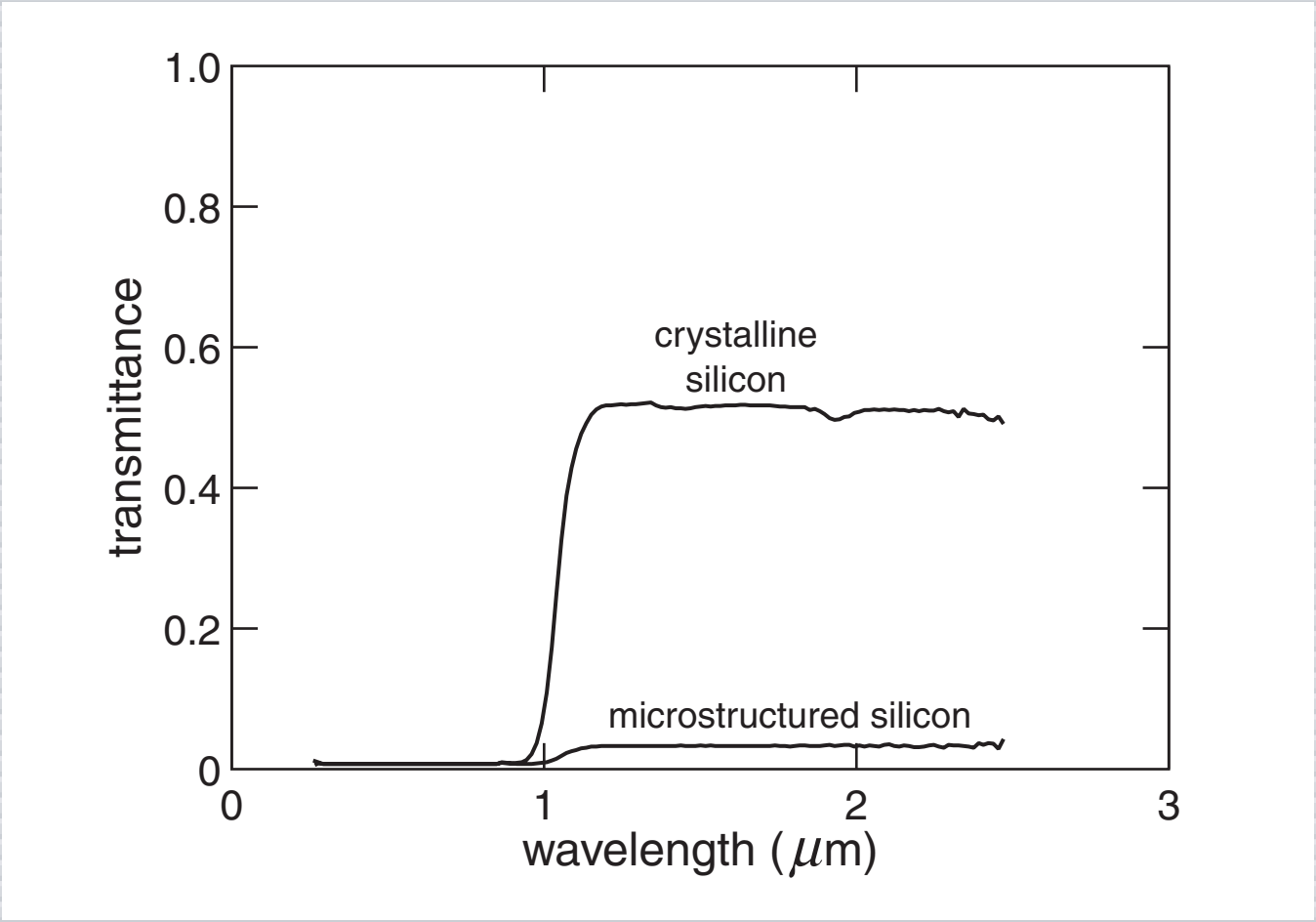
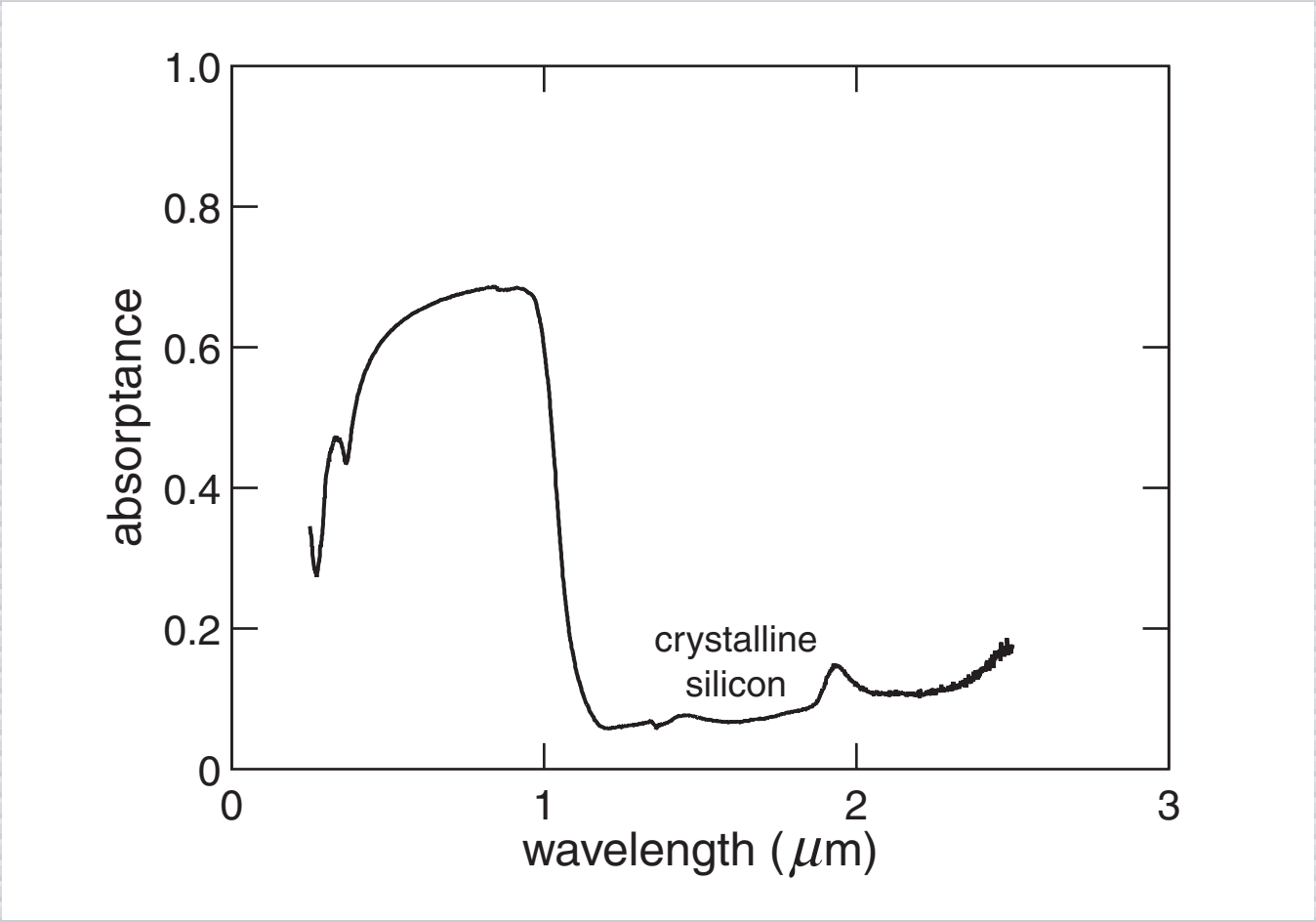


absorptance (1 – *R* – *T*)



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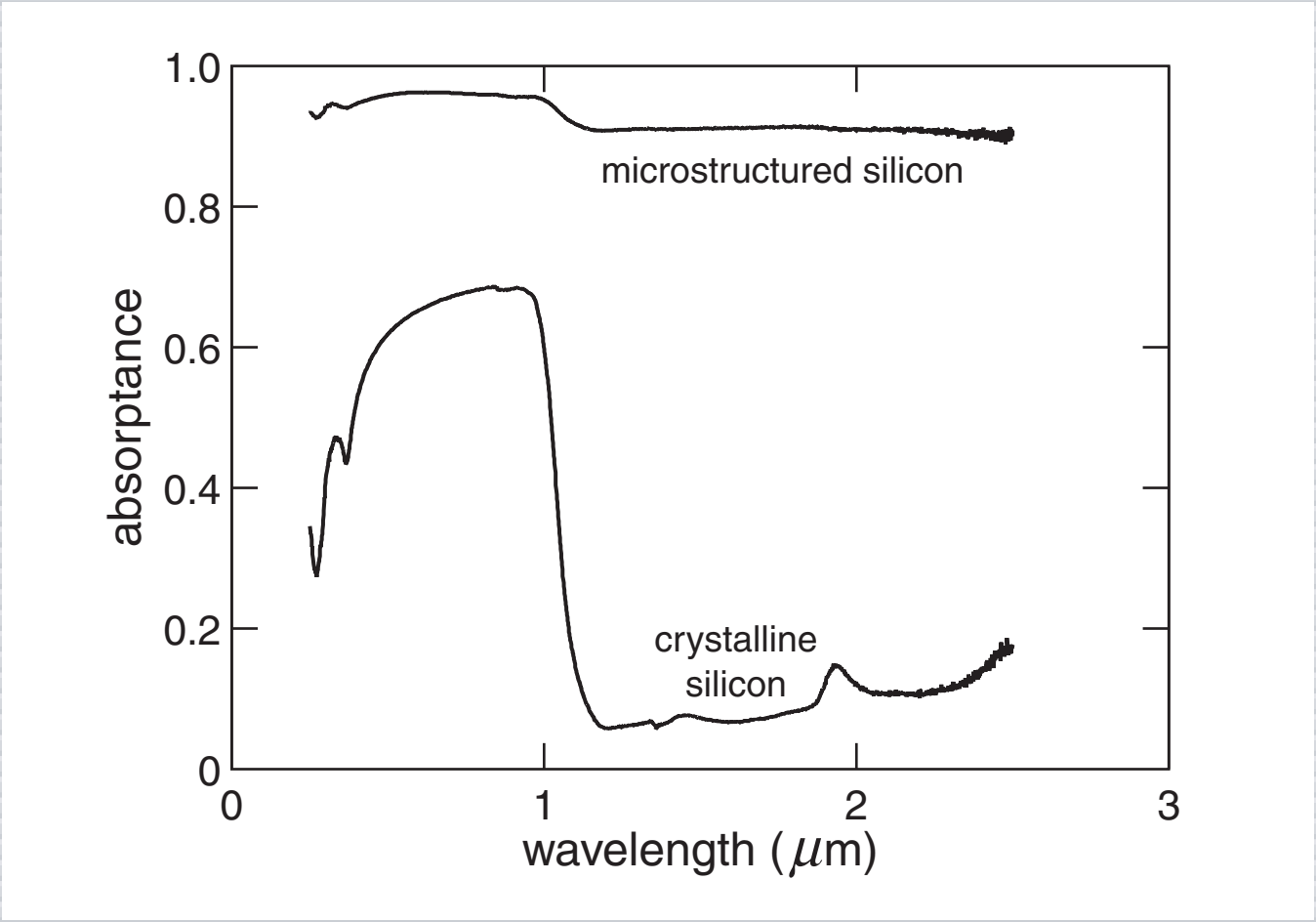

Appl. Phys. Lett. **78, 1850 (2001)**

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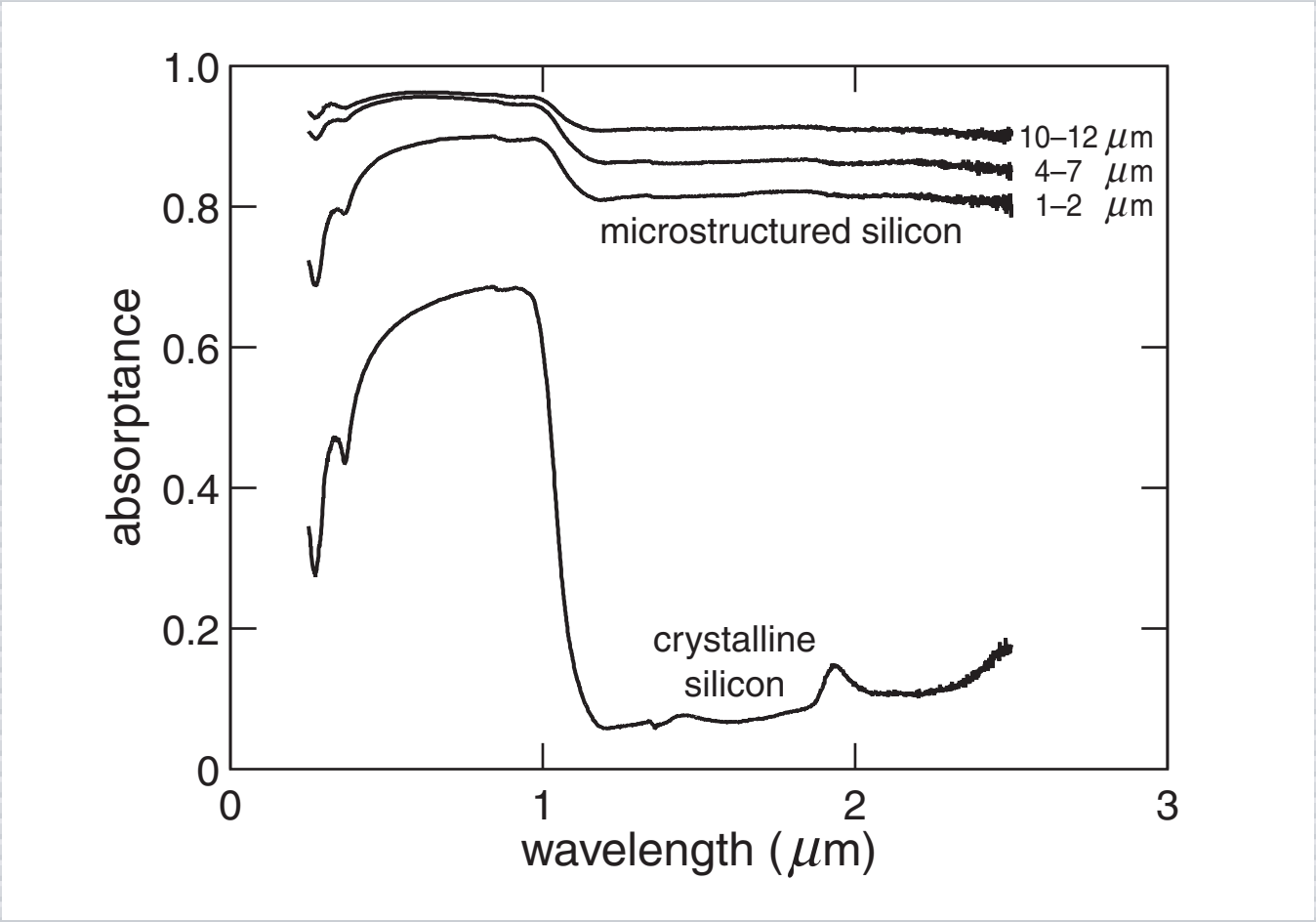
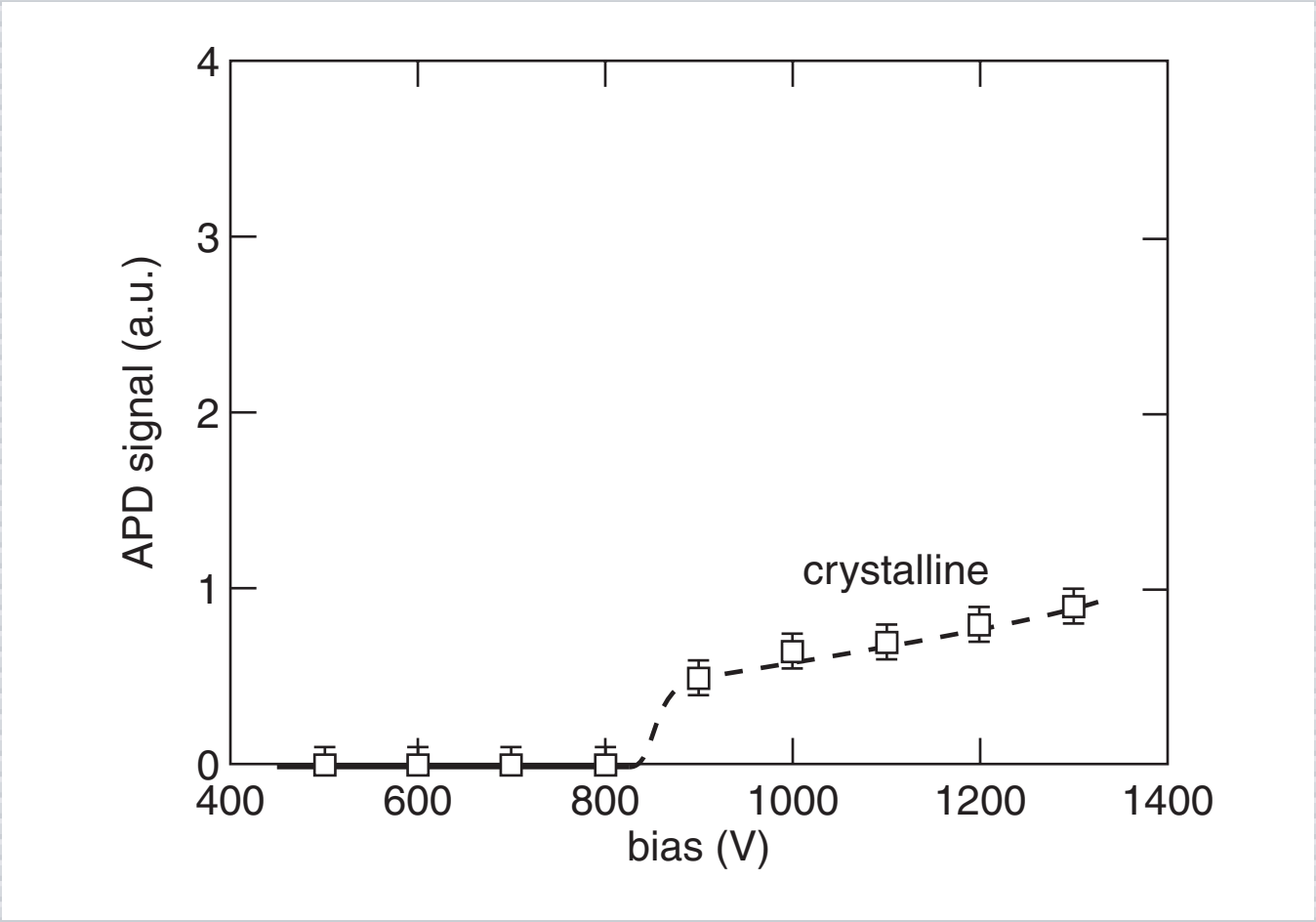


Appl. Phys. Lett. **78, 1850 (2001)**

avalanche photodiode response at 1.3 μm



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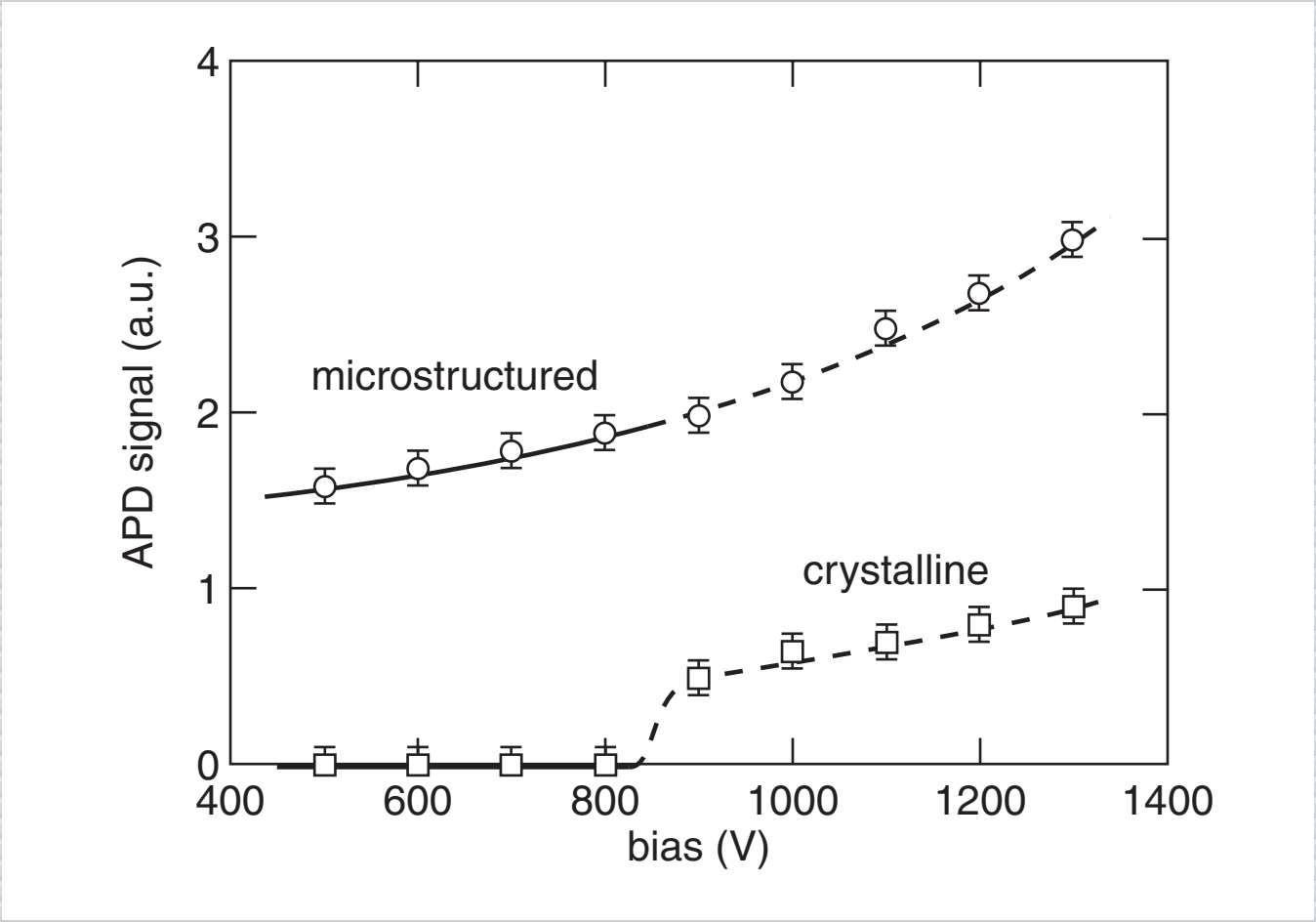
avalanche photodiode response at 1.3 μm



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**

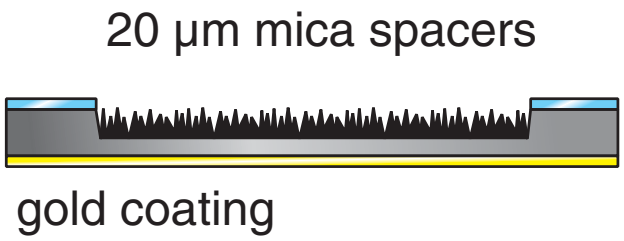
can spikes be used as field emitters?

field emission setup

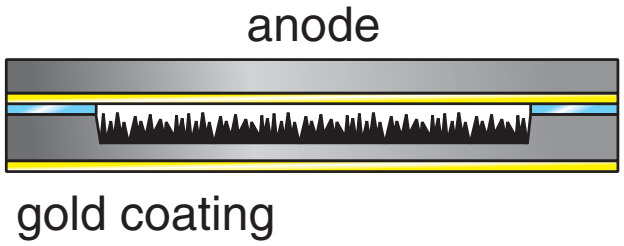
field emission setup

gold coating

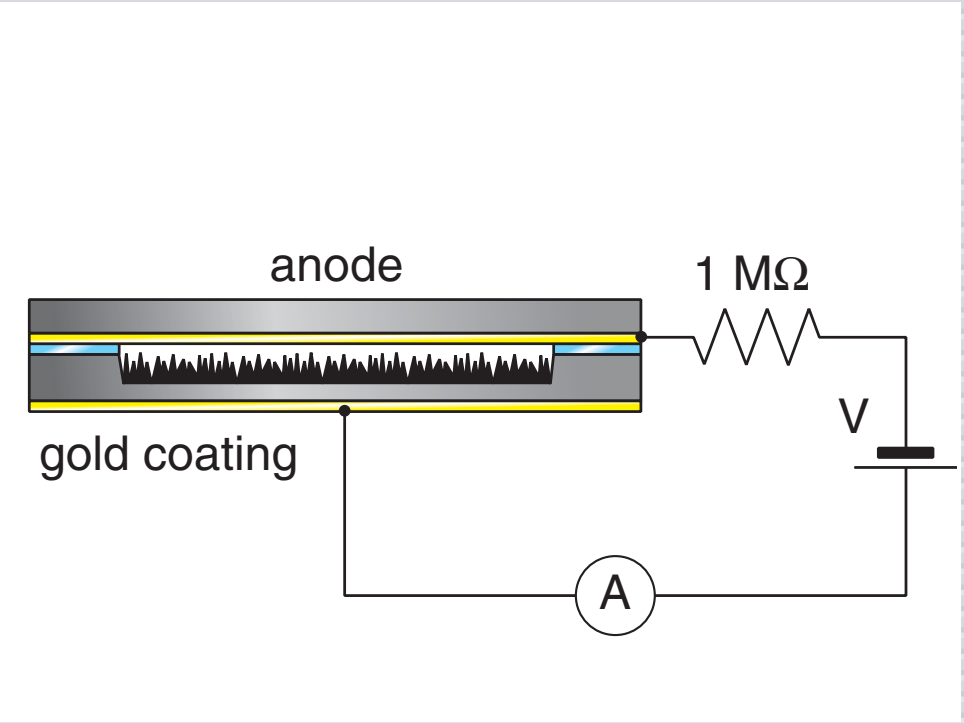
field emission setup



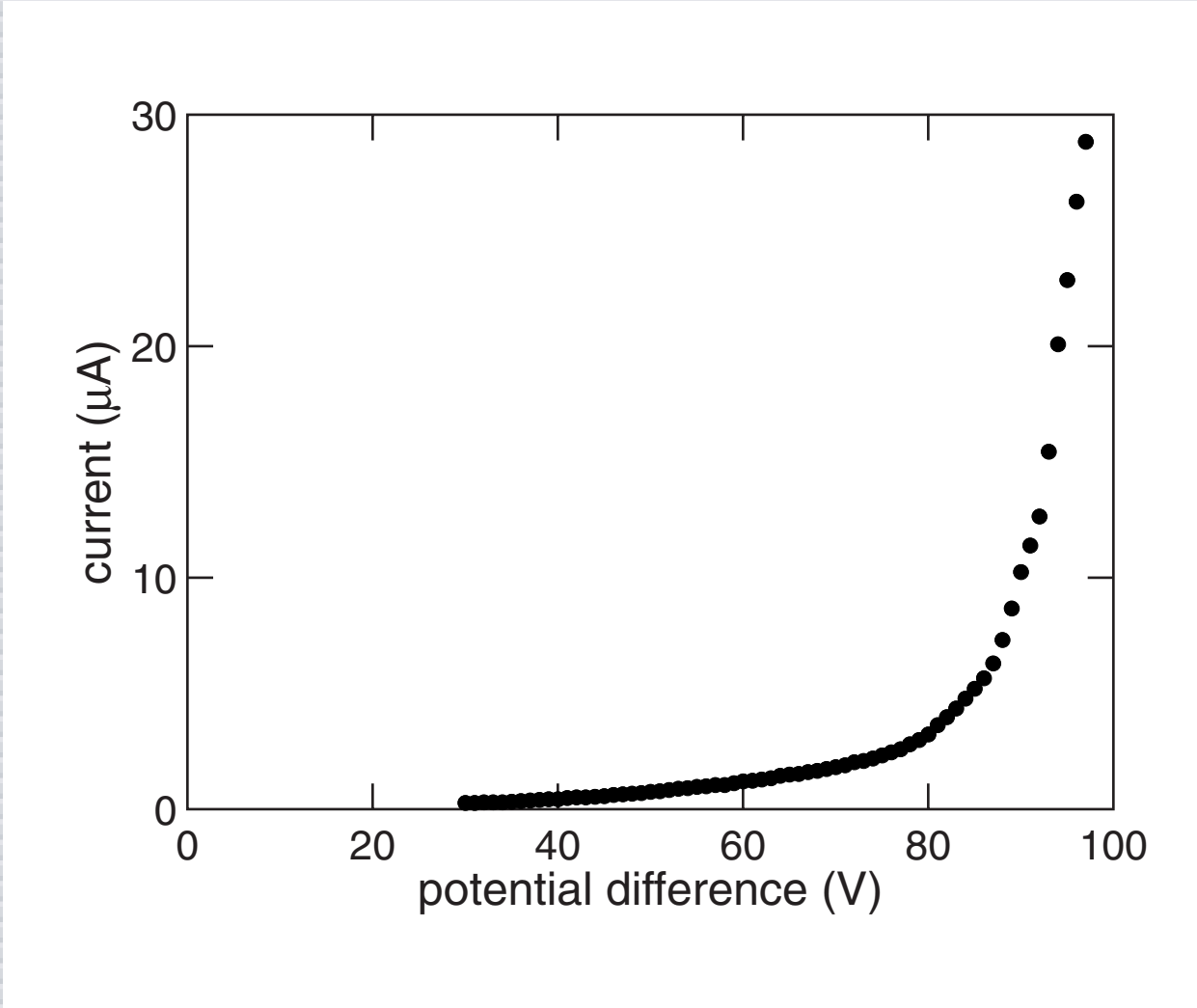
field emission setup



field emission setup



Properties



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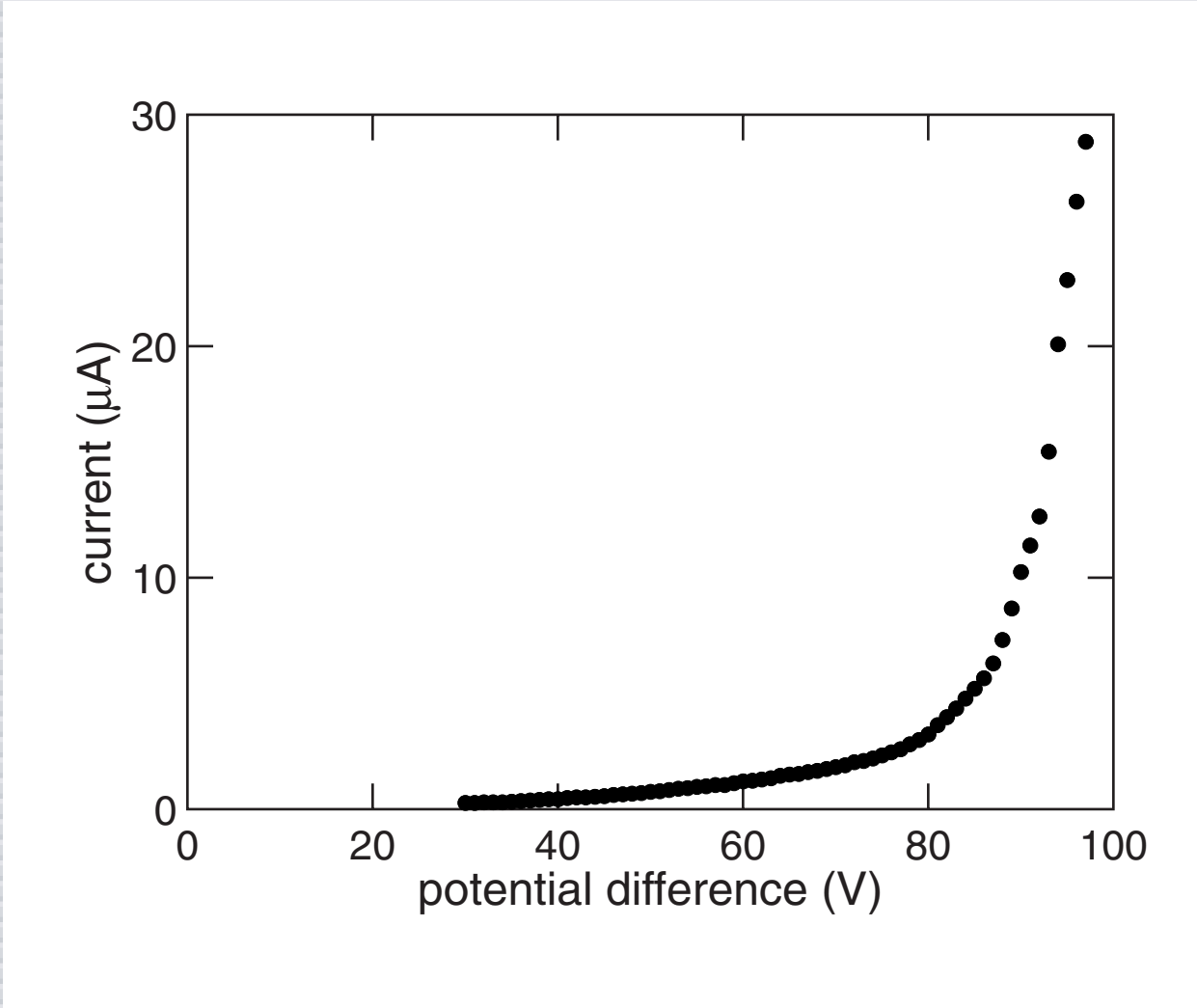
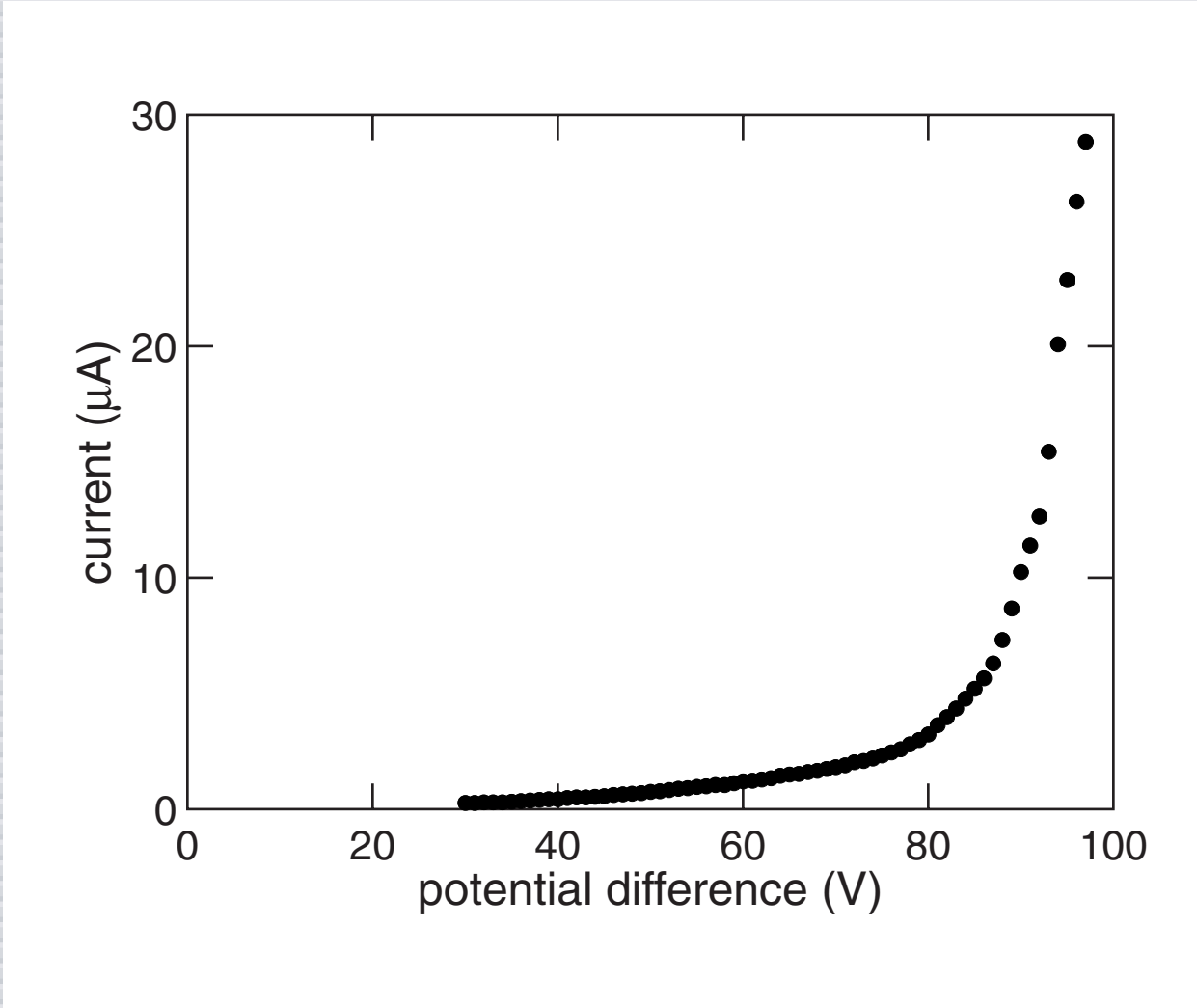


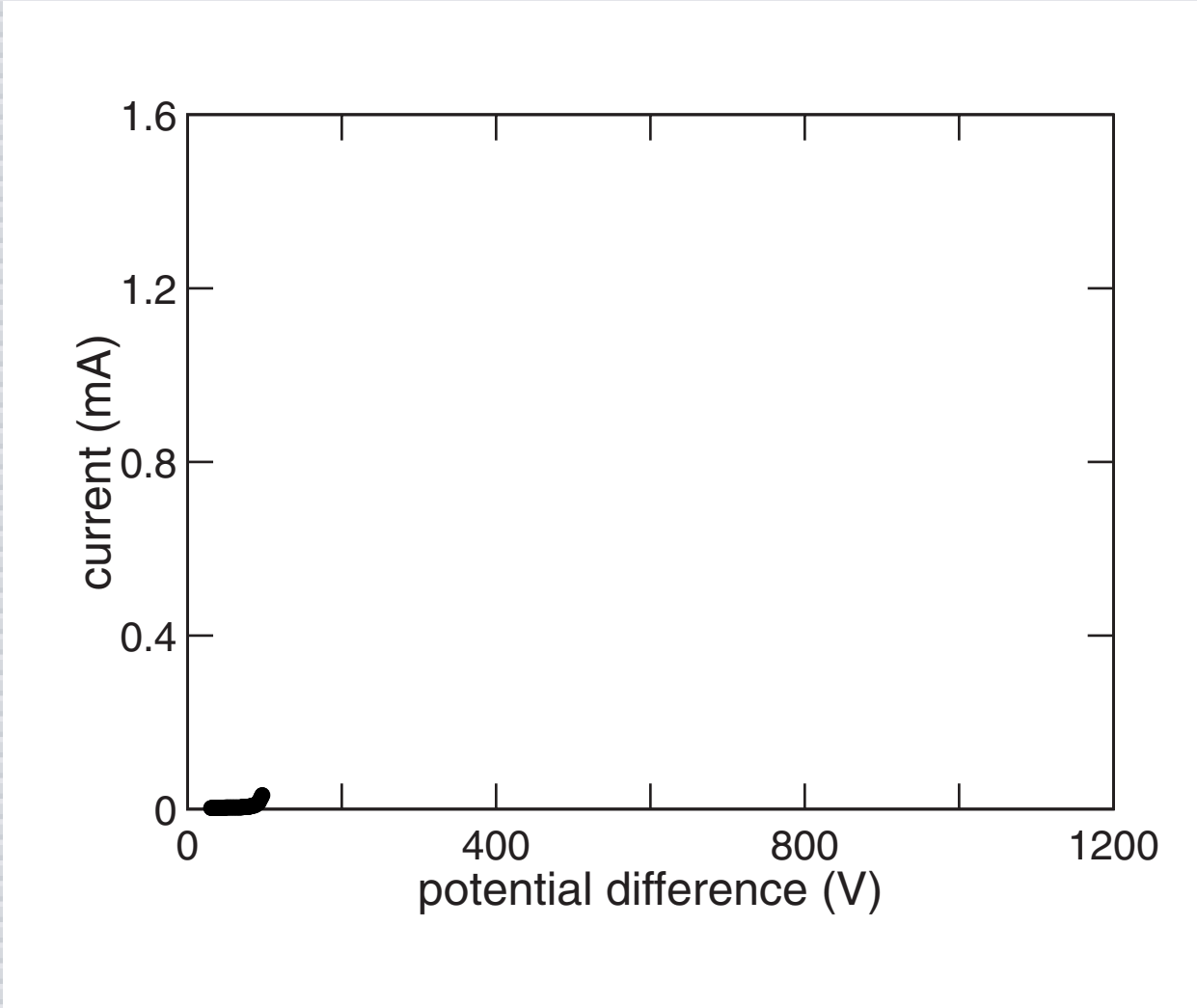
turn-on field (1 μA/cm^2): 1.2 V/μm

Properties



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

Properties



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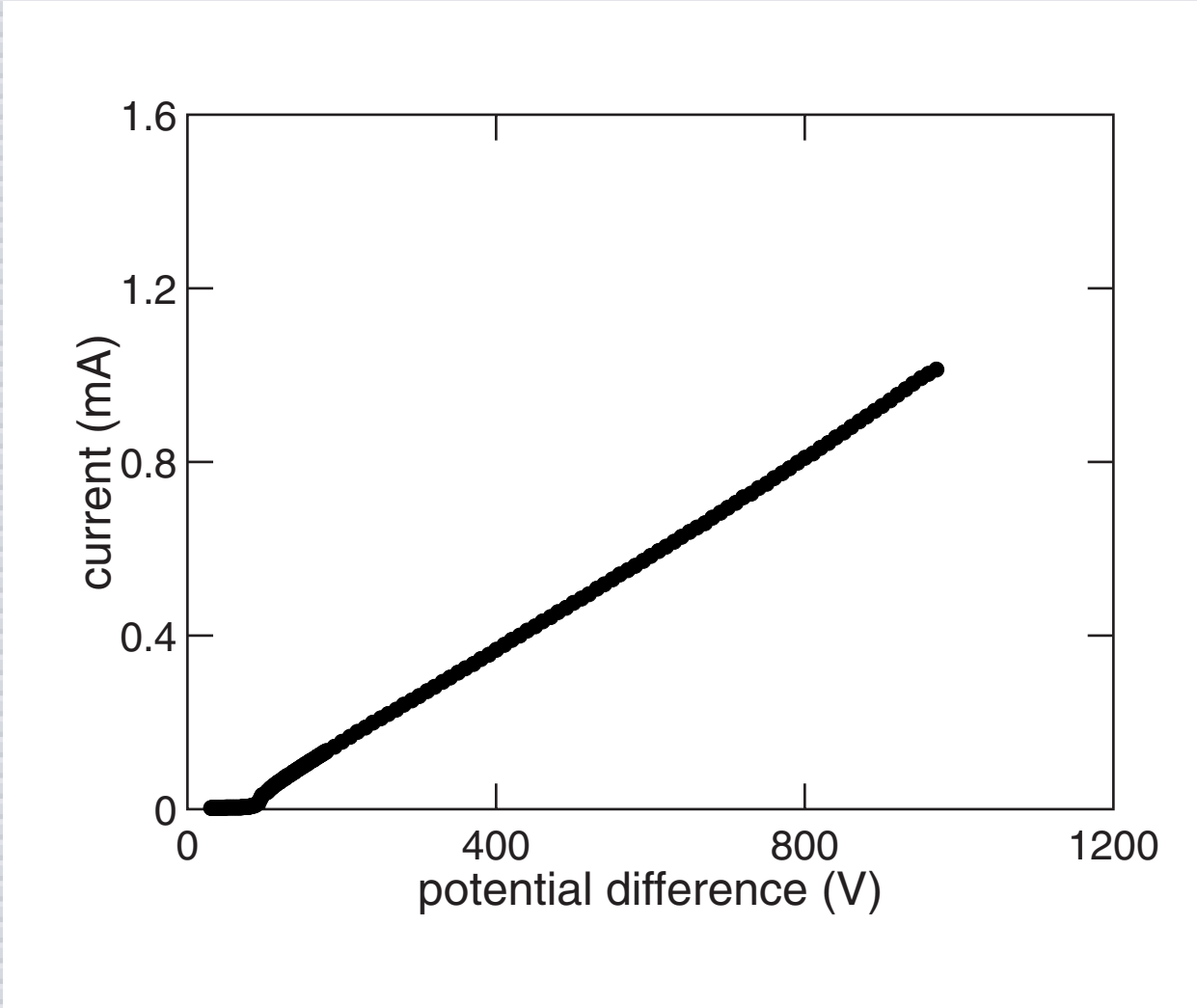

