

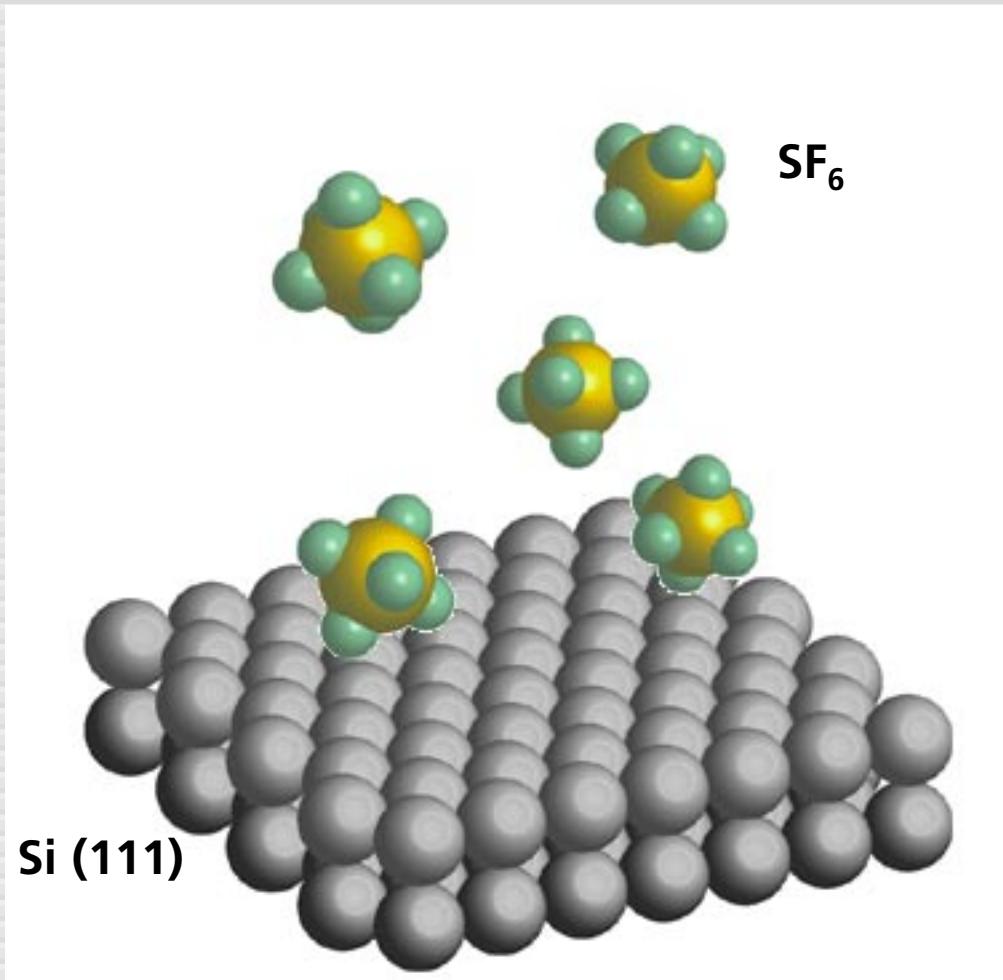
Fabrication of micrometer-sized conical field emitters using femtosecond laser-assisted etching of silicon

**Eric Mazur
Jim Carey
Catherine Crouch
Rebecca Younkin**

**MRS Spring Meeting
San Francisco, 20 April 2001**

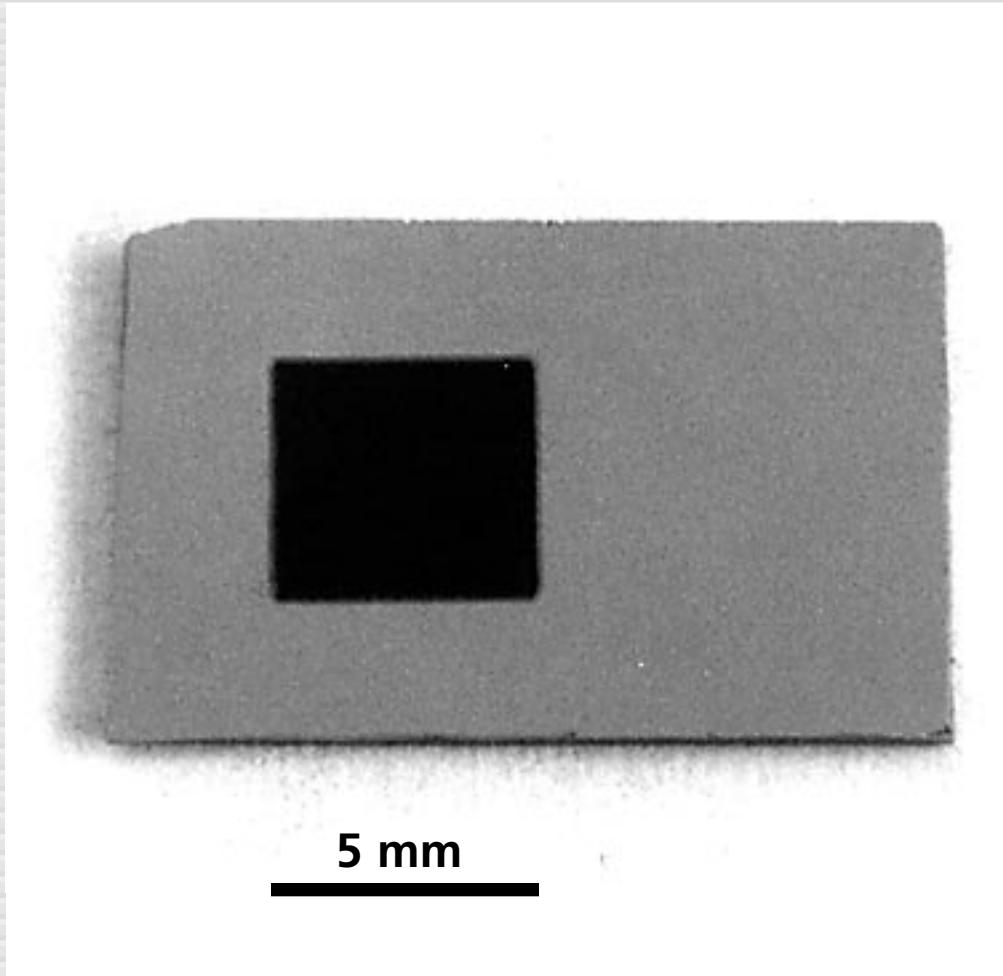


Introduction



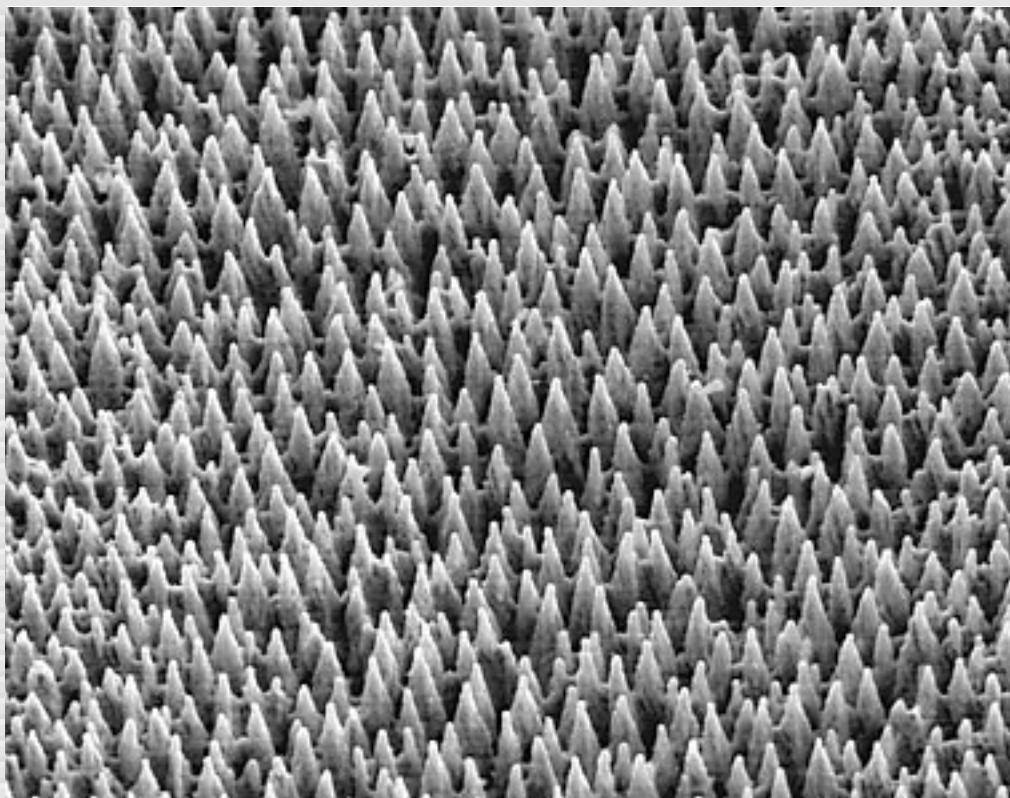
irradiate with 100-fs 10 kJ/m^2 pulses

Introduction



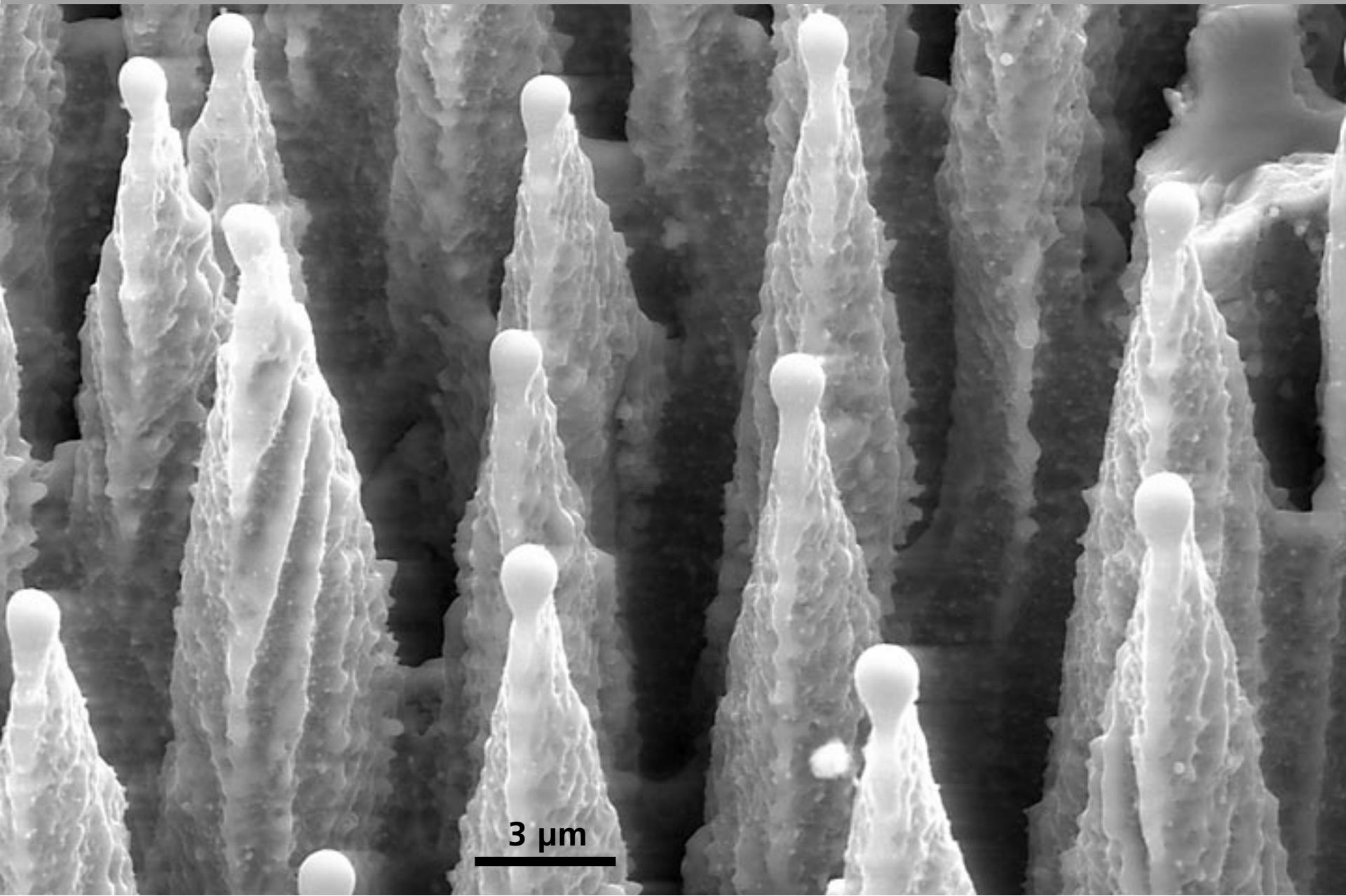
"black silicon"