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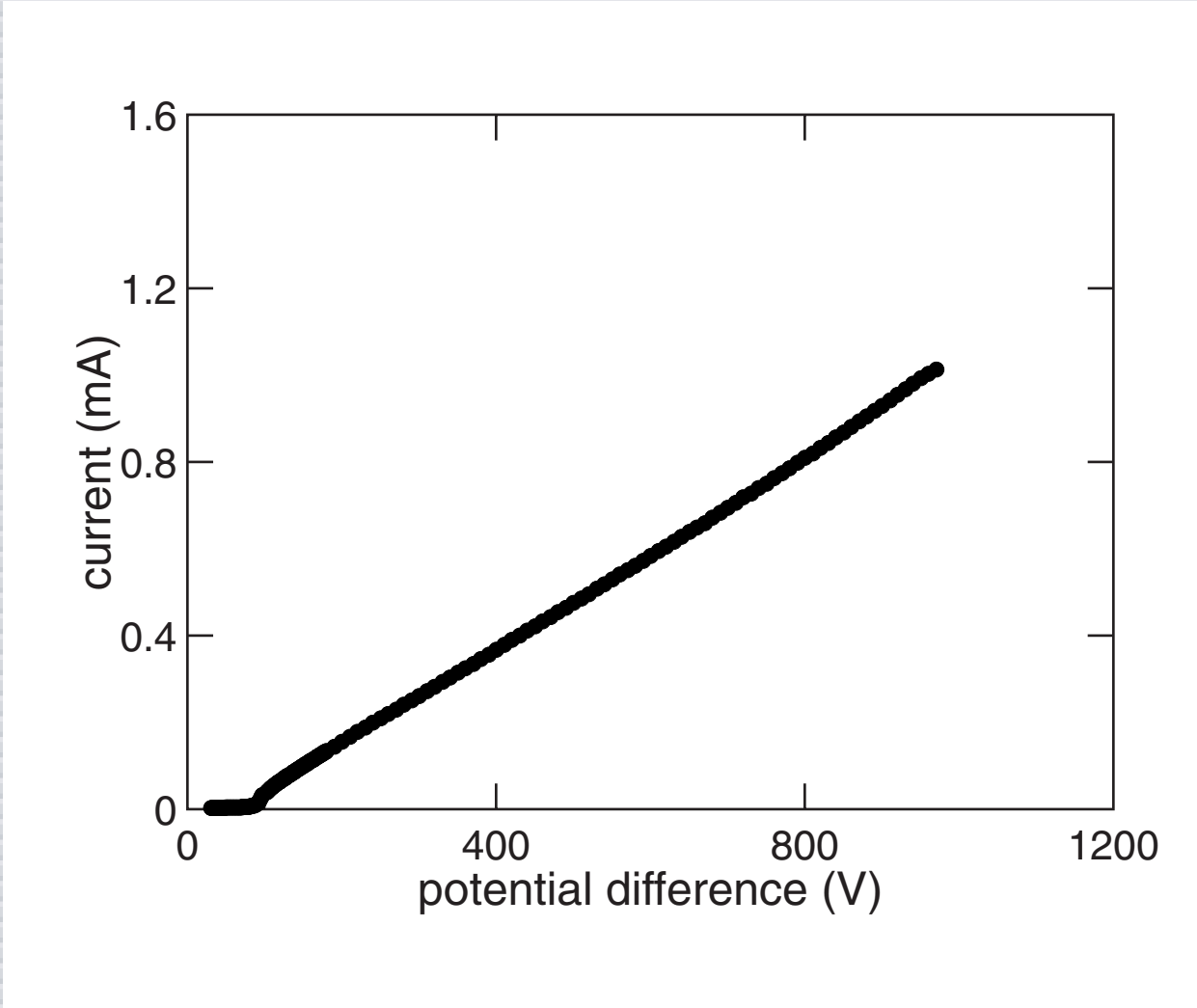
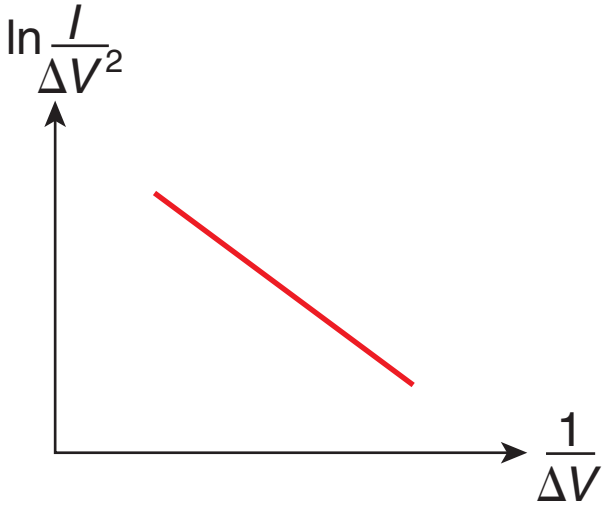


maximum current: 20 mA (4 mm^2 sample)

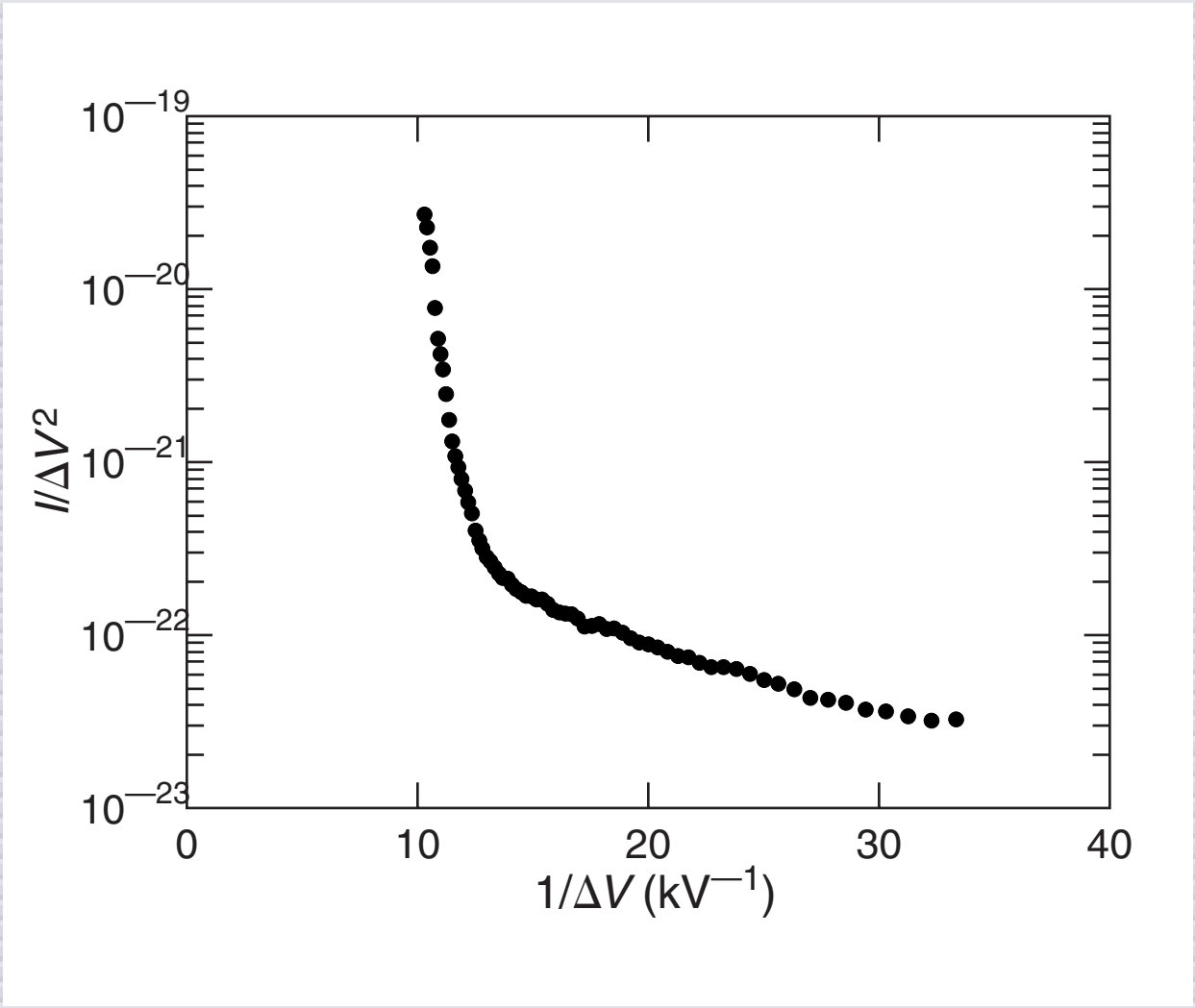
Properties

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



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

Properties



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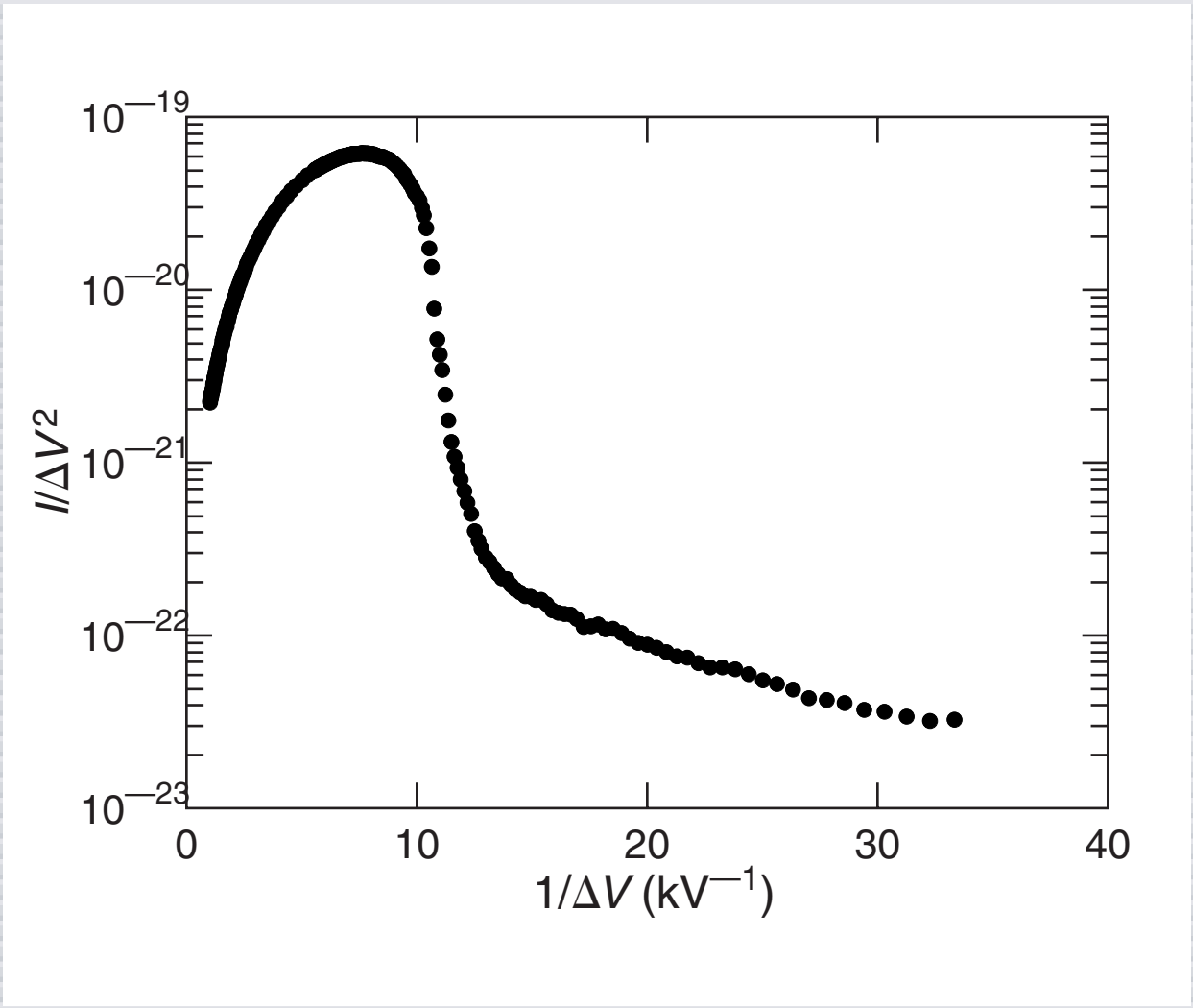


Properties

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:

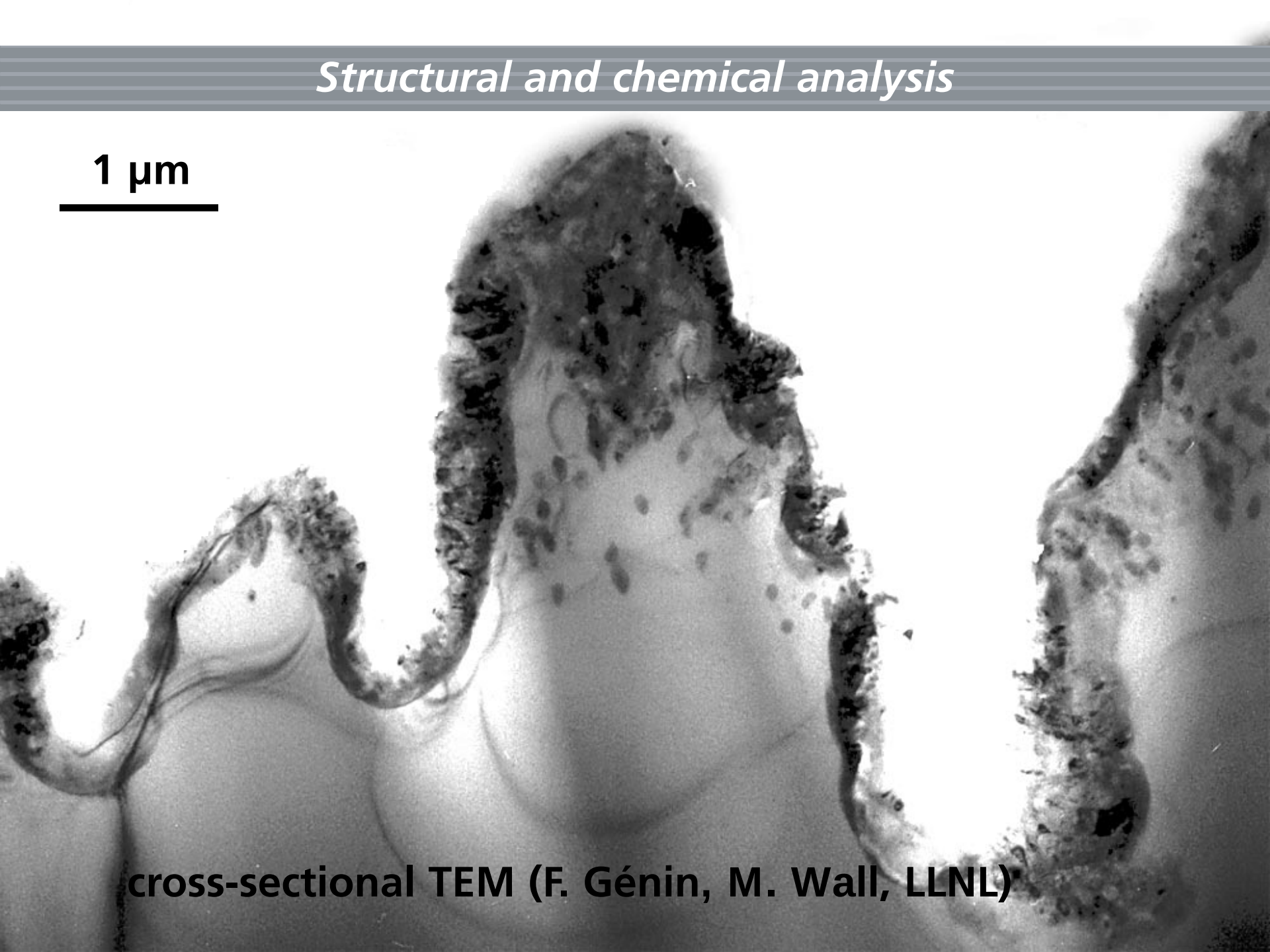
- **spikes retain crystalline order**
- **high density of defects**

Structural and chemical analysis

Secondary ion mass spectrometry:

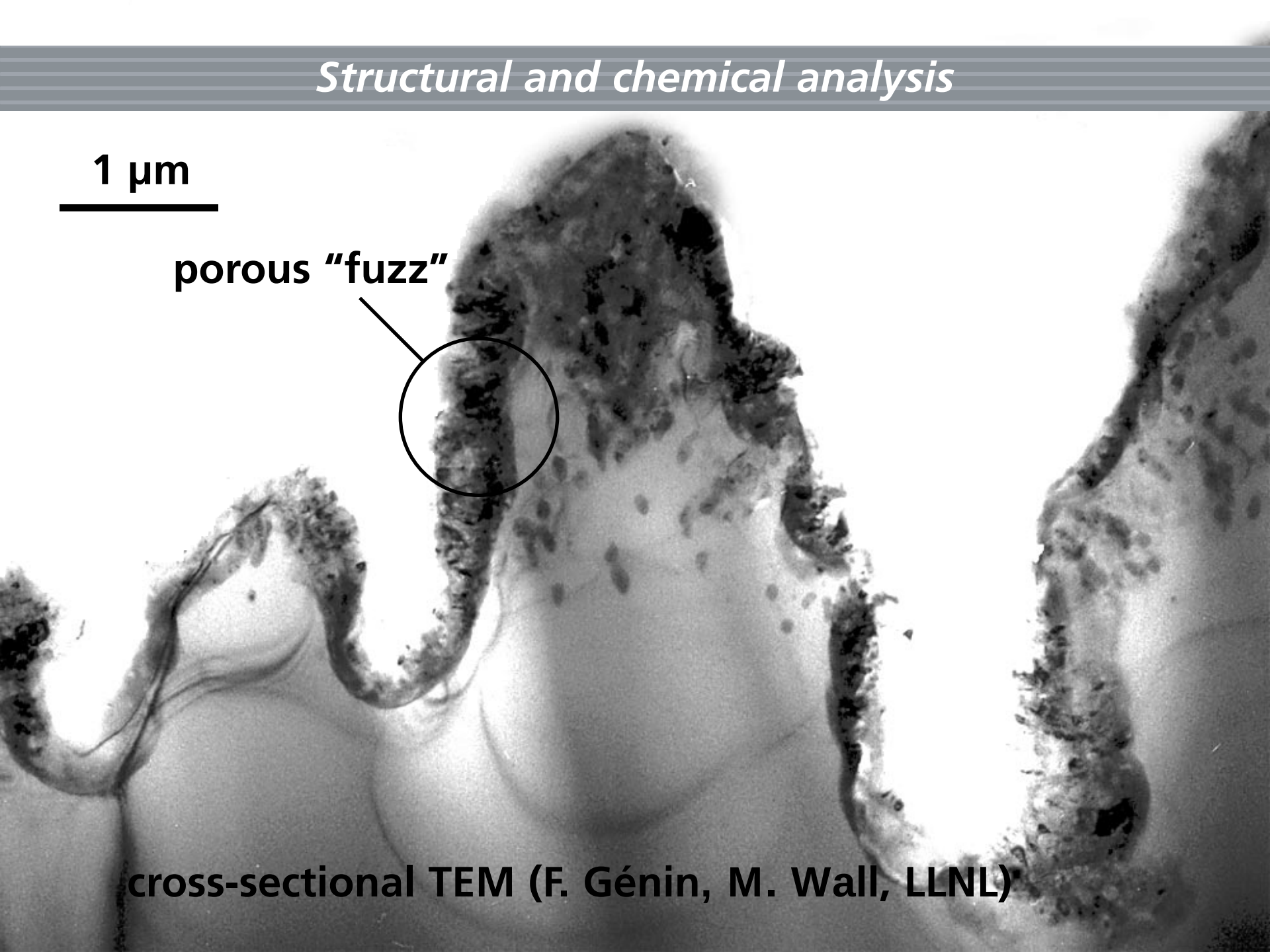
- **10^{20} cm^{-3} sulfur**
- **10^{17} cm^{-3} fluorine**

Structural and chemical analysis



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

Structural and chemical analysis



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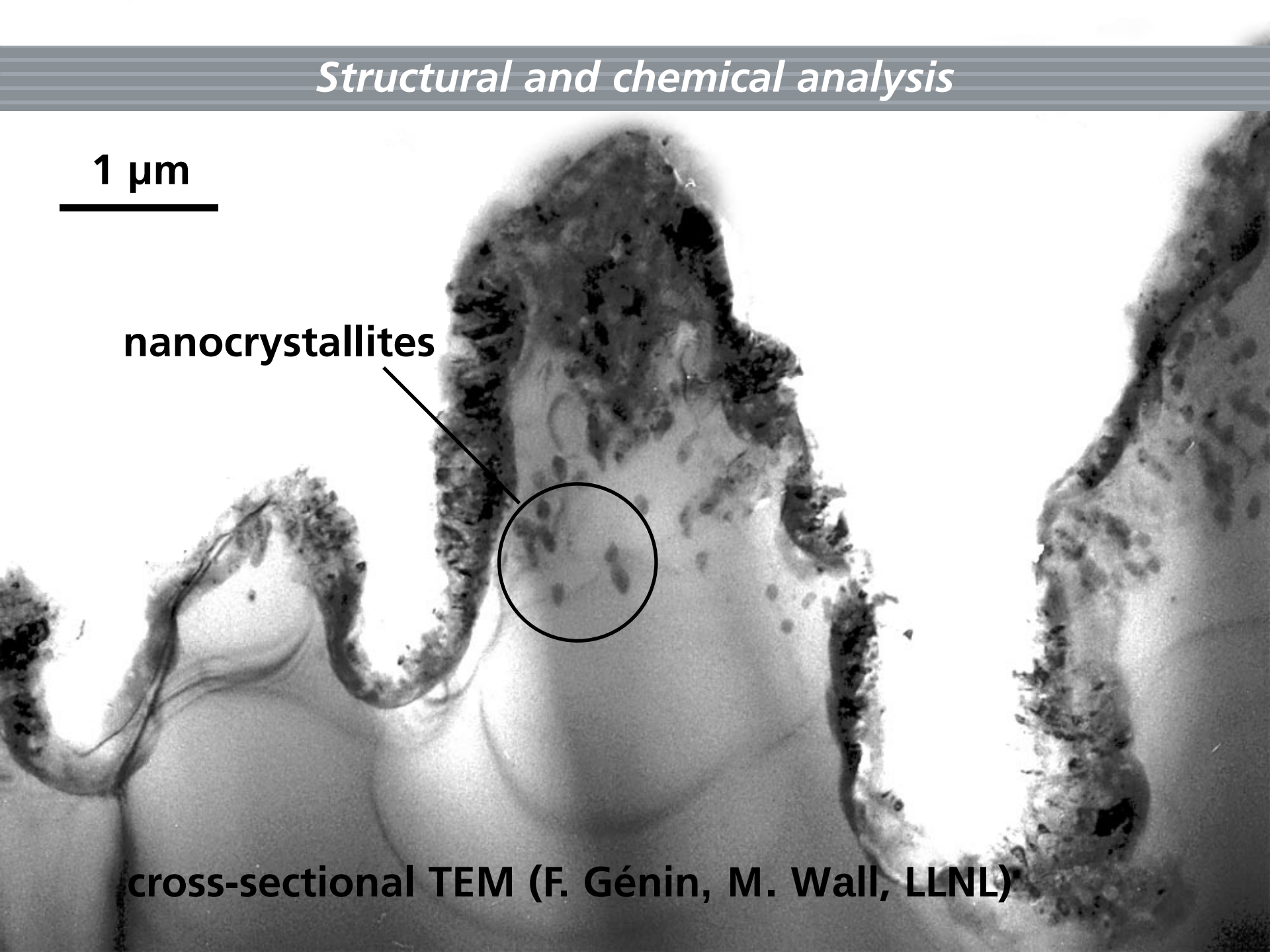
Structural and chemical analysis



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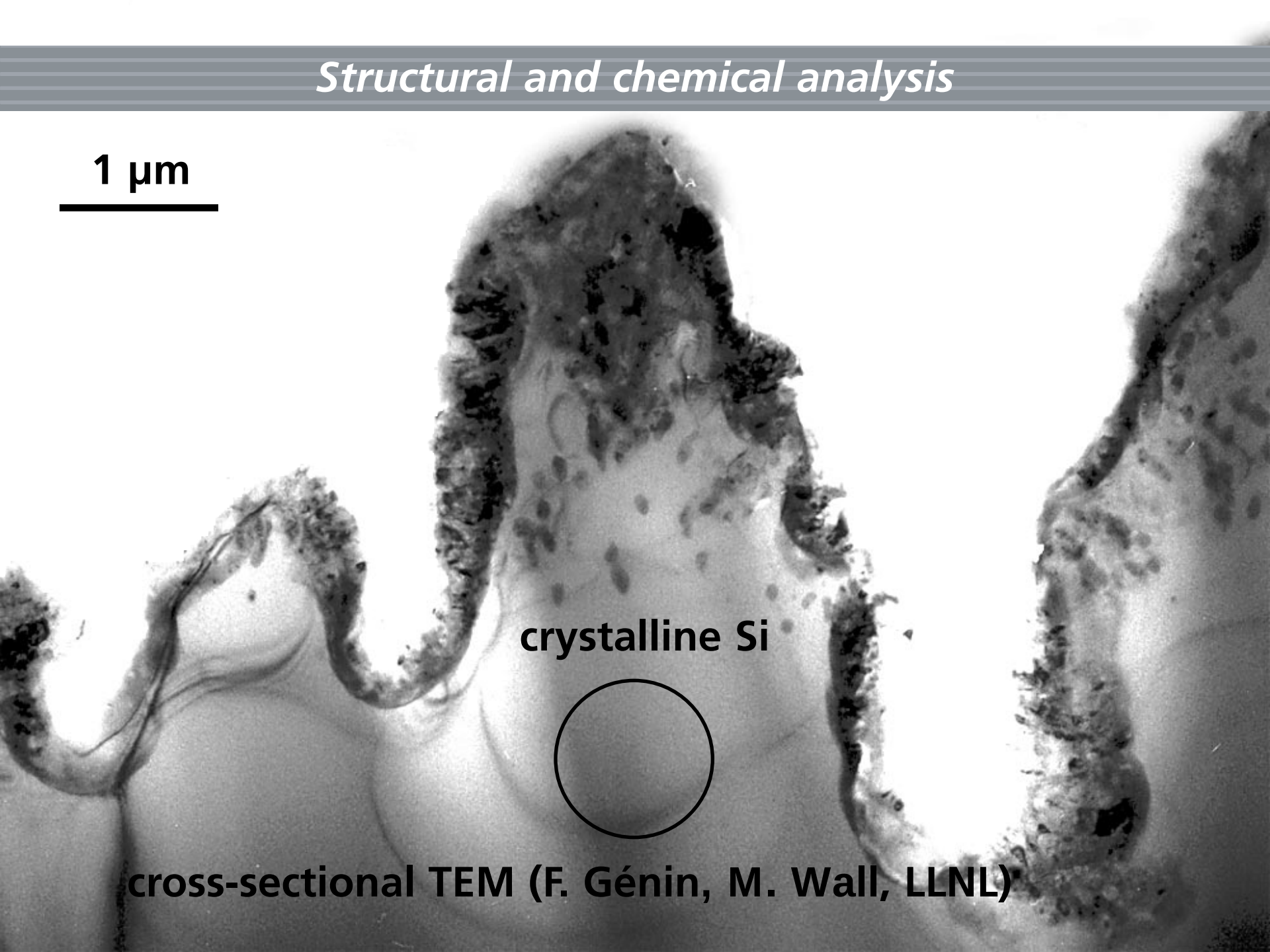

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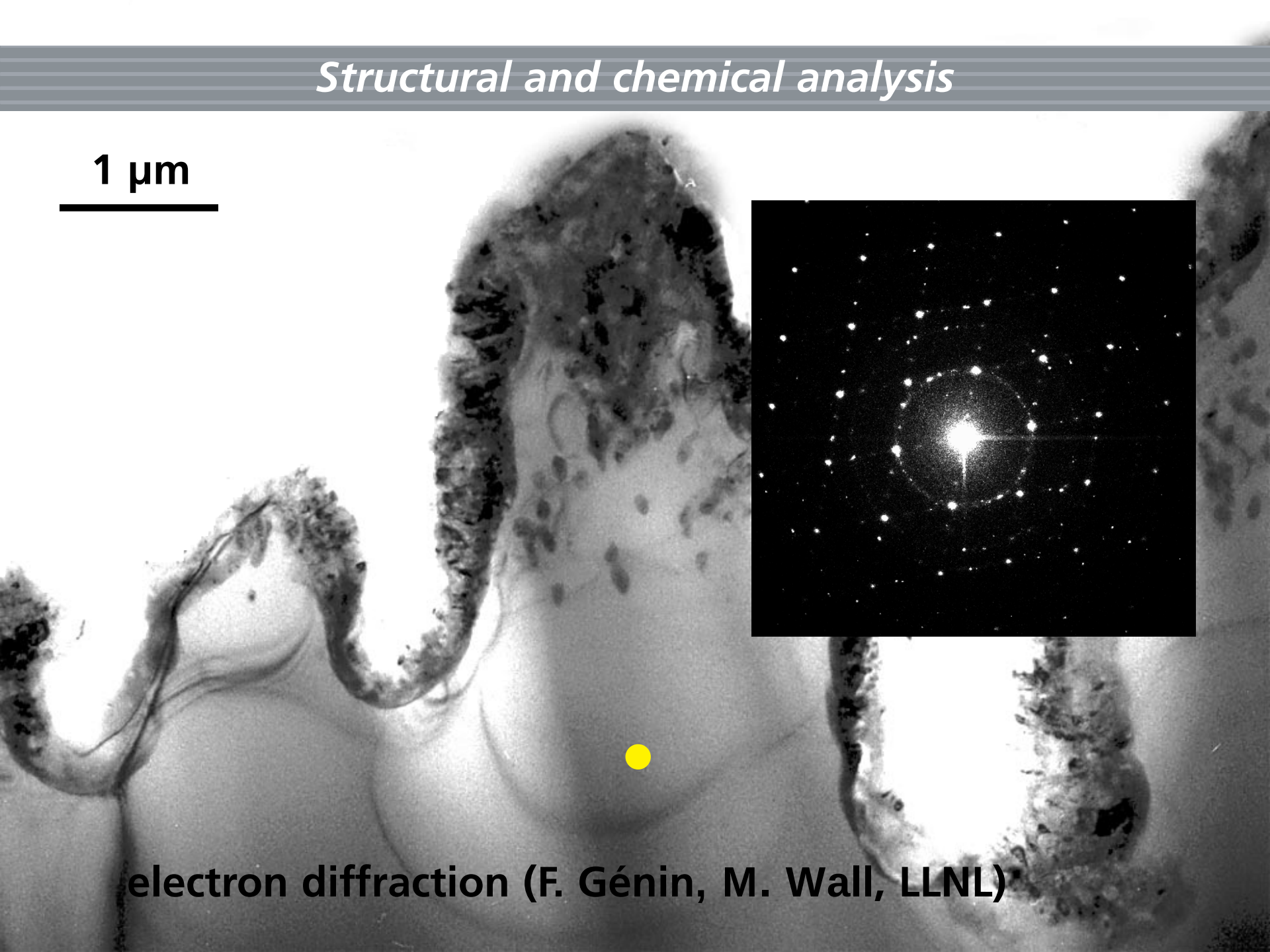
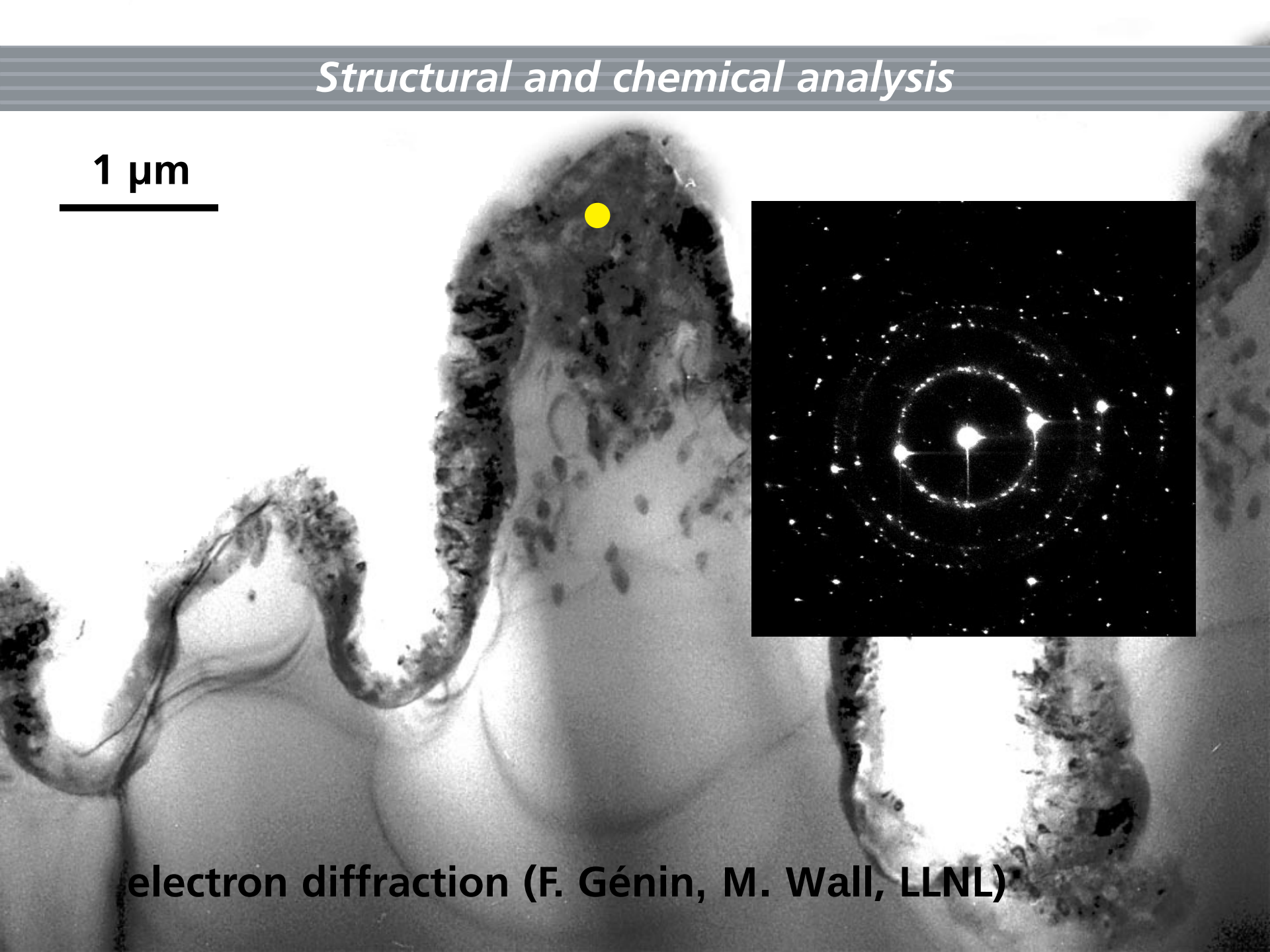


electron diffraction (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



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

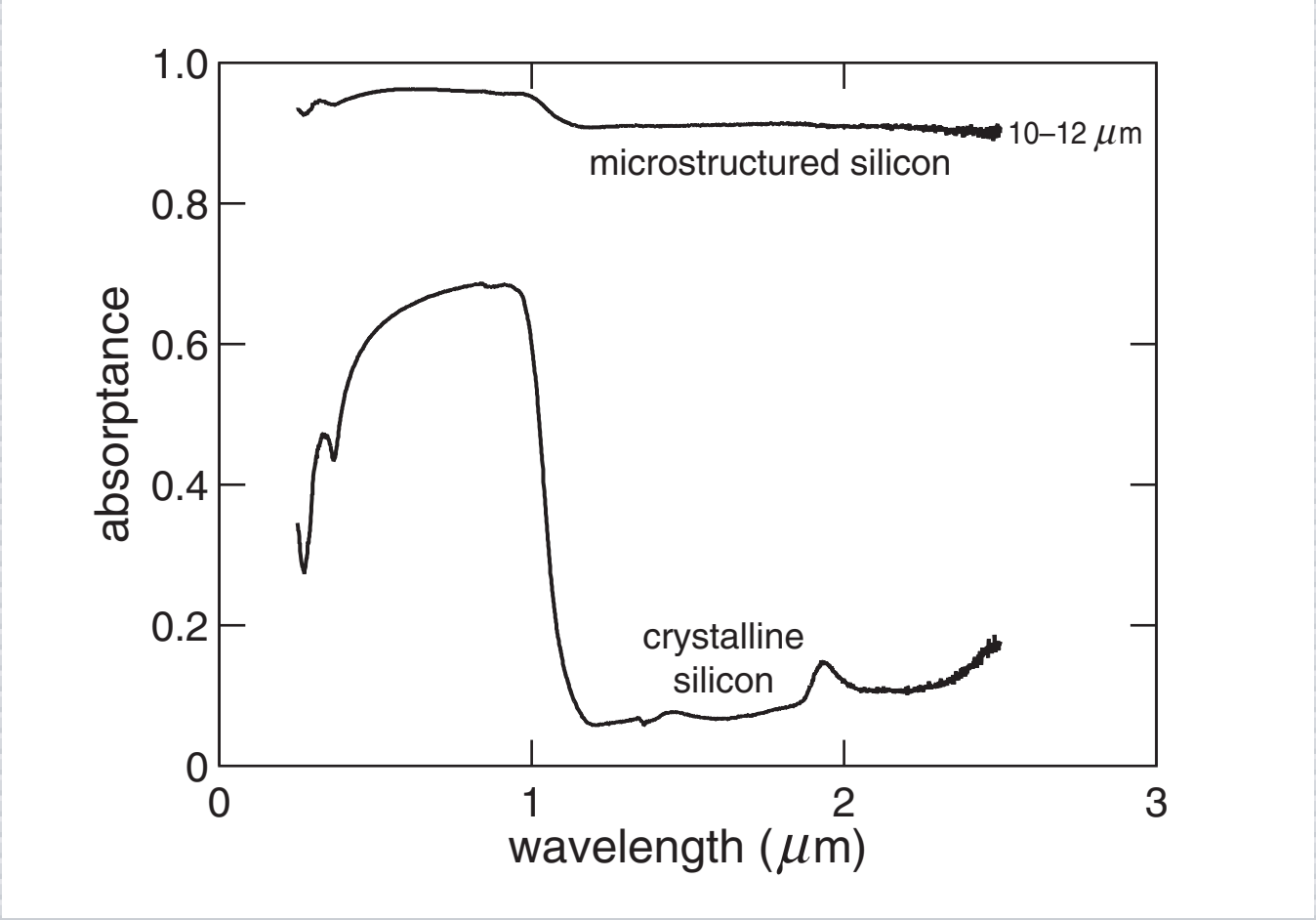
Structural and chemical analysis

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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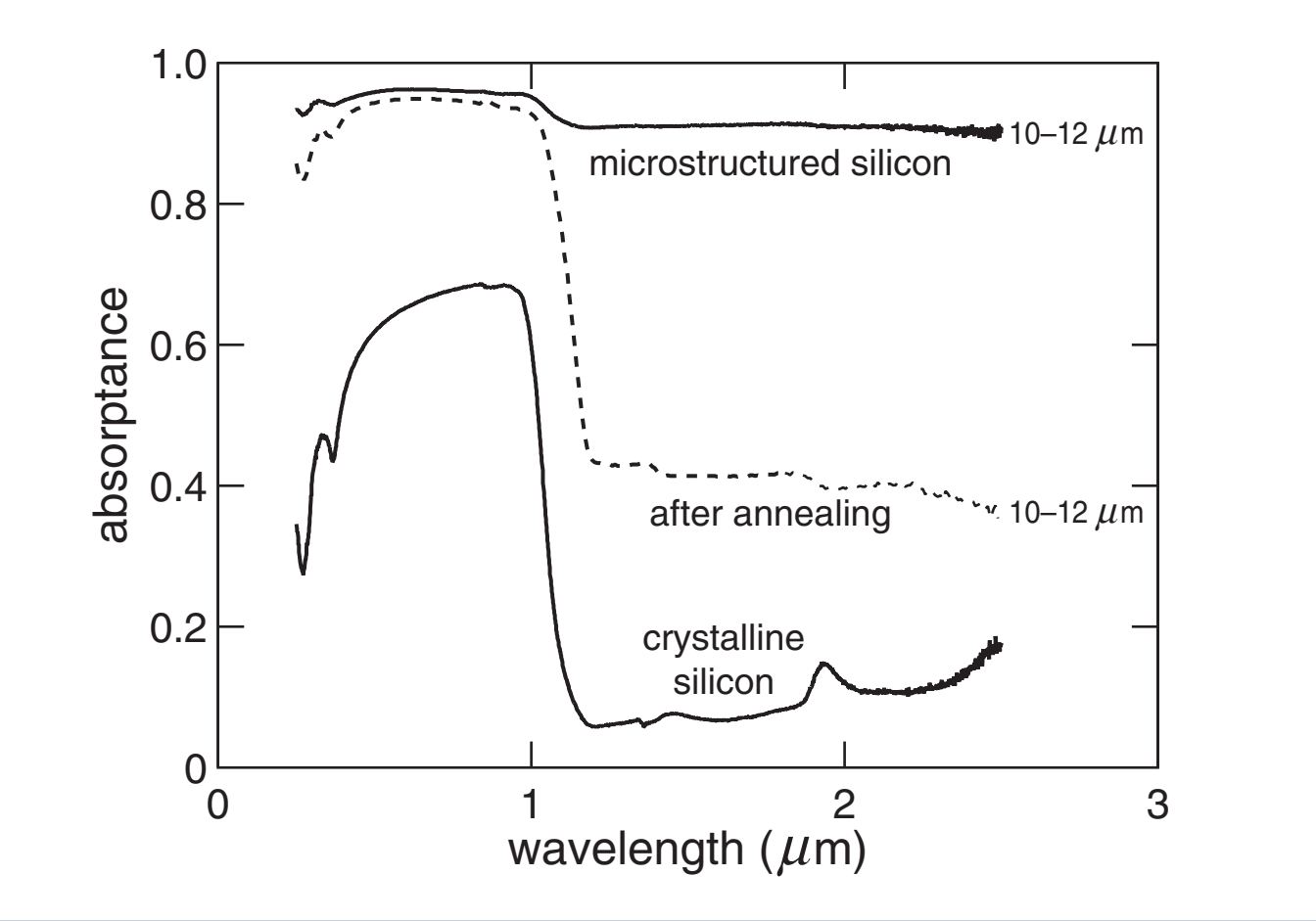