Introduction

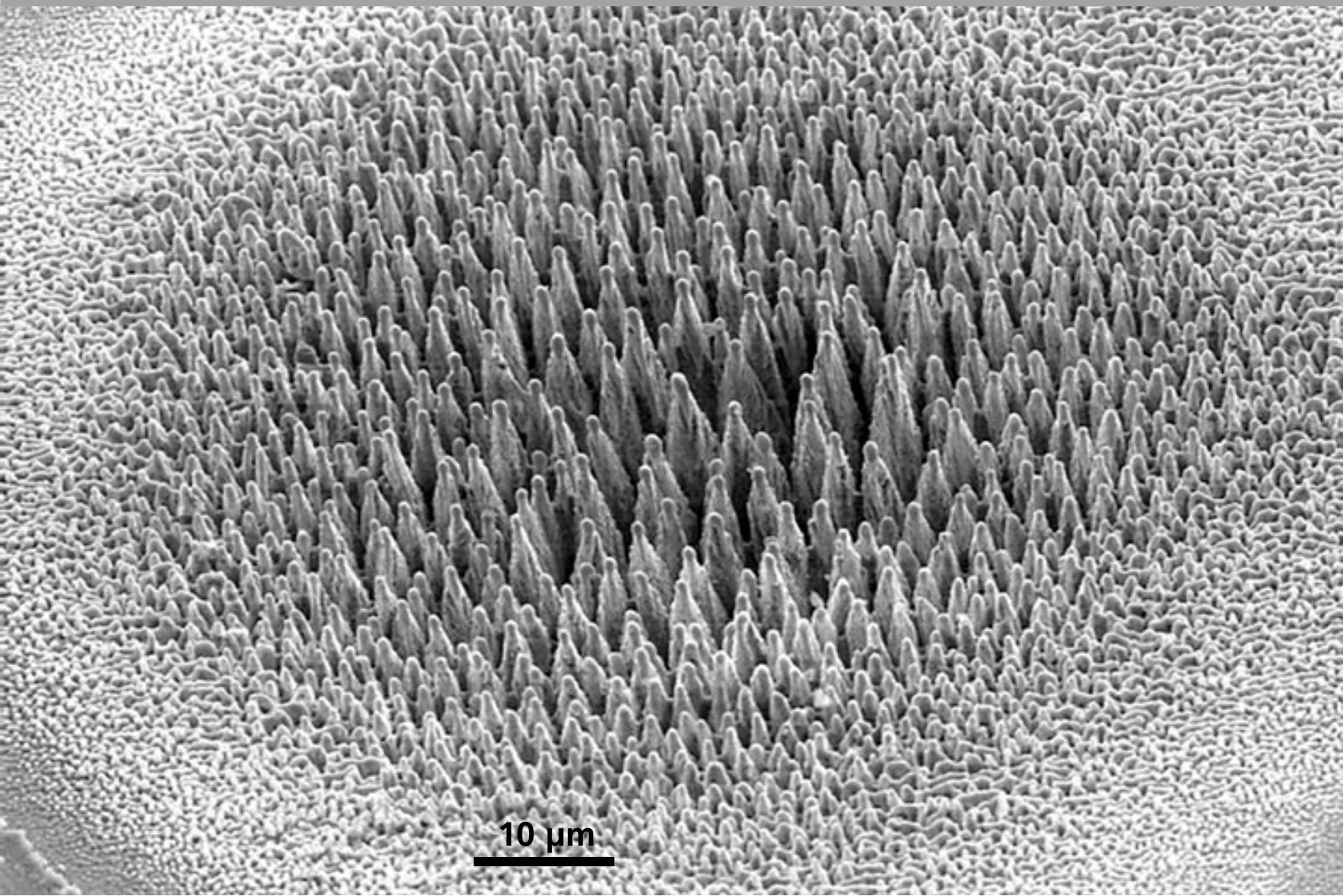


20 μm

Introduction



Introduction



Outline

- ▶ **Background**
- ▶ **Results**
- ▶ **Discussion**

x2000

#3548

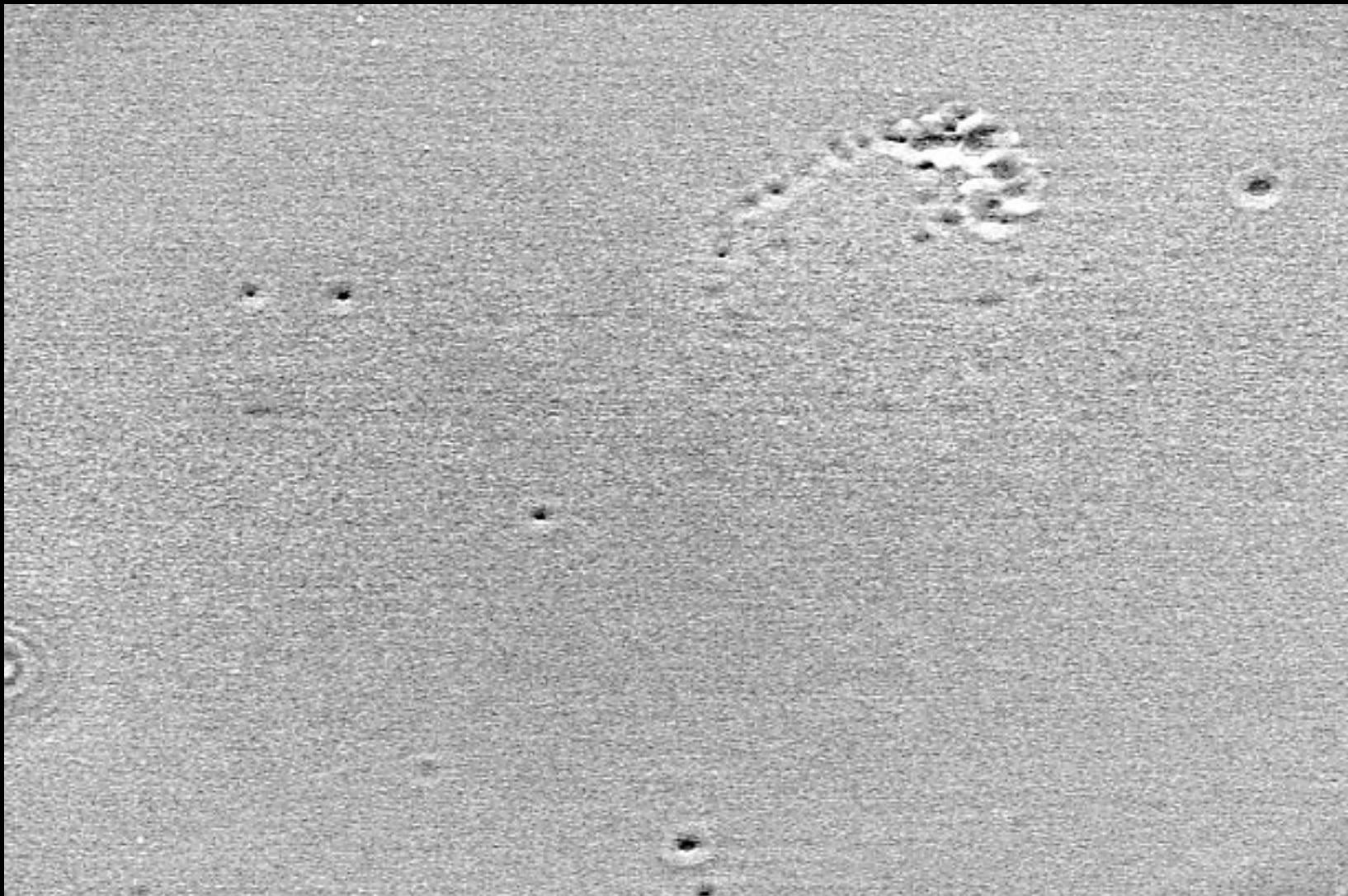
512 x 480

20 μ m

10kV

15mm

0000



x2000

#3548

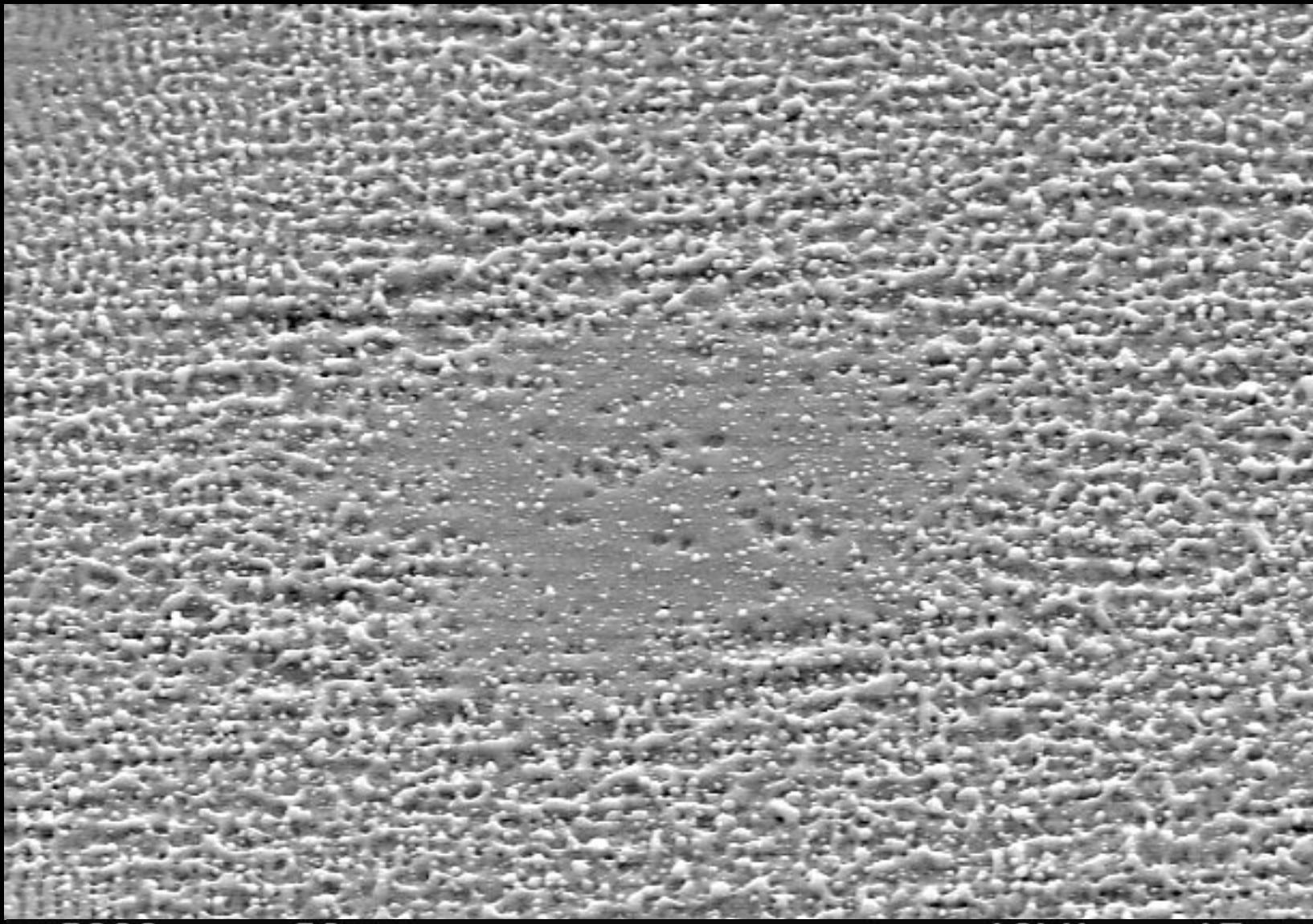
512 x 480

20 μm

10kV

15mm

0001



x2000

#3548

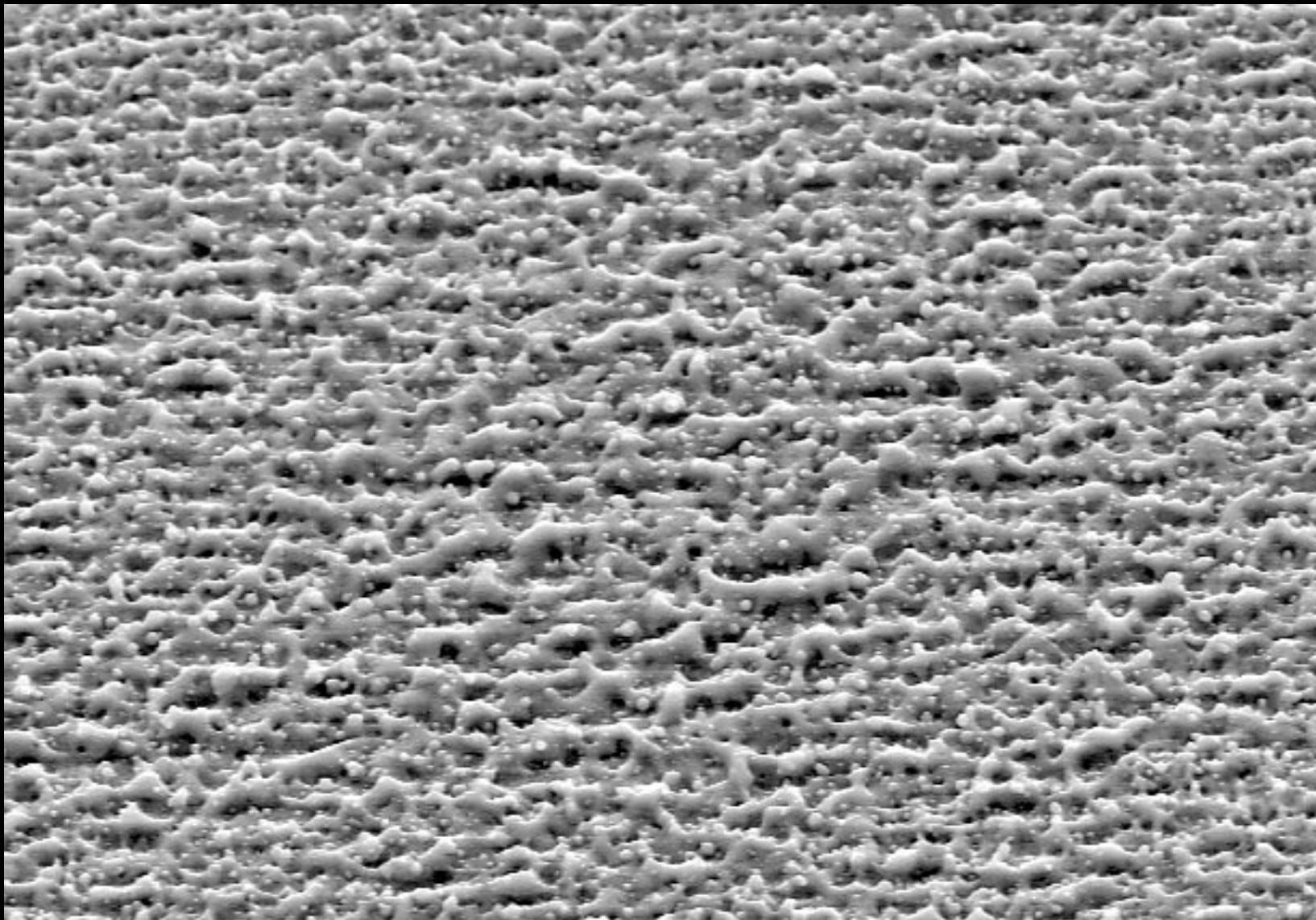
512 x 480

20 μm

10kV

15mm

0005



x2000

#3548

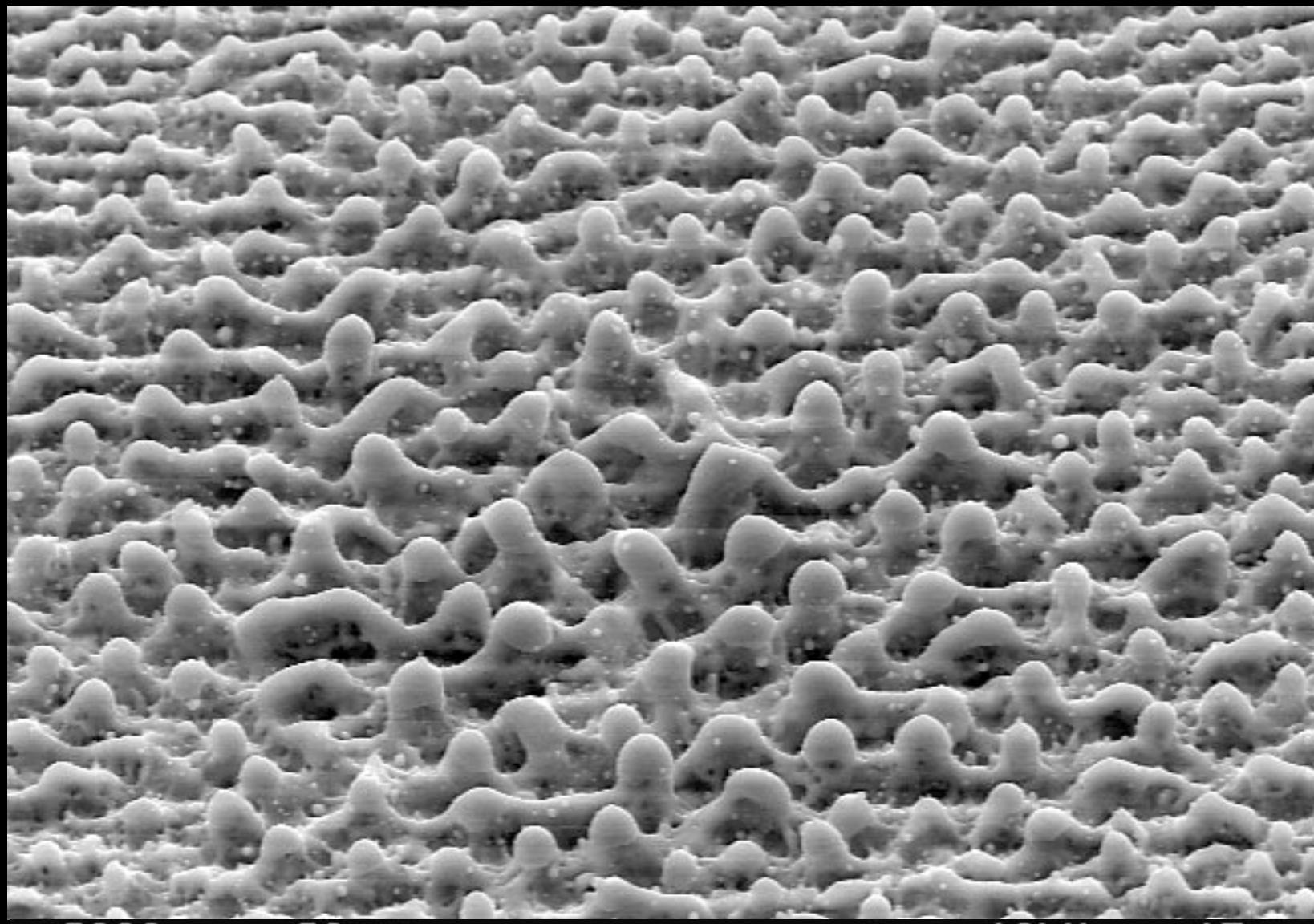
512 x 480

20 μm

10kV

15mm

0010



x2000

#3548

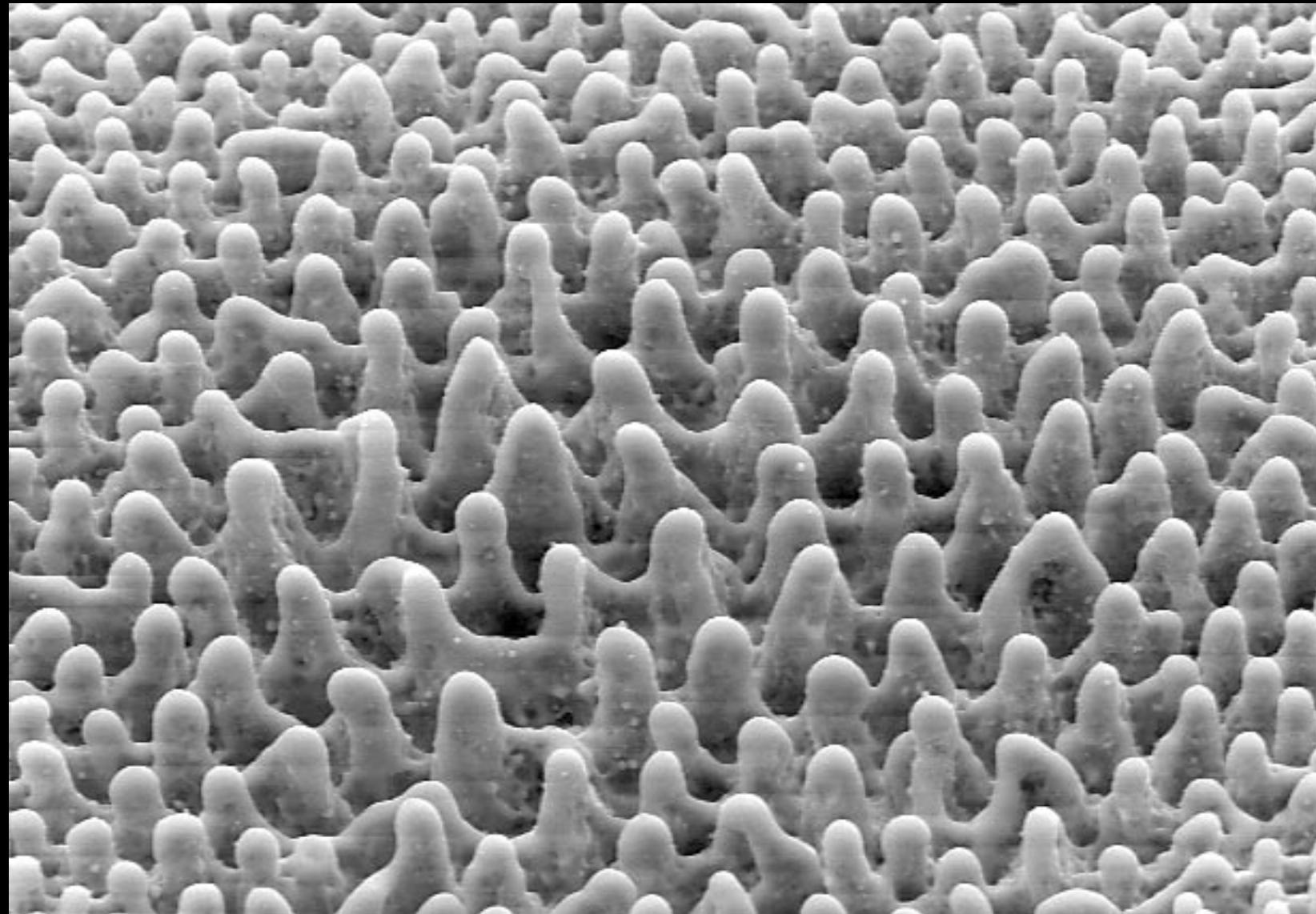
512 x 480

20 μm

10kV

15mm

0025



x2000

#3548

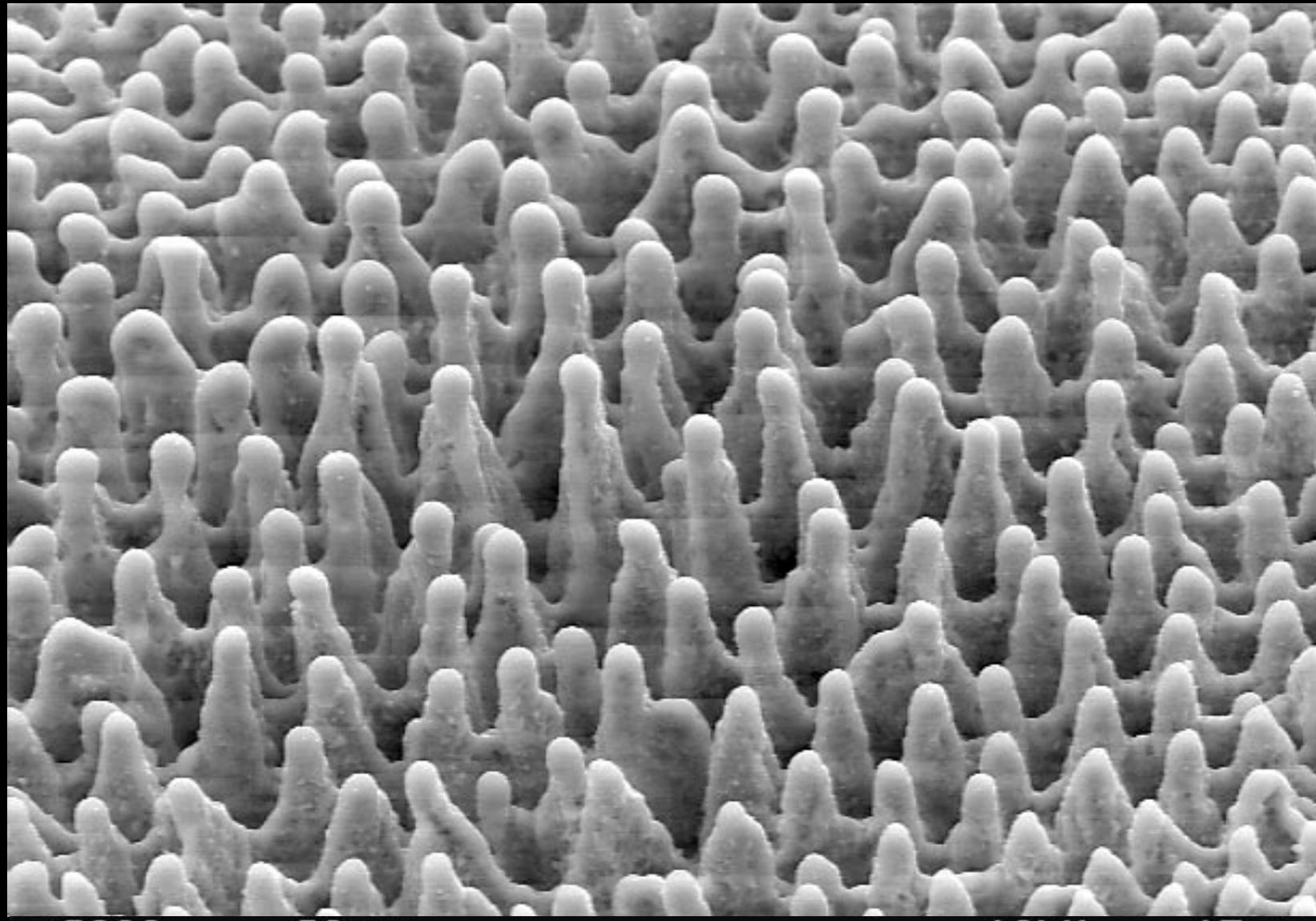
512 x 480

20 μm

10kV

15mm

0050



x2000

20 μm

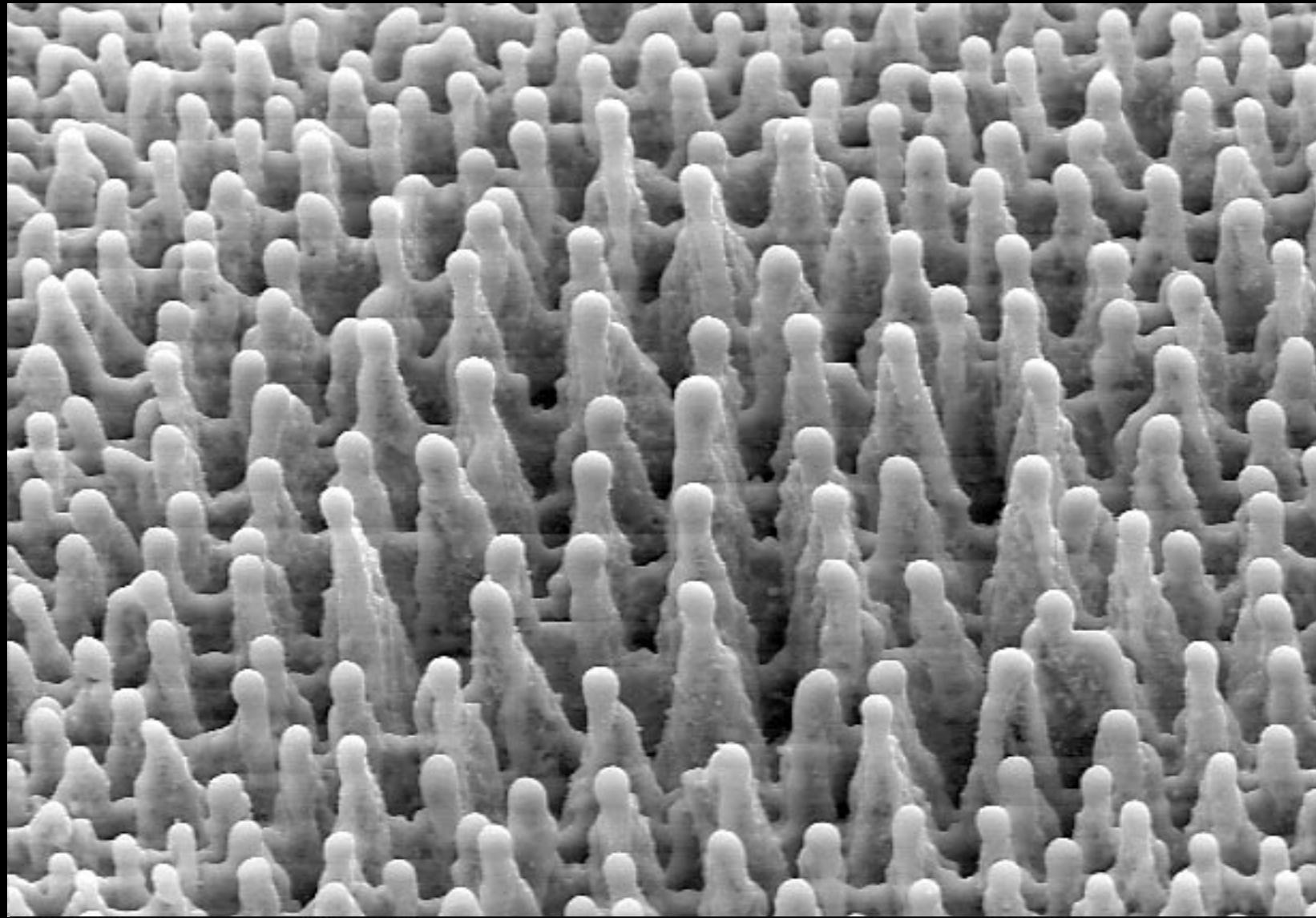
10kV

15mm

#3548

512 x 480

0075



x2000

#3548

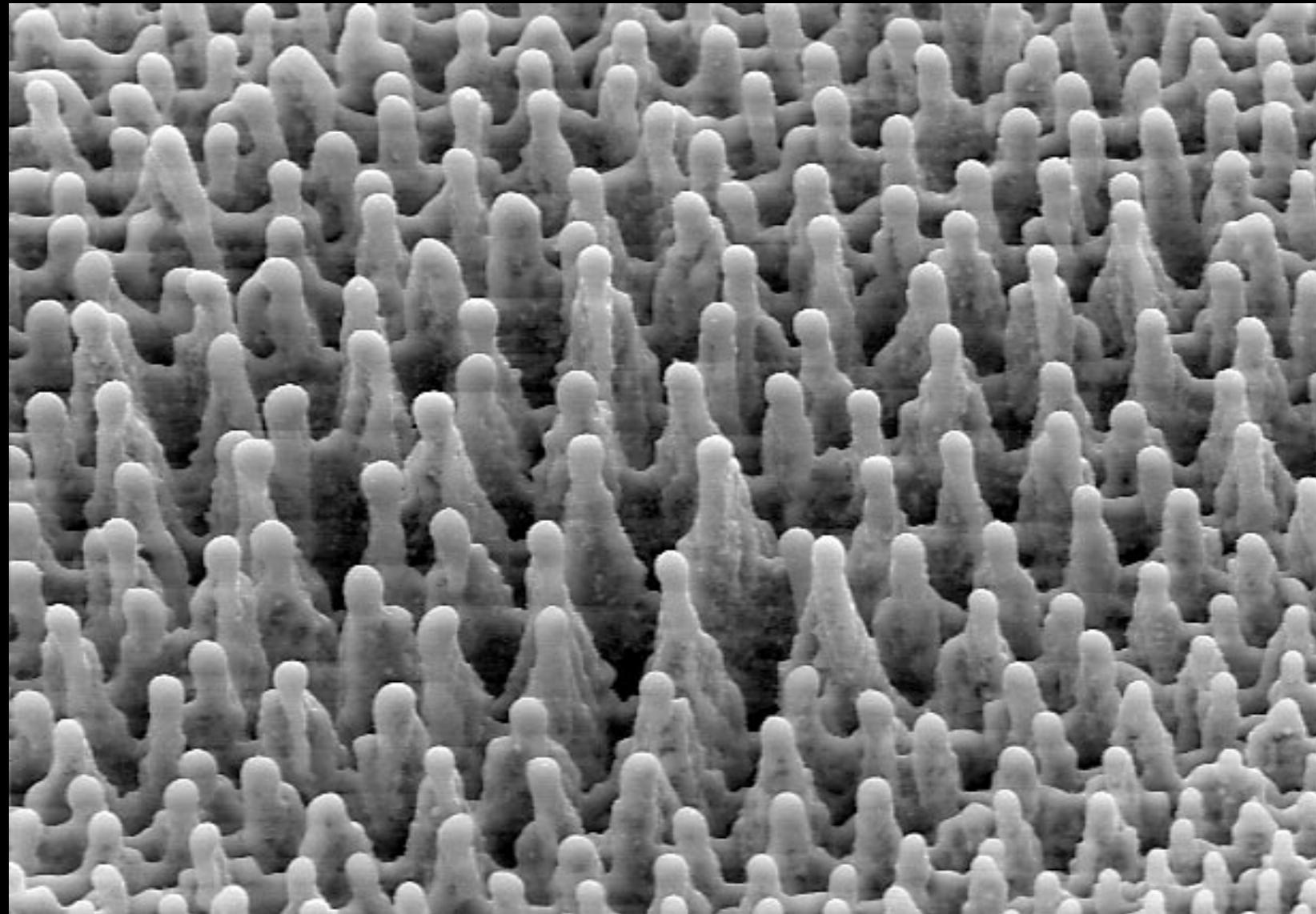