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Structural and chemical analysis

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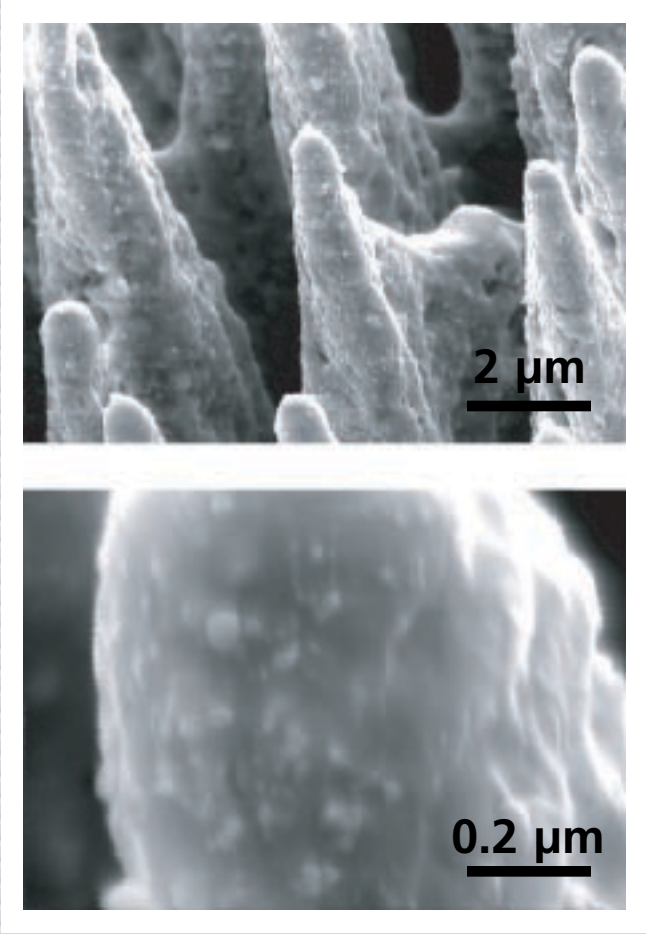

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Structural and chemical analysis

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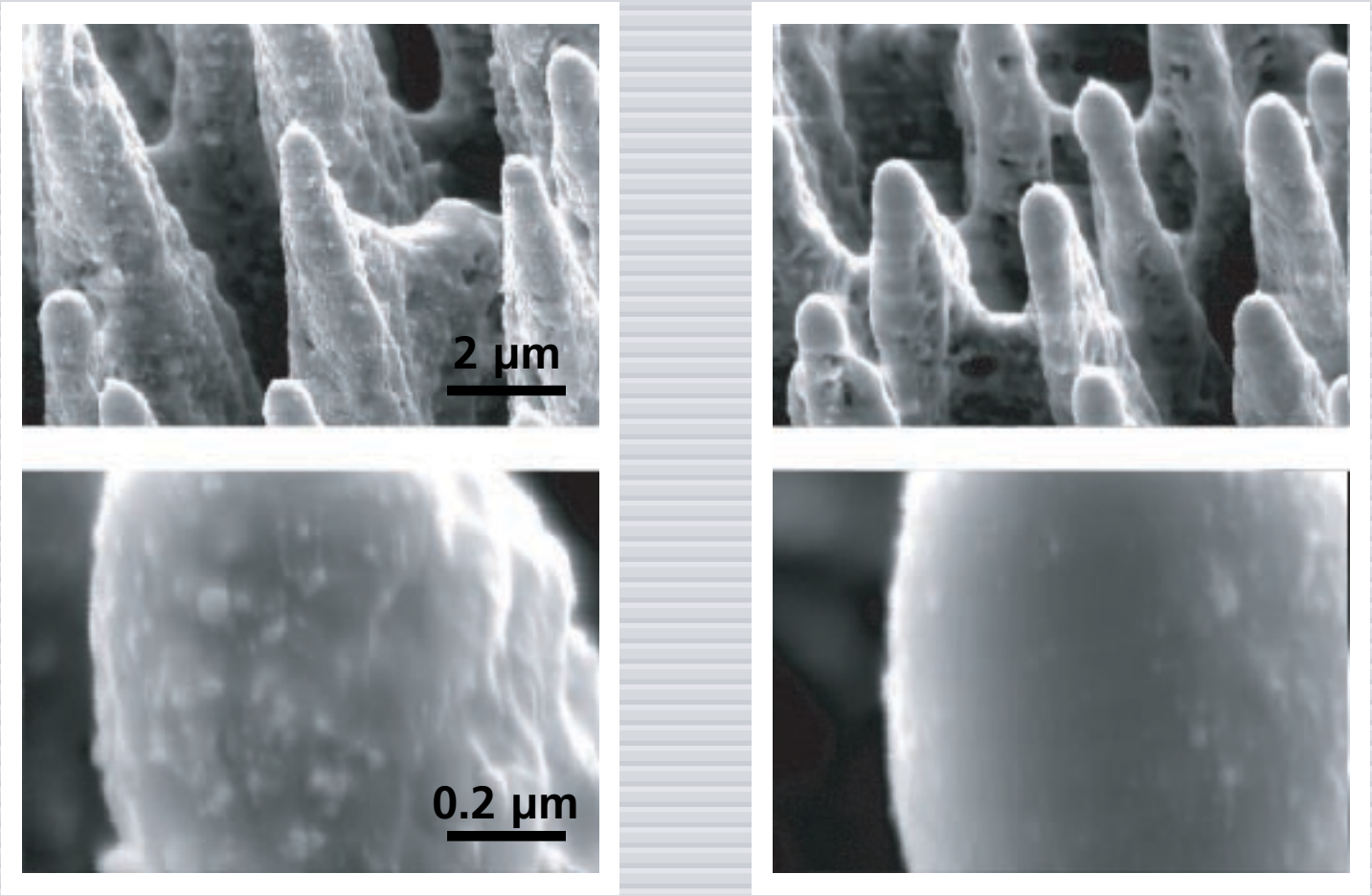


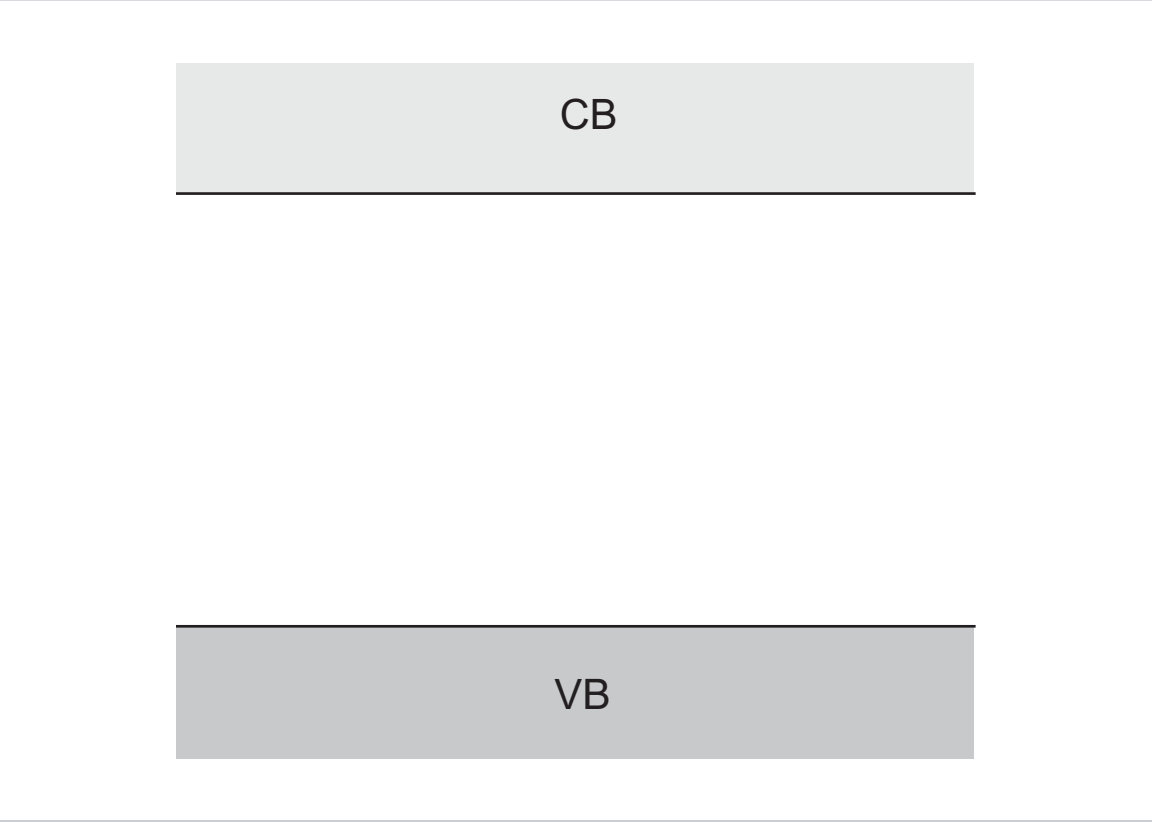
Appl. Phys. Lett. **78**, 1850 (2001)

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



Structural and chemical analysis

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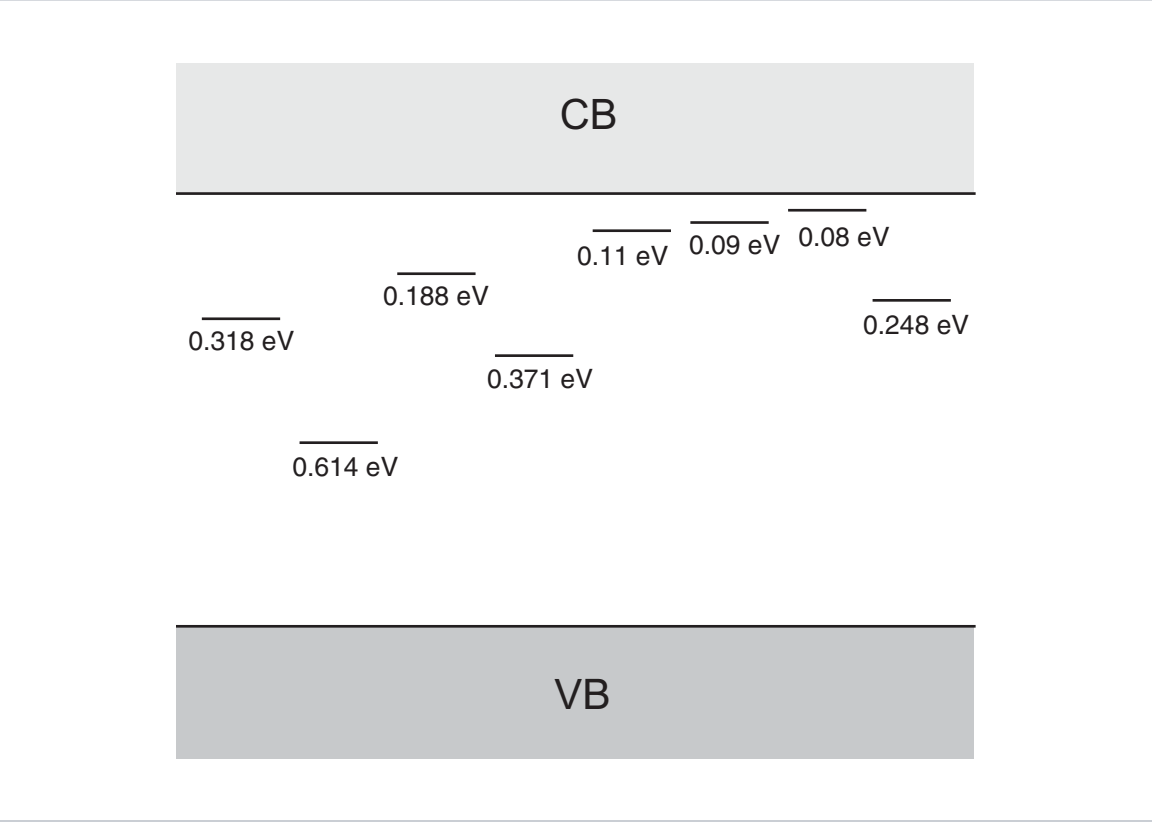
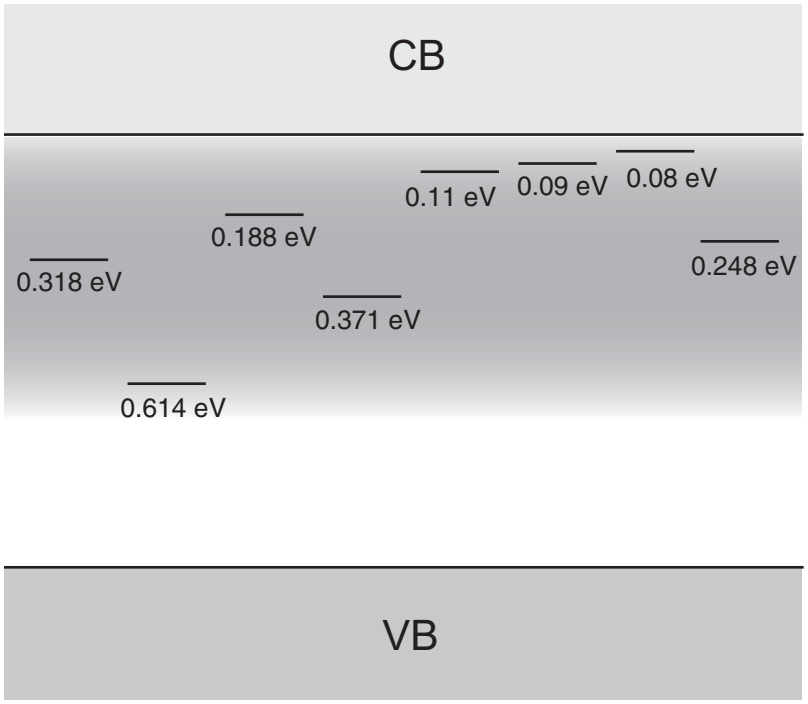
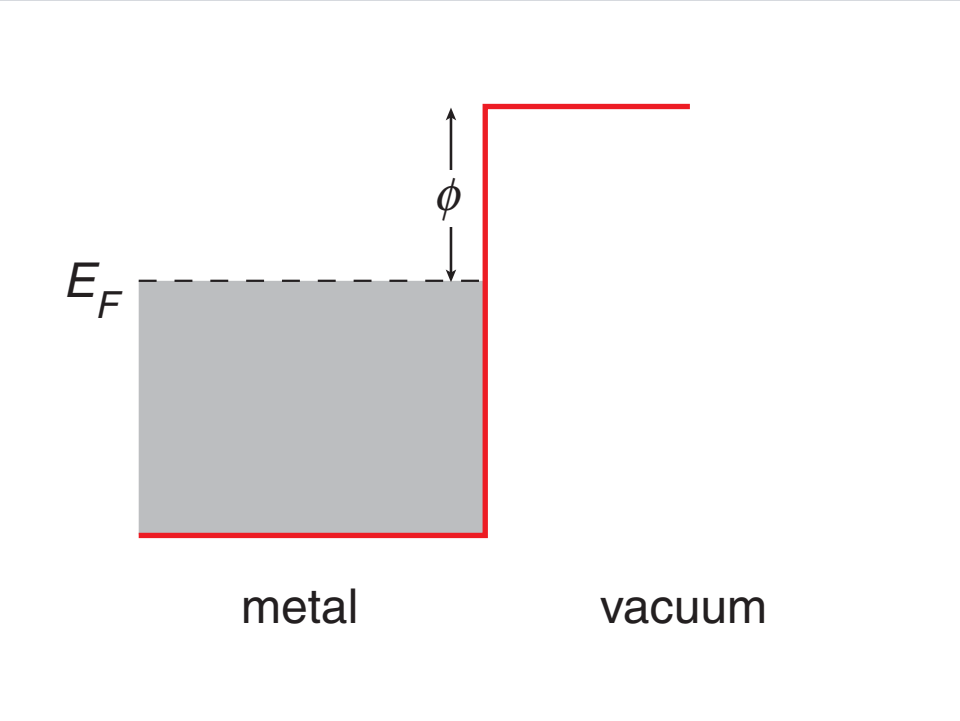


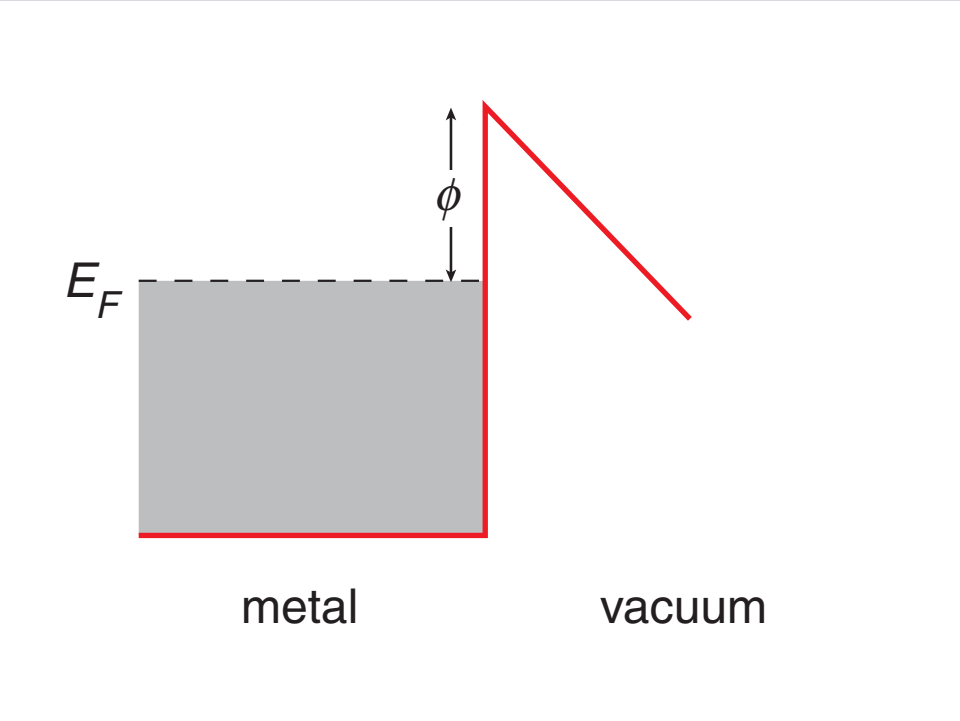
Janzén, *et al.*, *Phys. Rev. B* **29**,1907 (1984)

states broaden into a band

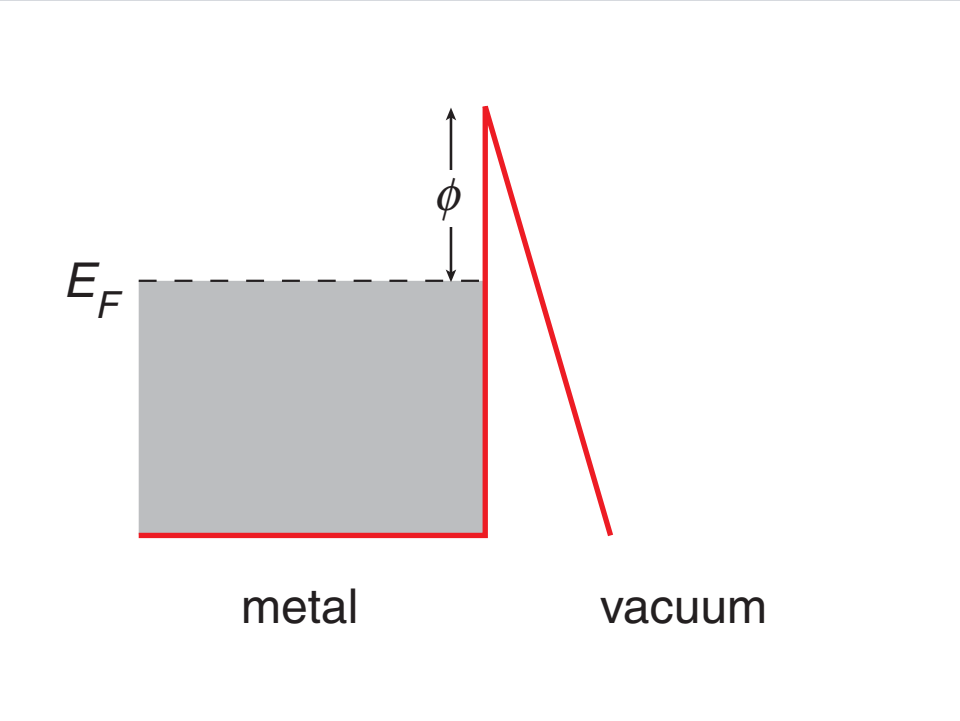


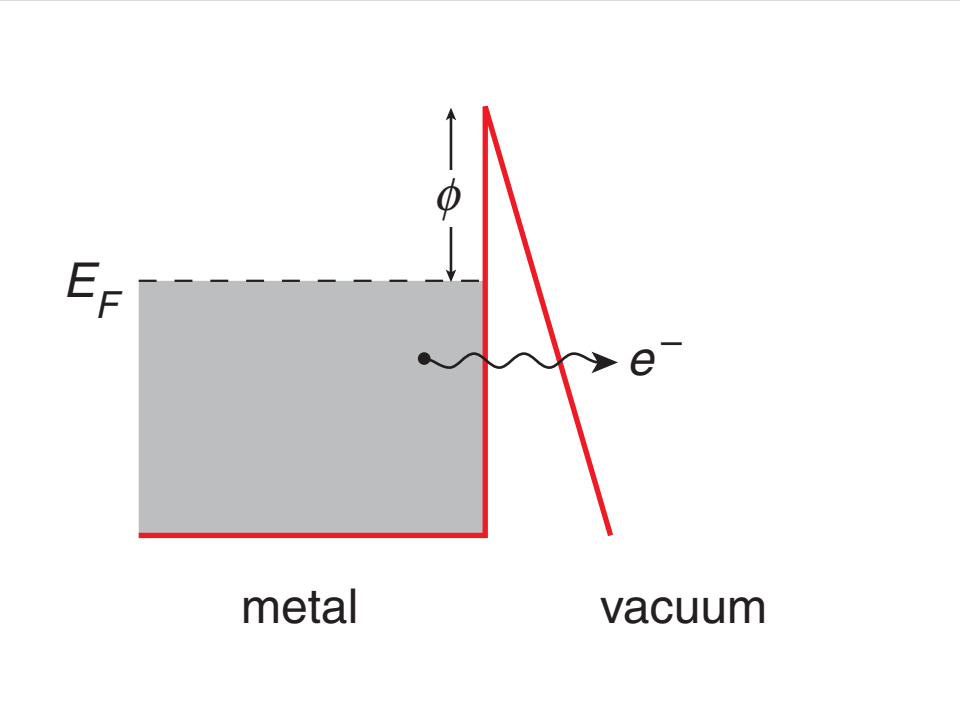

ϕ
E_F
metal
vacuum

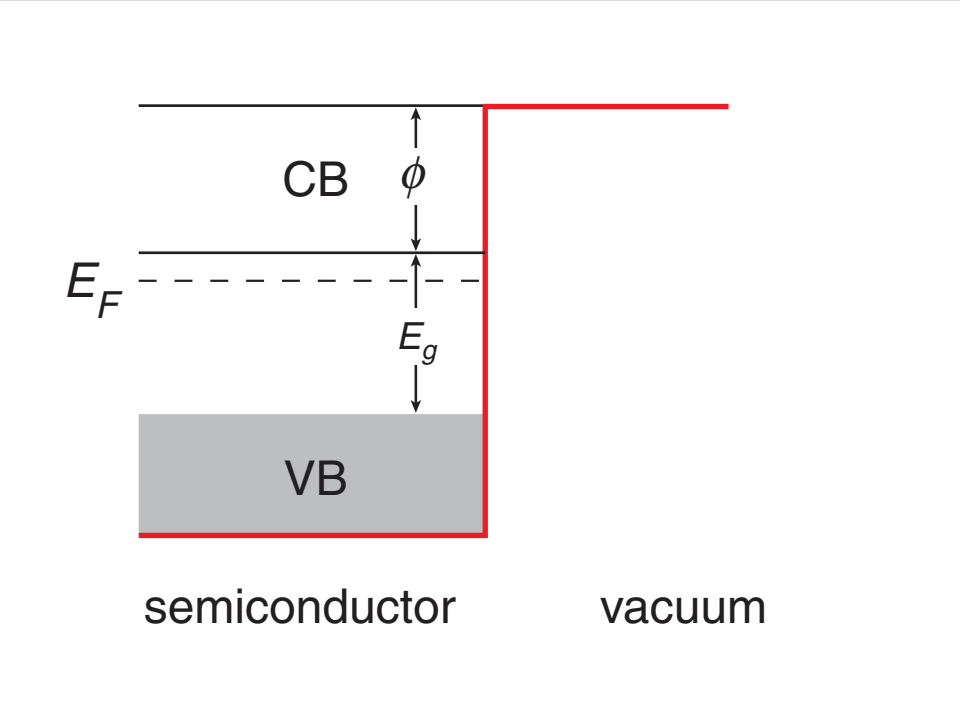
Structural and chemical analysis



Structural and chemical analysis




ϕ
E_F
e^-
metal
vacuum


CB
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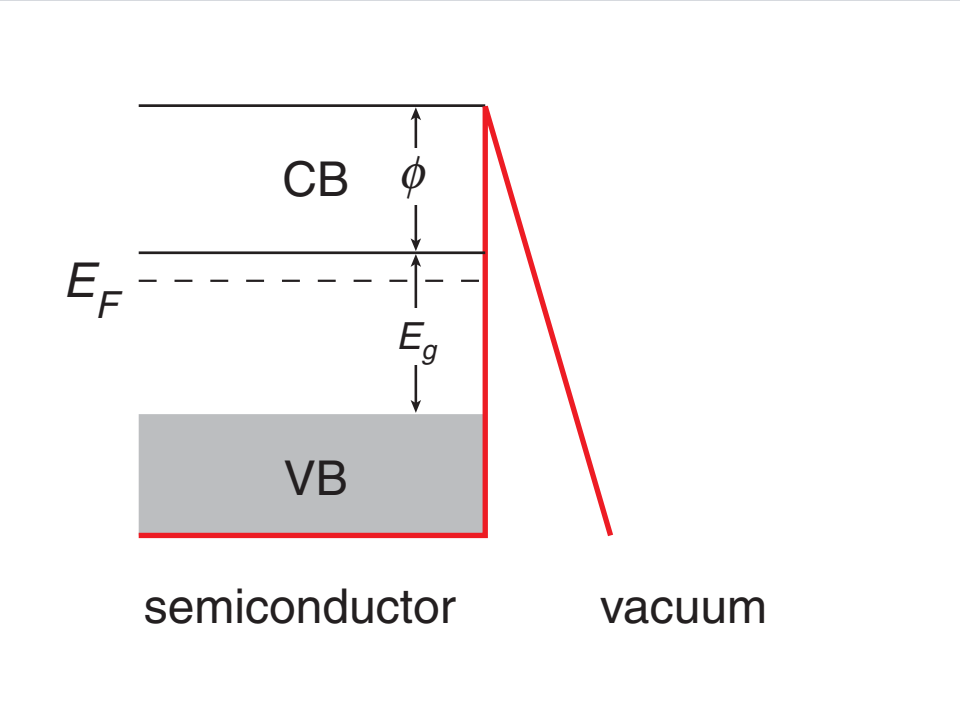
E_F
E_g
VB
semiconductor
vacuum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semiconductor
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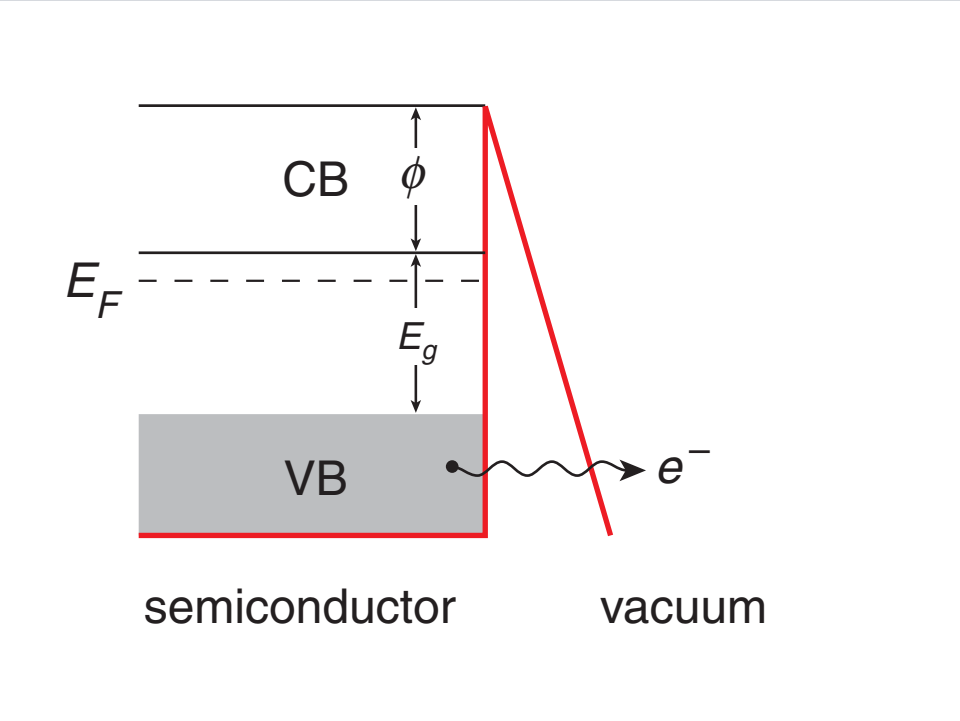
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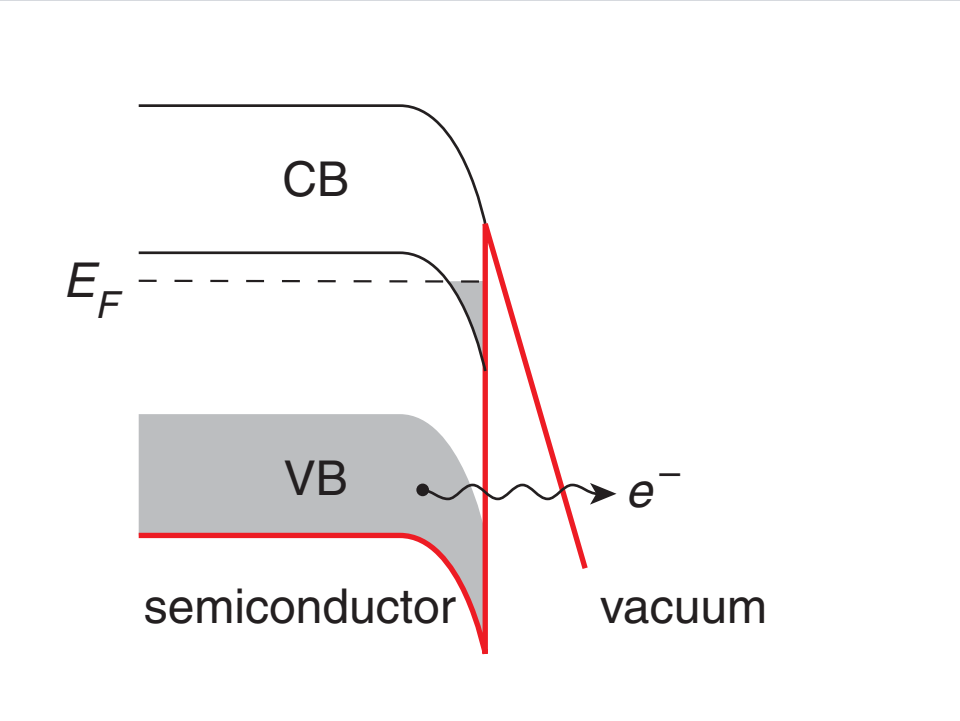
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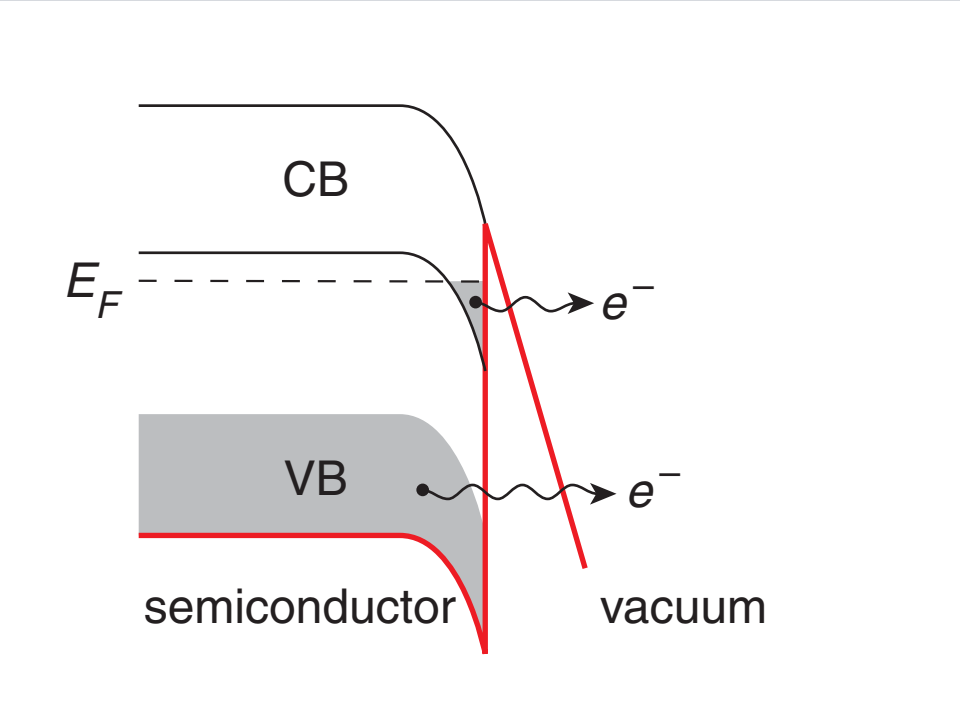
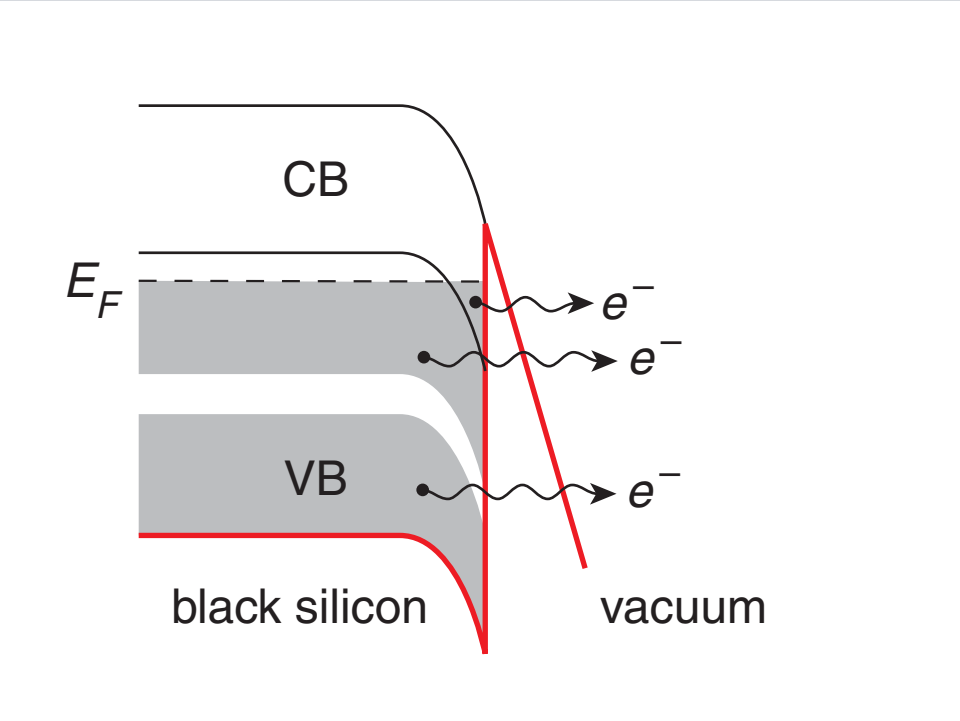
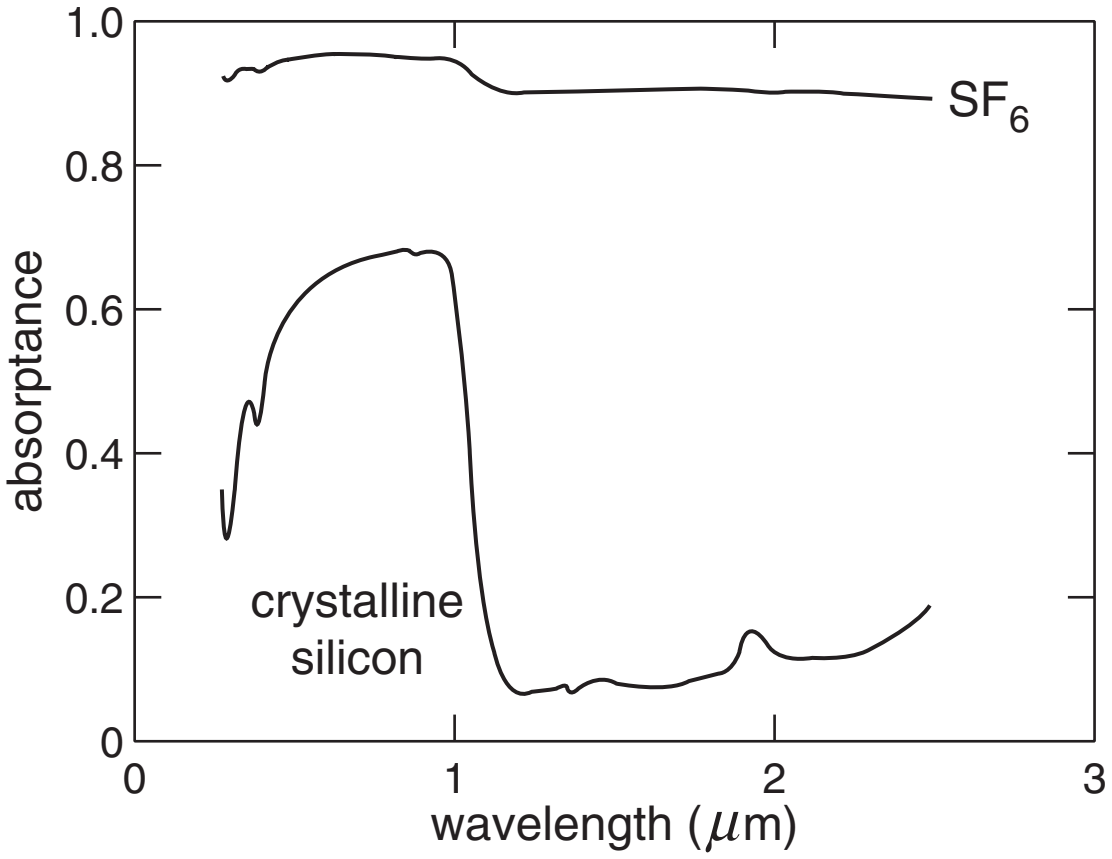
Structural and chemical analysis



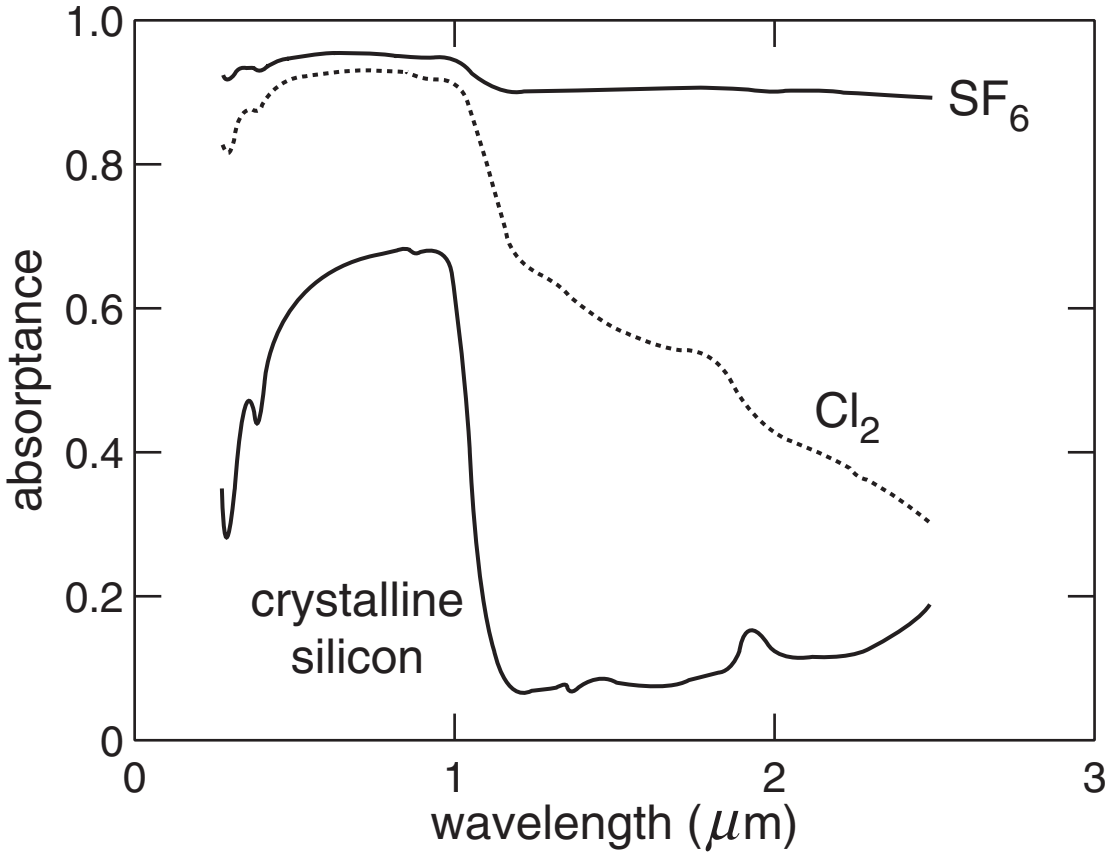
sulfur band provides additional electrons