512 x 480

20 μm

10kV

15mm

0100



x2000

#3548

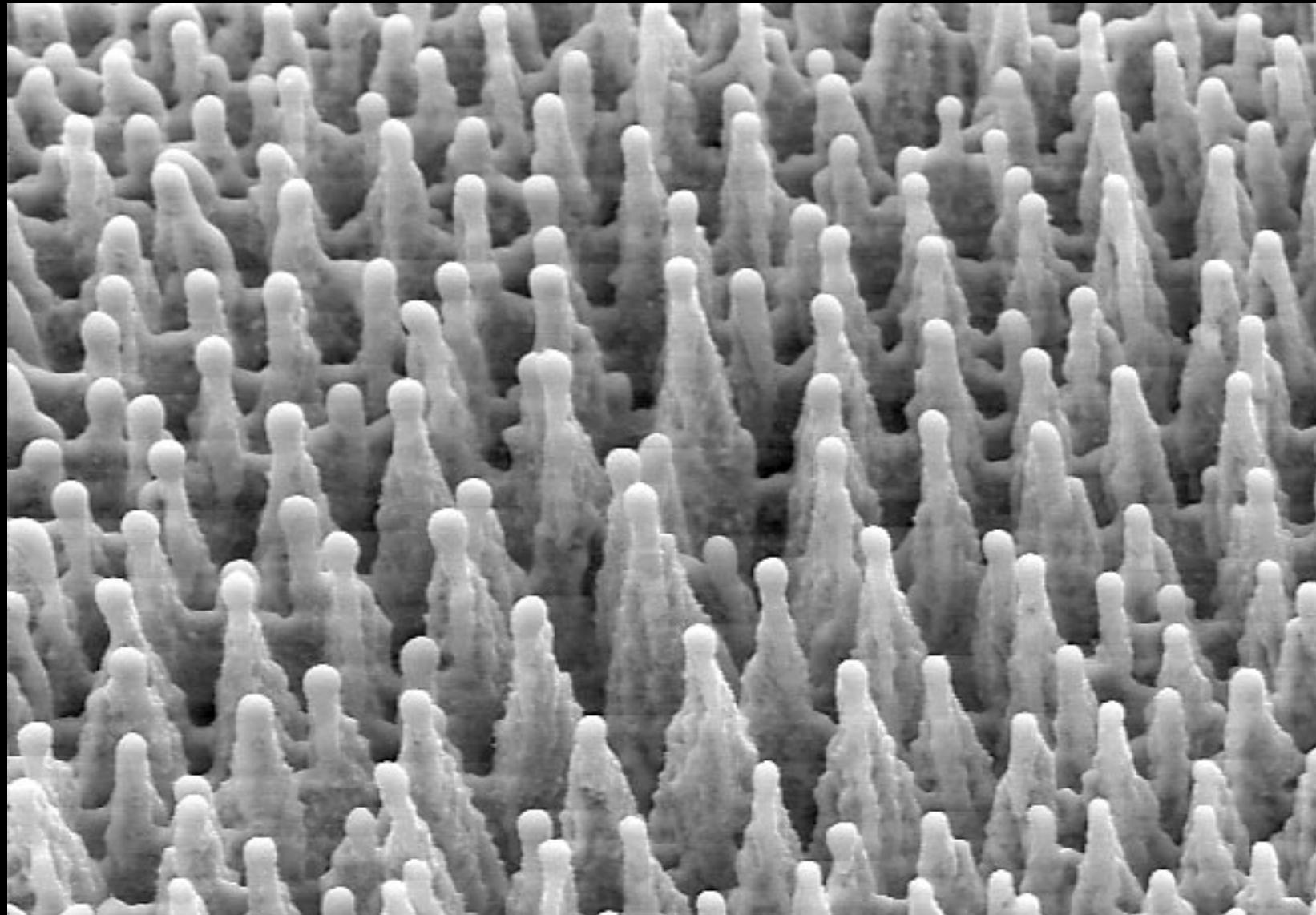
512 x 480

20 μm

10kV

15mm

0125



x2000

#3548

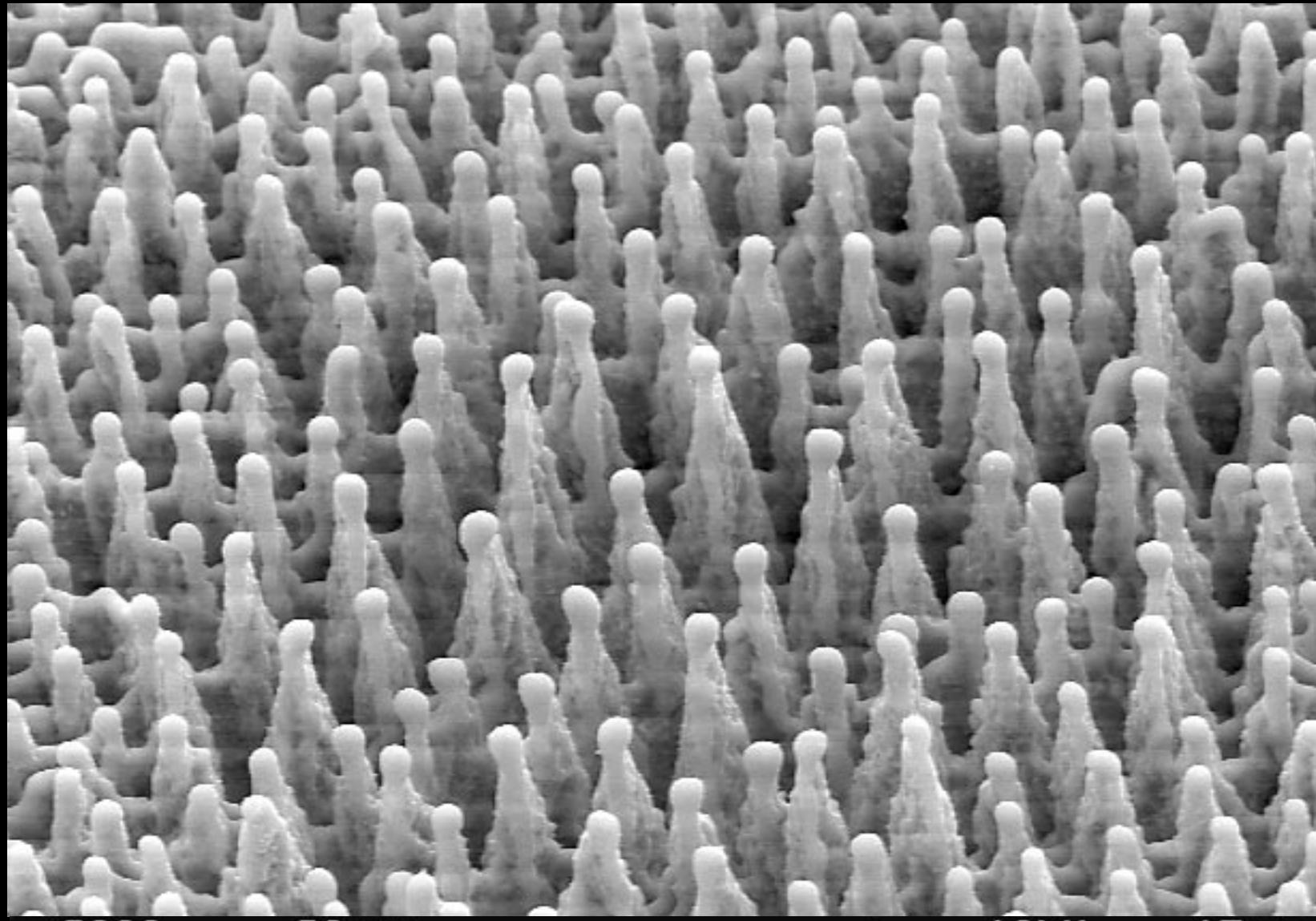
512 x 480

20 μm

10kV

15mm

0250



x2000

#3548

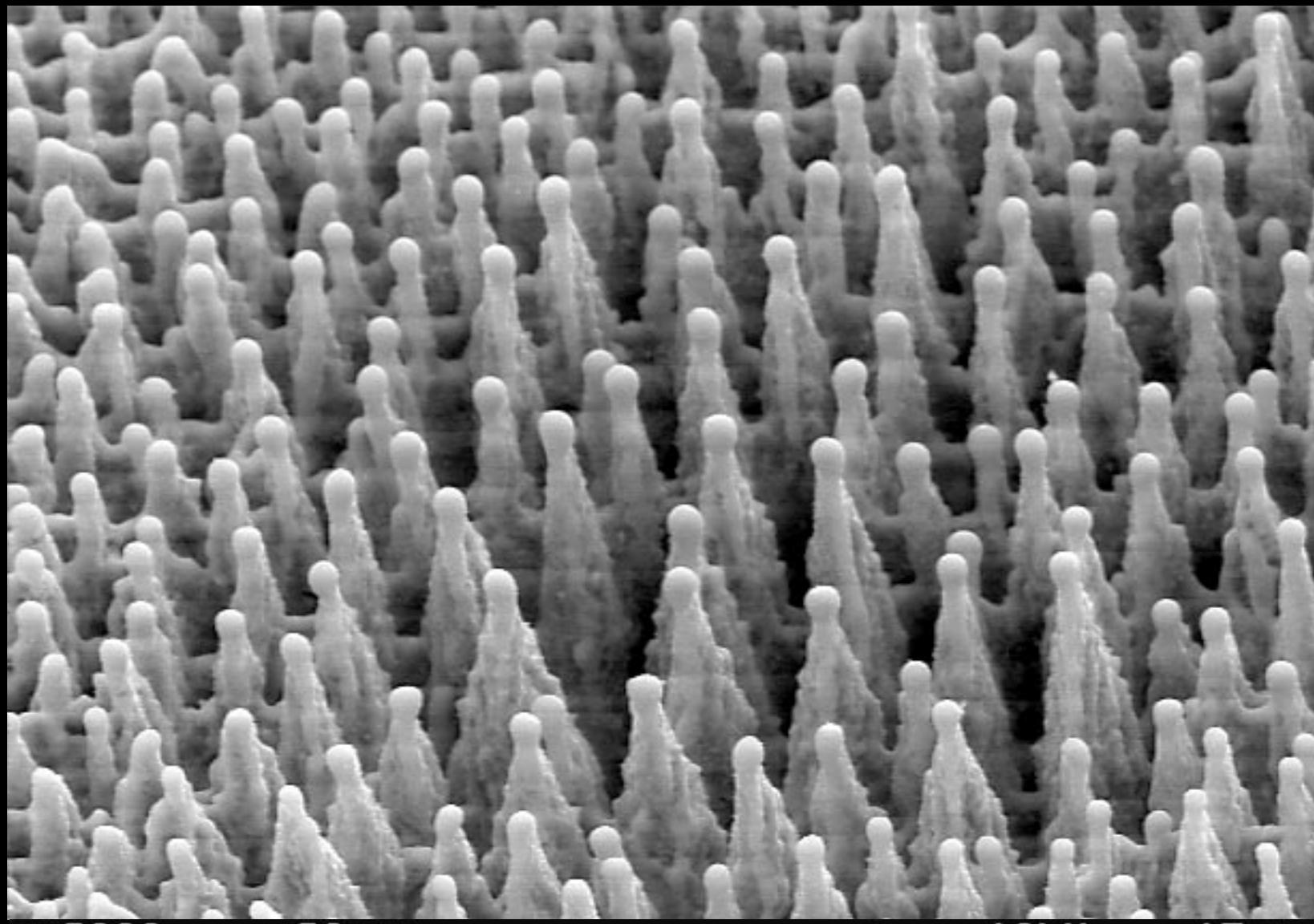
512 x 480

20 μm

10kV

15mm

0300



x2000

#3548

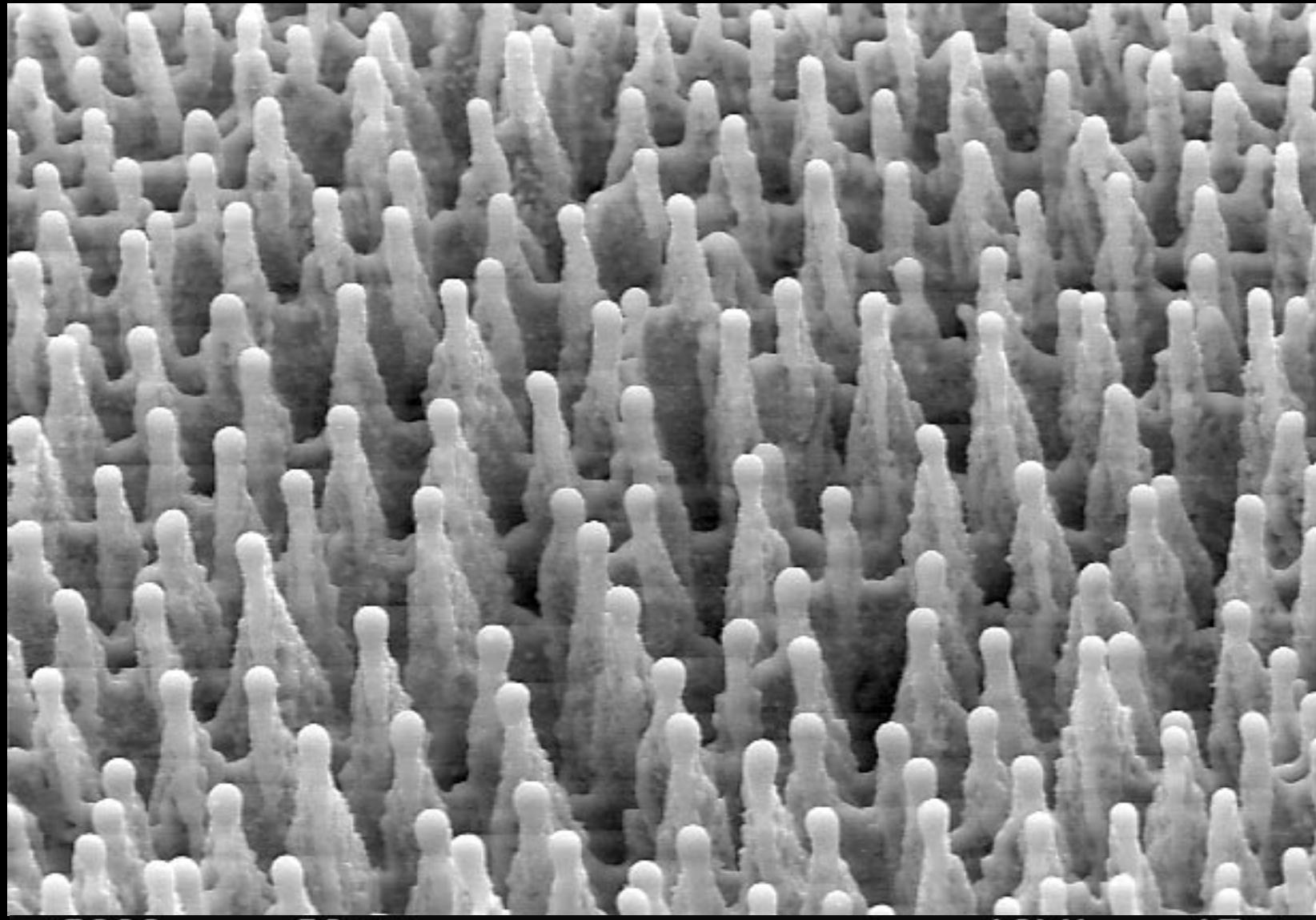
512 x 480

20 μm

10kV

15mm

0400



x2000

20 μm

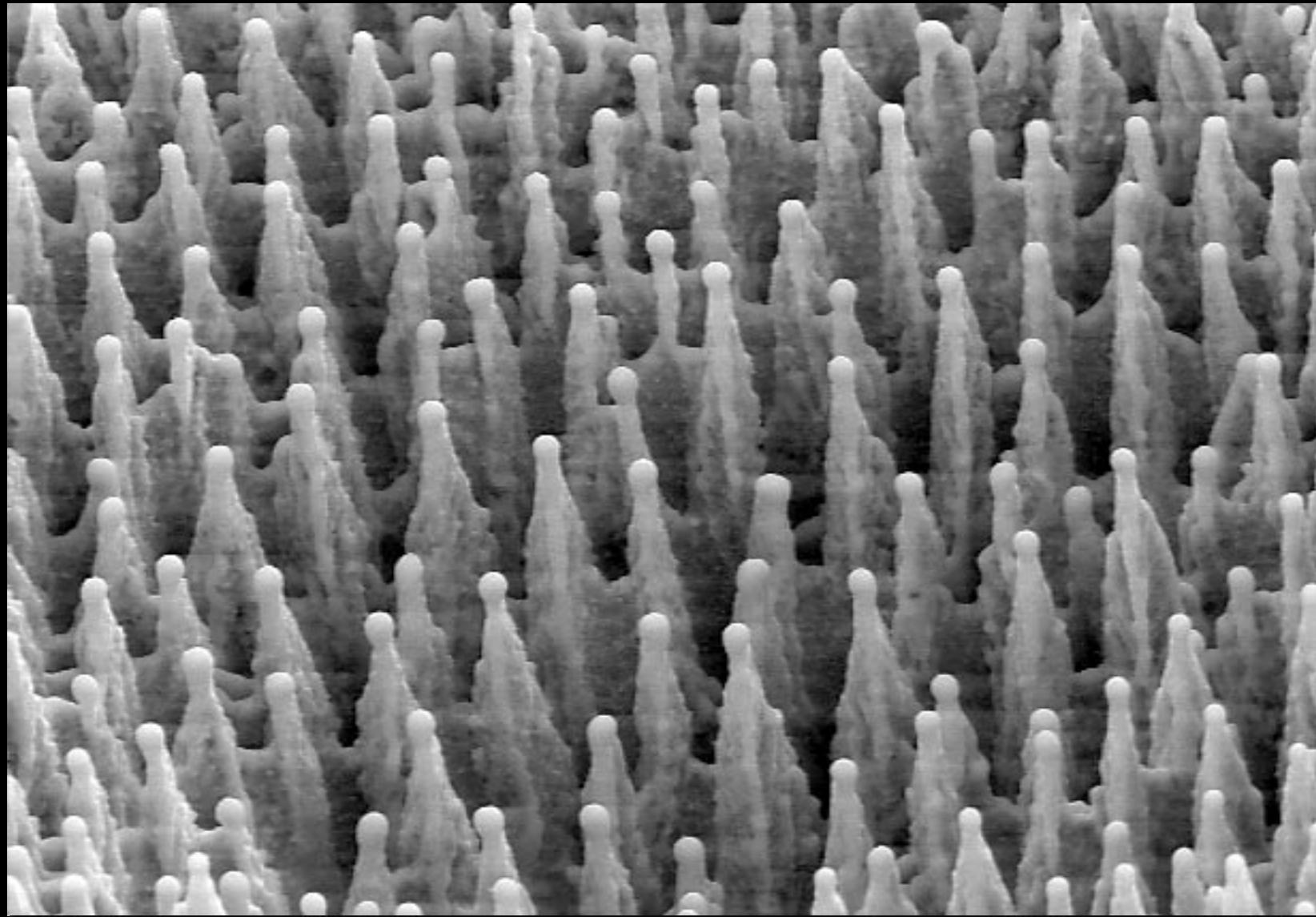
10kV

15mm

#3548

512 x 480

0500



x2000

20 μm

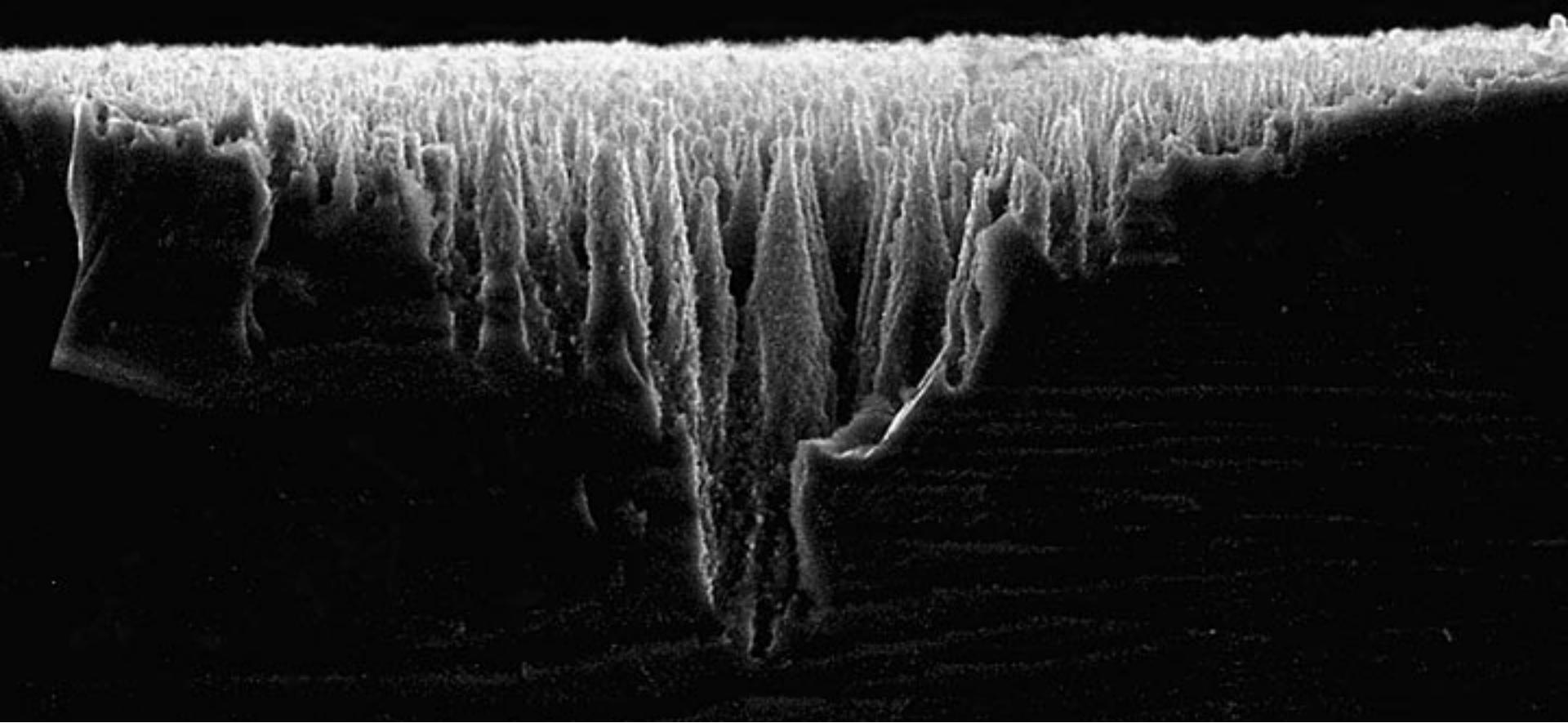
10kV

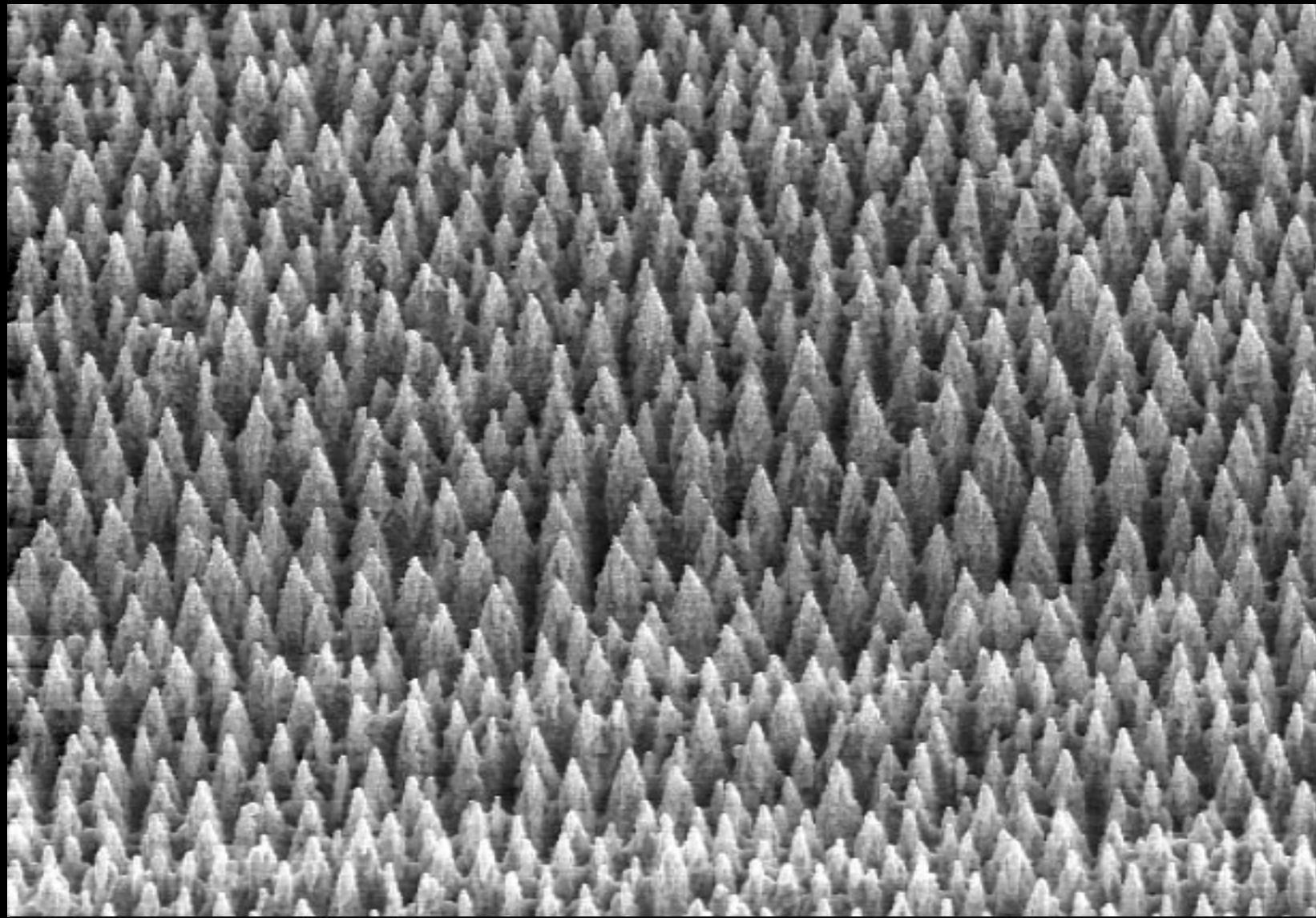
15mm

#3548

512 x 480

1000





x2000

#3548

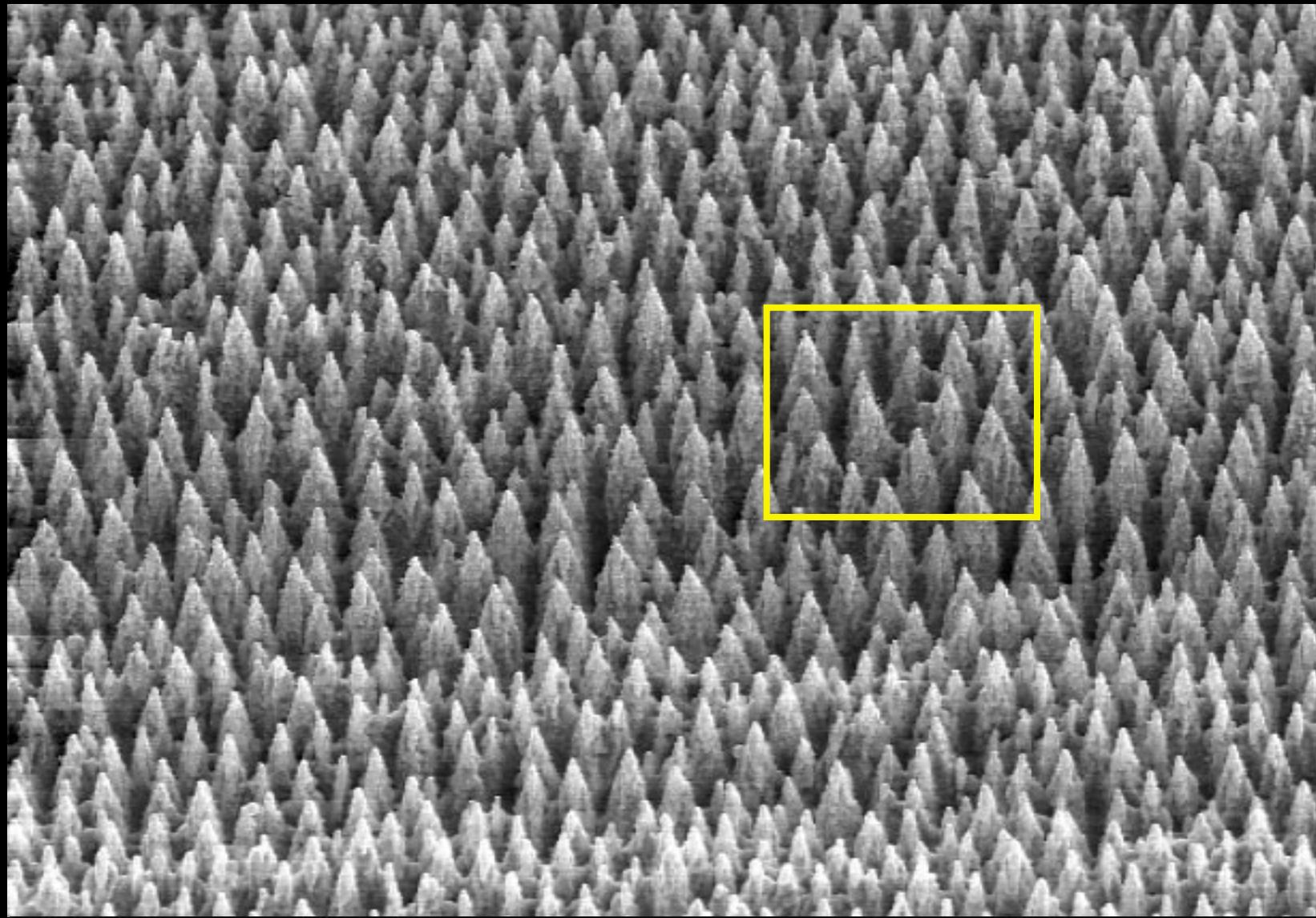
512 x 480

20 μm

10kV

15mm

scanned



x2000

#3548

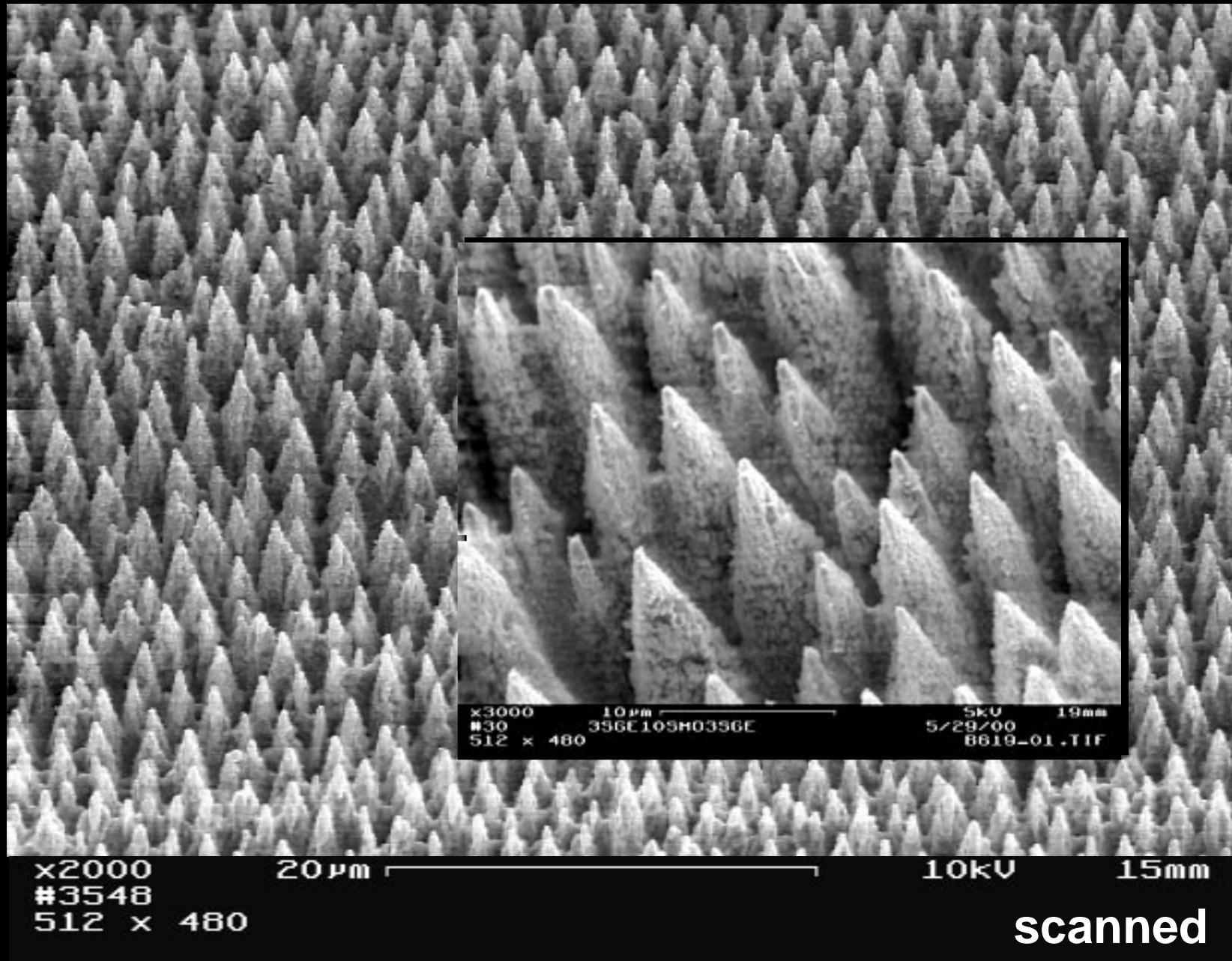
512 x 480

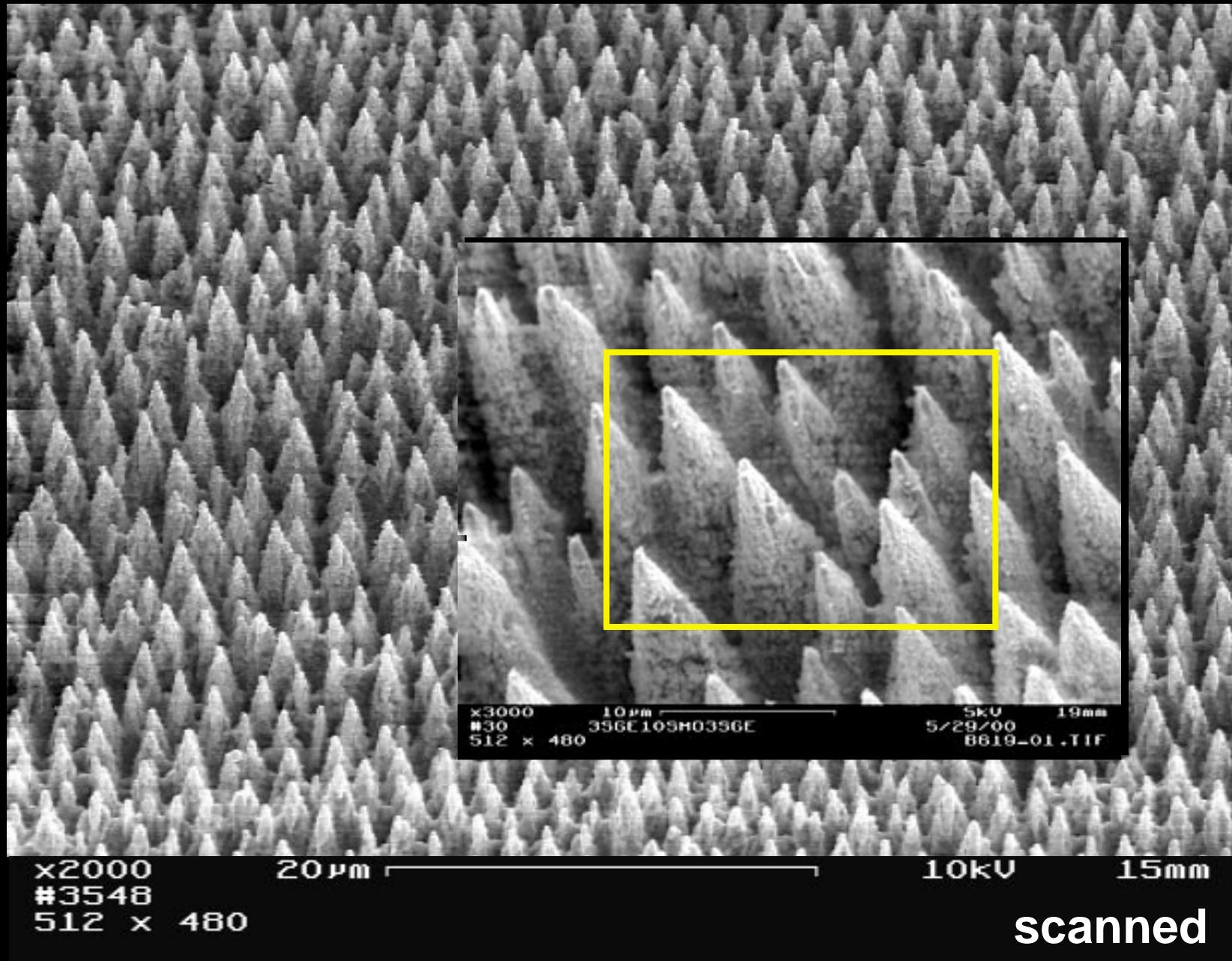