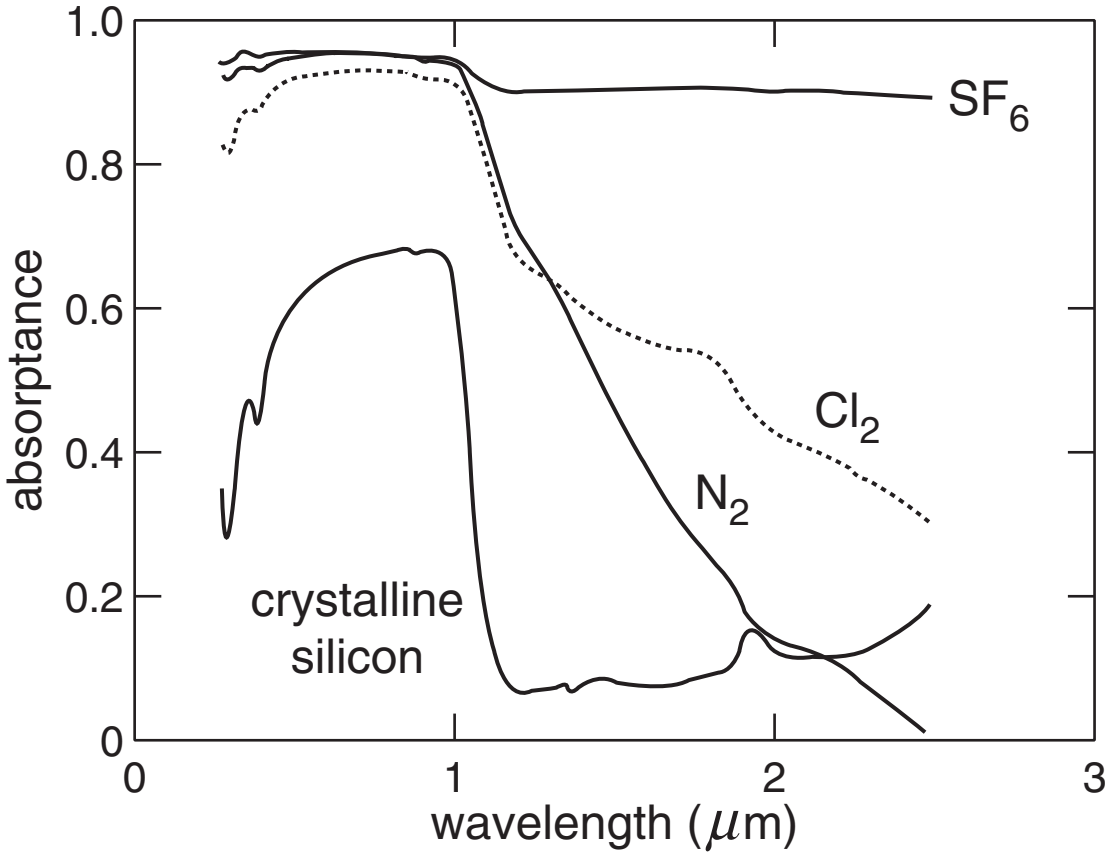
effect of ambient gas on absorptance



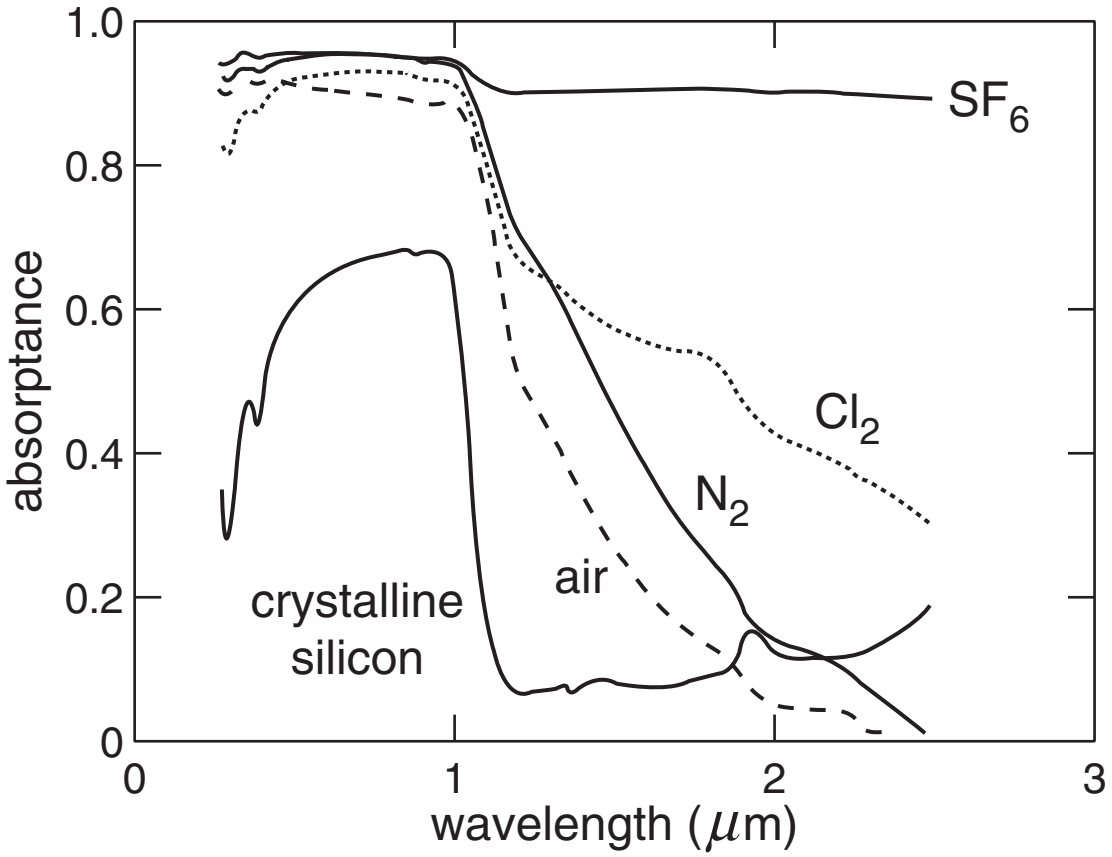
effect of ambient gas on absorptance



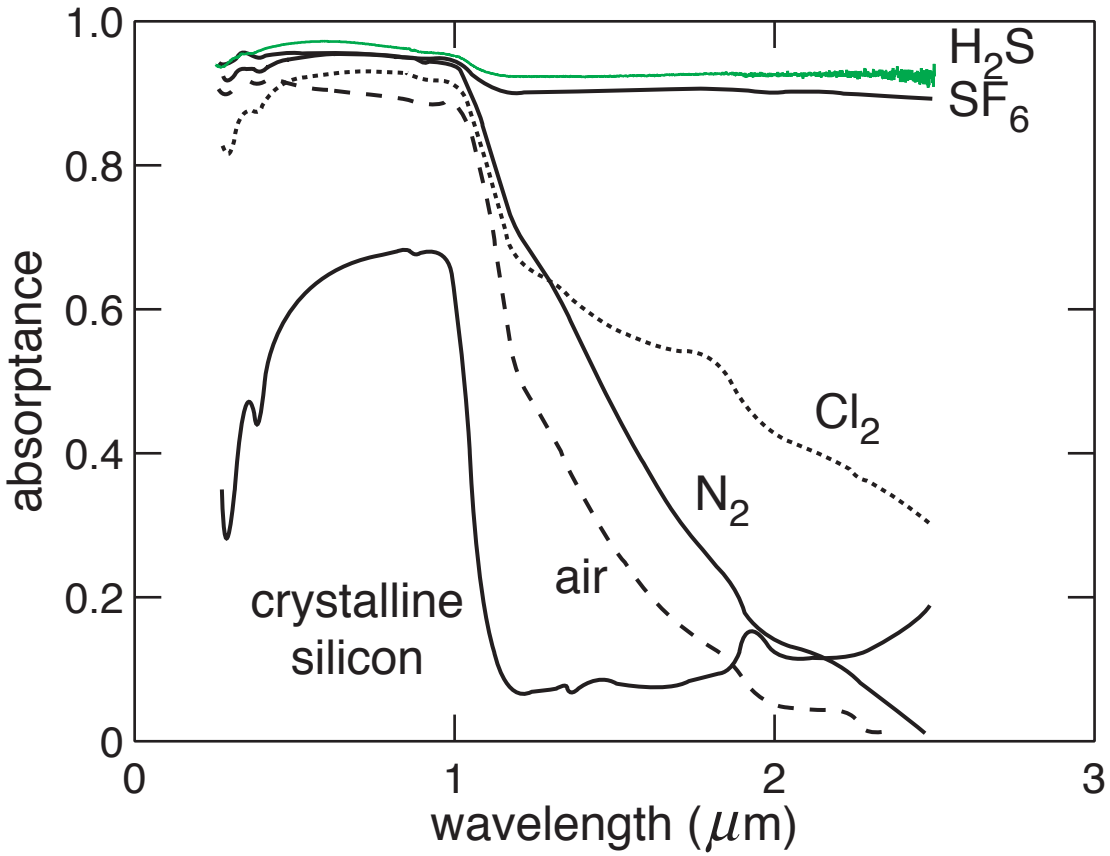
effect of ambient gas on absorptance



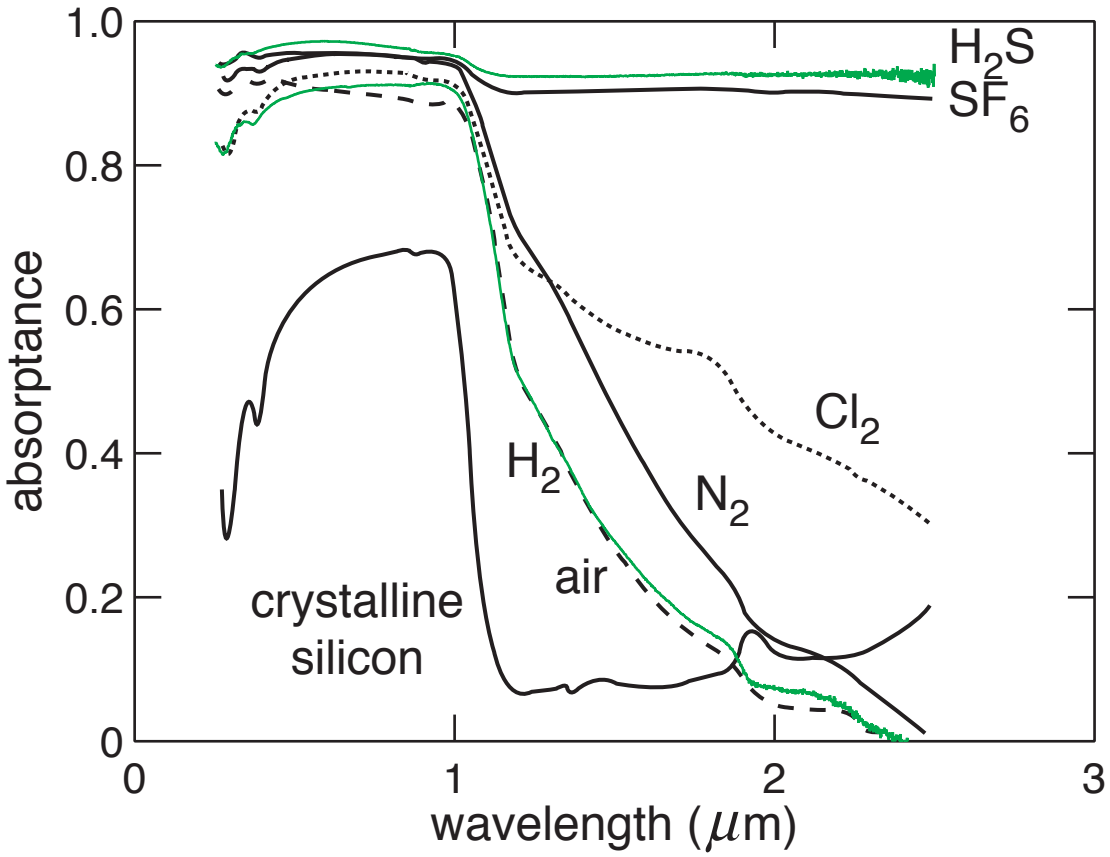
effect of ambient gas on absorptance



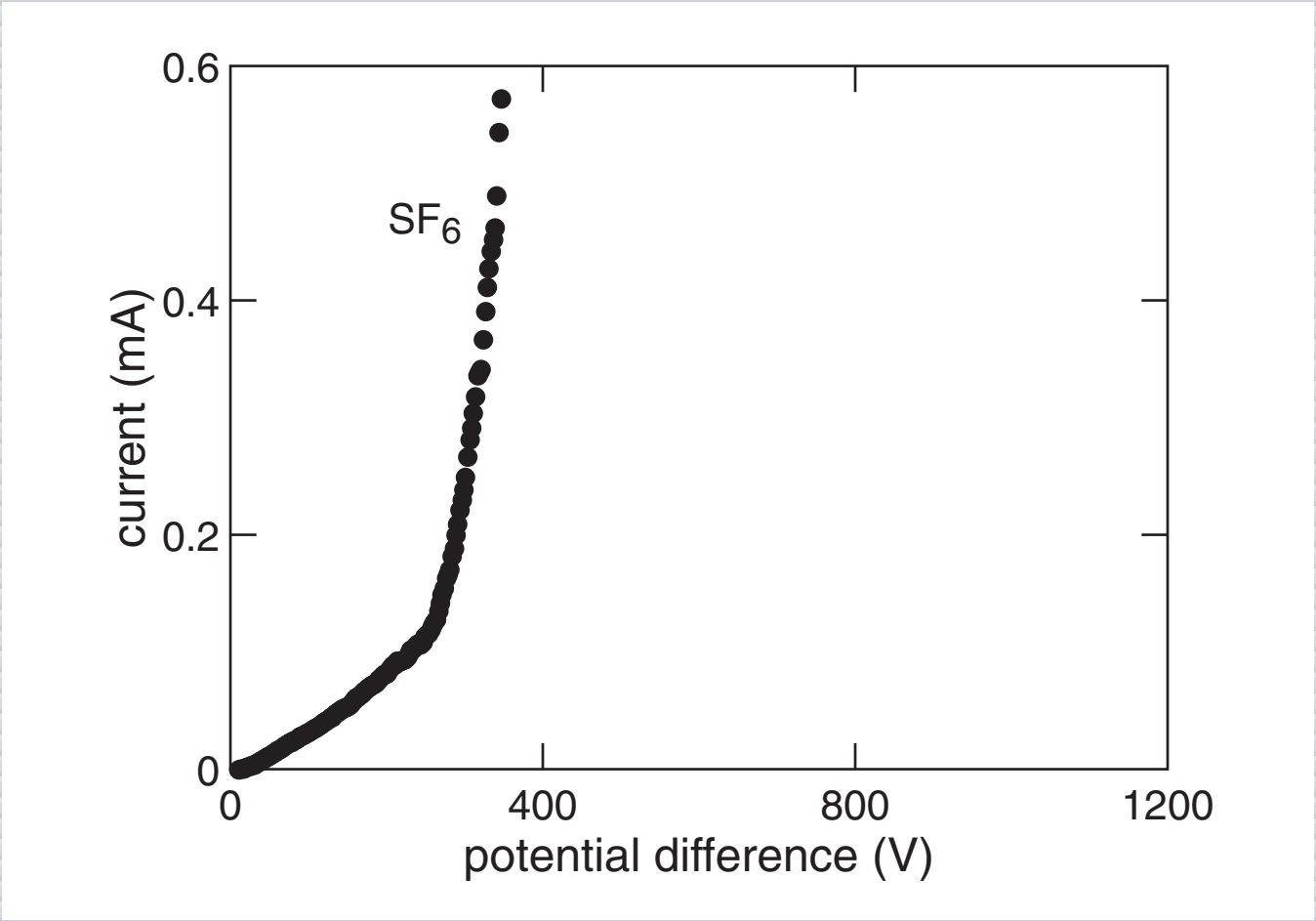
effect of ambient gas on absorptance



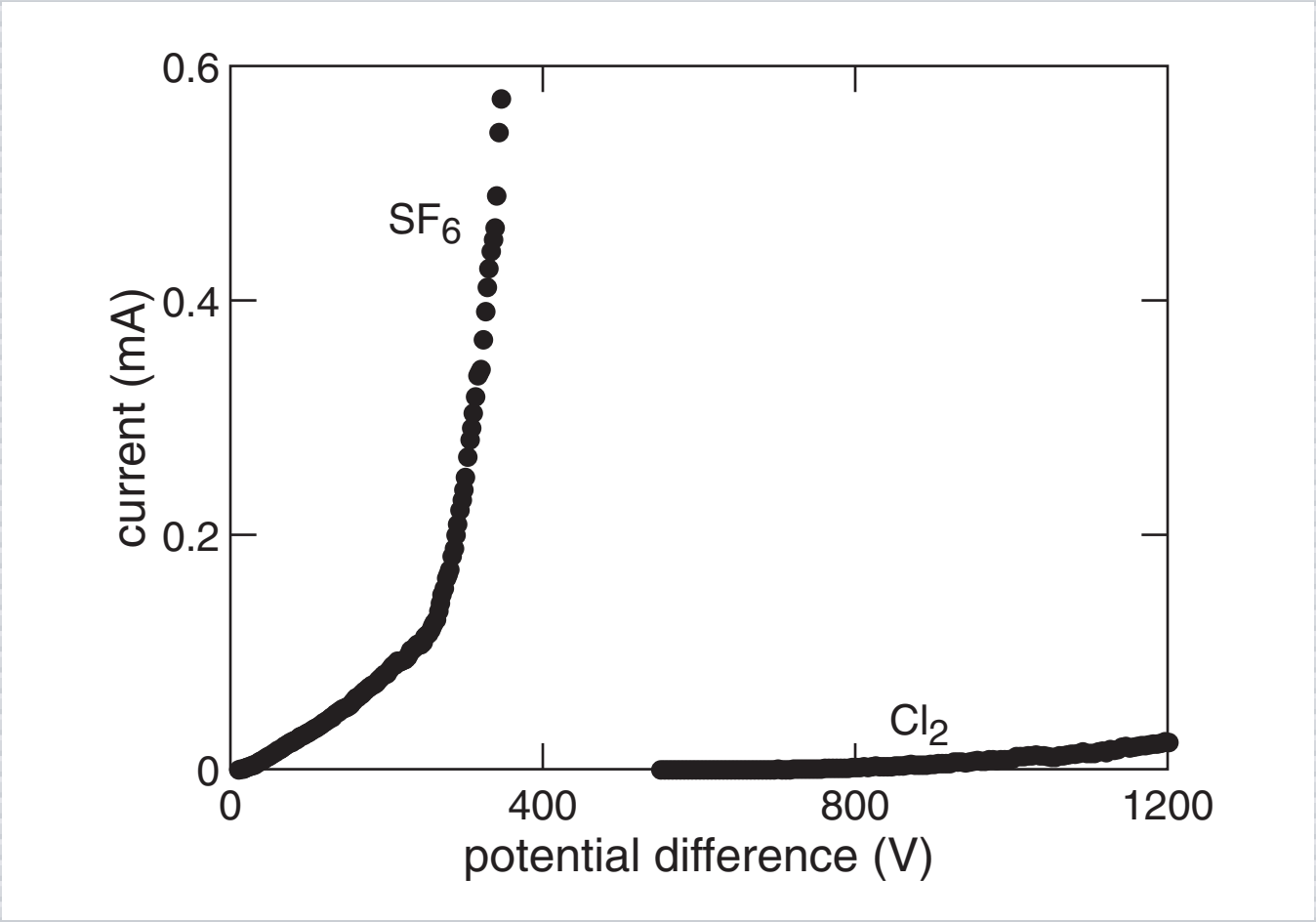
effect of ambient gas on absorptance



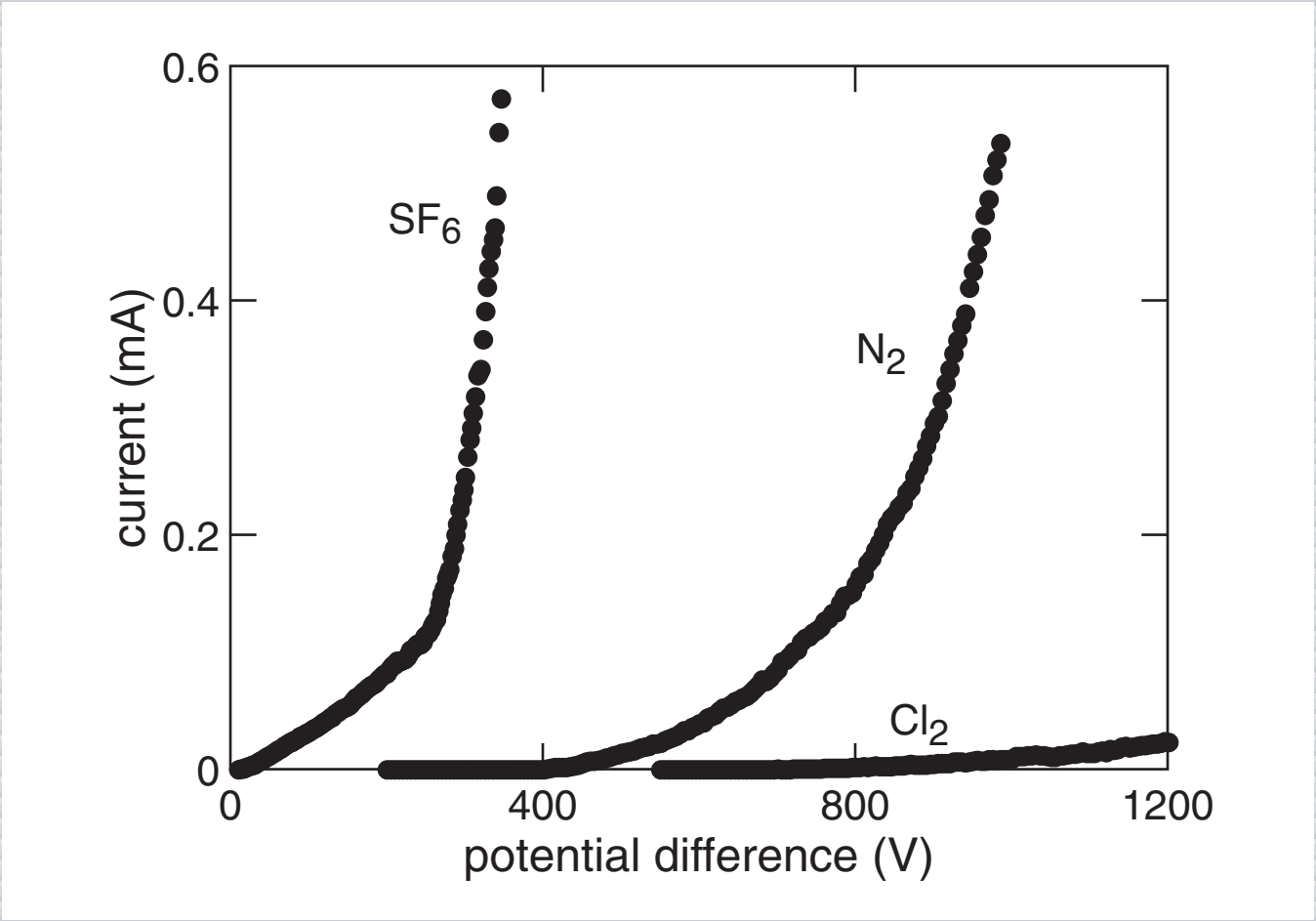
effect of ambient gas on field emission



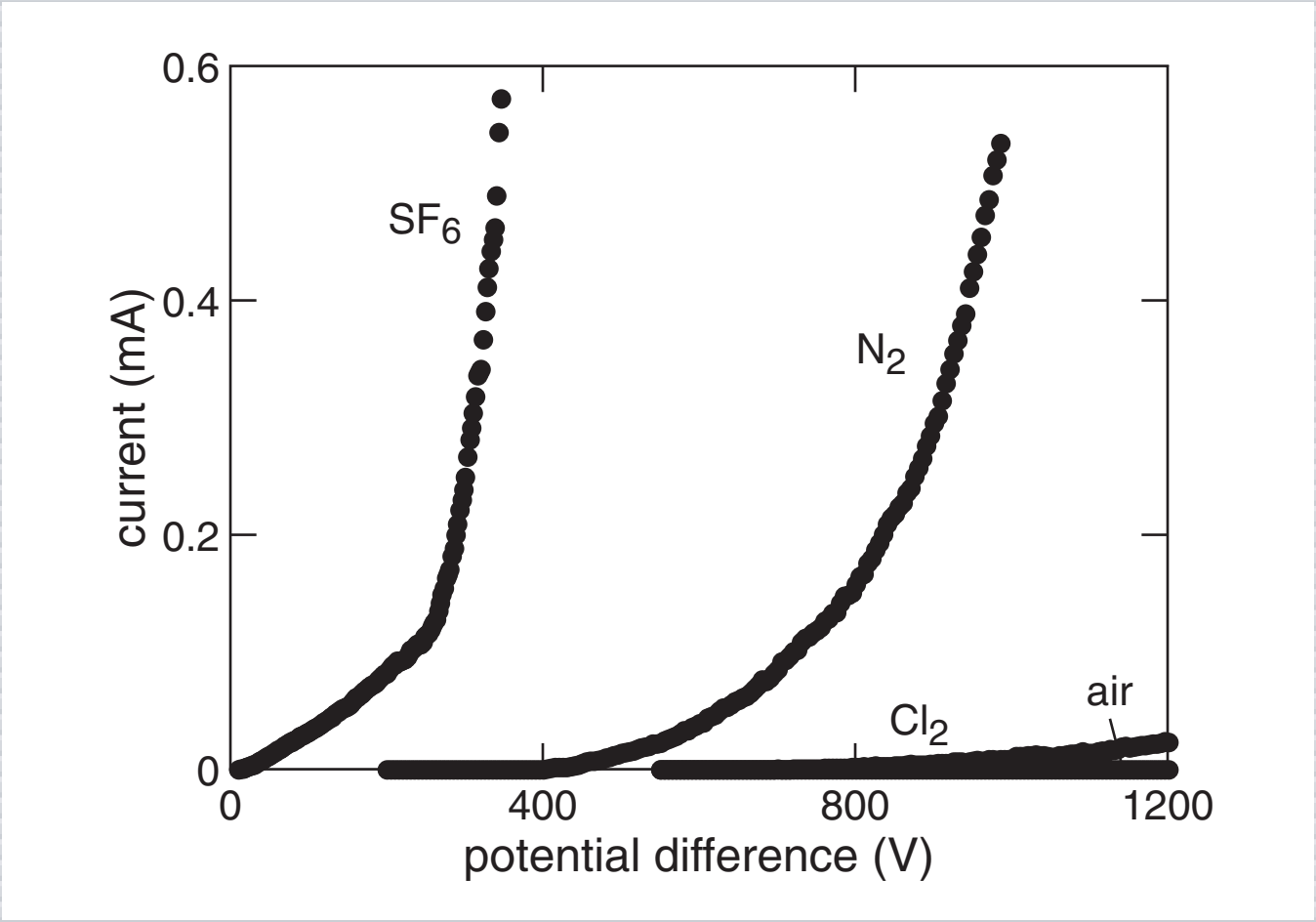
effect of ambient gas on field emission

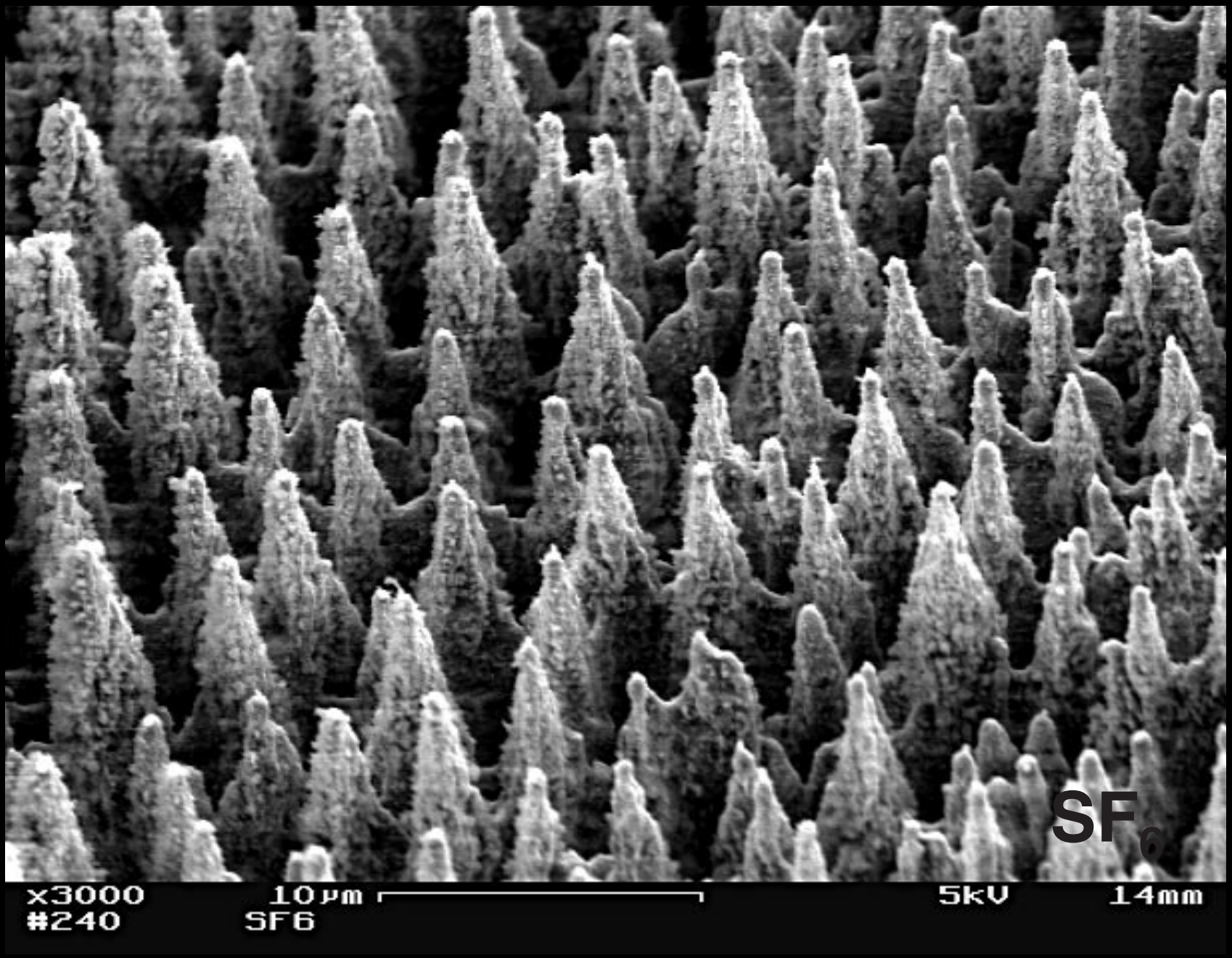


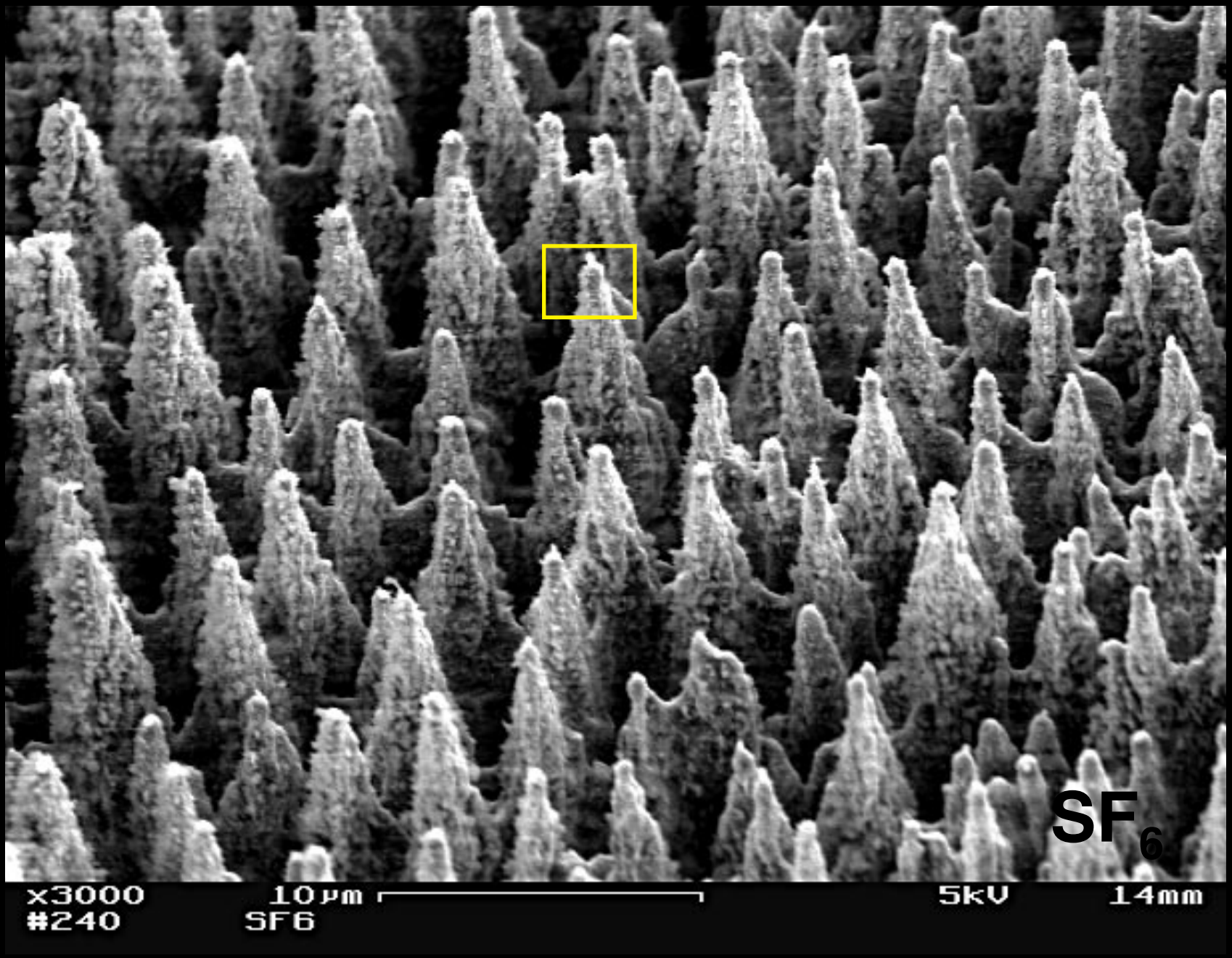
effect of ambient gas on field emission



effect of ambient gas on field emission




SF6
x3000
#240
10µm
SF6
5kV
14mm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x3000
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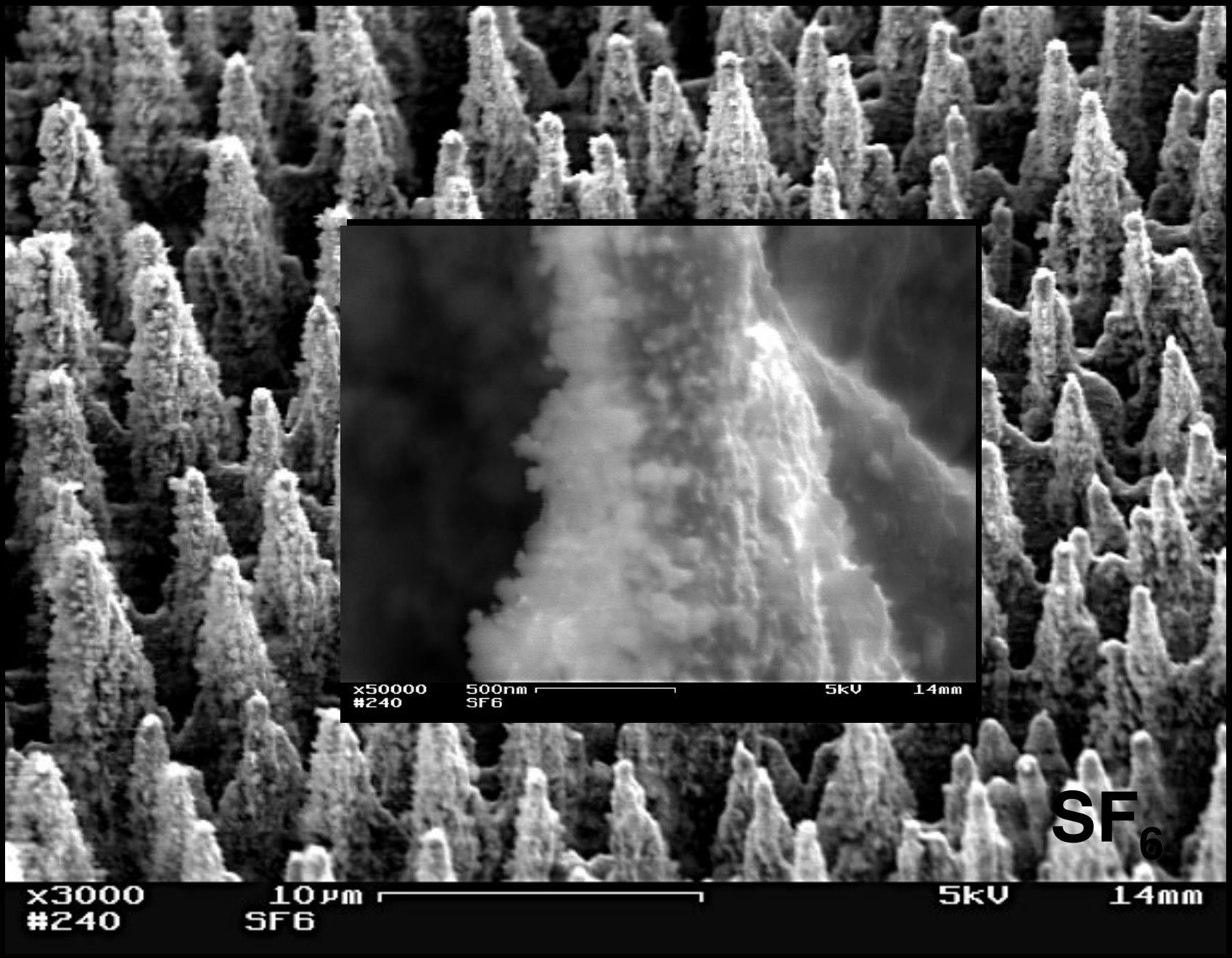
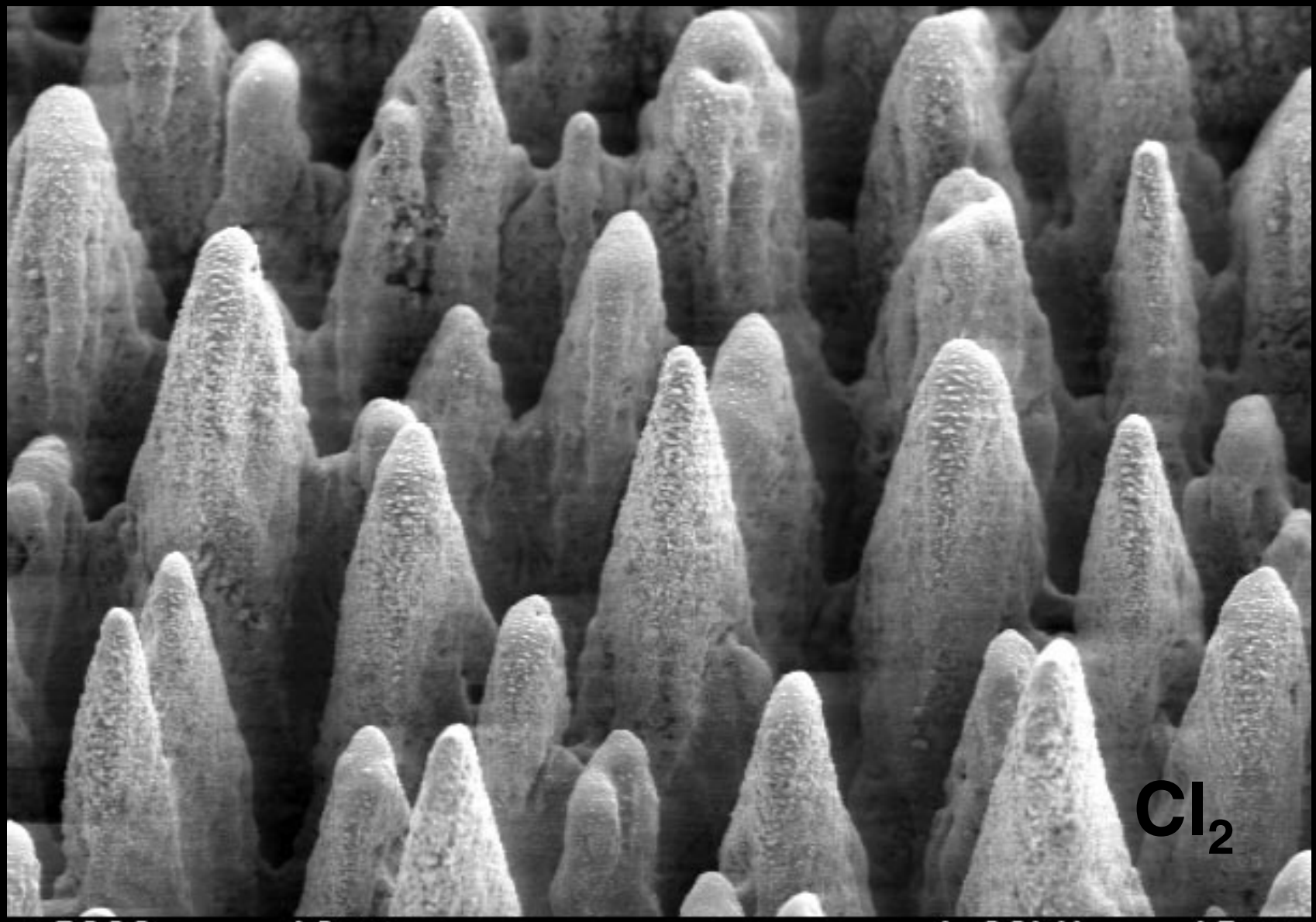
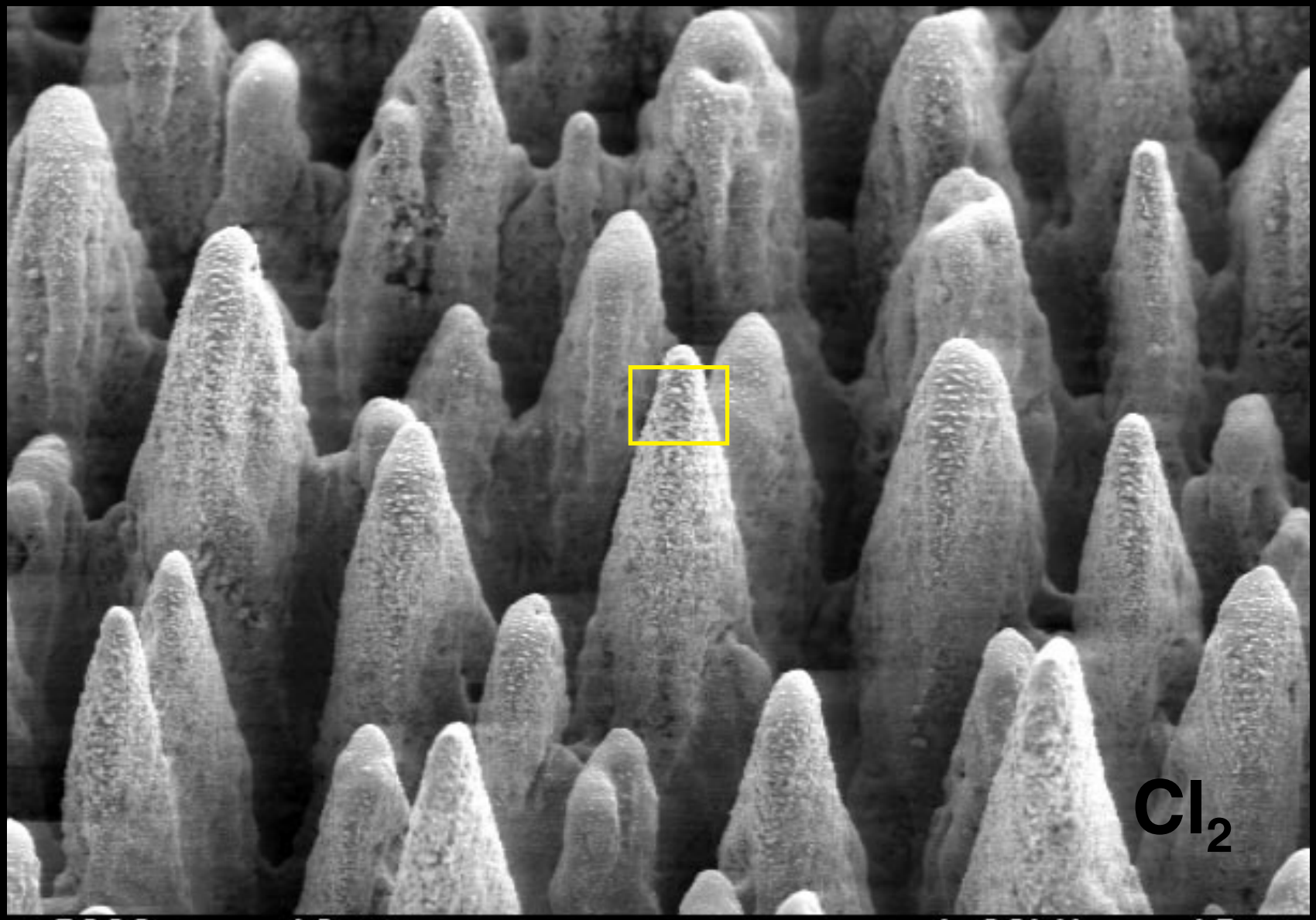
10µm
SF6
5kV
14mm