20 μm

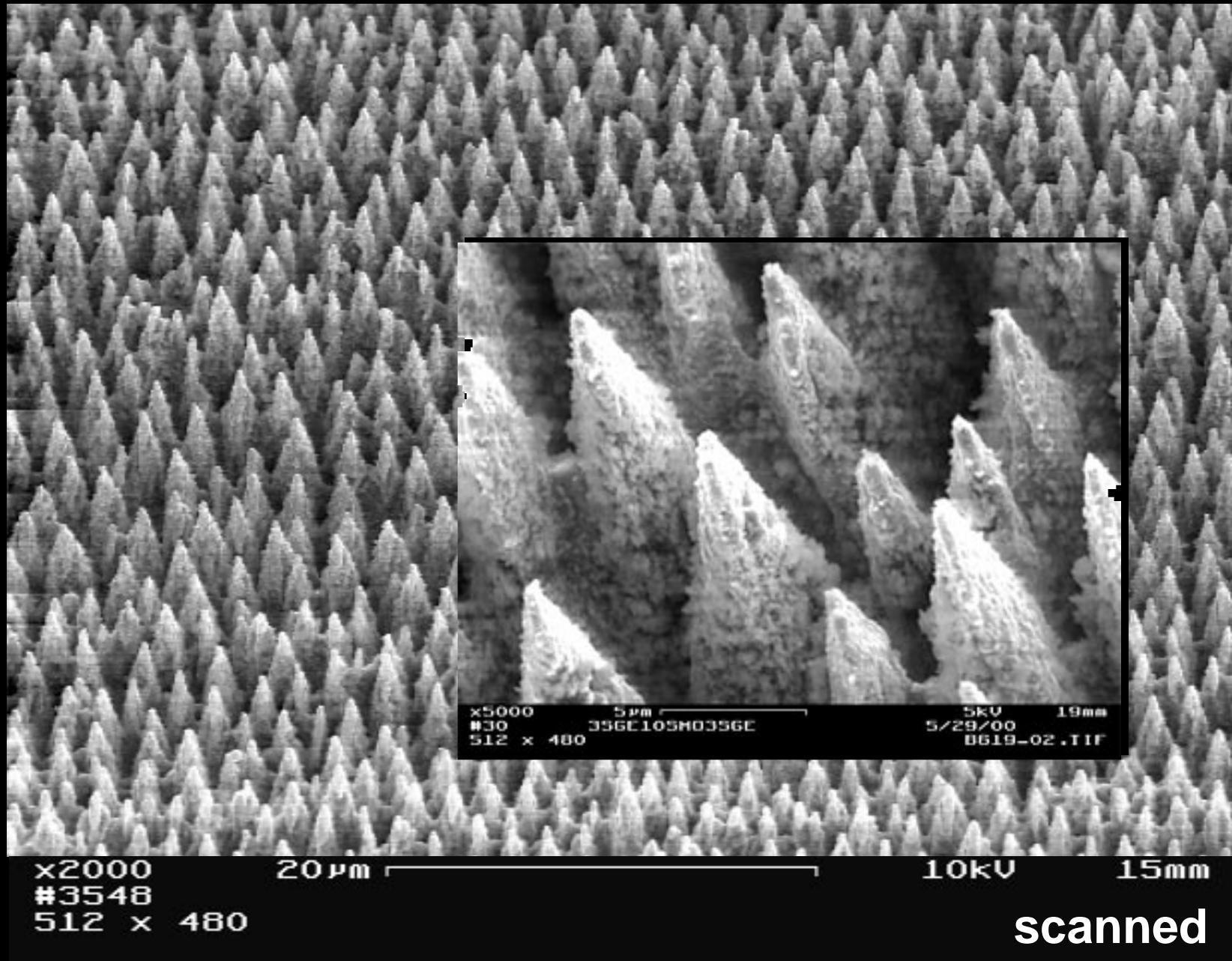
10kV

15mm

scanned

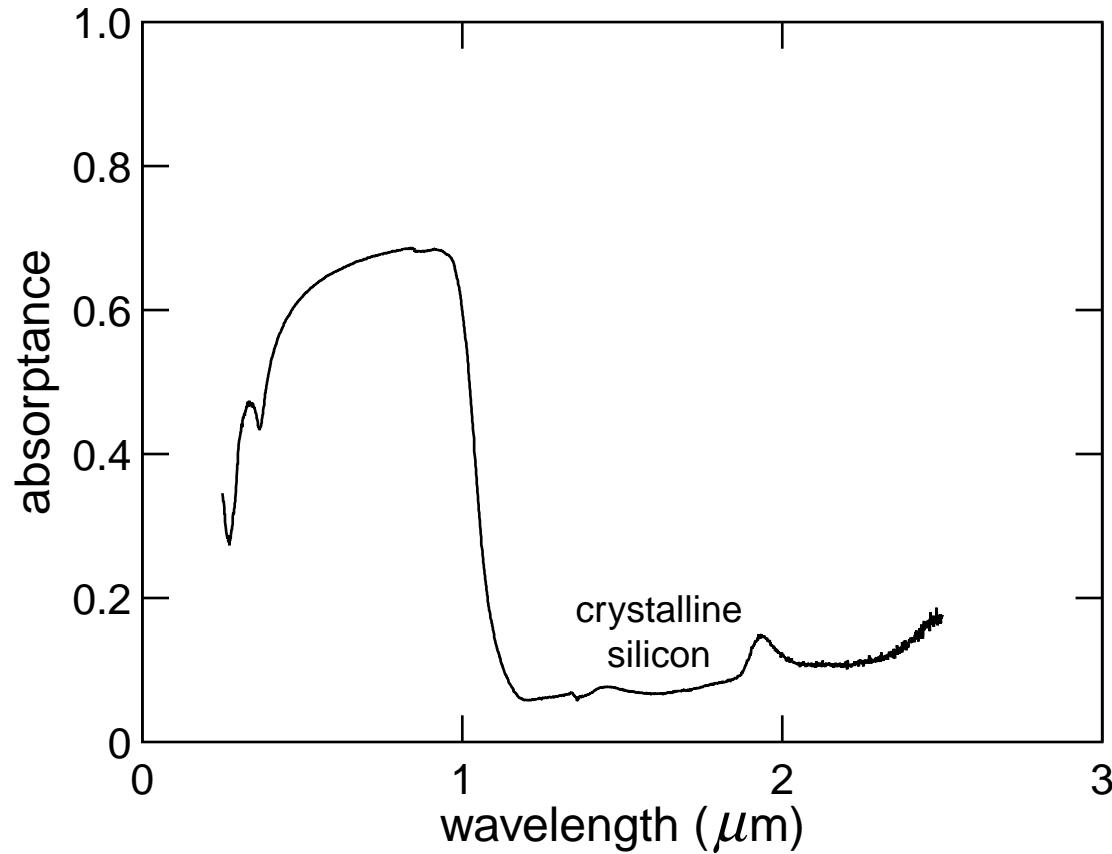






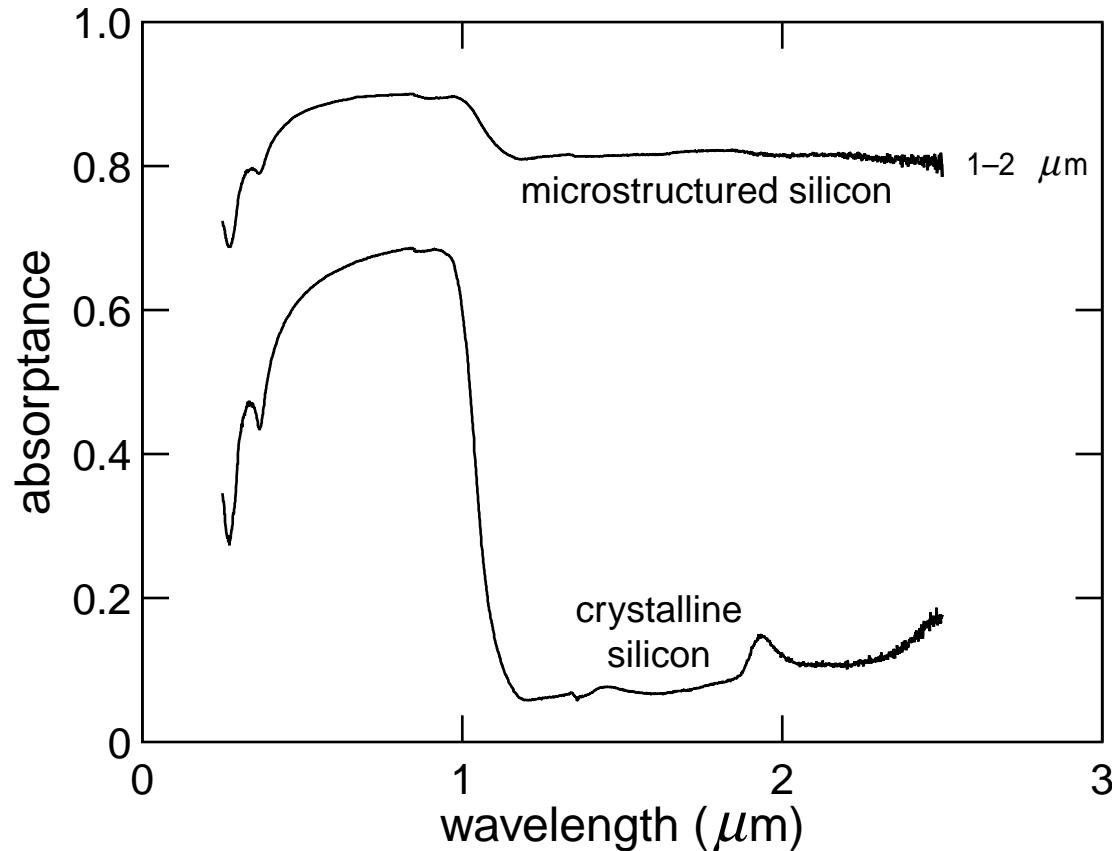
Background

absorptance



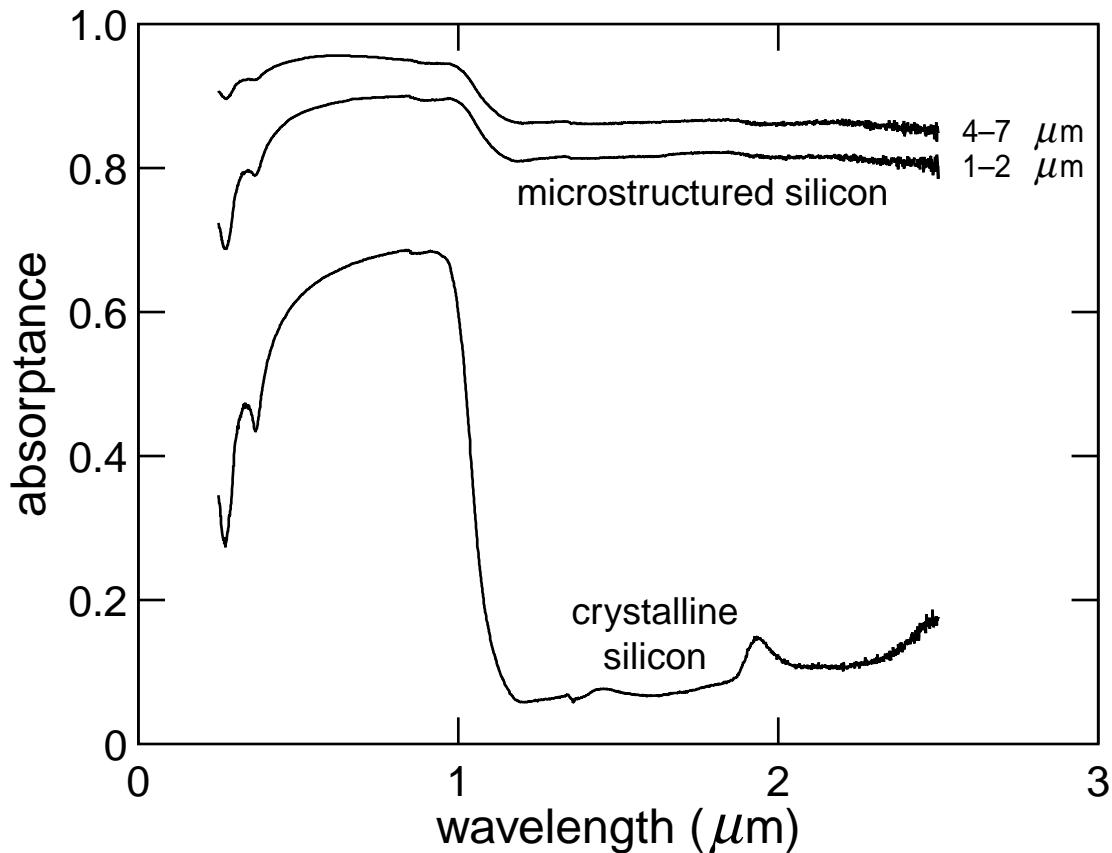
Background

absorptance



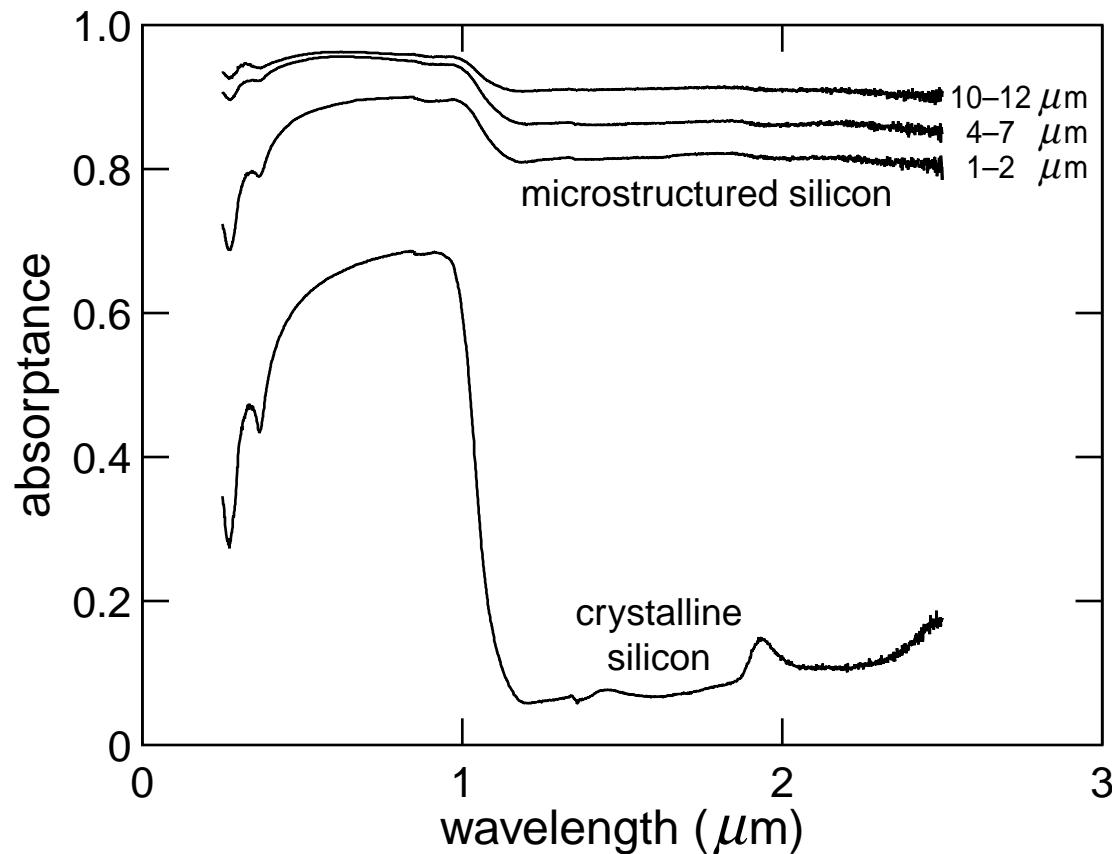
Background

absorptance



Background

absorptance



Background

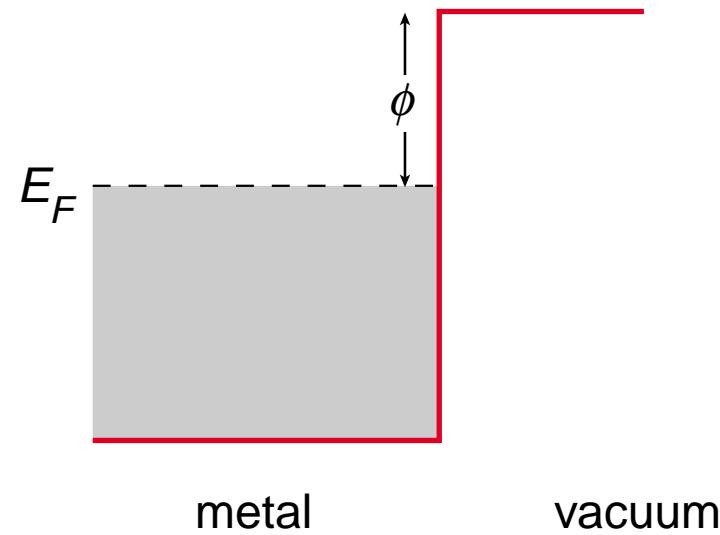
Points to keep in mind:

- ▶ **one-step, maskless process**
- ▶ **large area with uniform high density of spikes**
- ▶ **band structure change**

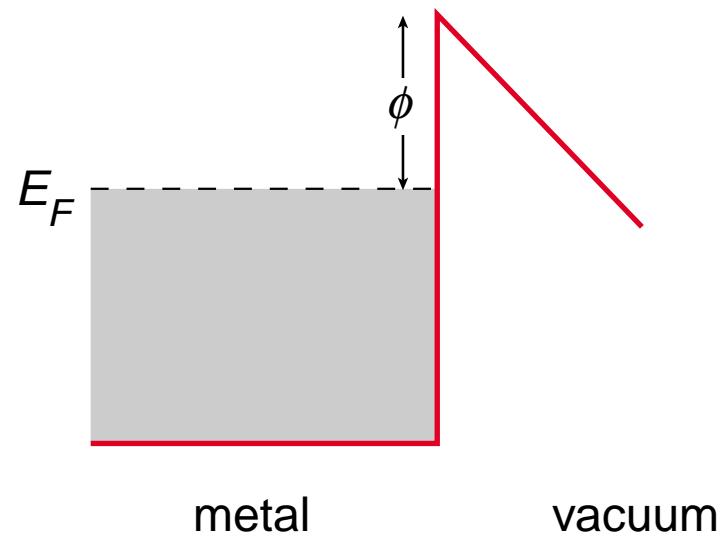
Outline

- ▶ **Background**
- ▶ **Results**
- ▶ **Discussion**

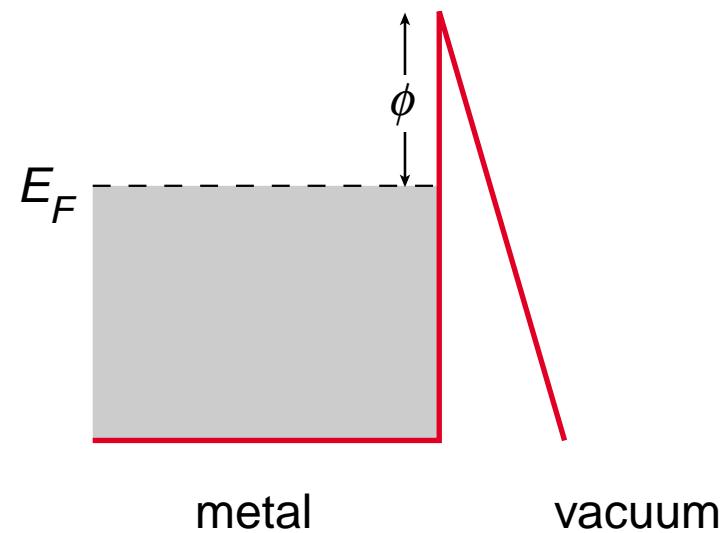
Field emission



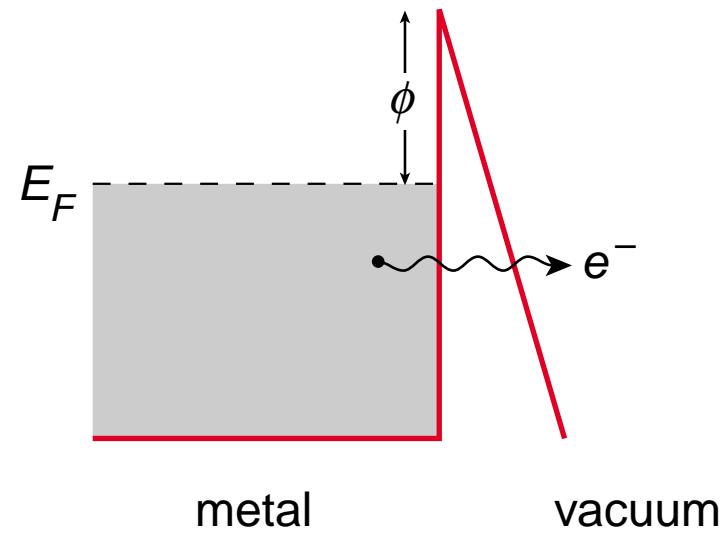
Field emission



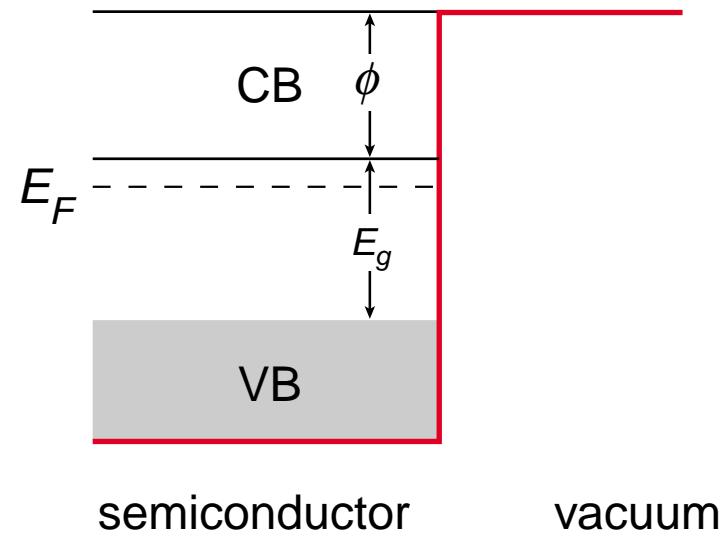
Field emission



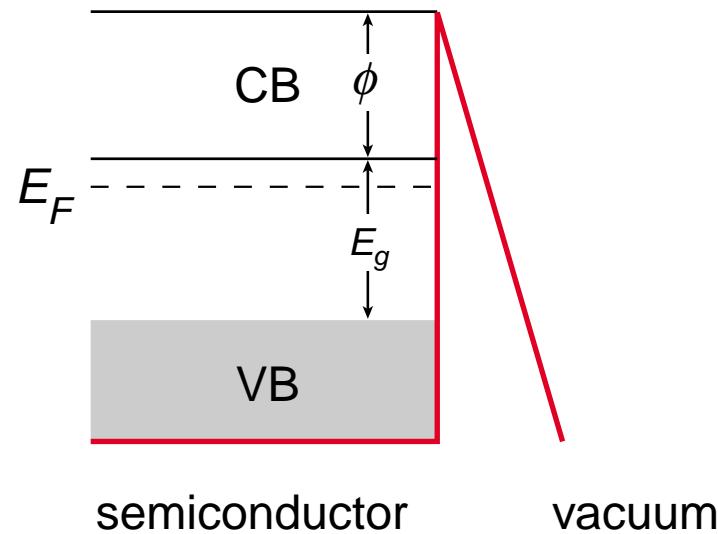
Field emission



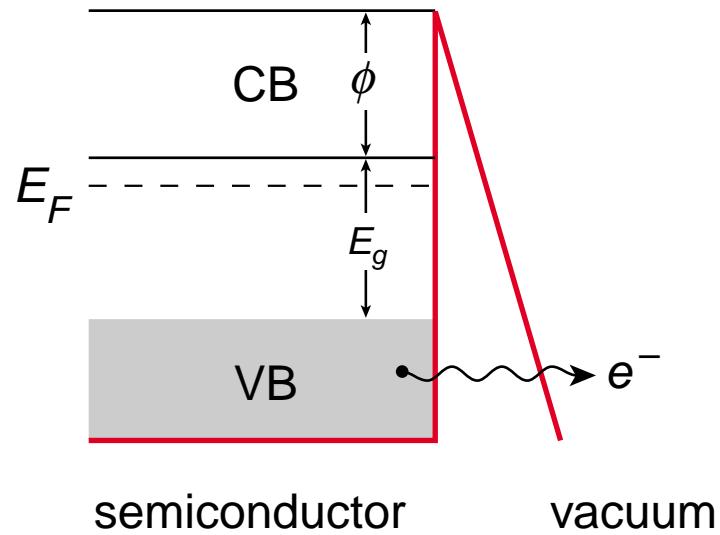
Field emission



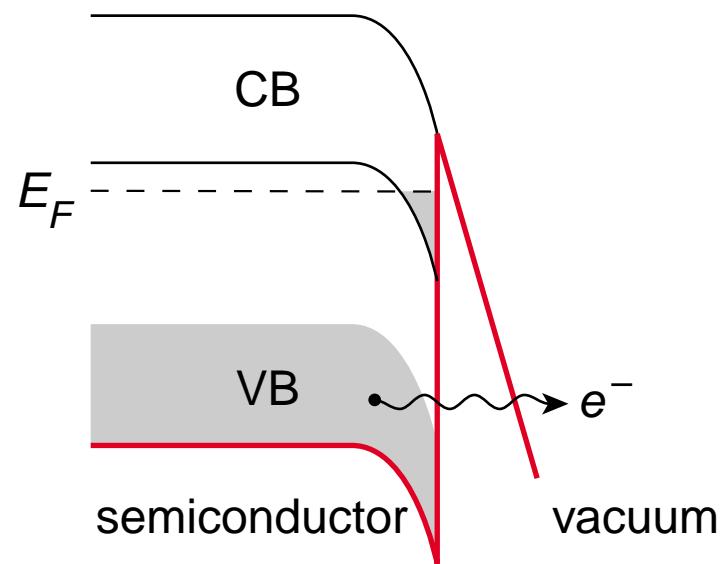
Field emission



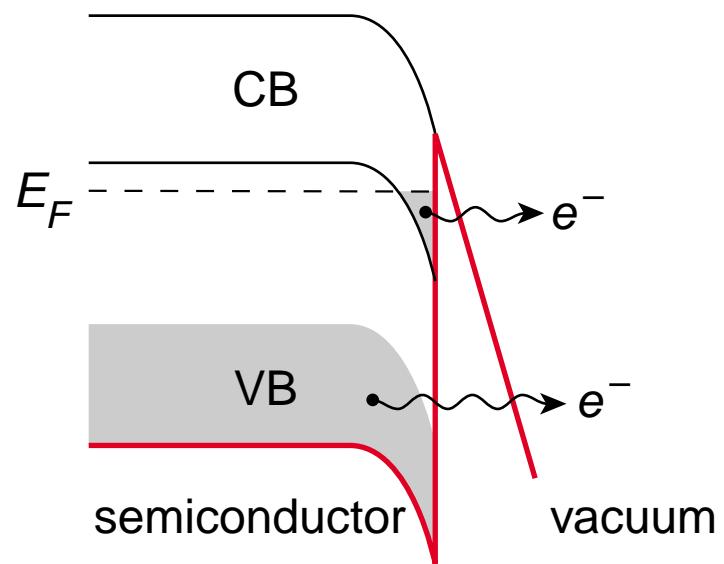
Field emission



Field emission

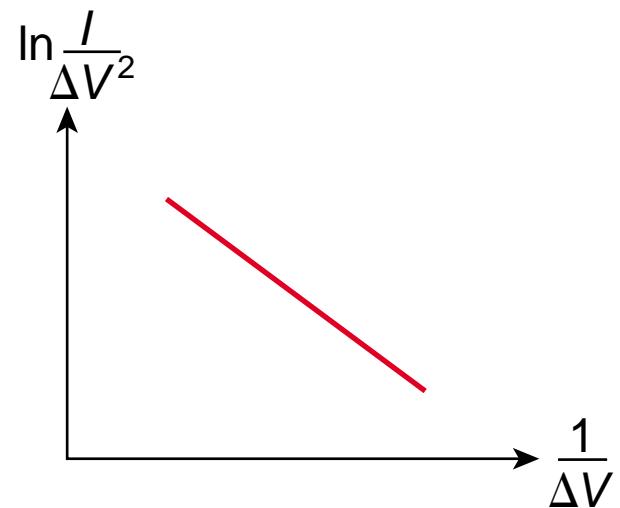


Field emission