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


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


Cl_2
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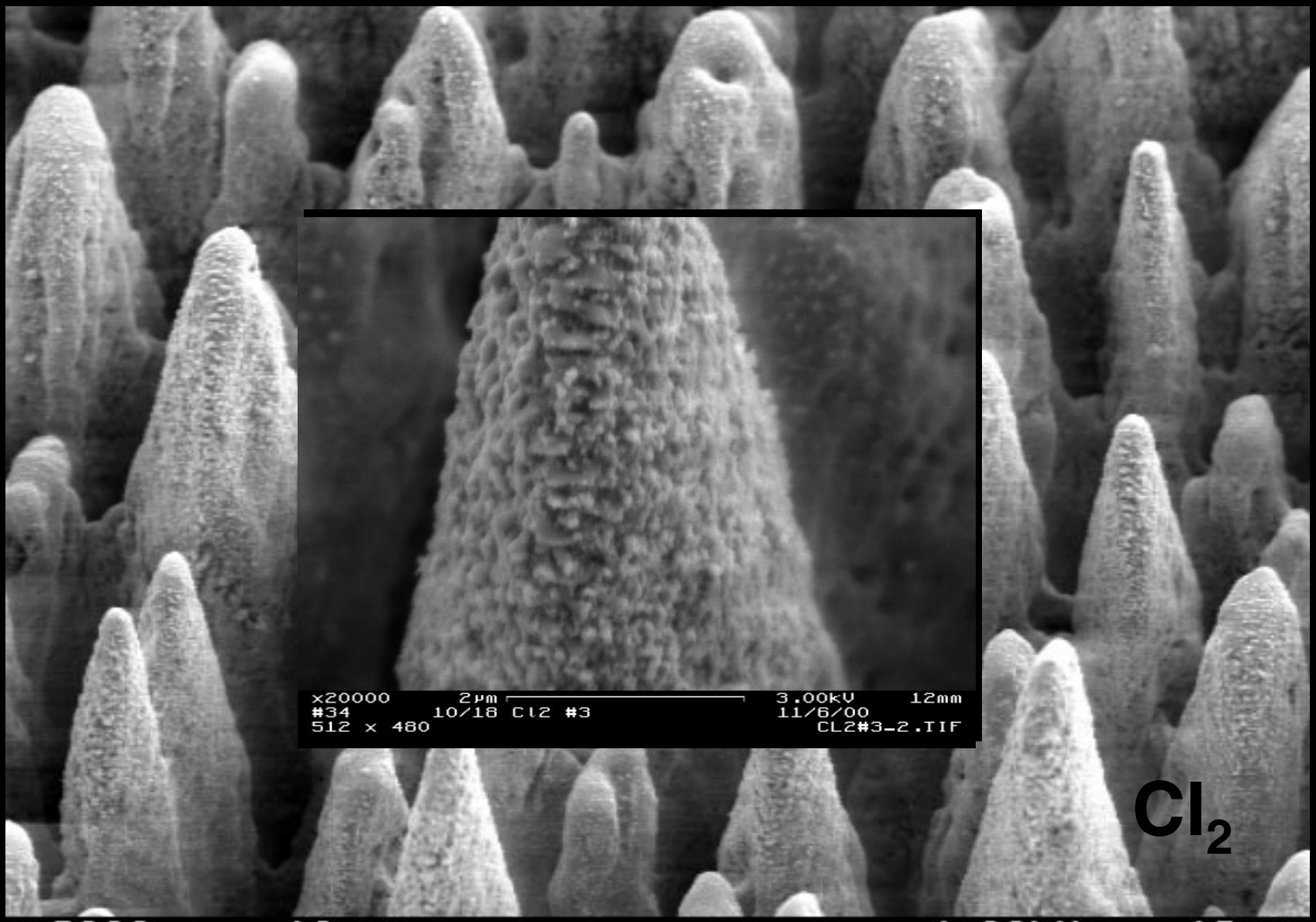
x20000 2µm 3.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
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Cl_2
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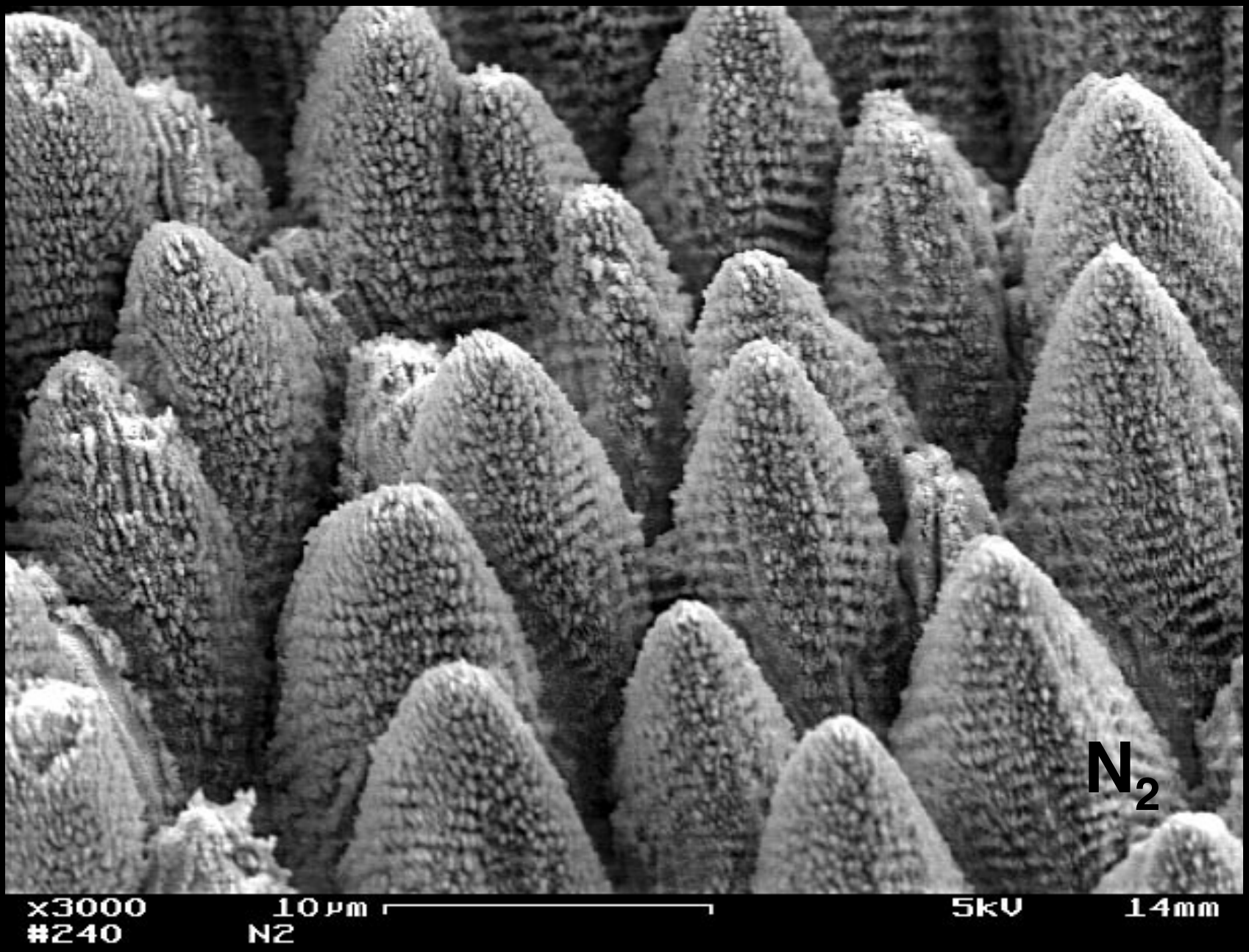
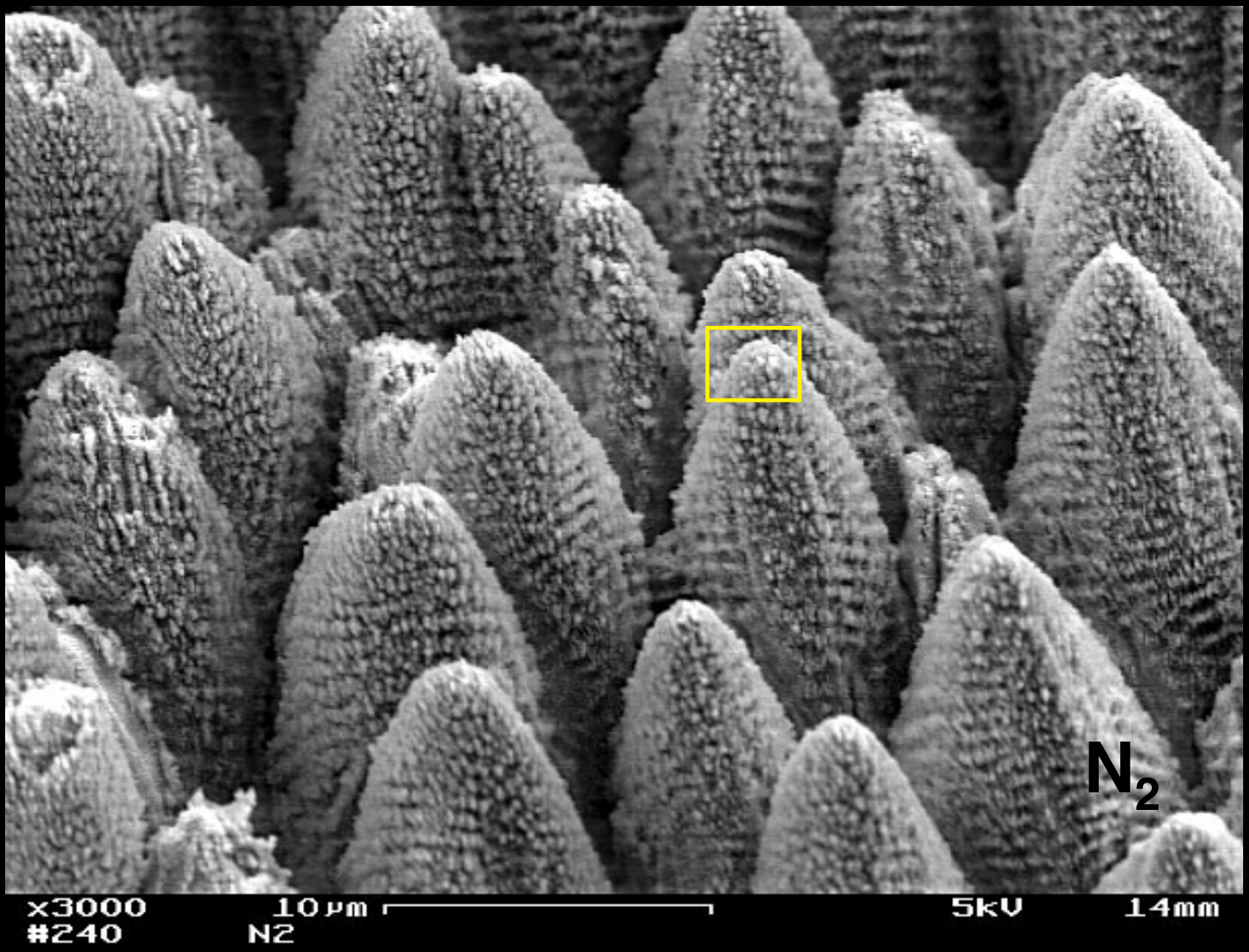
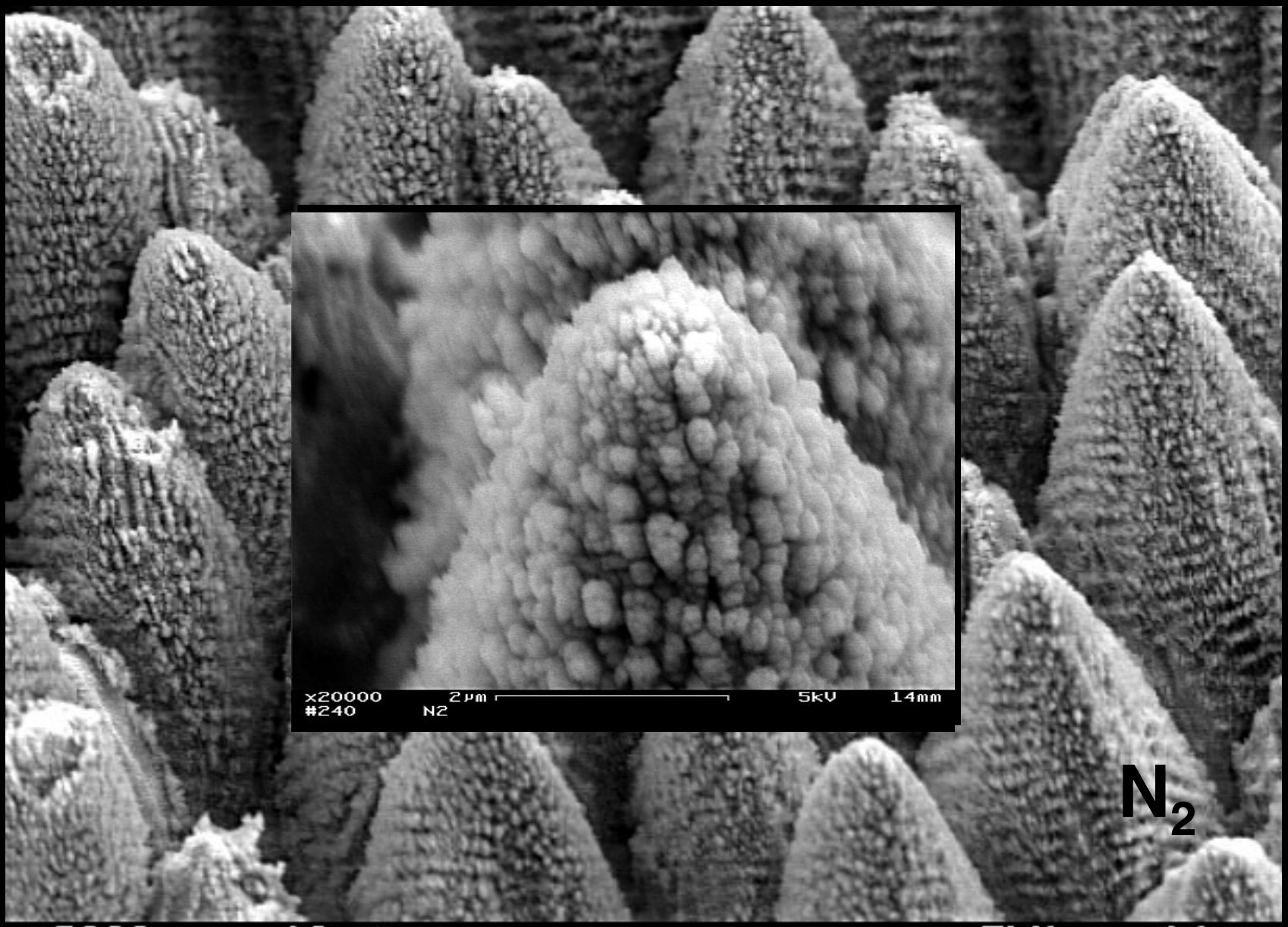

N_2
x3000
#240
10 µm
N2
5kV
14mm


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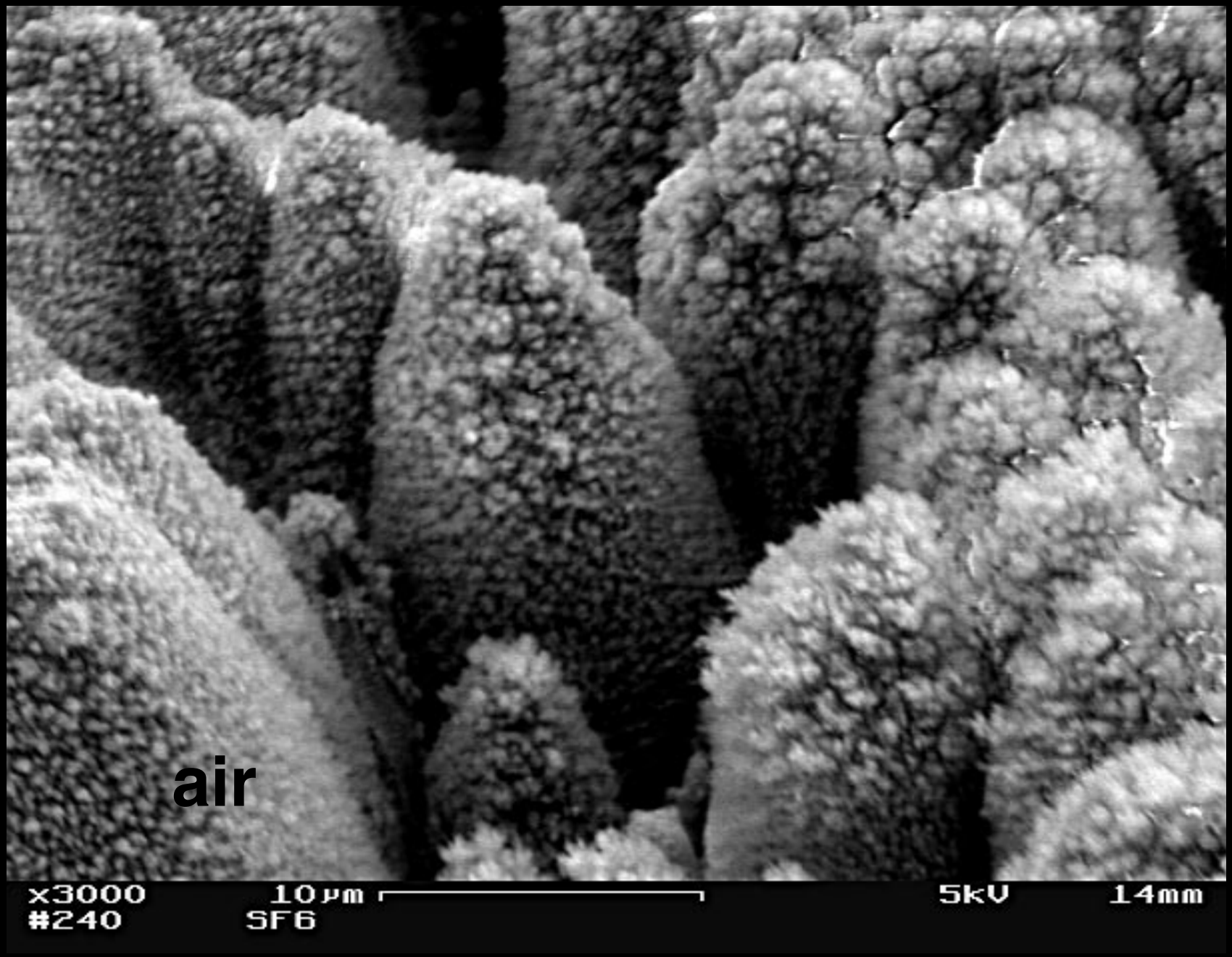
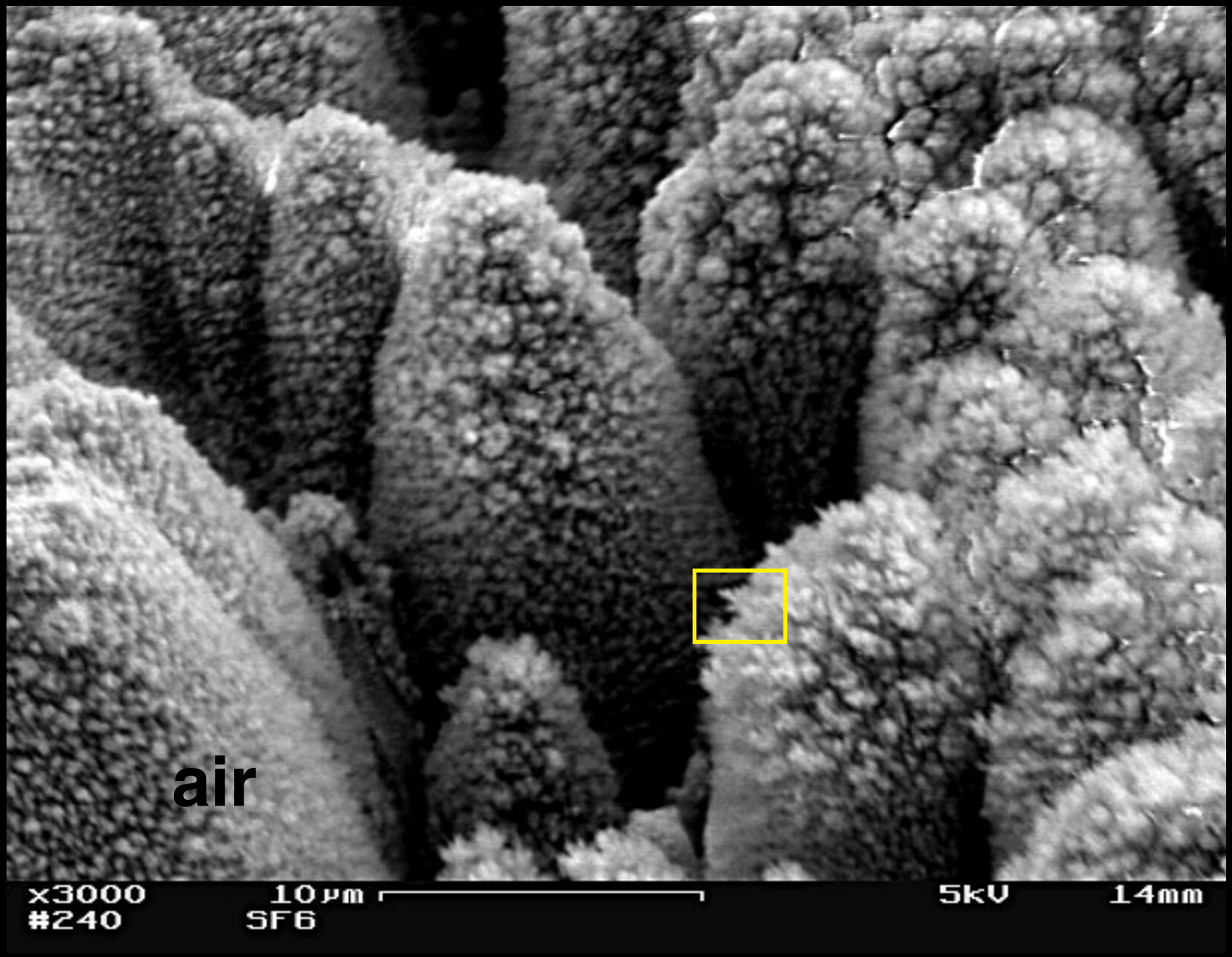
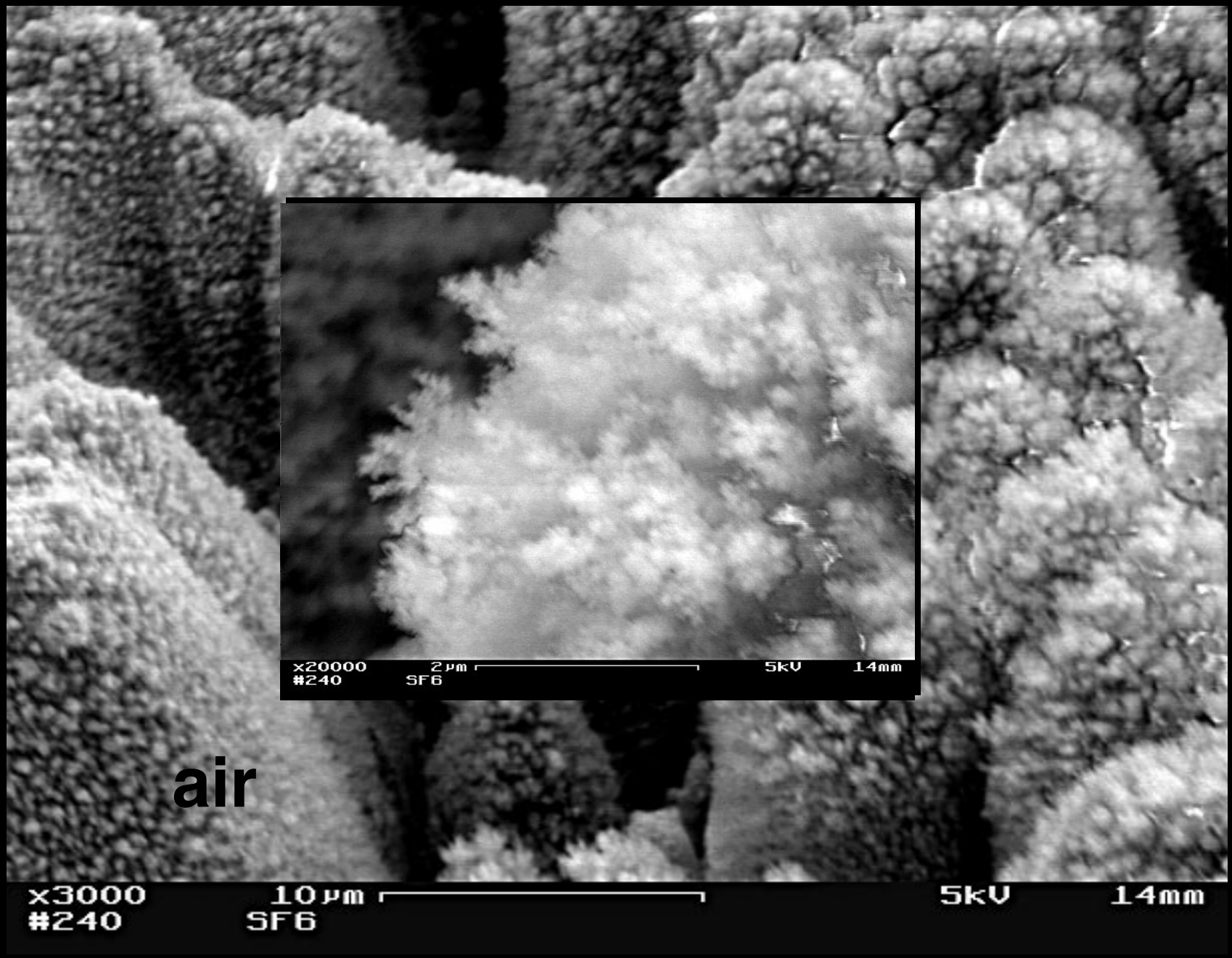
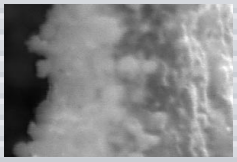
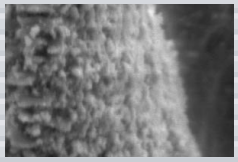
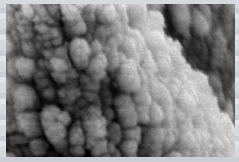
#240 N2
N_2
x3000 10µm 5kV 14mm
#240 N2


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				

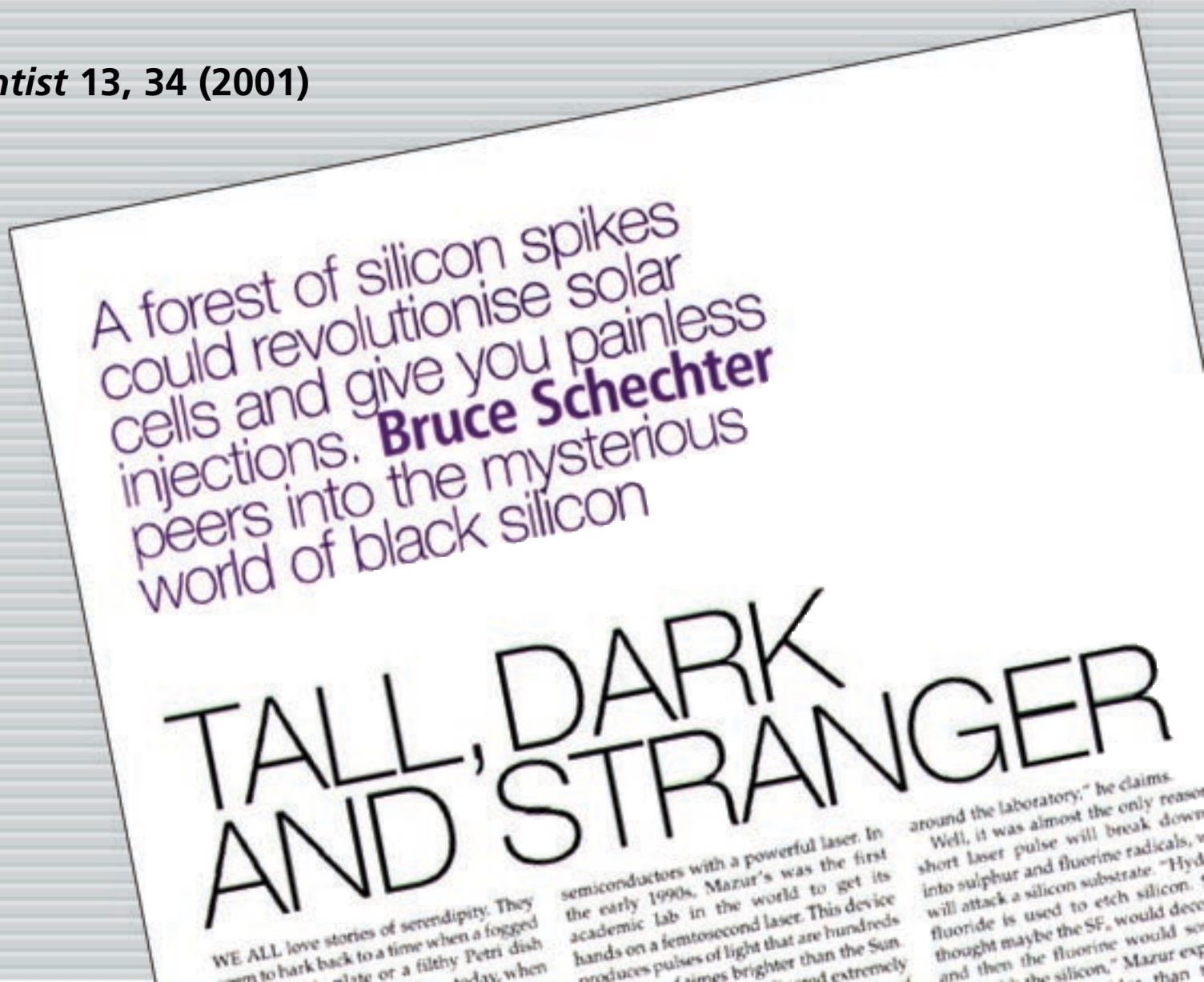
Structural and chemical analysis

- 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.

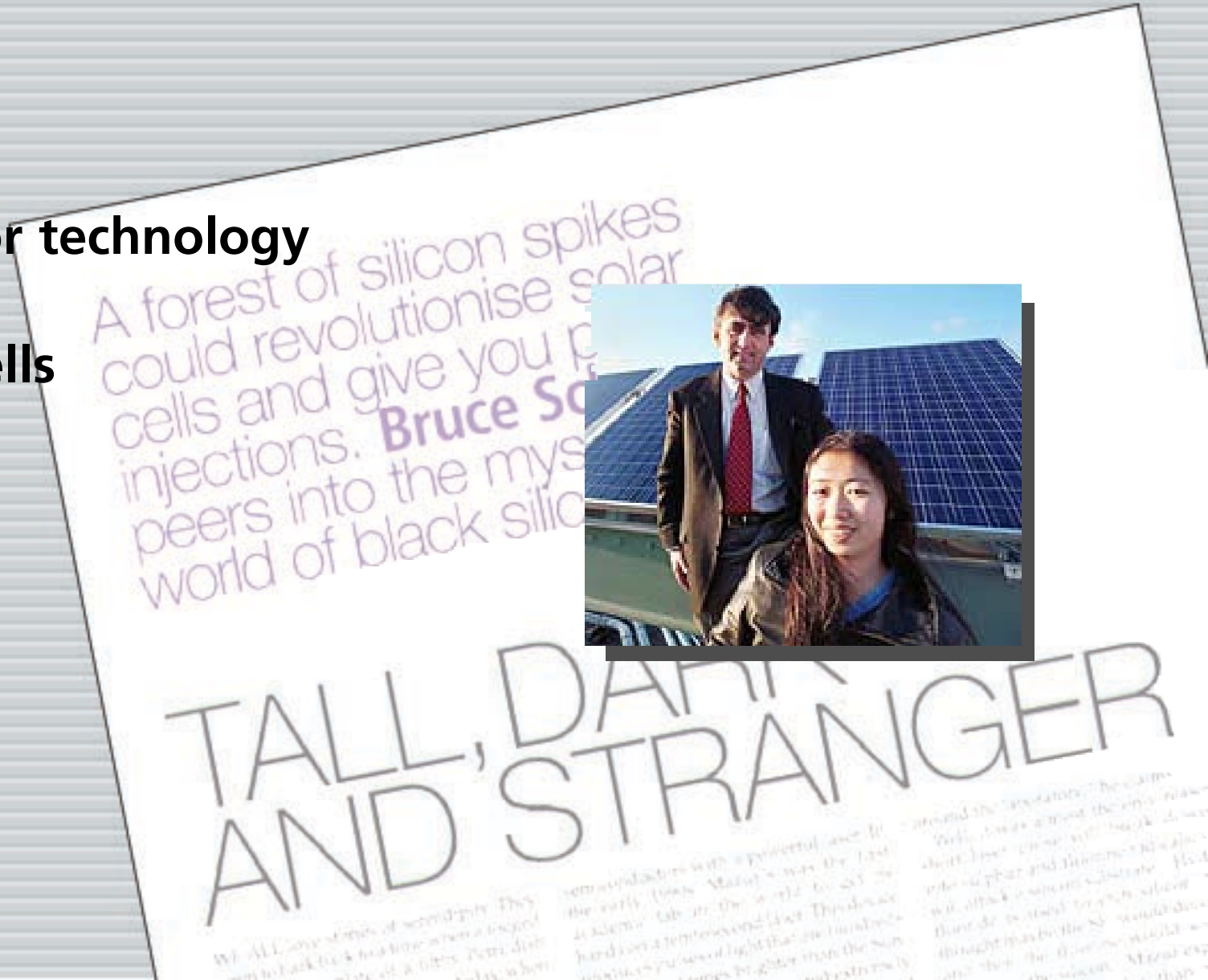
Well, it was almost the only reason short laser pulse will break down into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrofluoride is used to etch silicon. thought maybe the SF_6 would decompose and then the fluorine would react with the silicon," Mazur explains, than

Outlook

- **detector technology**

Outlook

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

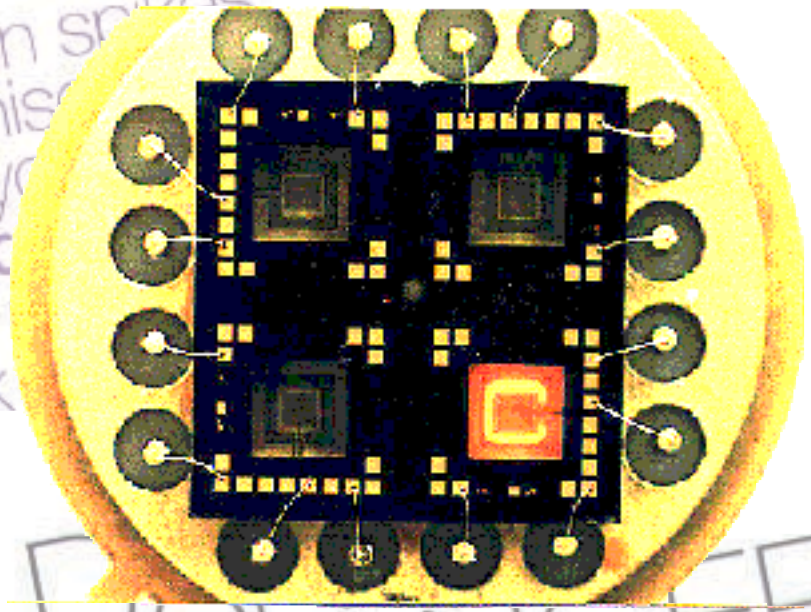


Outlook

- detector technology
- solar cells
- display technology

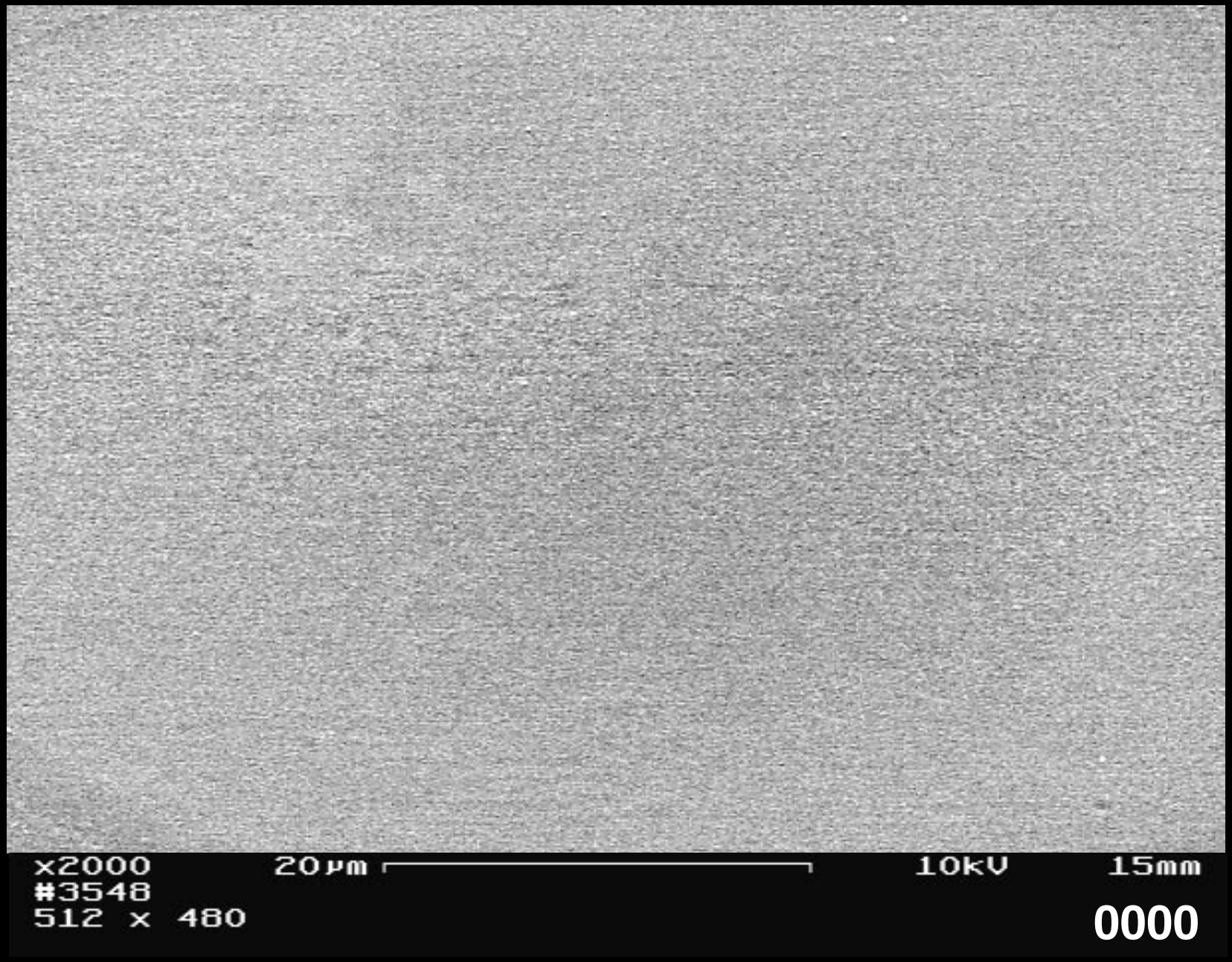
Outlook

- detector technology
- solar cells
- display technology
- sensors



Outlook

- development of spikes
- spike formation through grids
- cell adhesion
- functionalization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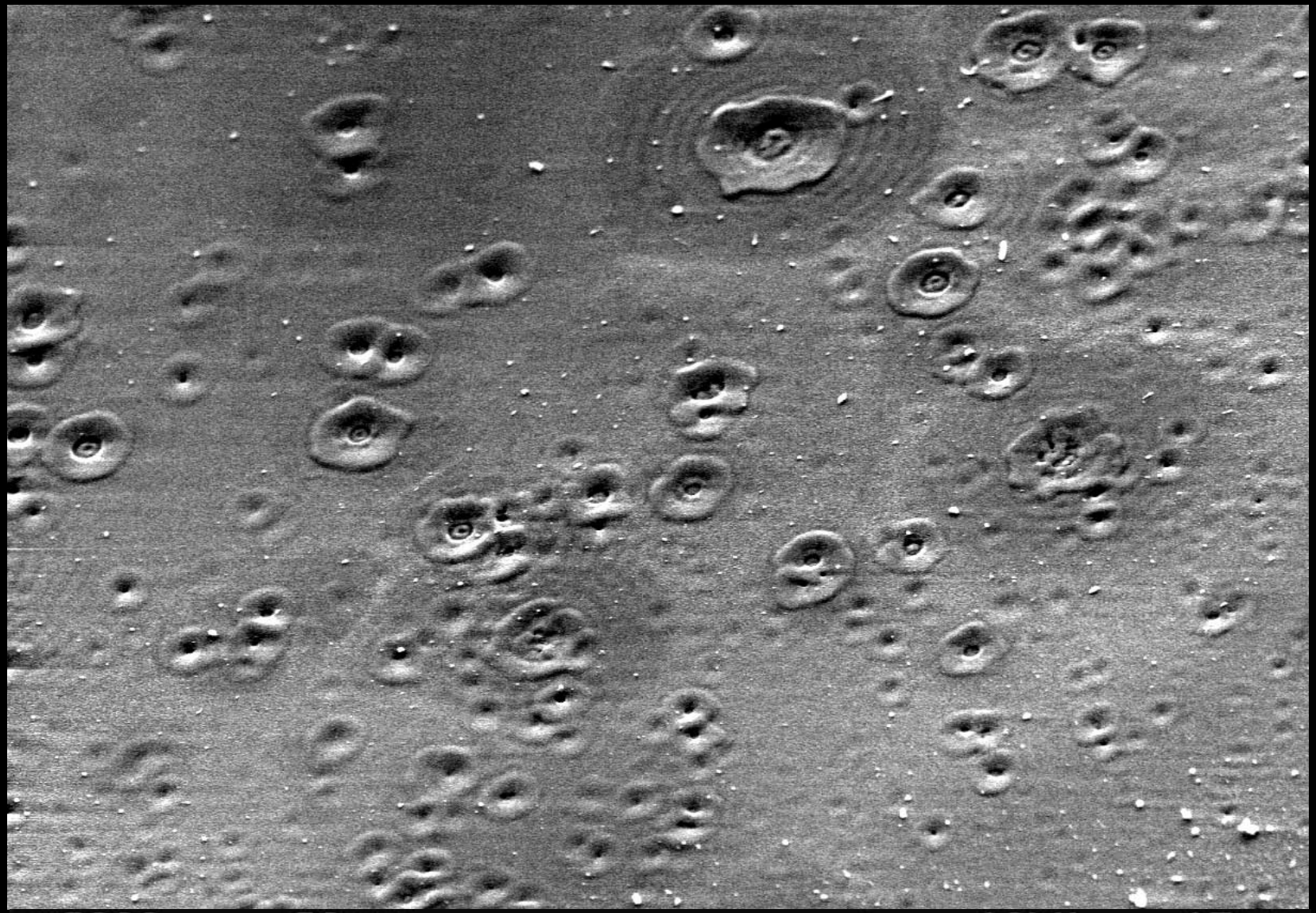
#3548
512 x 480
20µm
10kV
15mm
0000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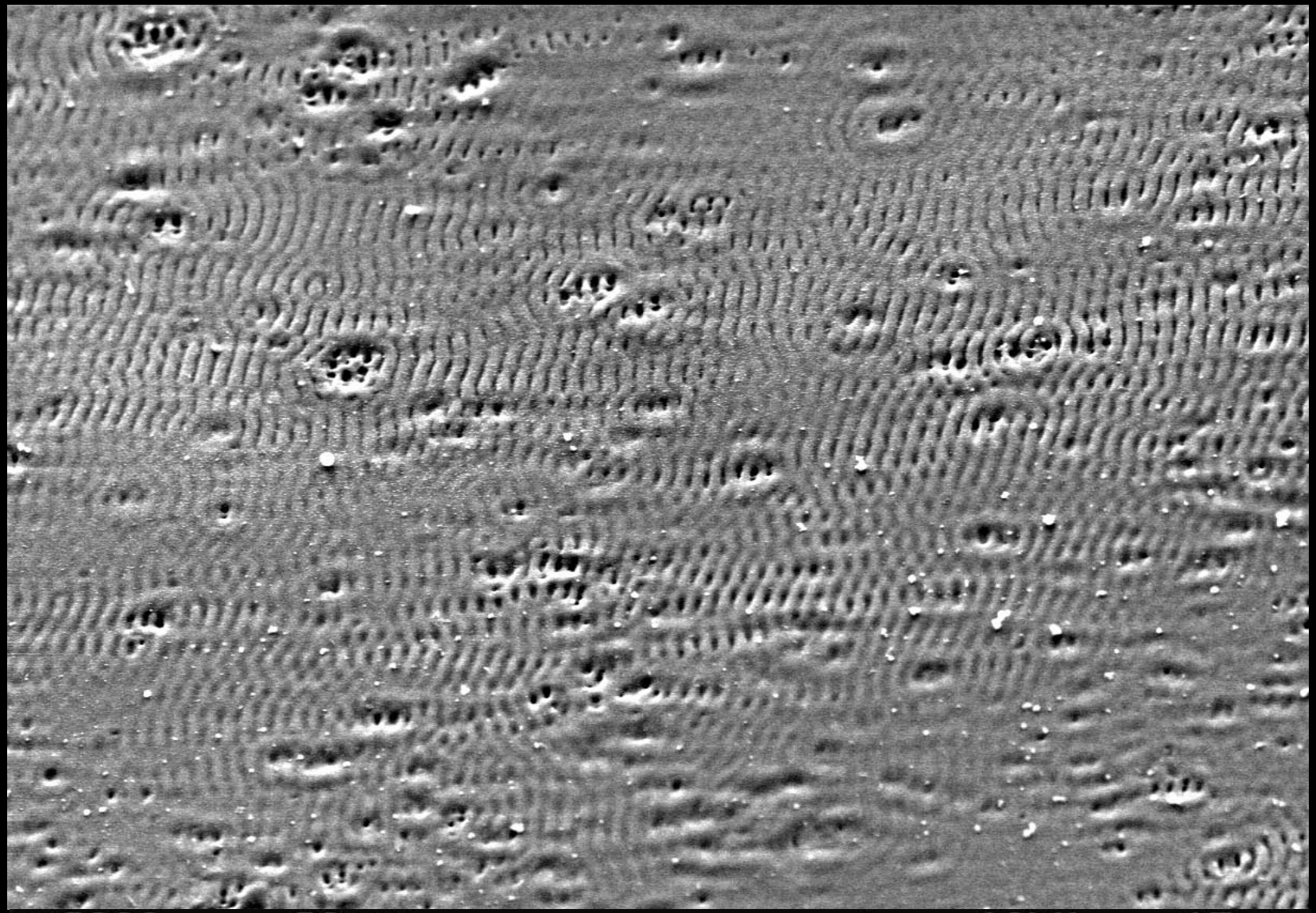
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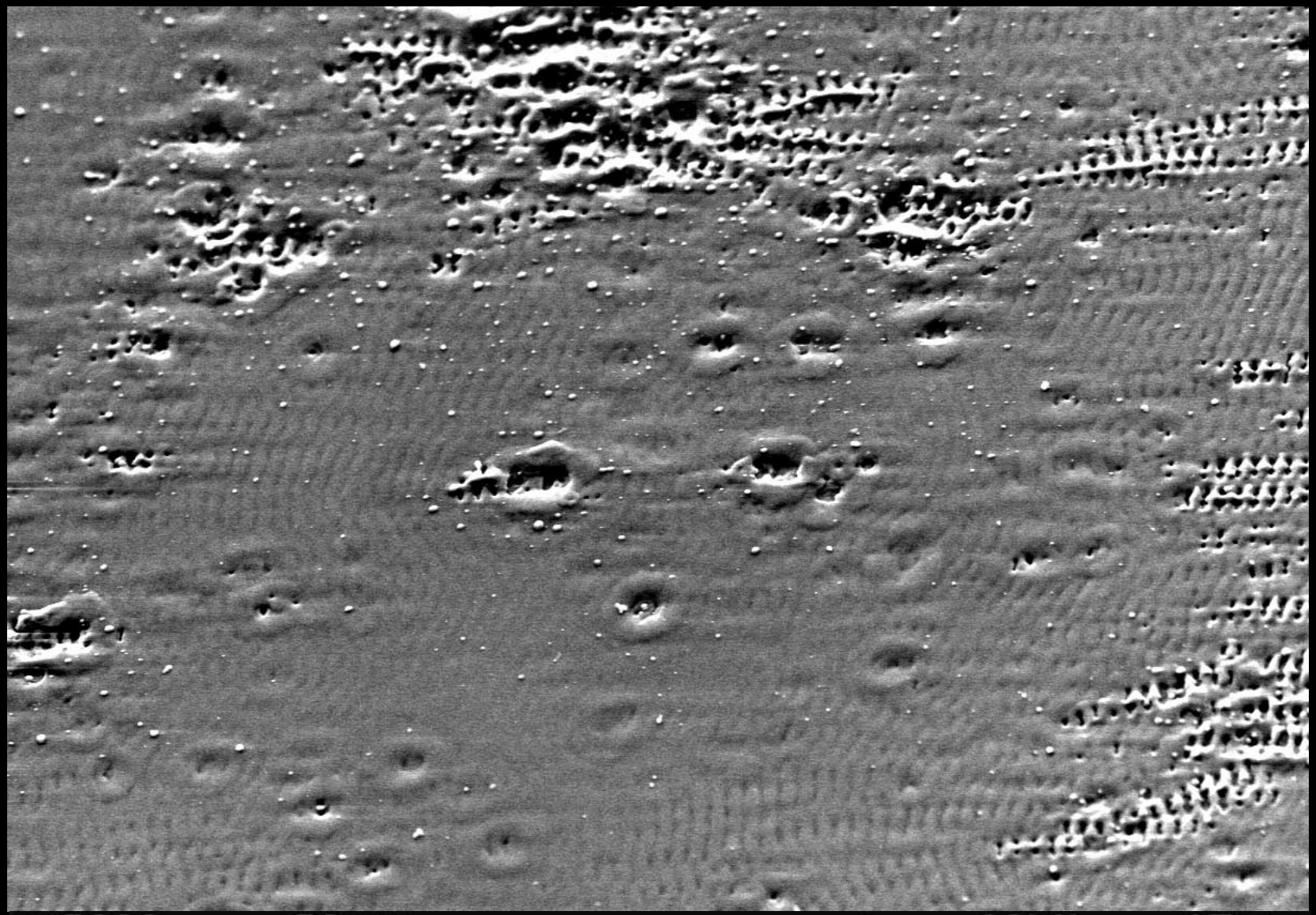
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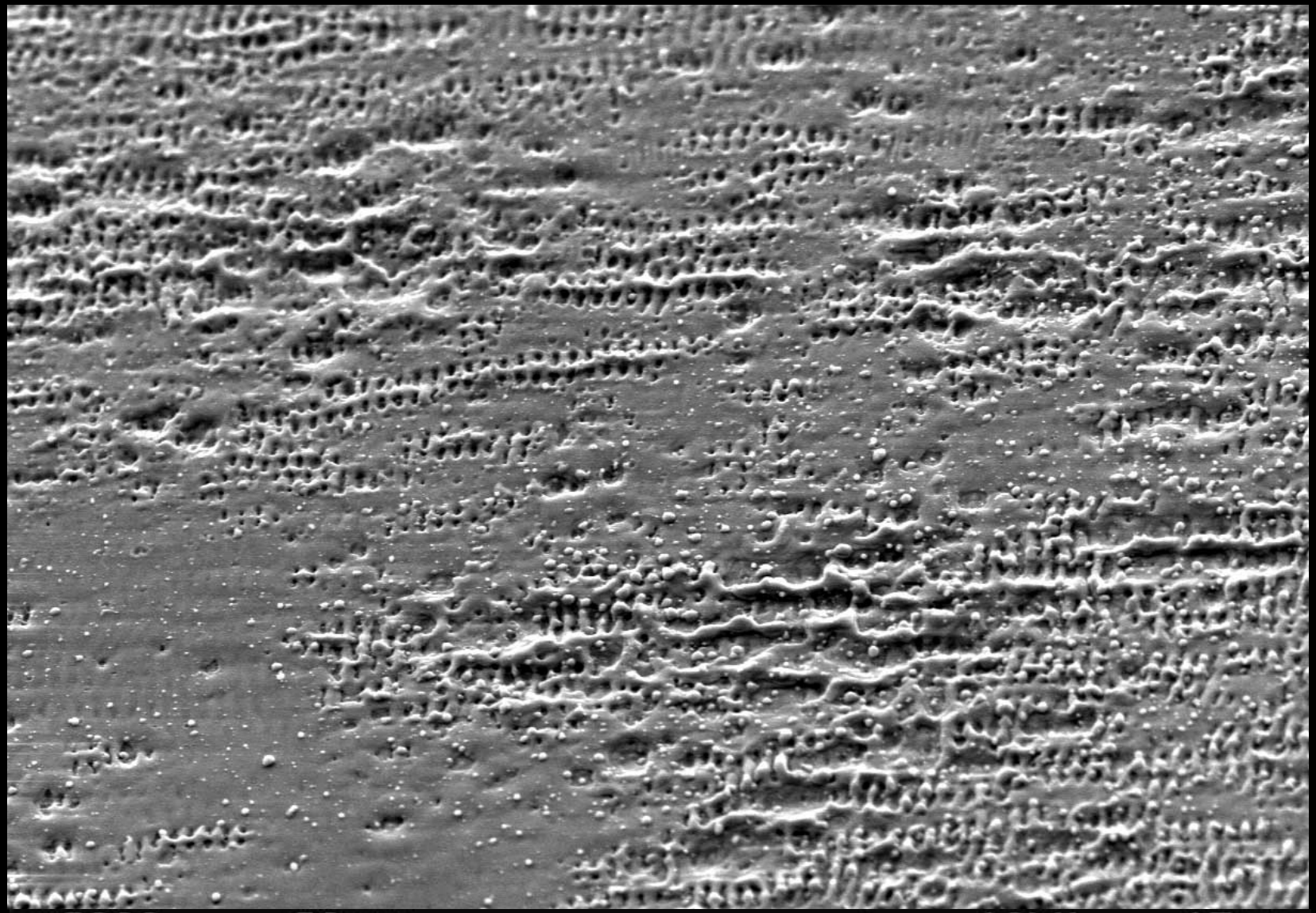
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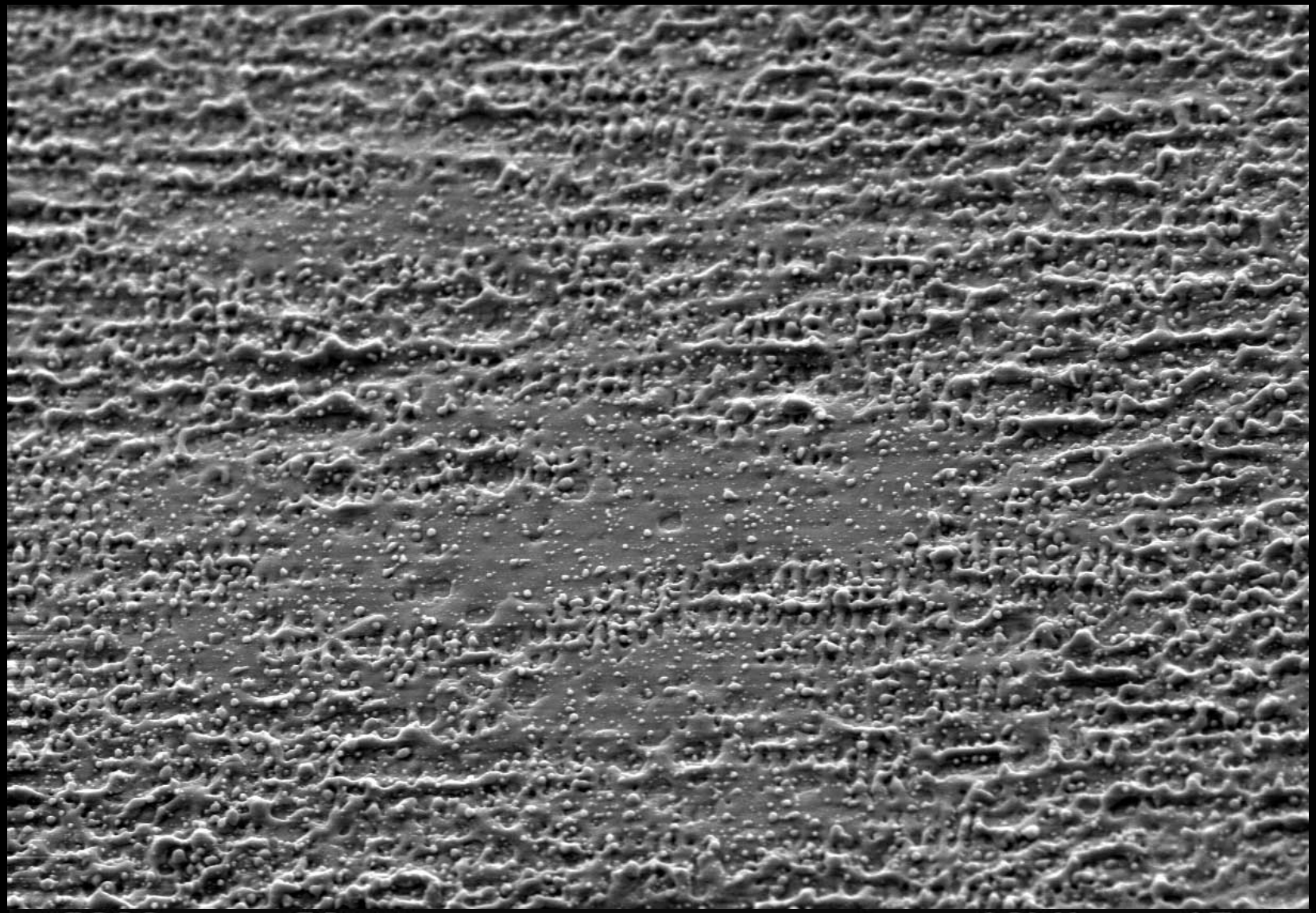
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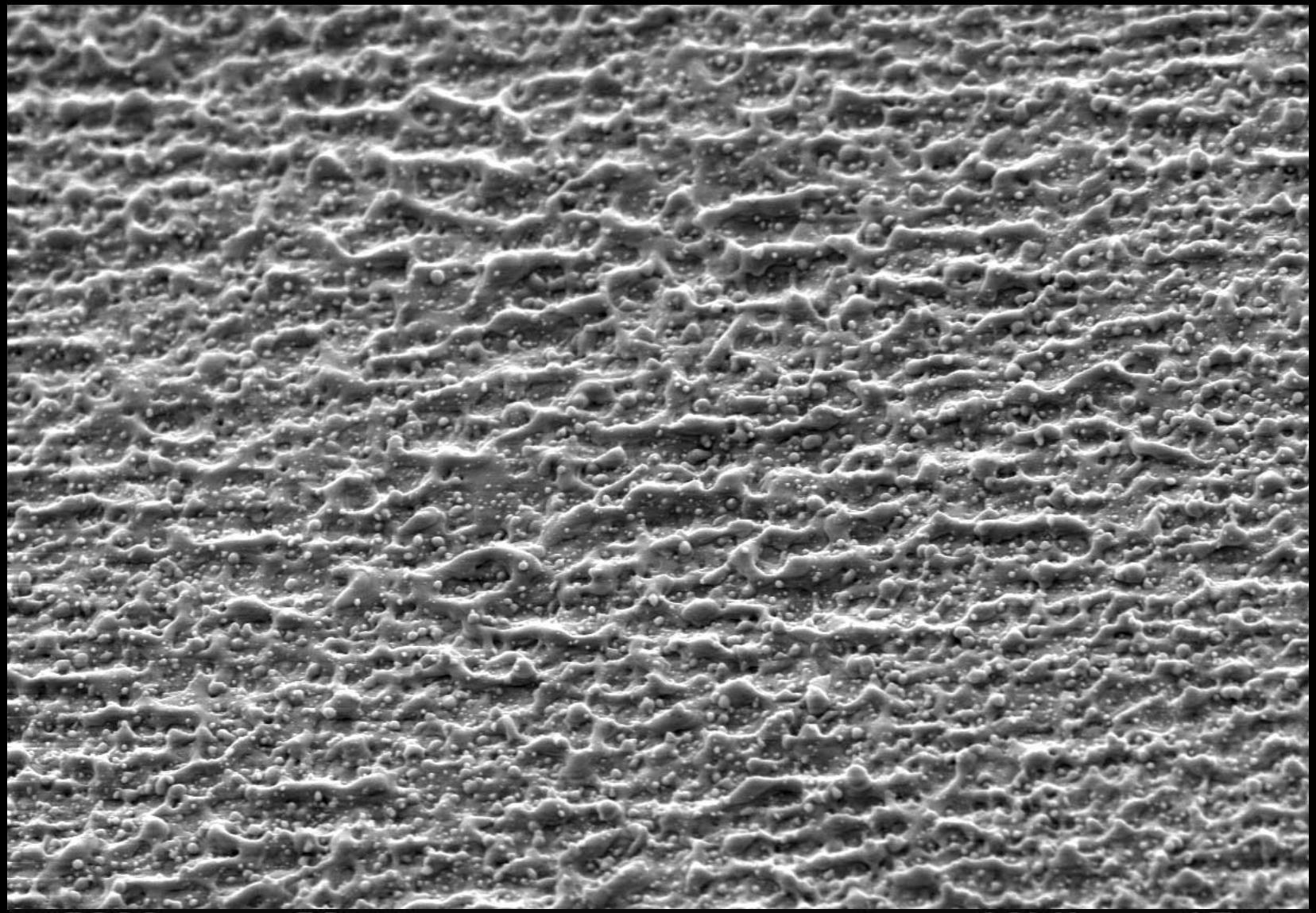
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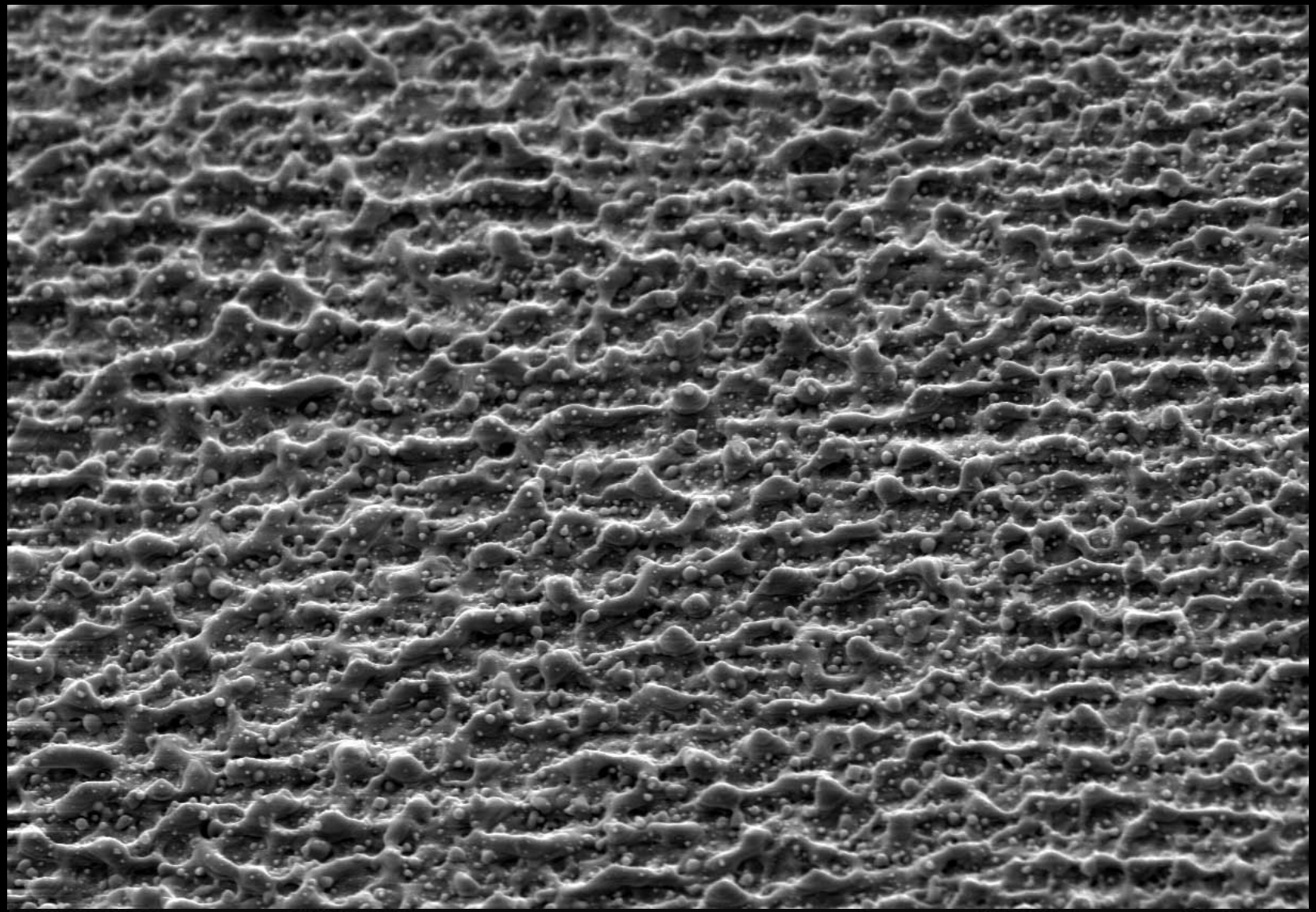
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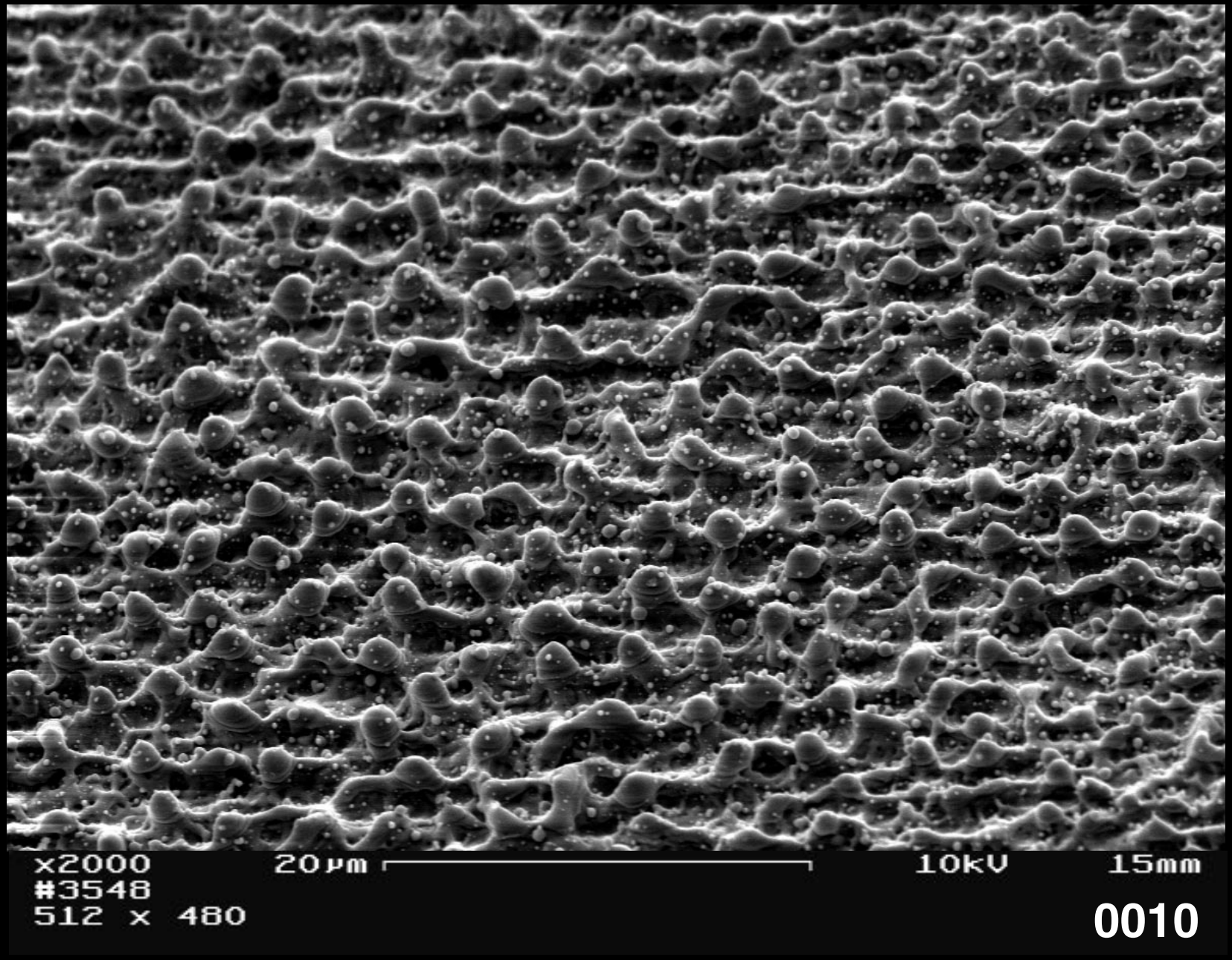
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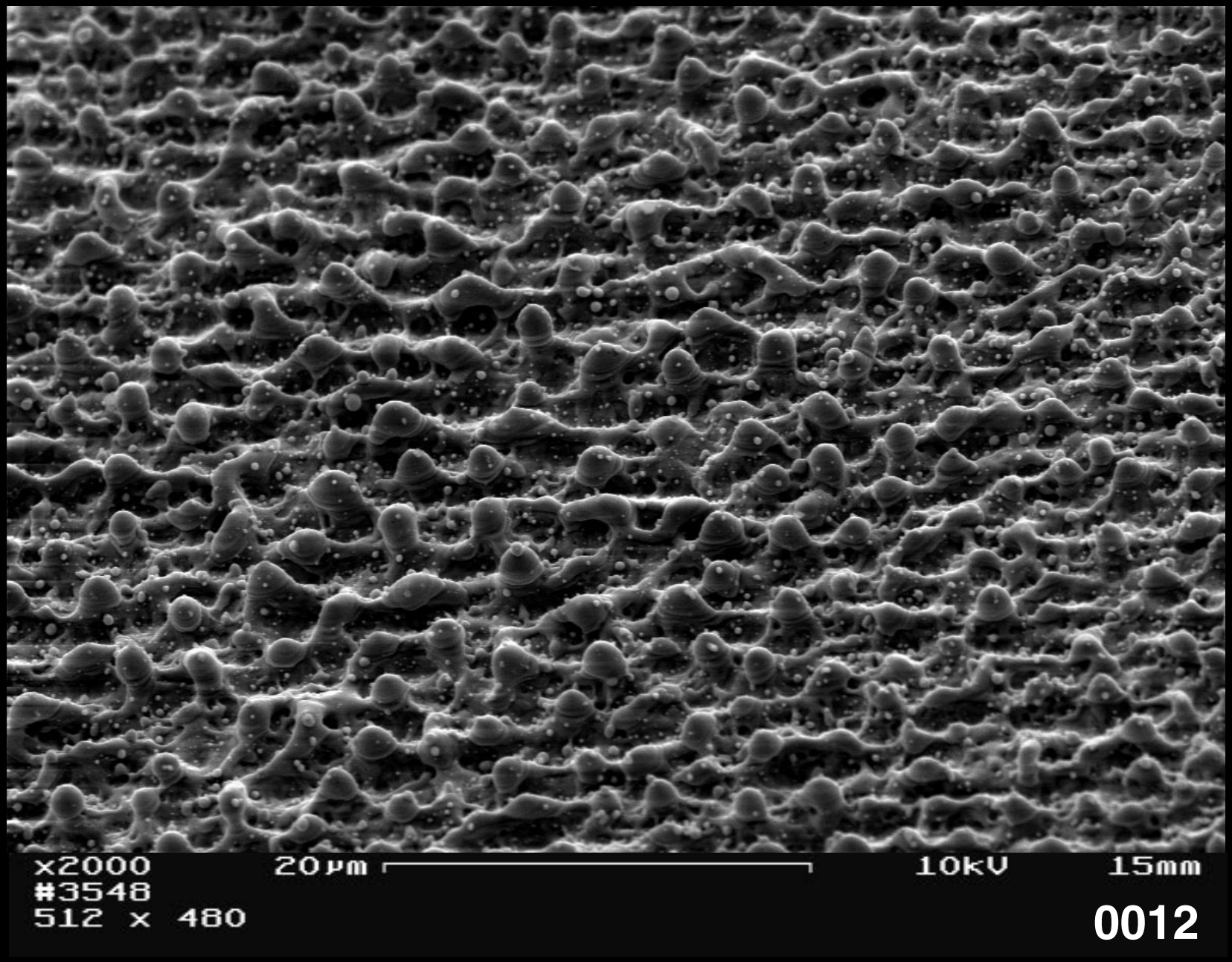
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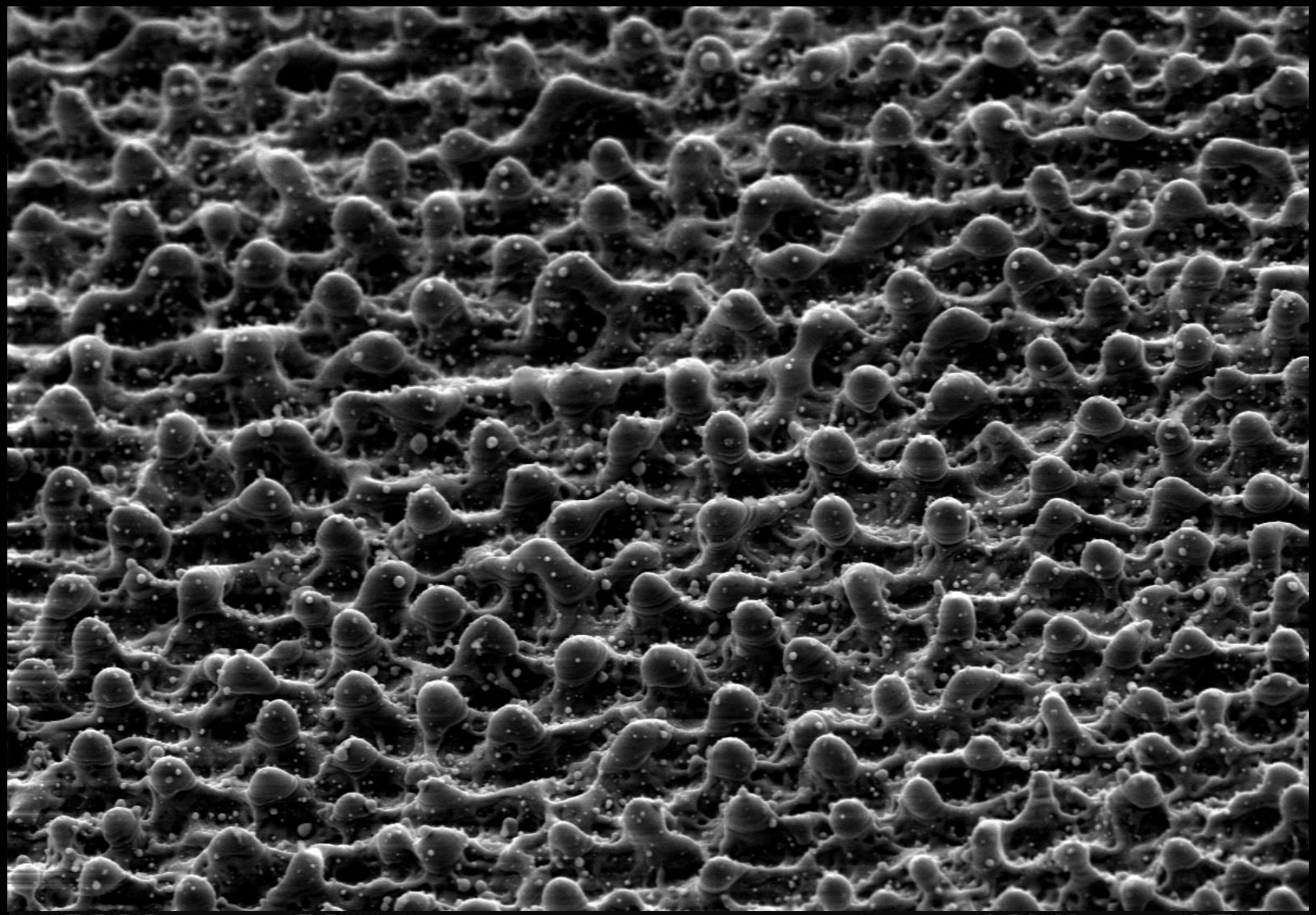
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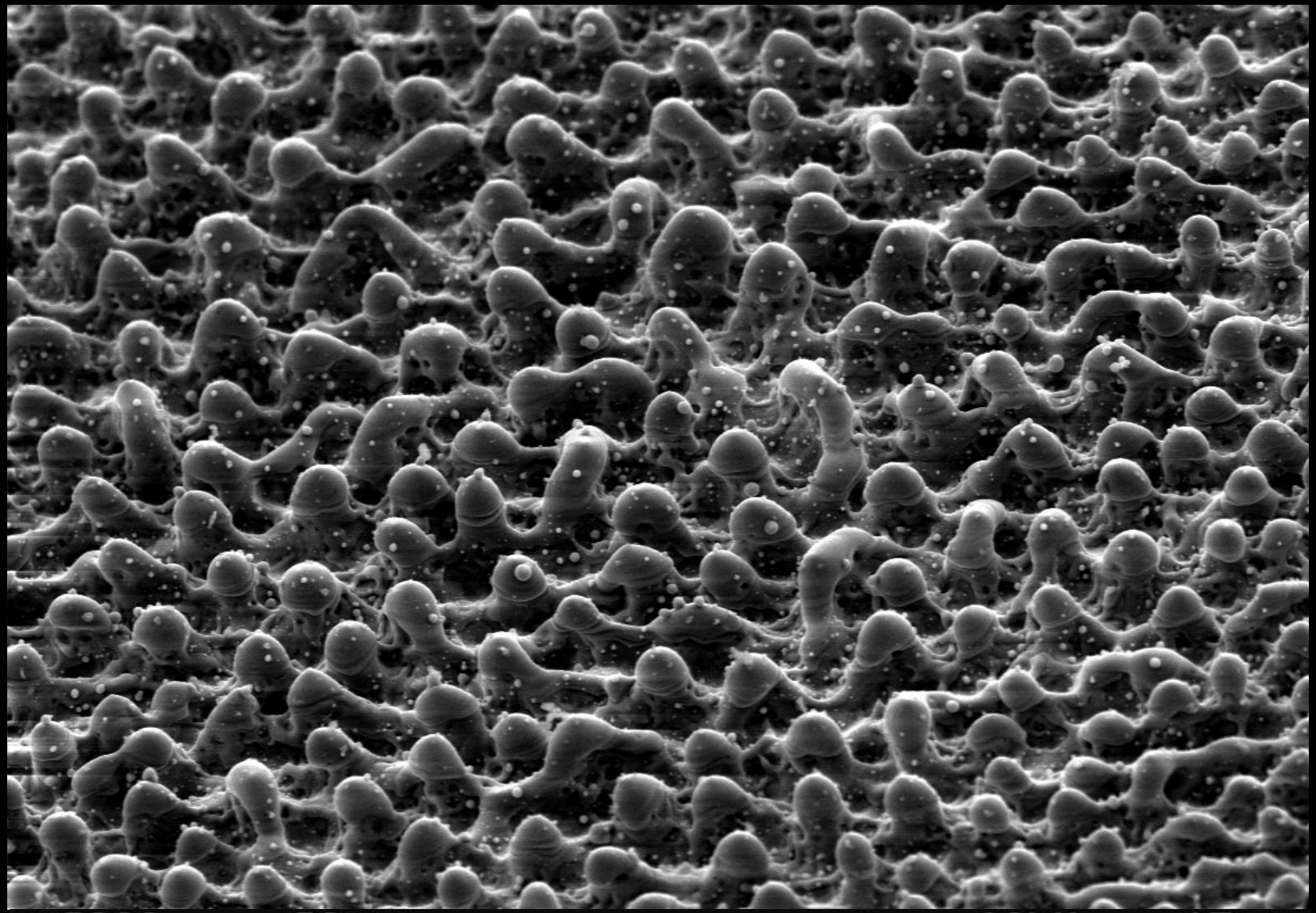
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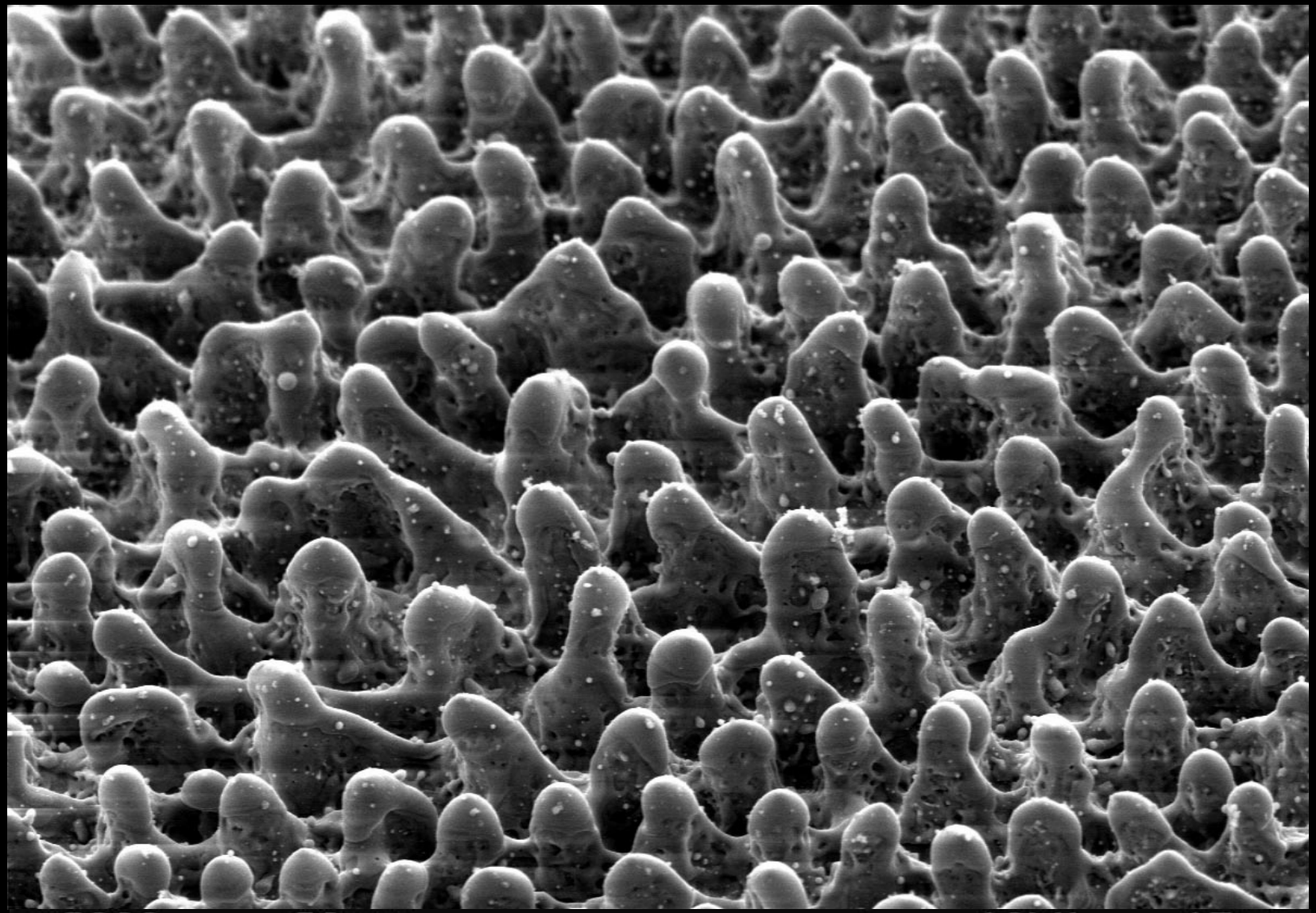
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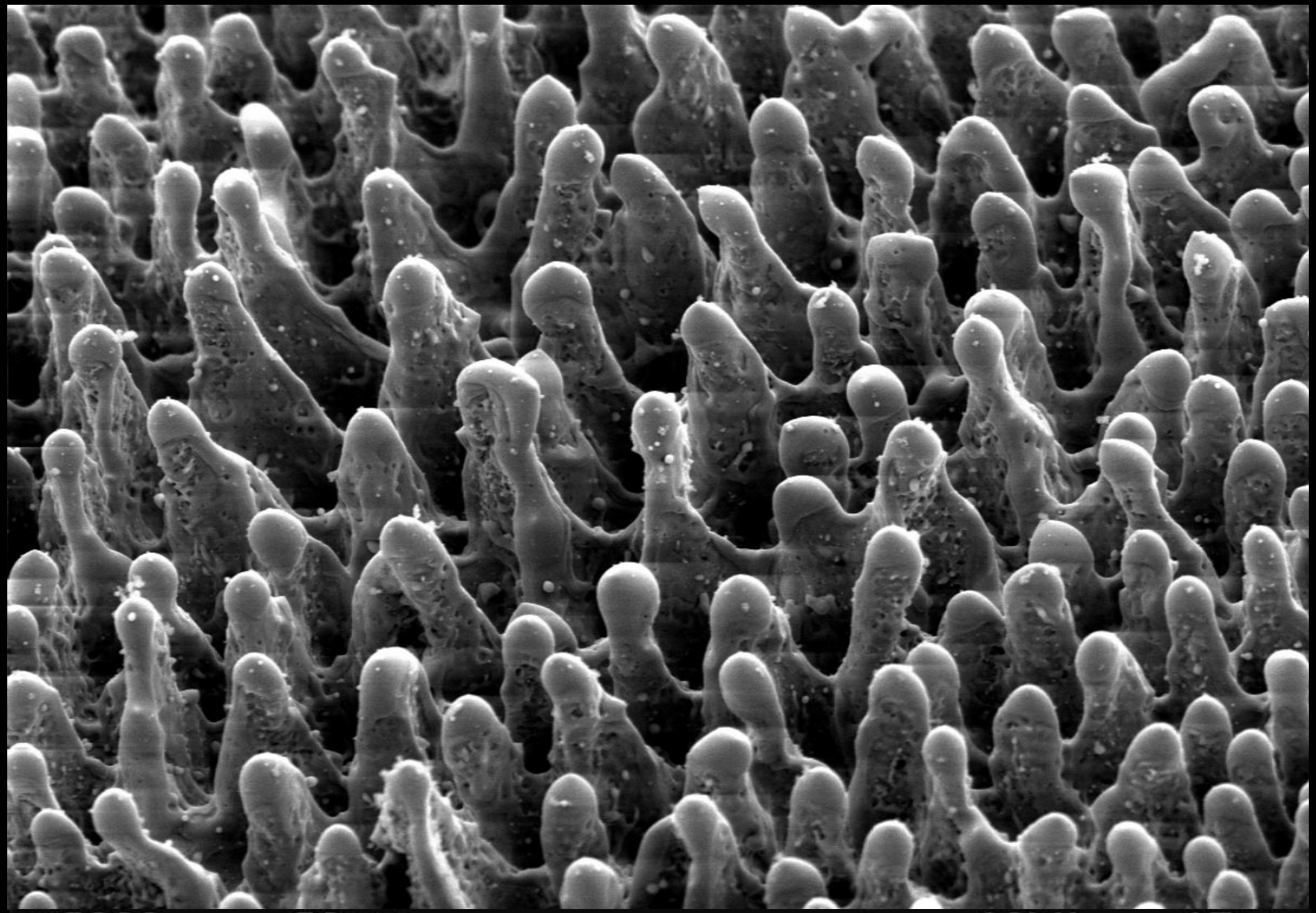
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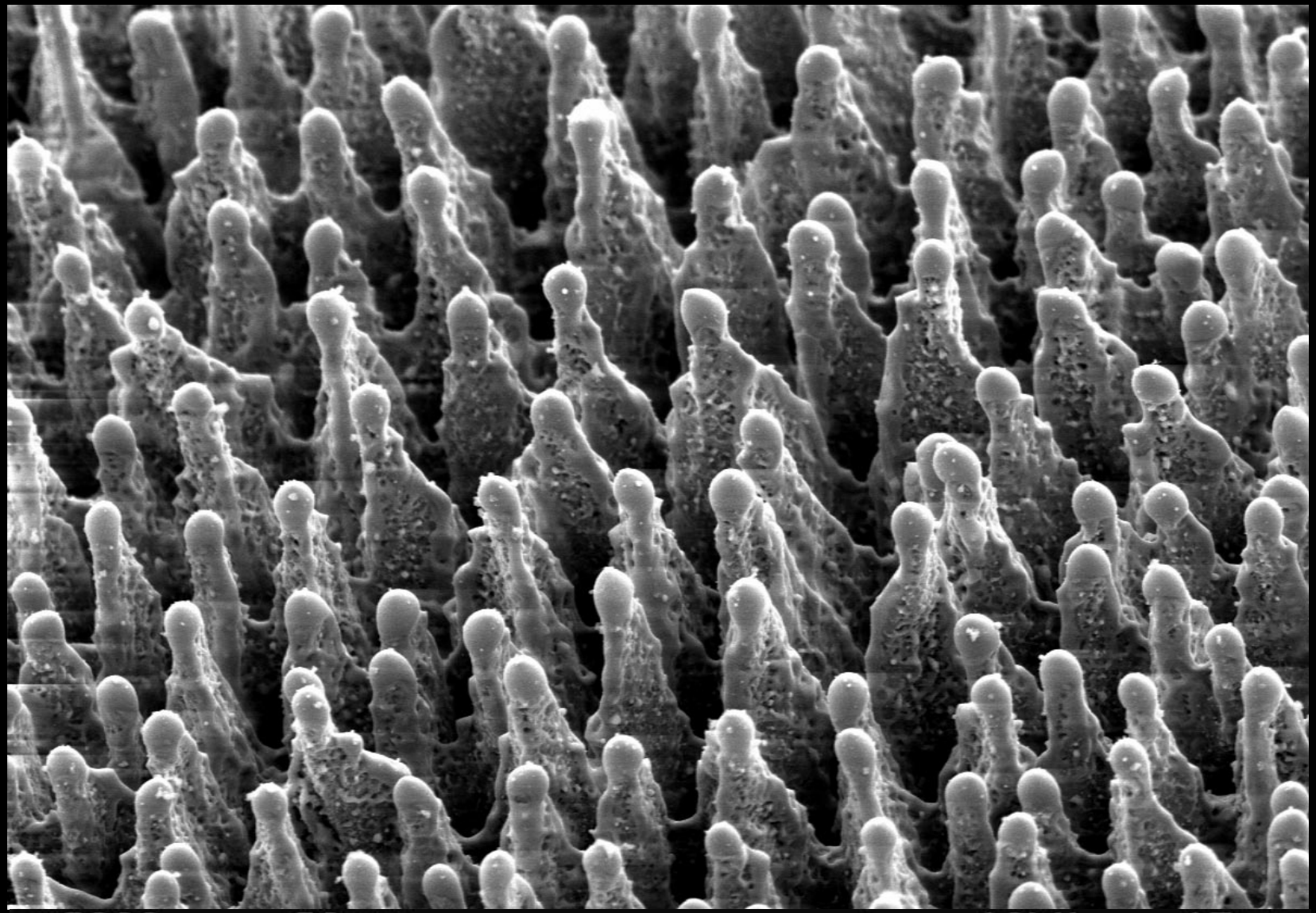
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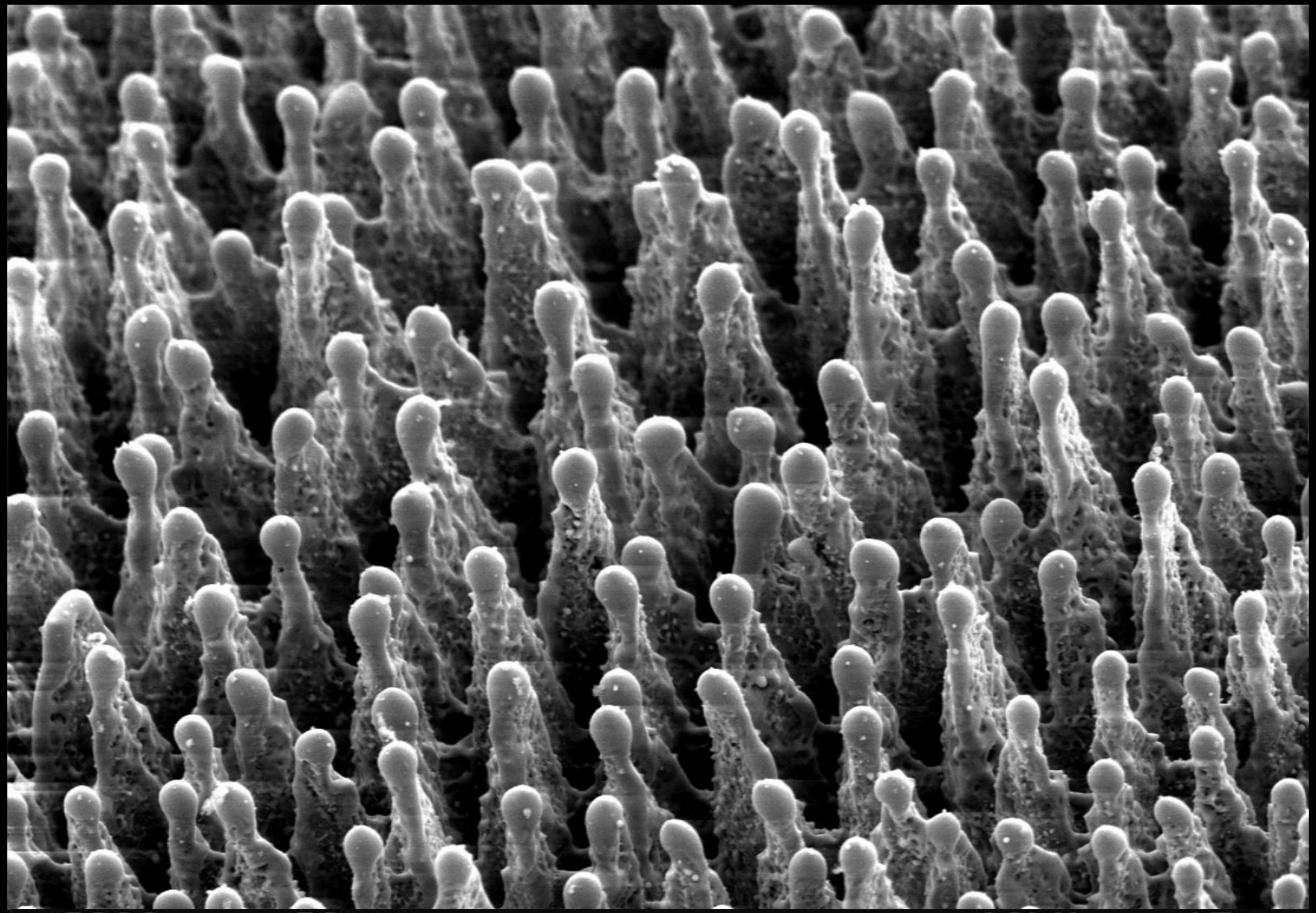
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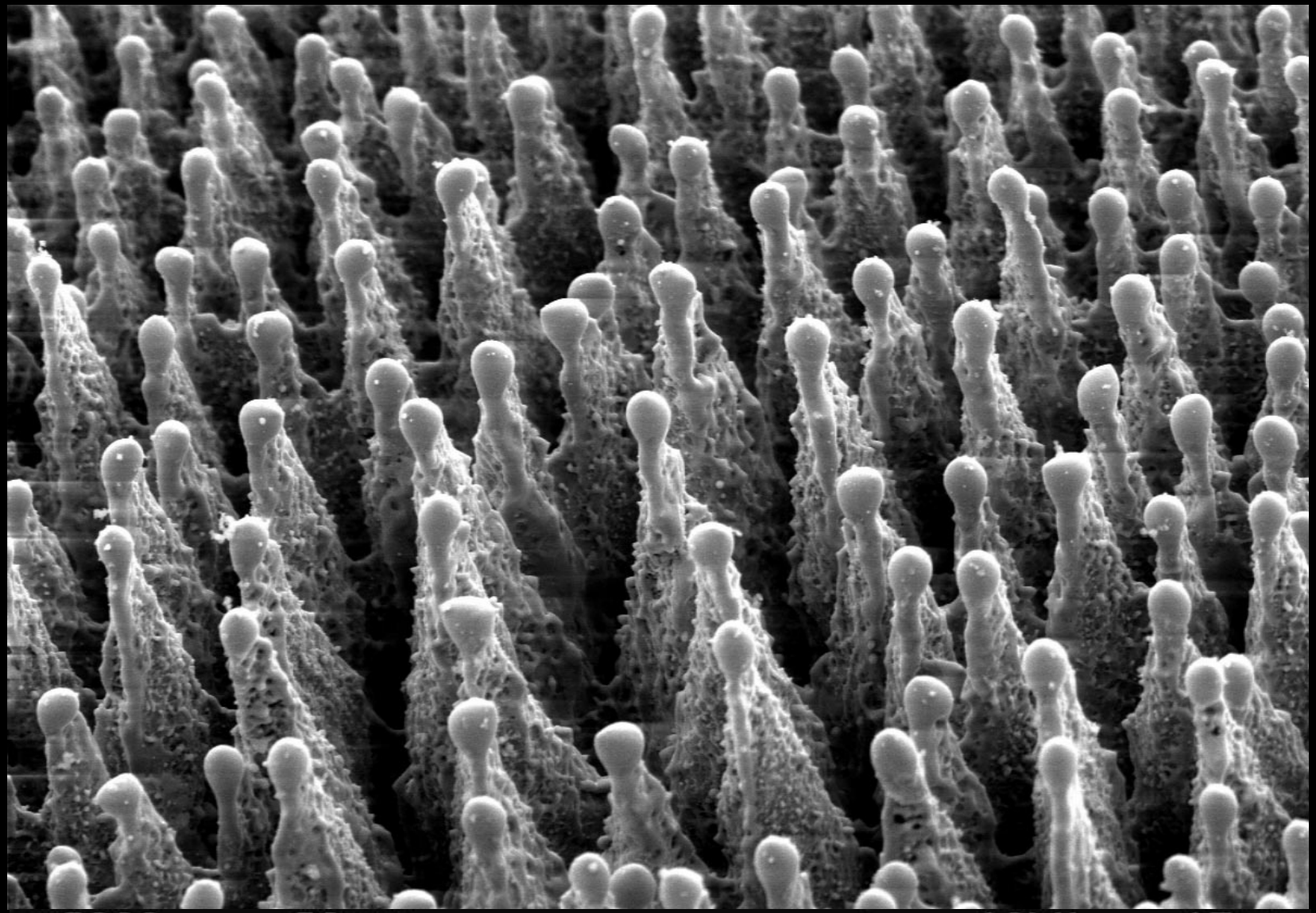
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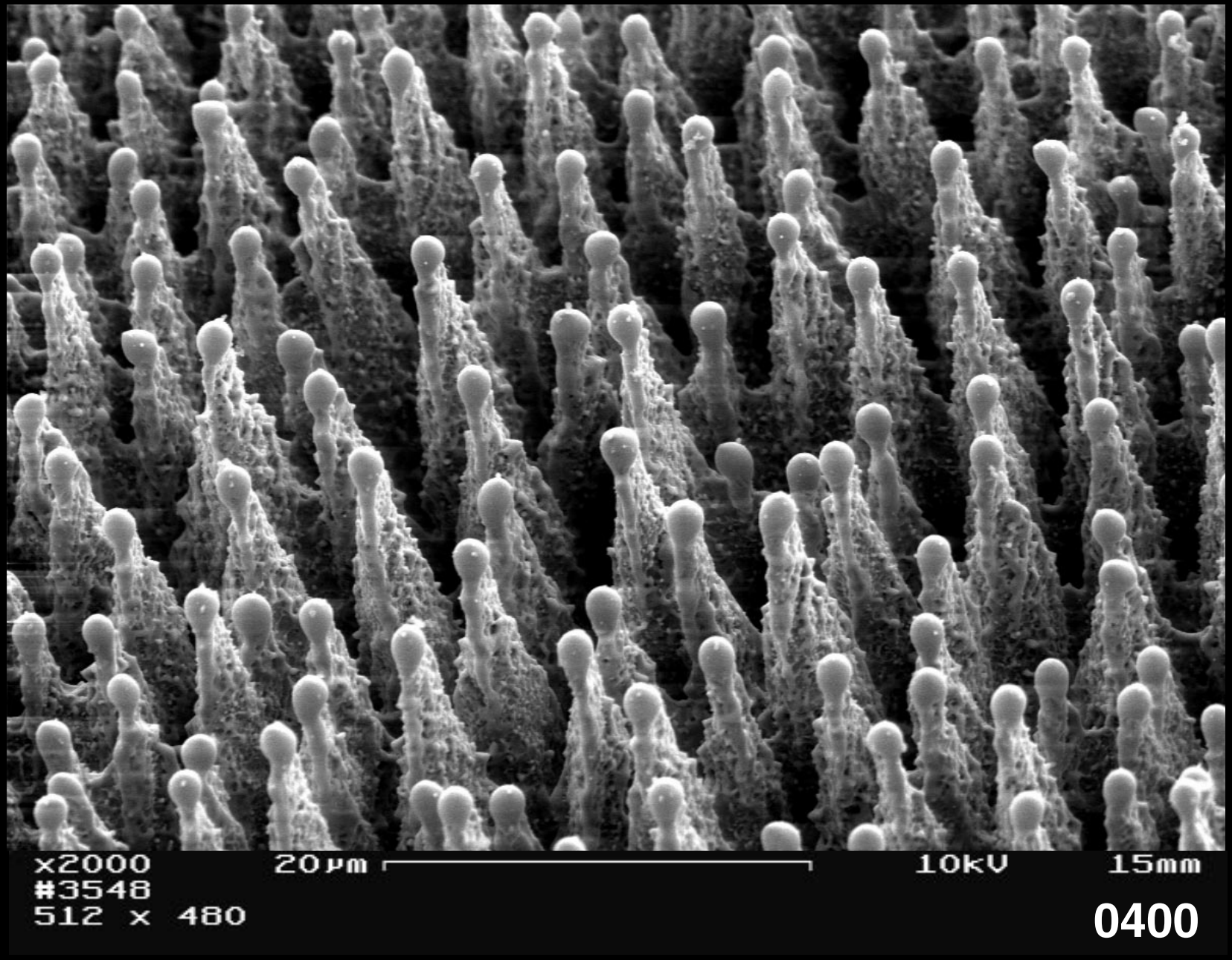
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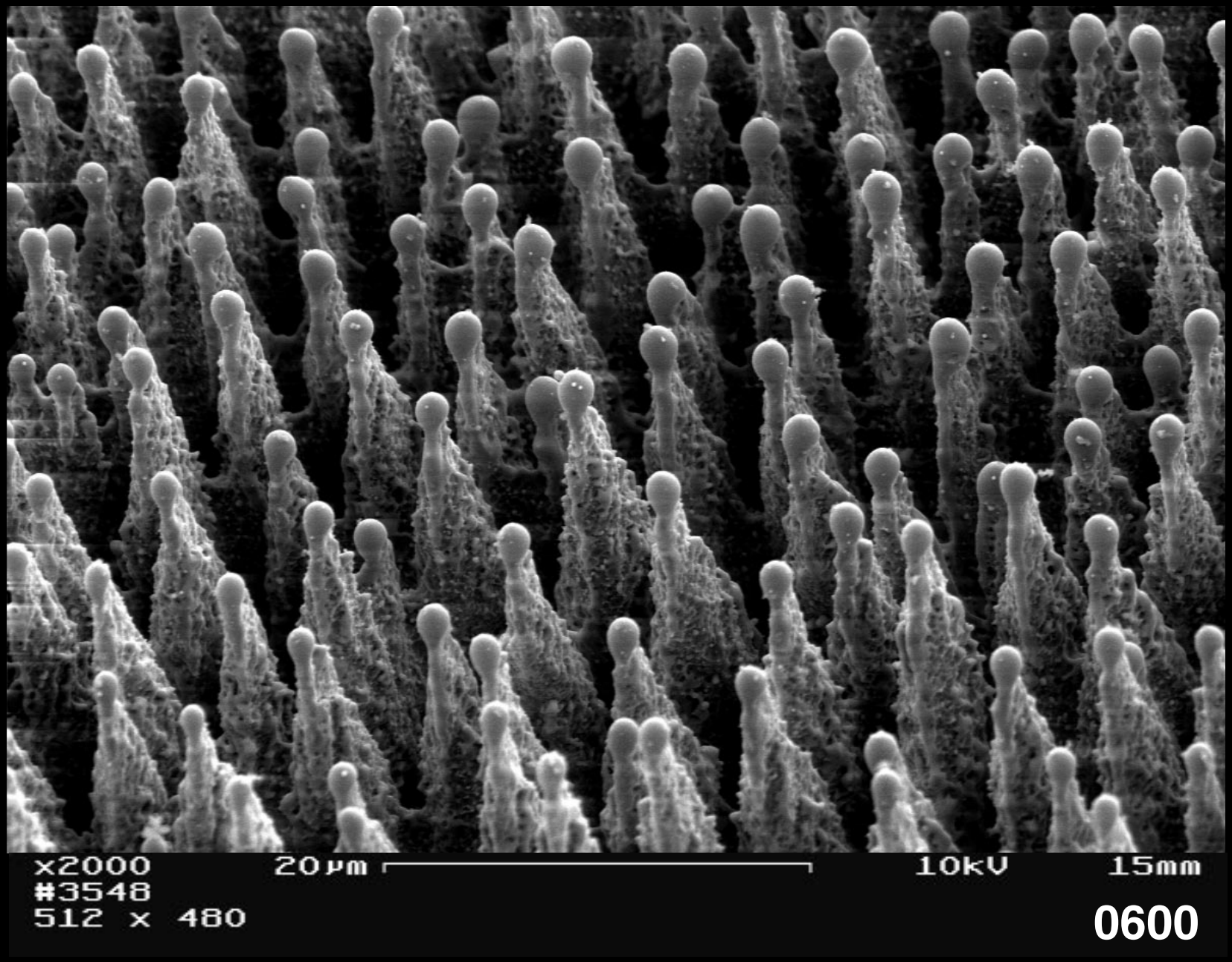
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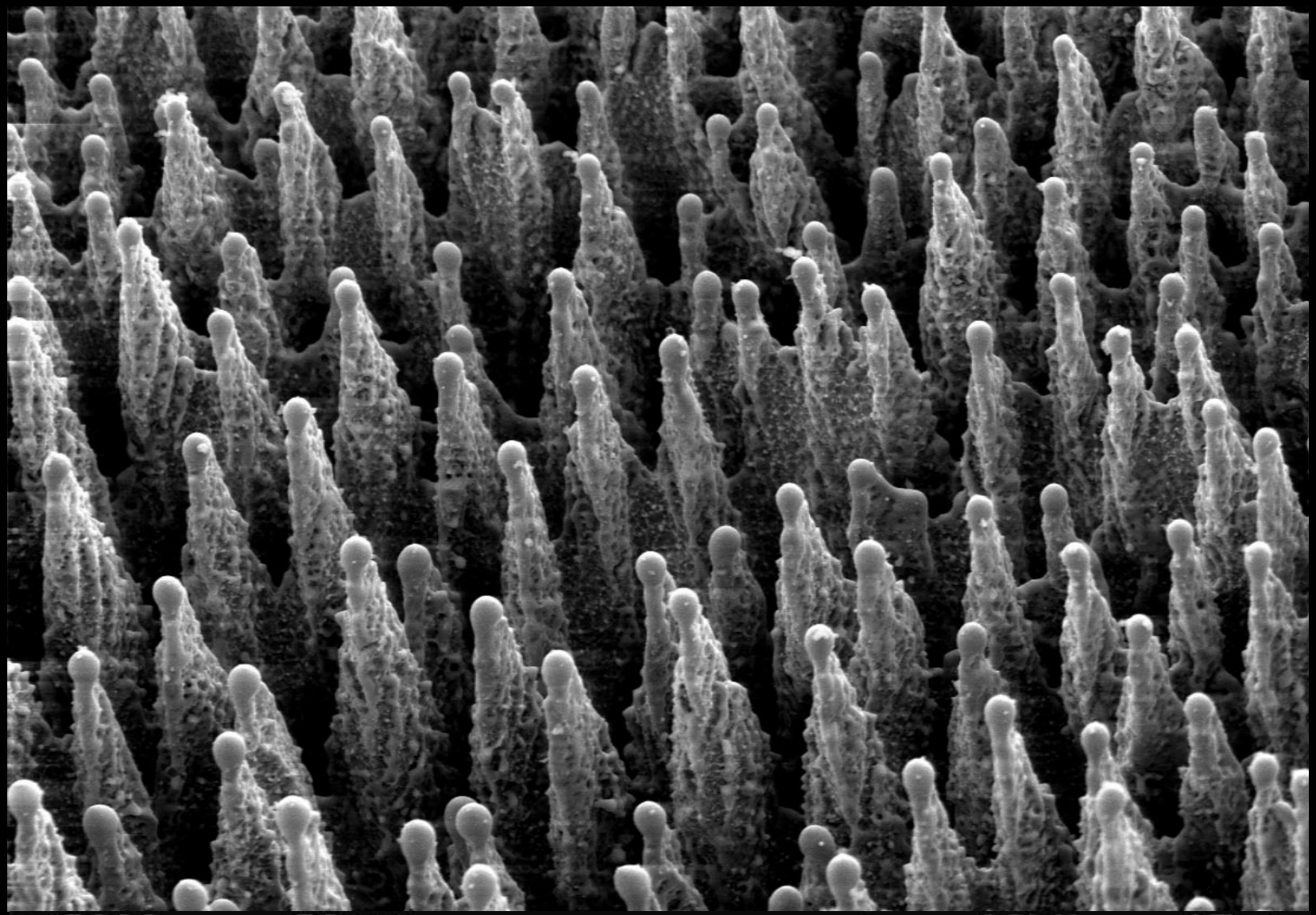
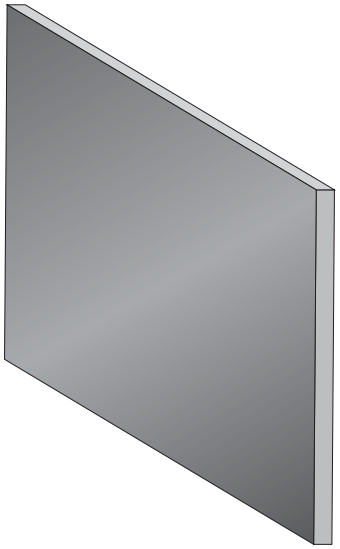

x2000
#3548
512 x 480
20µm
10kV
15mm
1000

Outlook

can ordering of spikes be improved by using a grid?

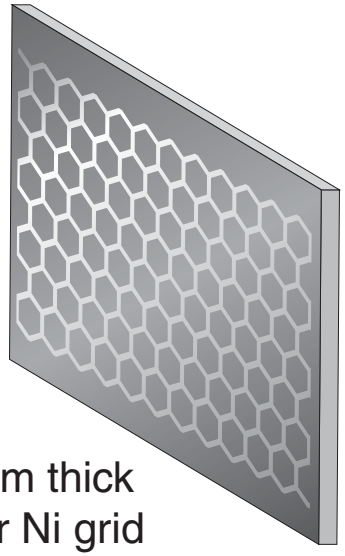
Outlook



Si or Ti substrate

Outlook

place grid in front of substrate

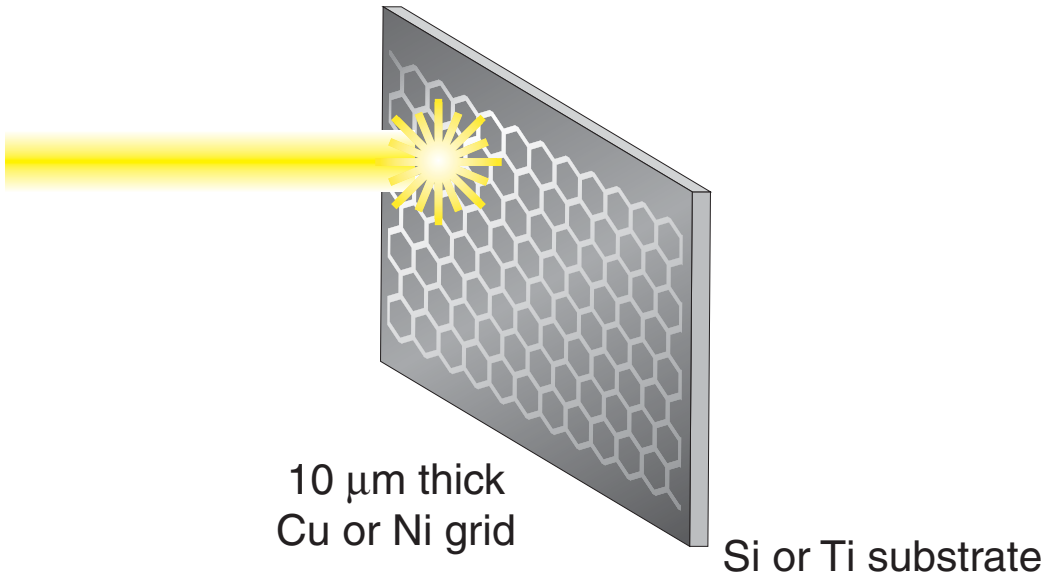


10 μm thick
Cu or Ni grid

Si or Ti substrate

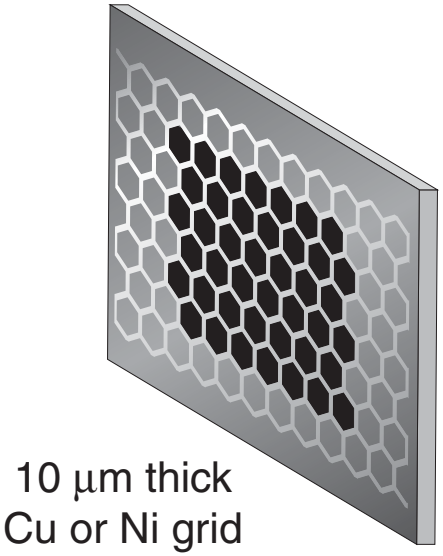
Outlook

scan laser beam



Outlook

scan laser beam

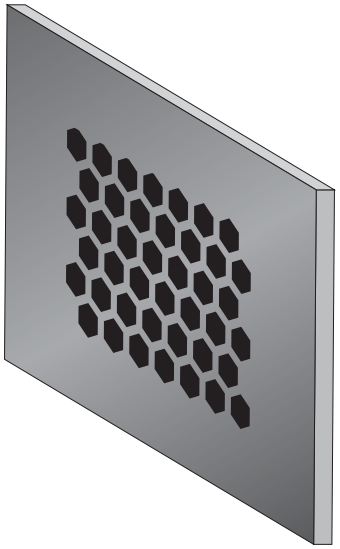


10 μm thick
Cu or Ni grid

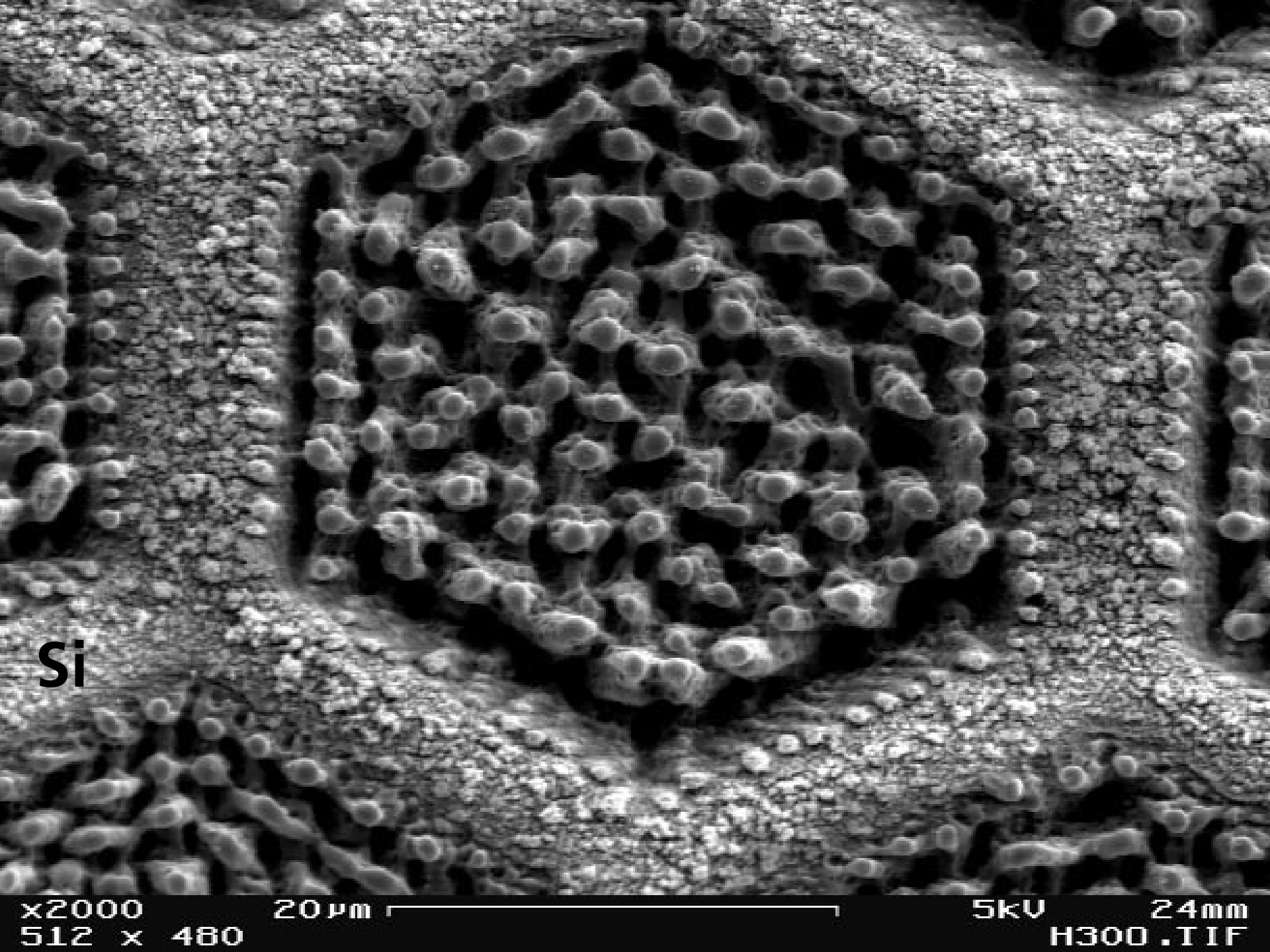
Si or Ti substrate

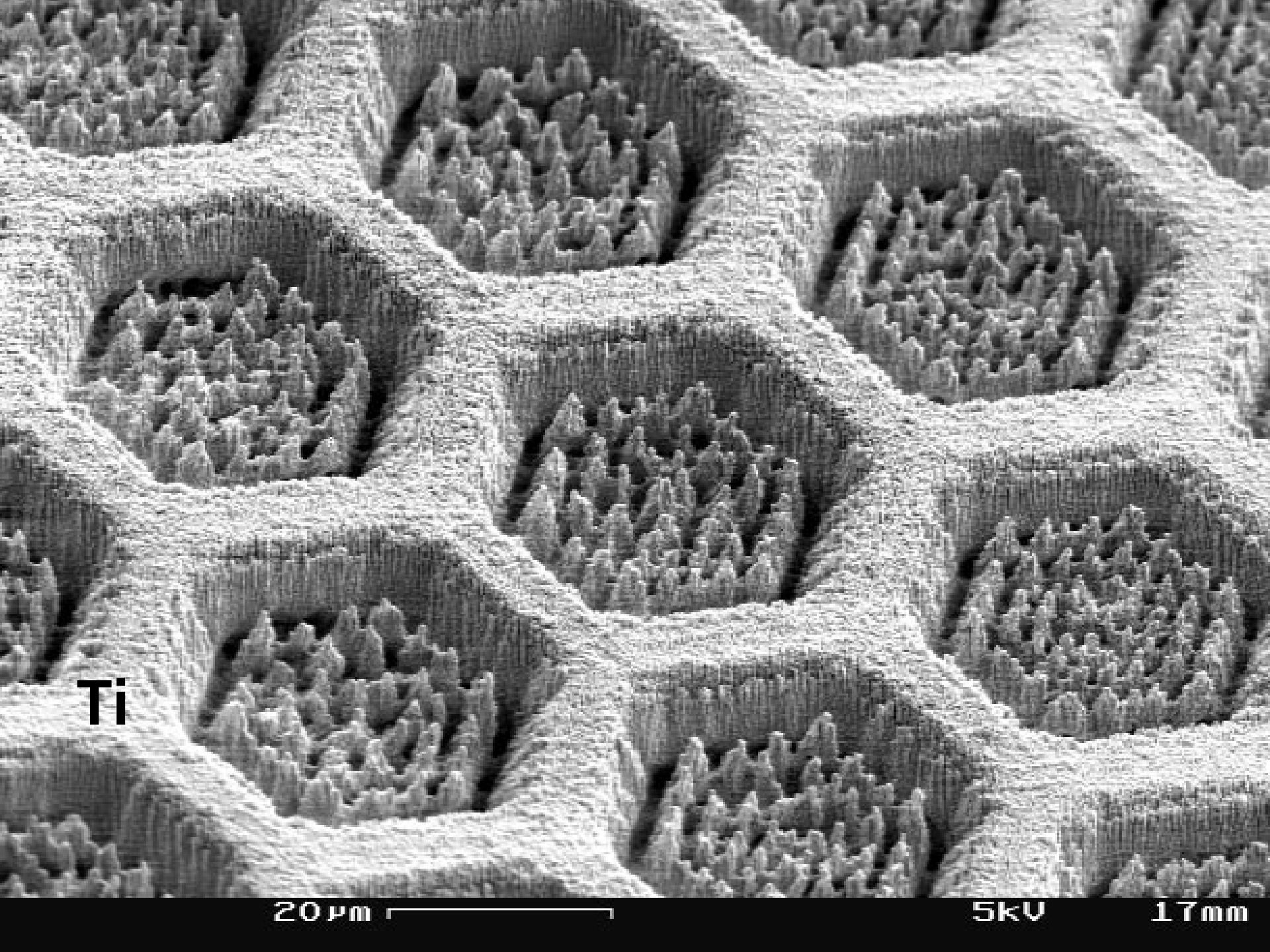
Outlook

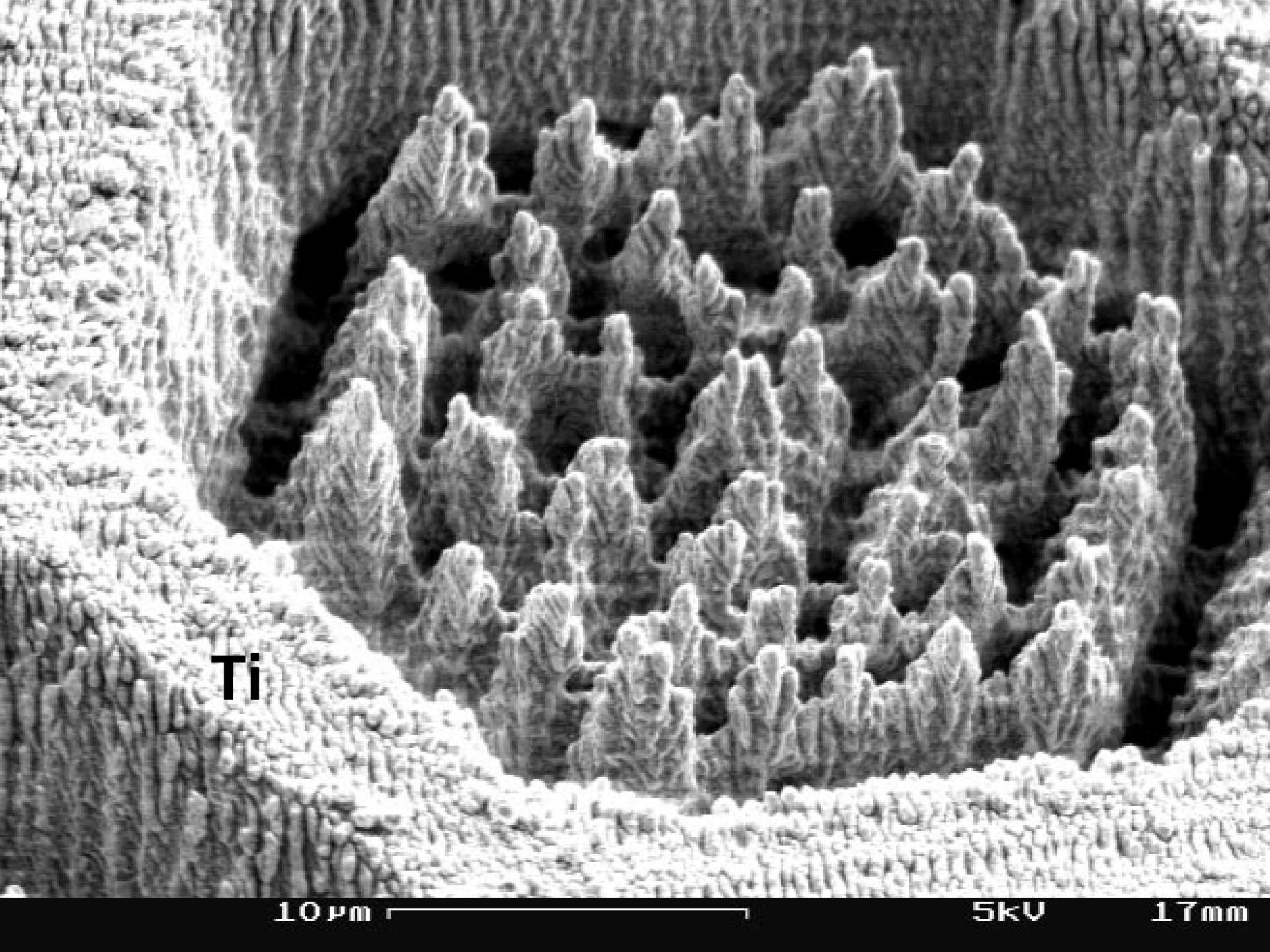
remove grid



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**

Summary

Microstructured silicon

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

Summary

Microstructured silicon

- **fabricated by simple, maskless process**
- **can be integrated with microelectronics**
- **generates IR photocurrent**
- **provides stable, high field emission current**

Summary

Microstructured silicon

- **fabricated by simple, maskless process**
- **can be integrated with microelectronics**
- **generates IR photocurrent**
- **provides stable, high field emission current**
- **is durable**


GORDON McKAY
LABORATORY OF
APPLIED SCIENCE

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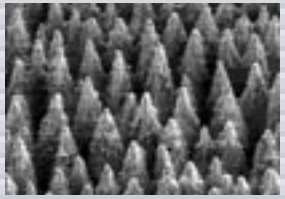
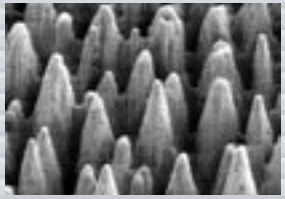
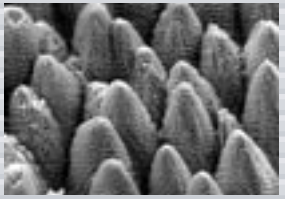
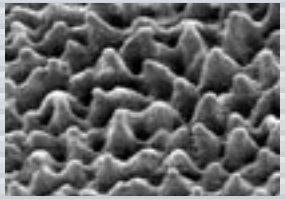
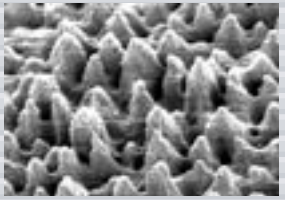
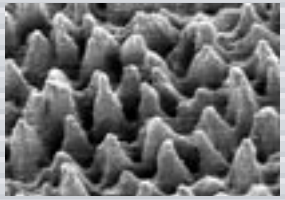
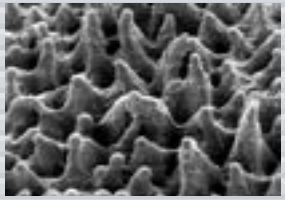
Dr. John Chervinsky (Harvard University)
Prof. Cynthia Friend (Harvard University)
Prof. Mike Aziz (Harvard University)

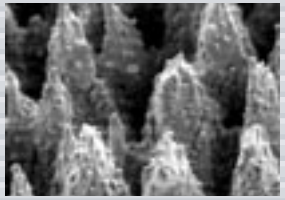
For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu

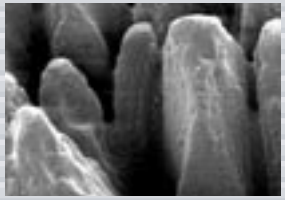
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti		reacts			

Only in SF_6:



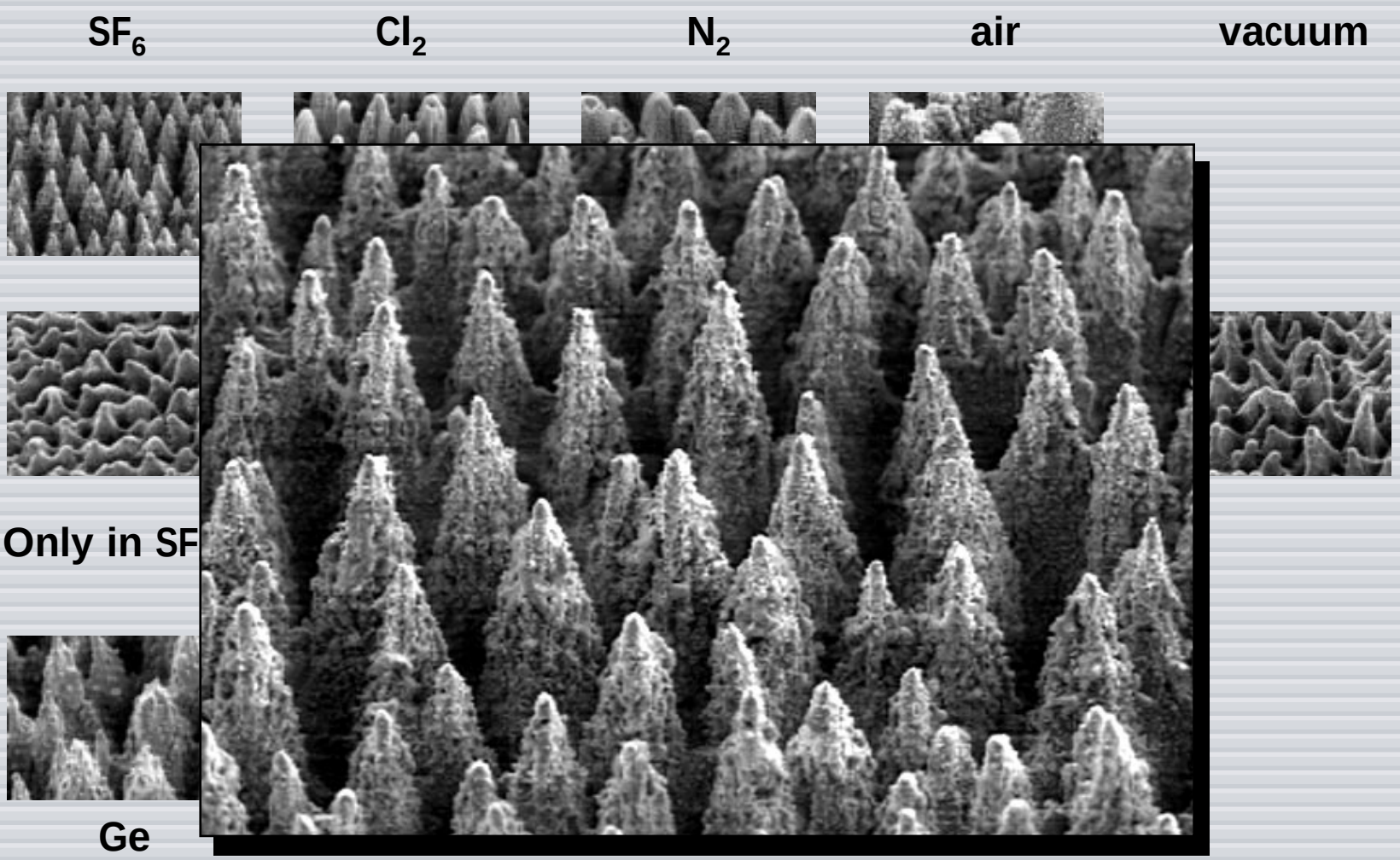
Ge



InP

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

Materials



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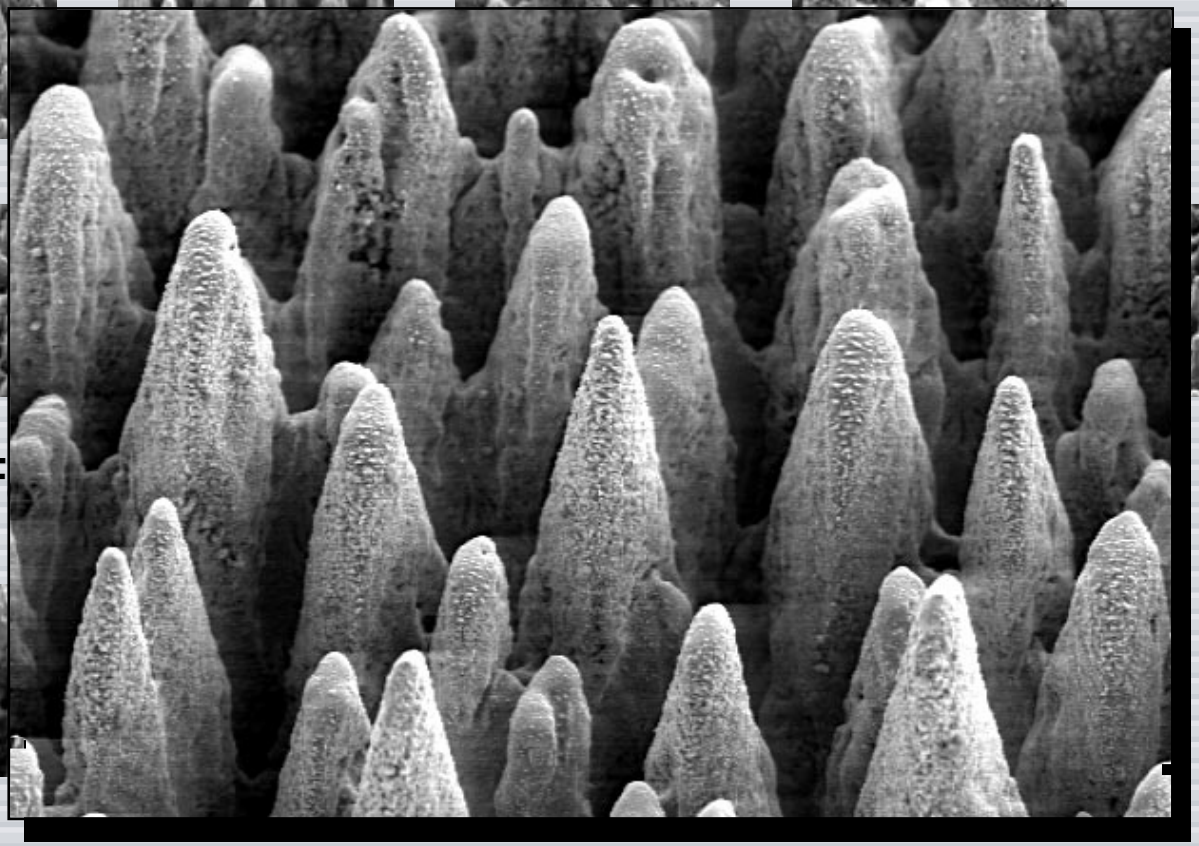
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Only in SF					
Ge					



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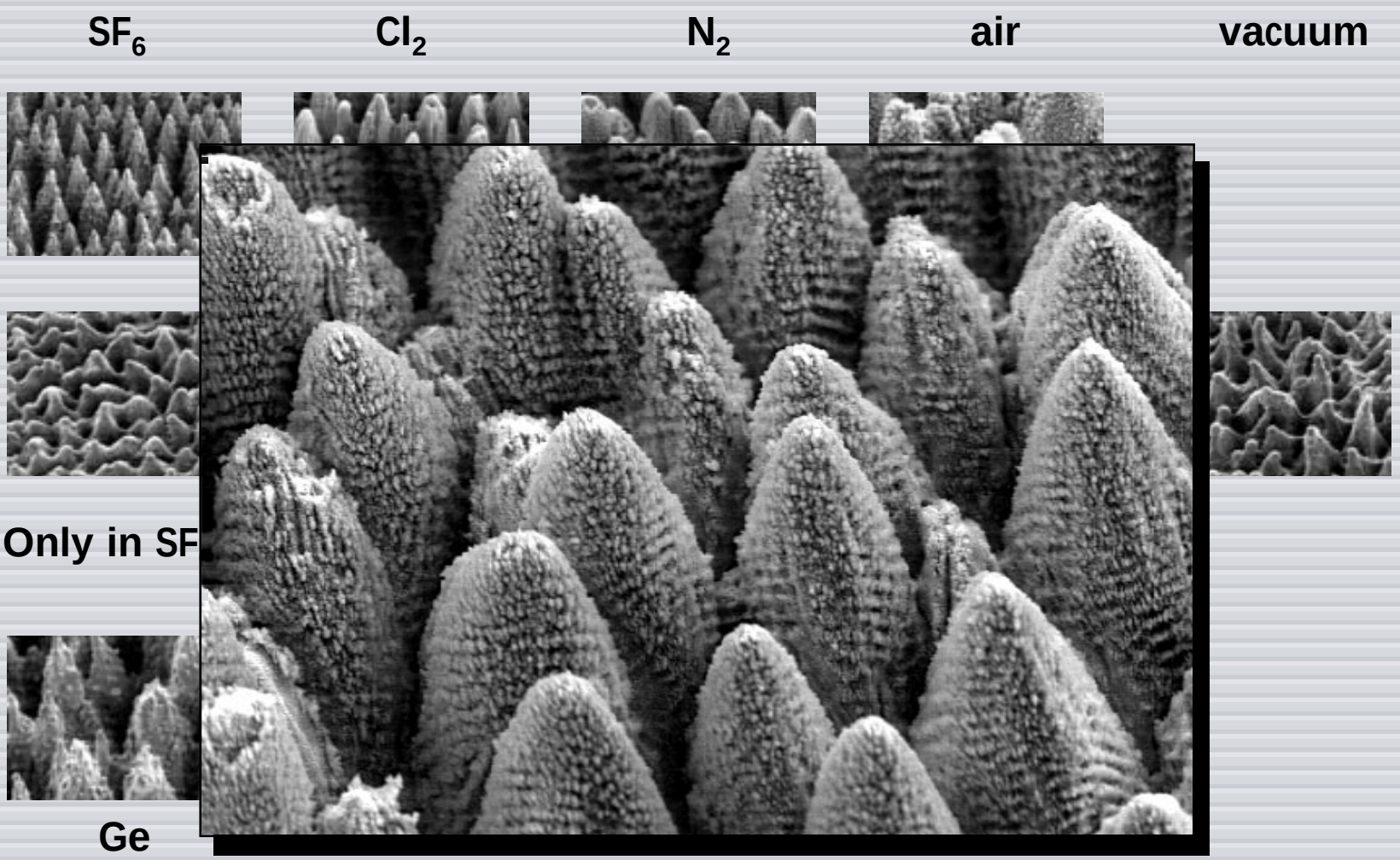
Materials



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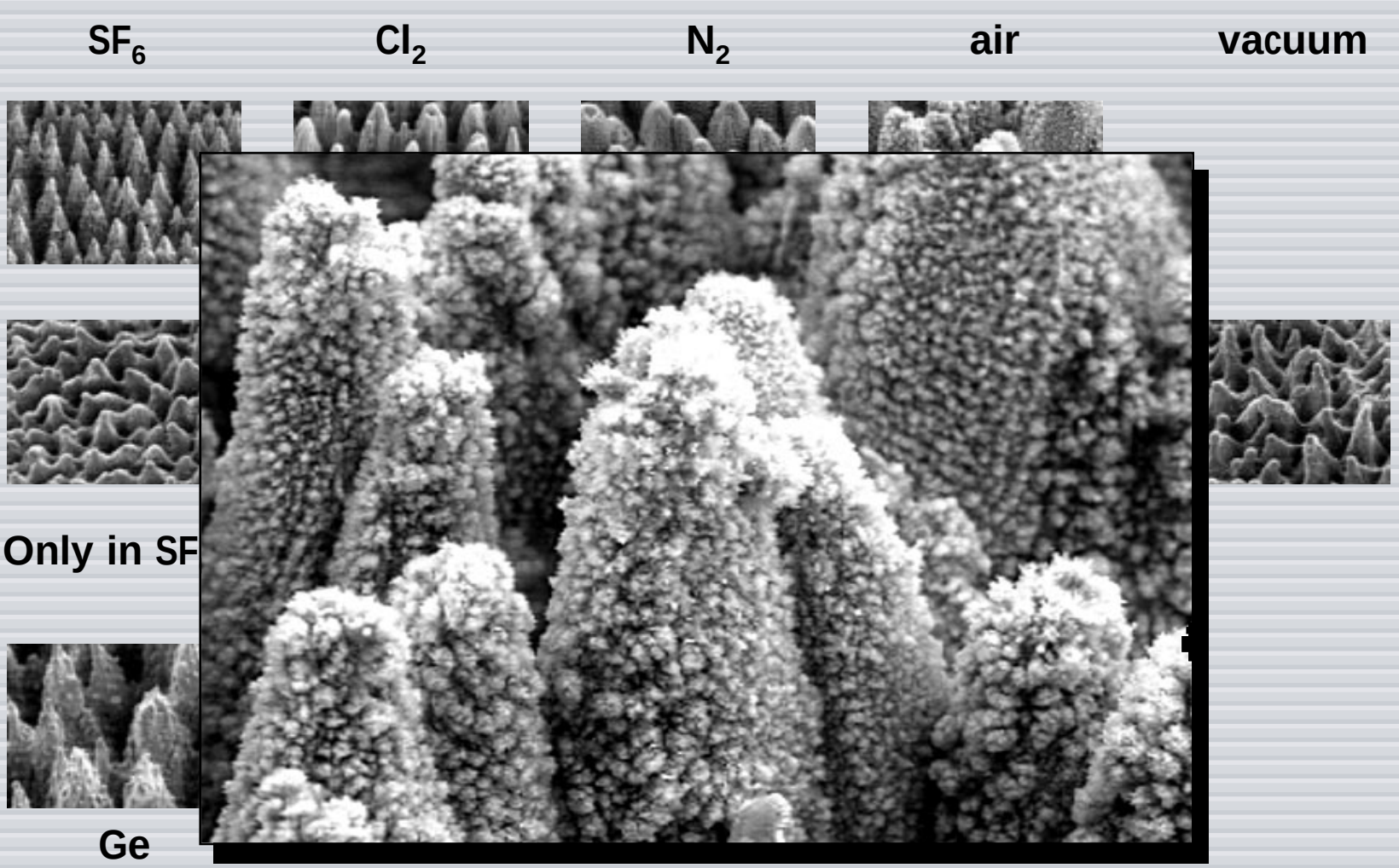
Materials



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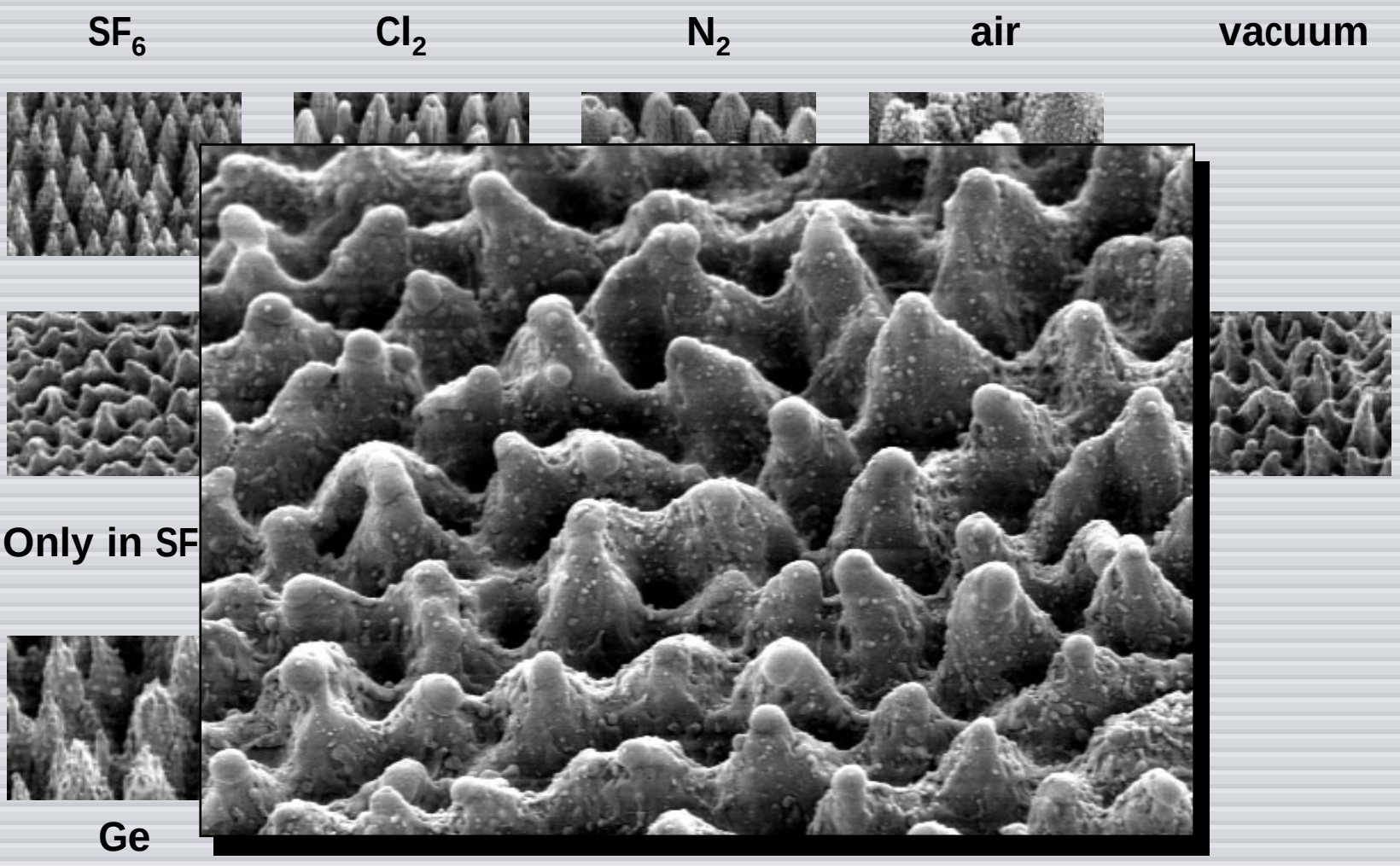
Materials



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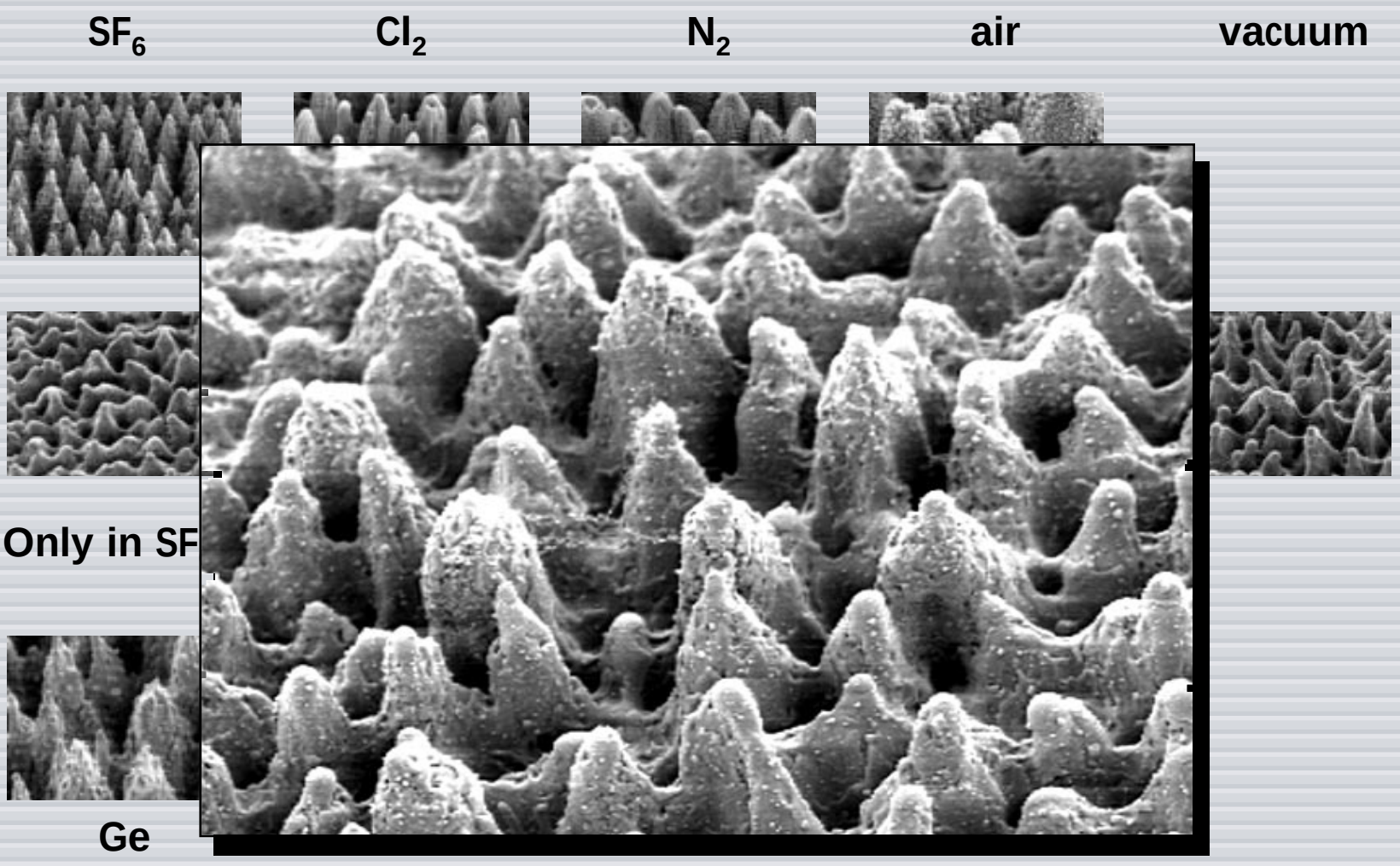
Materials



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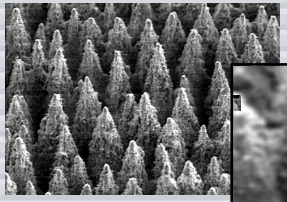
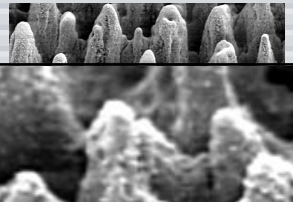
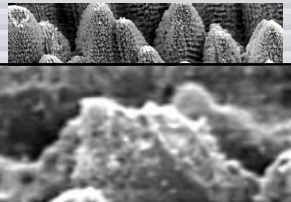
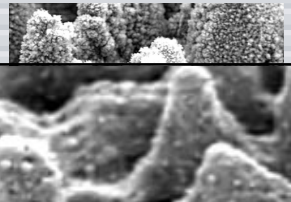
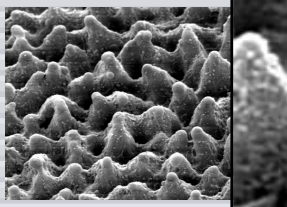
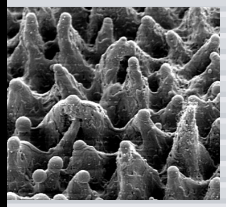
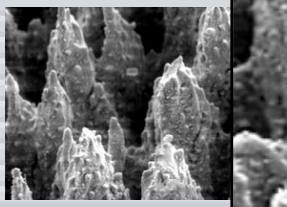
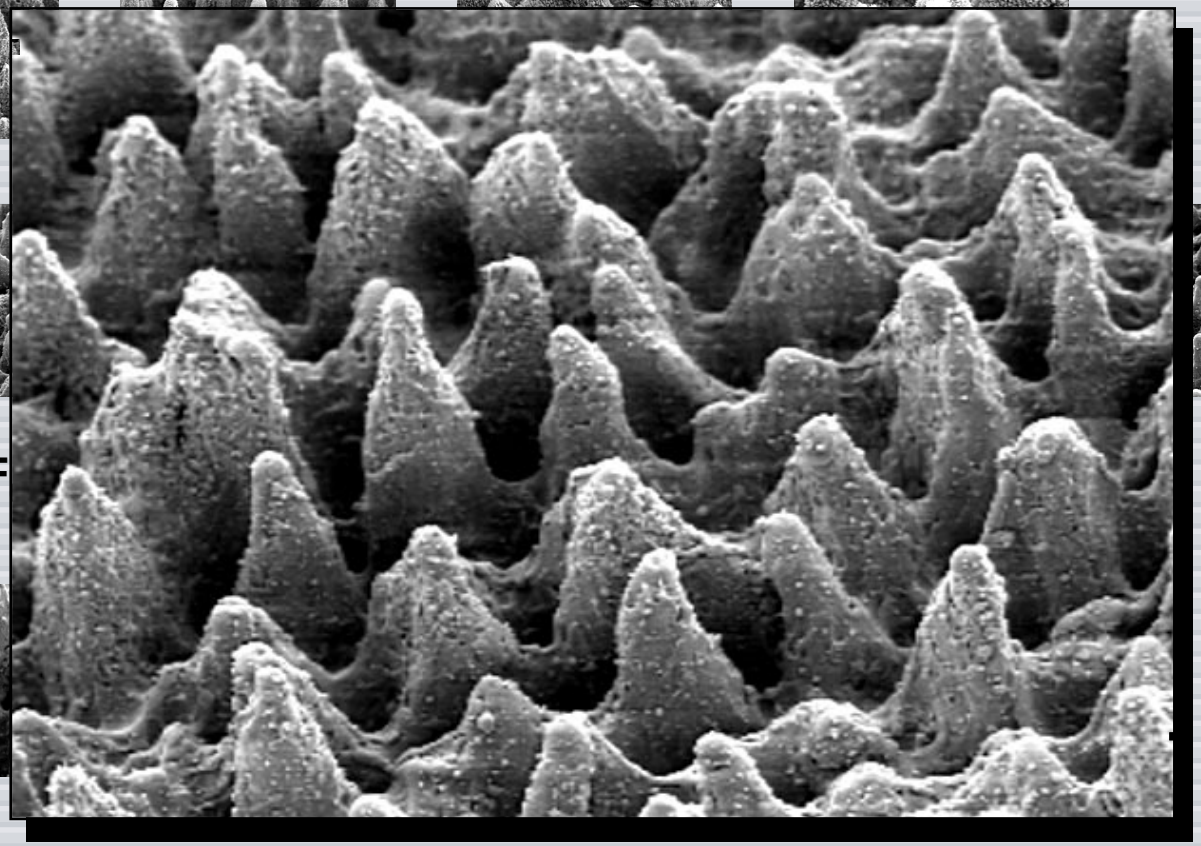
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Only in SF					
Ge					



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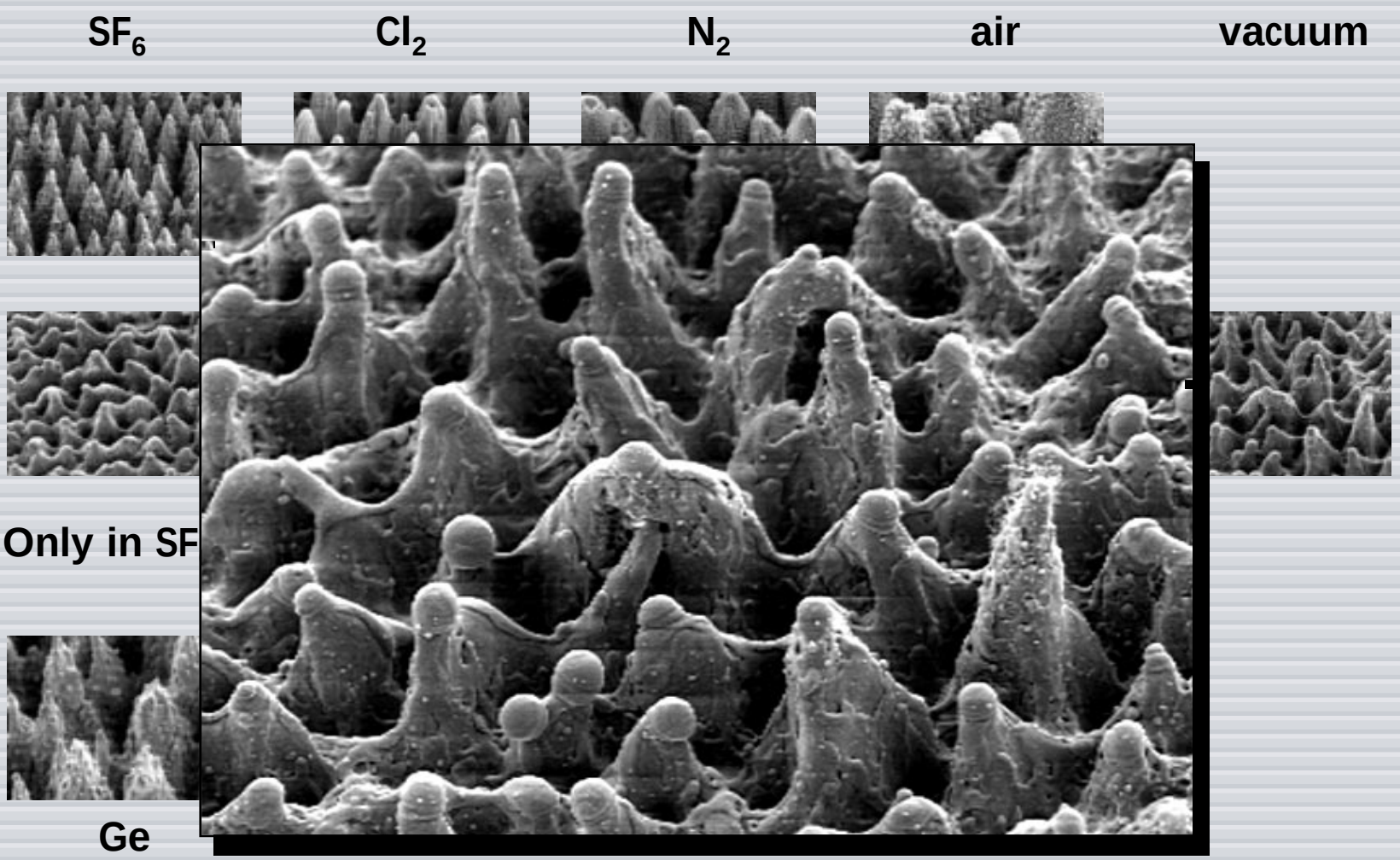
Materials



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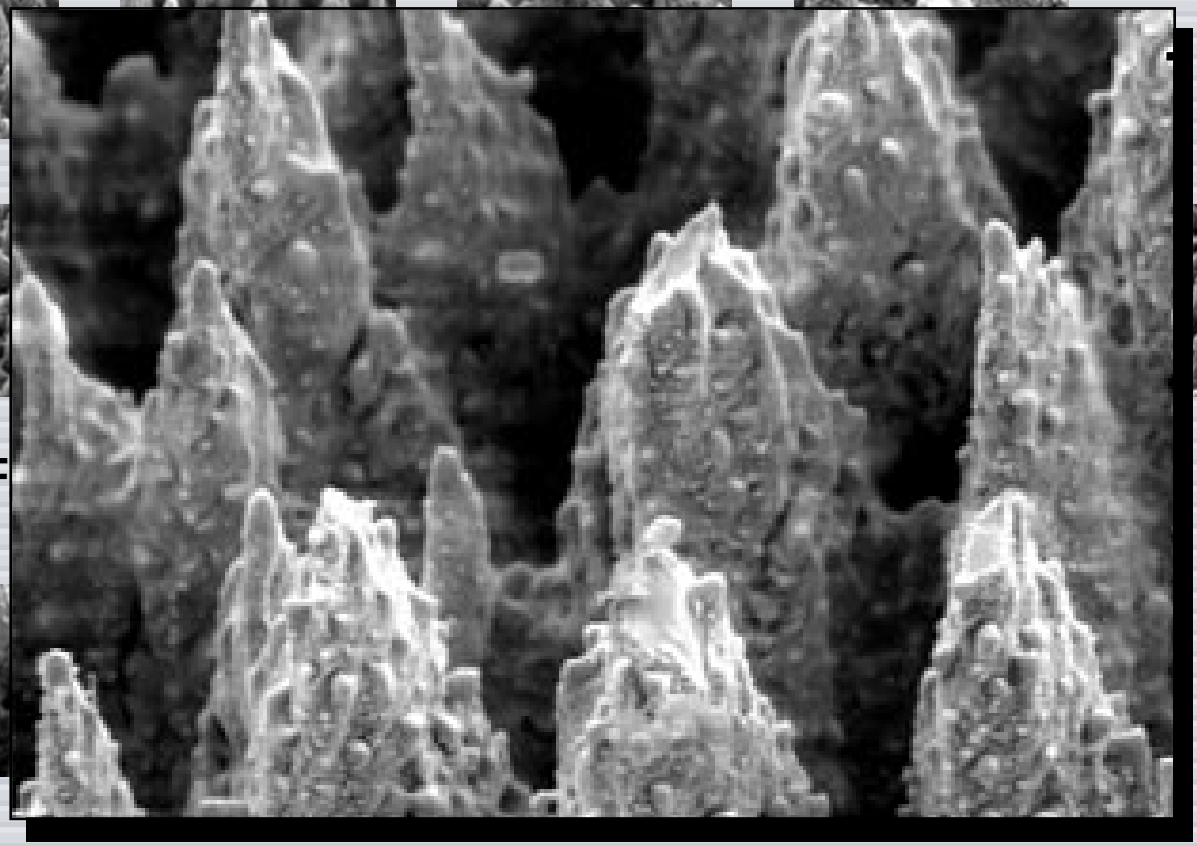
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					



Only in SF_6

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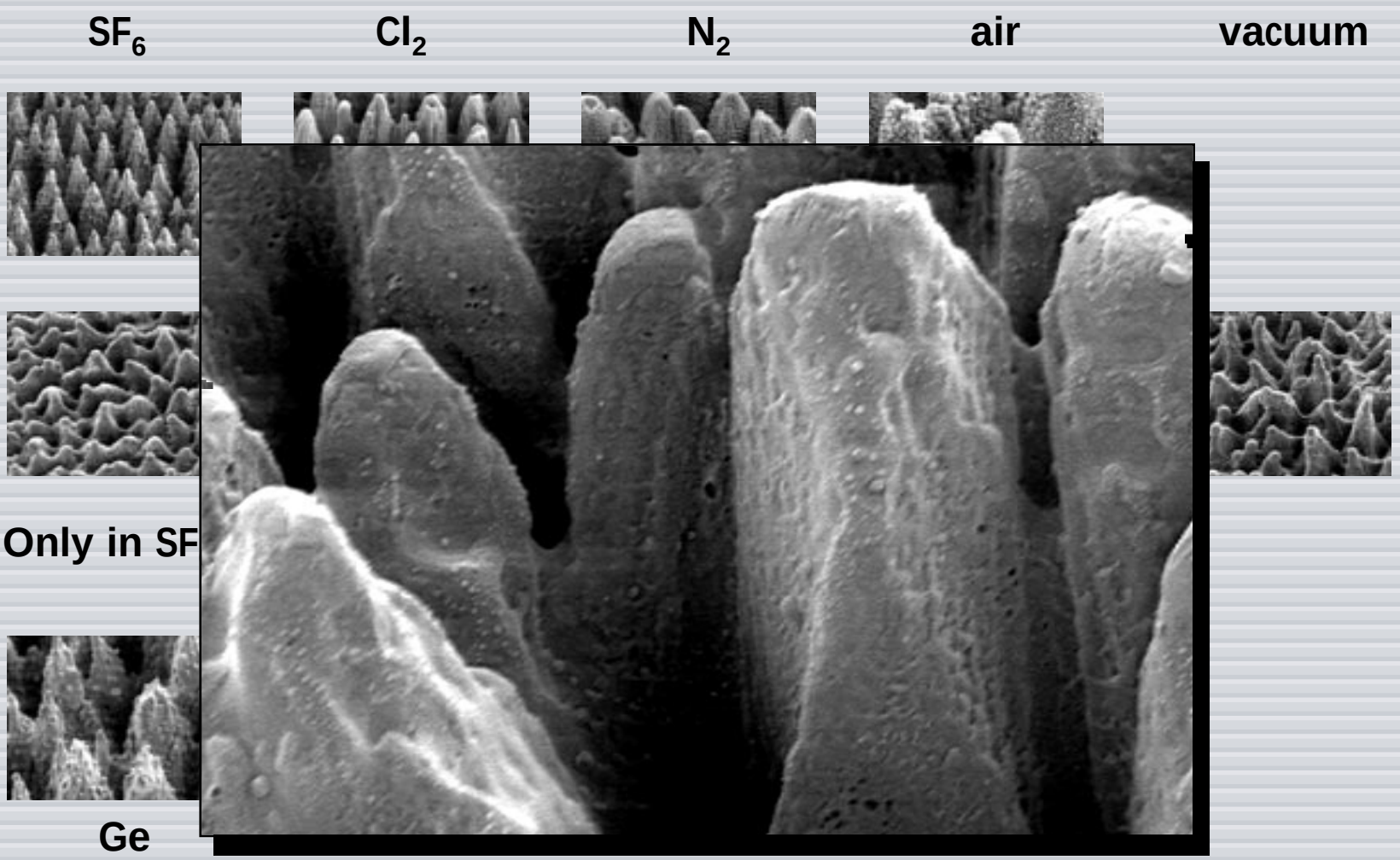
Materials



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