Field emission

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



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

Setup



Setup



gold coating

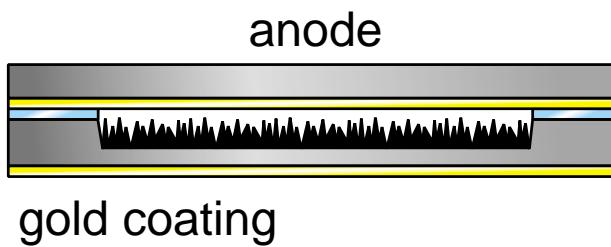
Setup

20 μm mica spacers

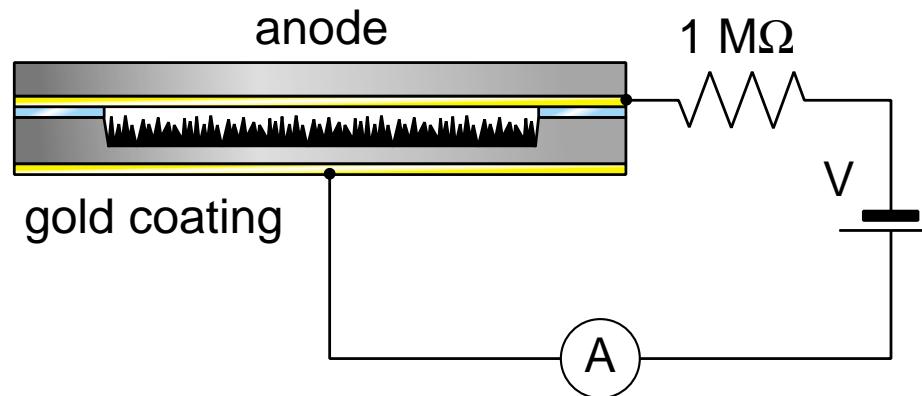


gold coating

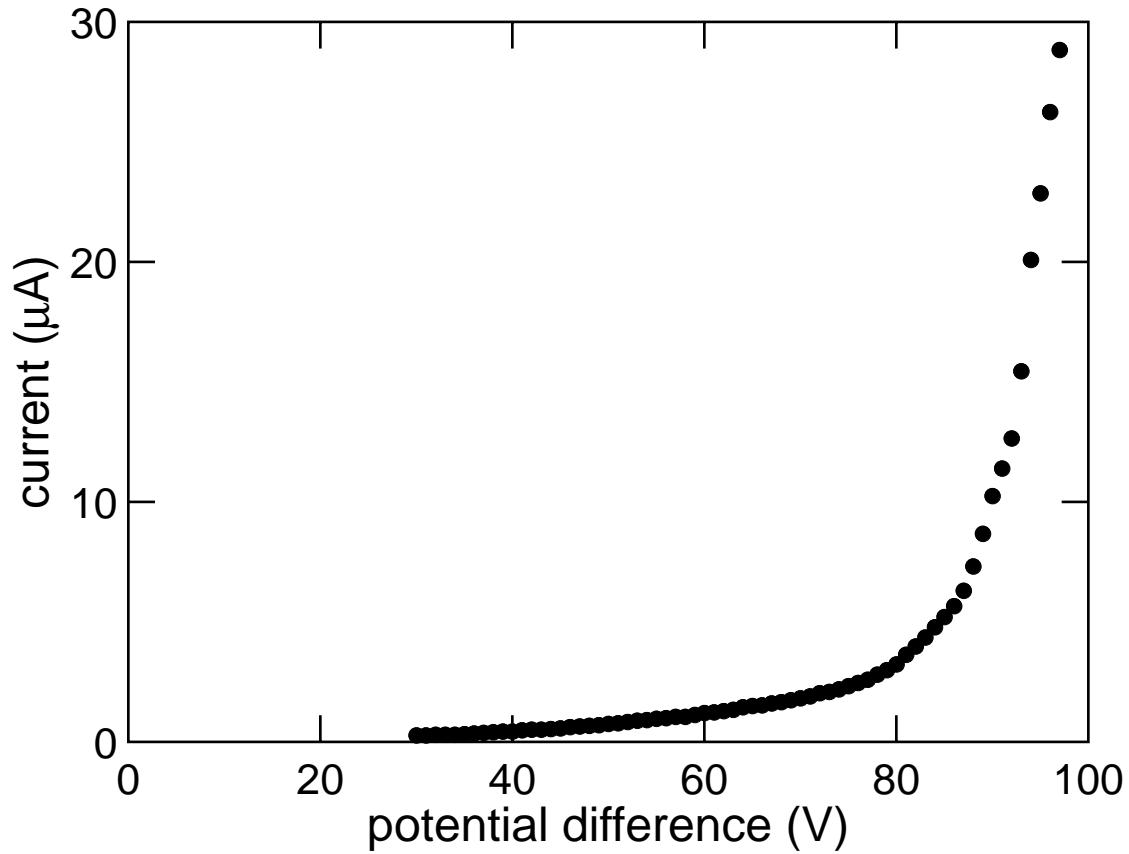
Setup



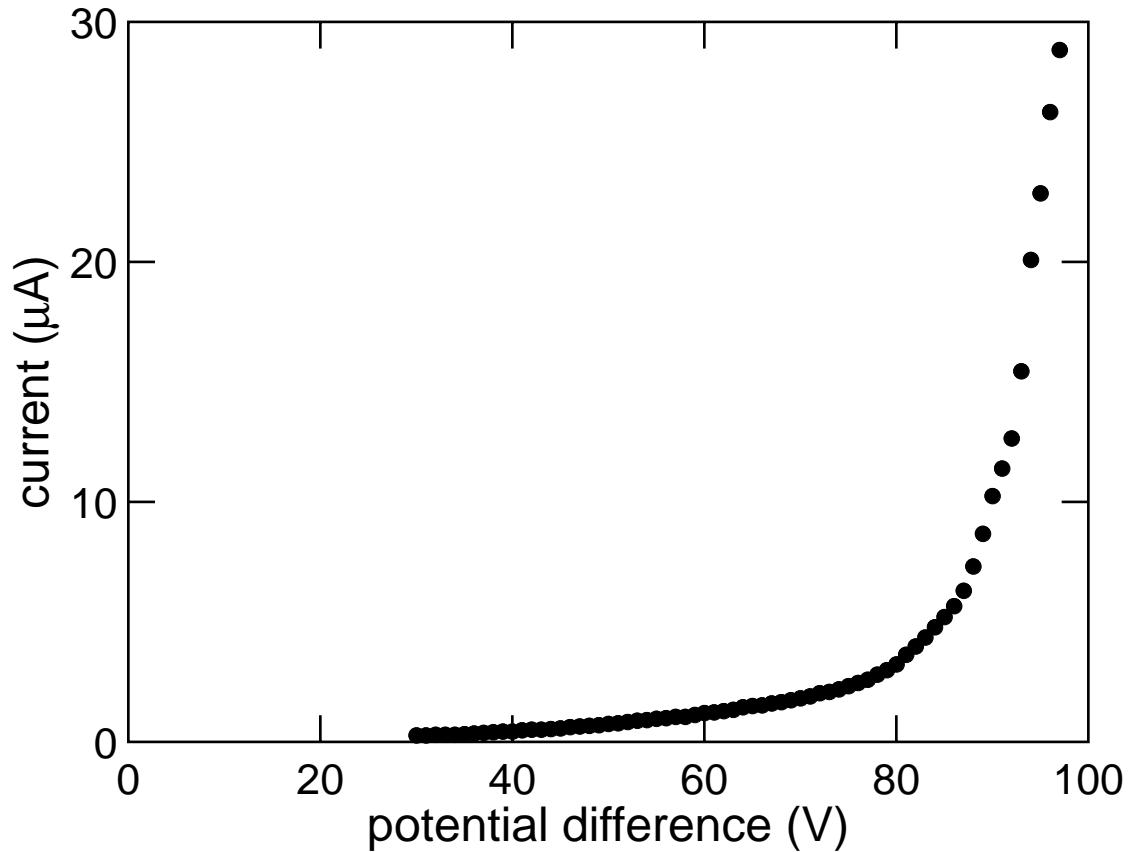
Setup



Results

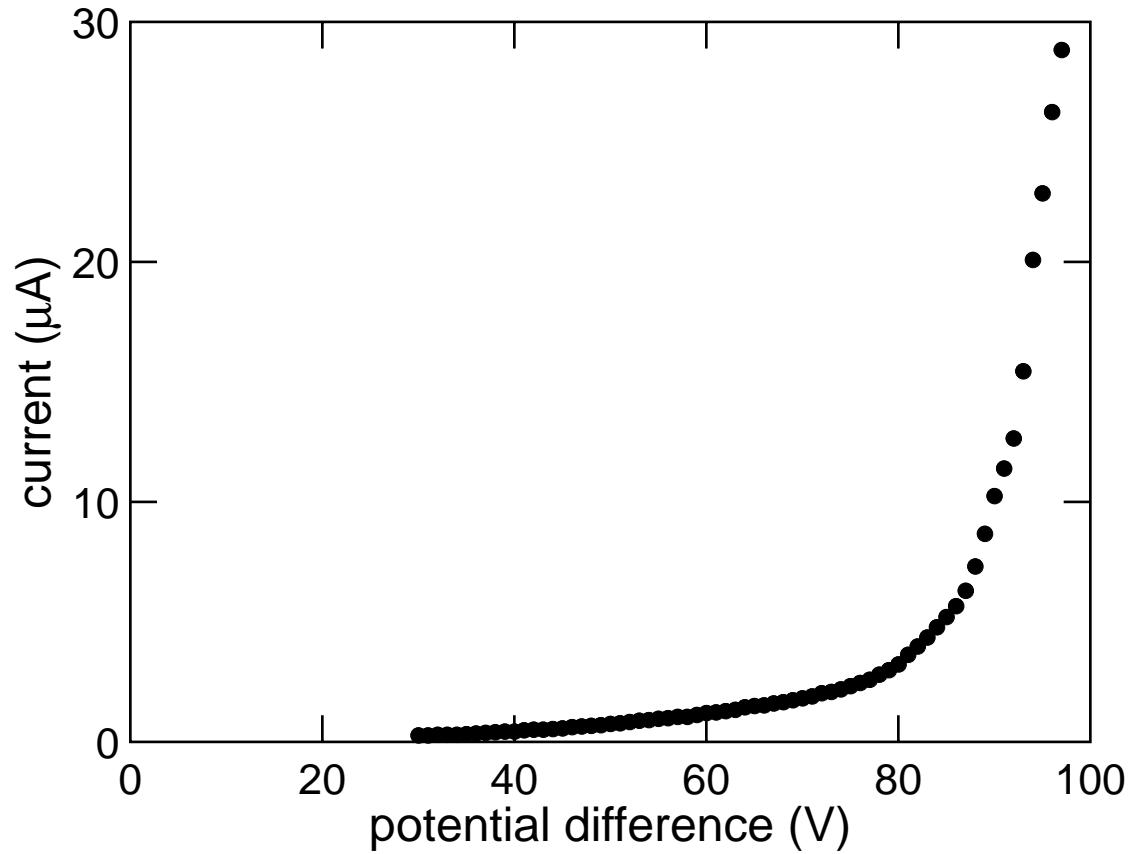


Results



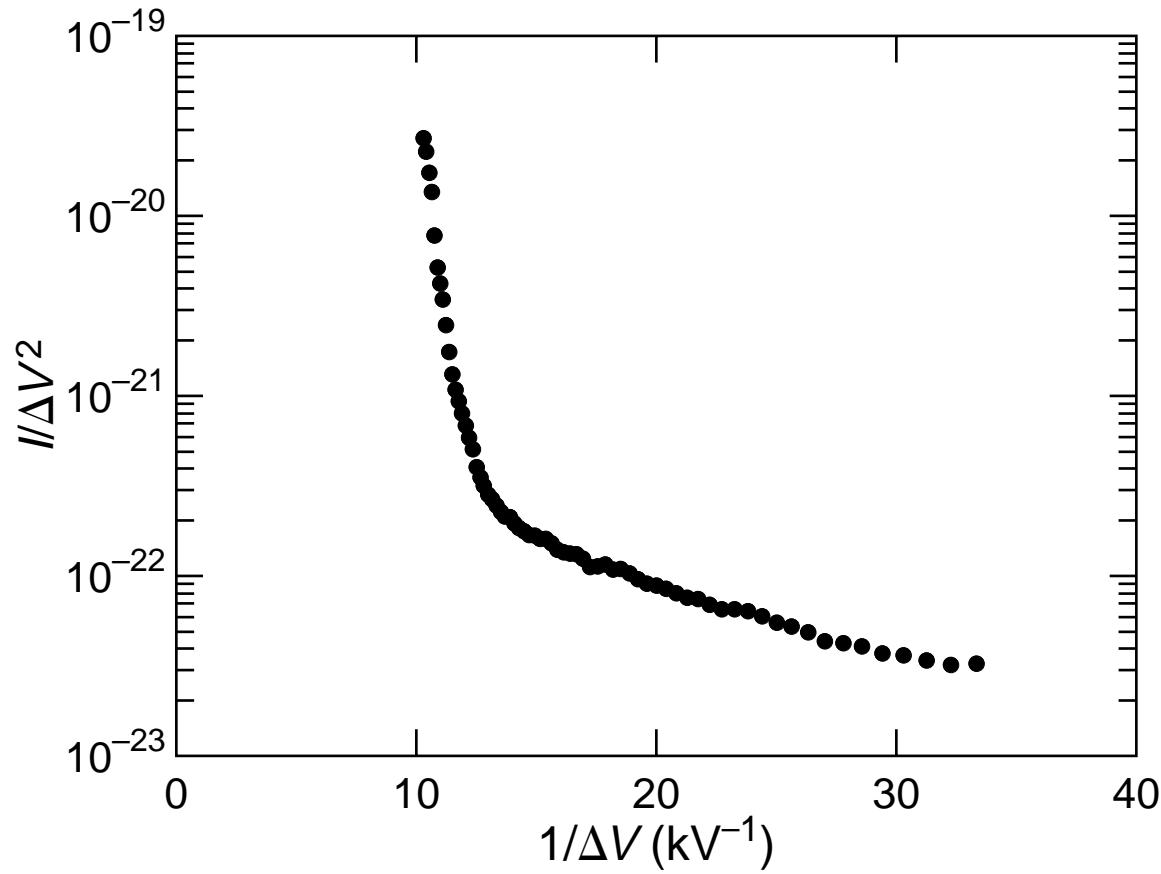
turn-on field (1 μA/cm²): 1.3 V/μm

Results

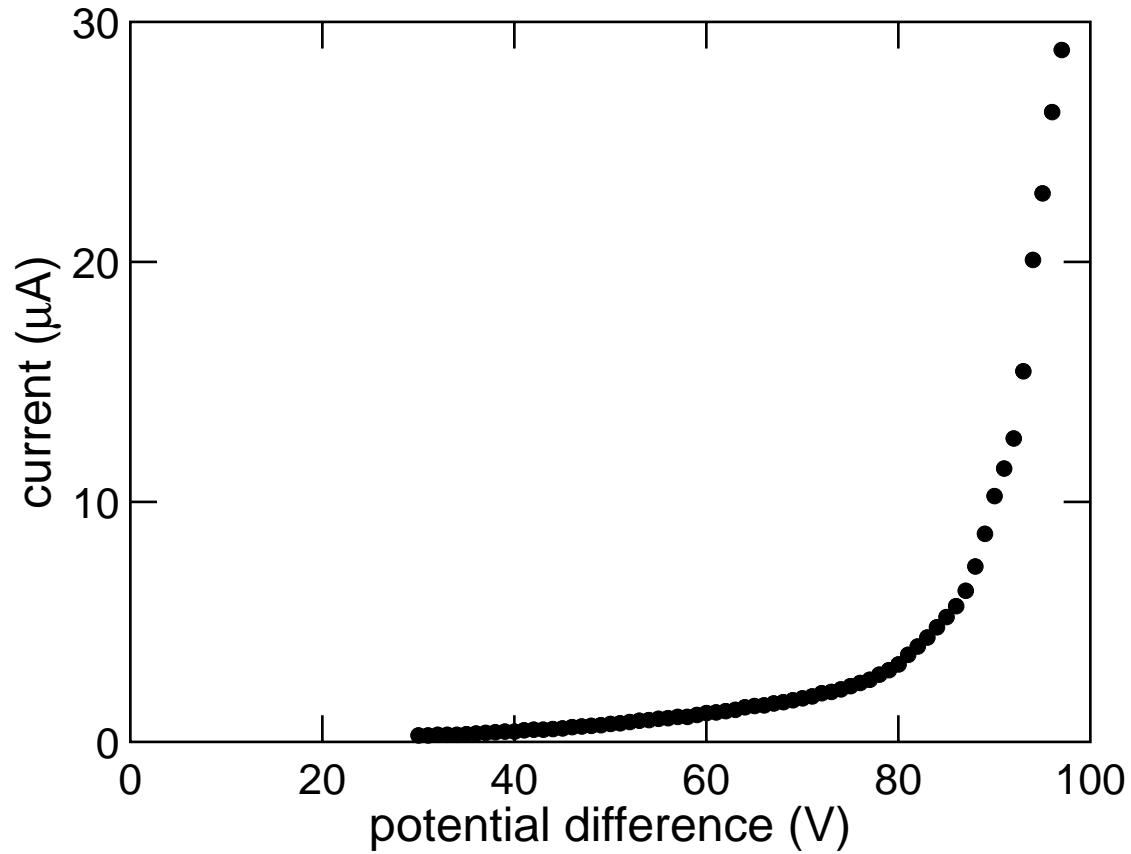


threshold field ($10 \mu\text{A}/\text{cm}^2$): $2.15 \text{ V}/\mu\text{m}$

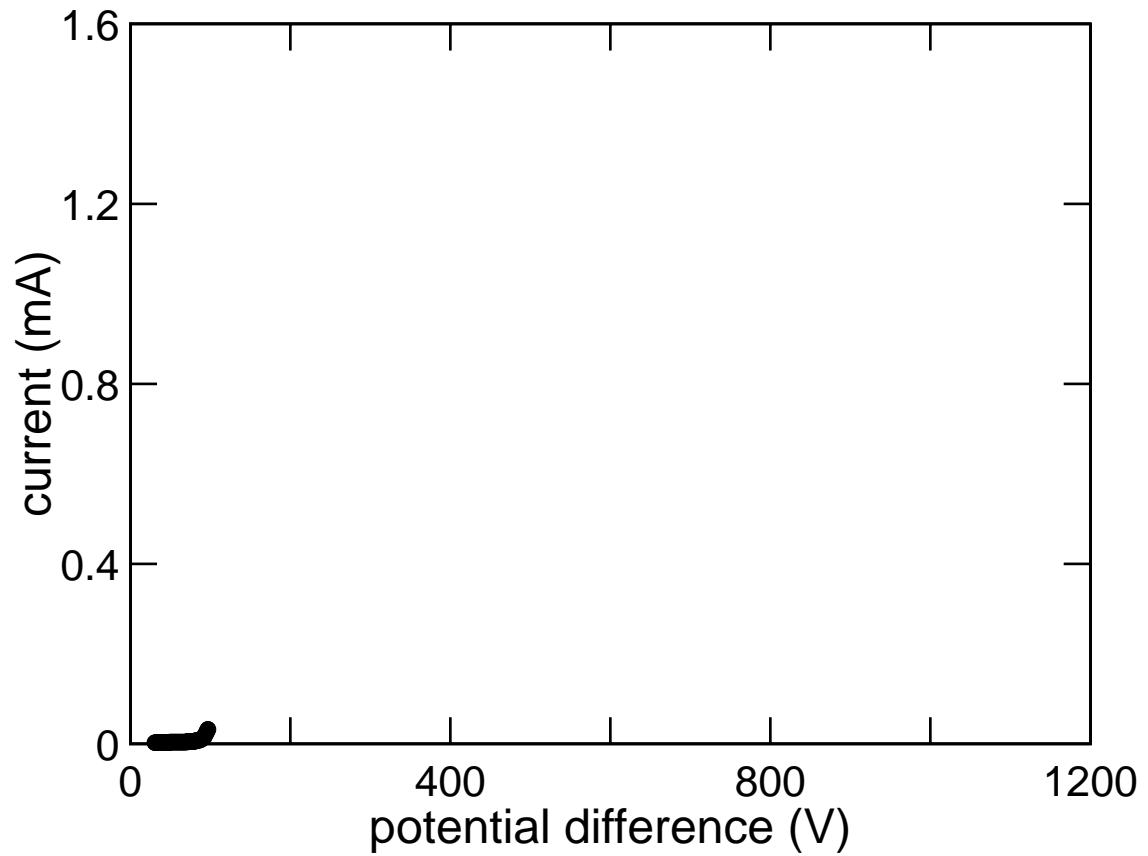
Results



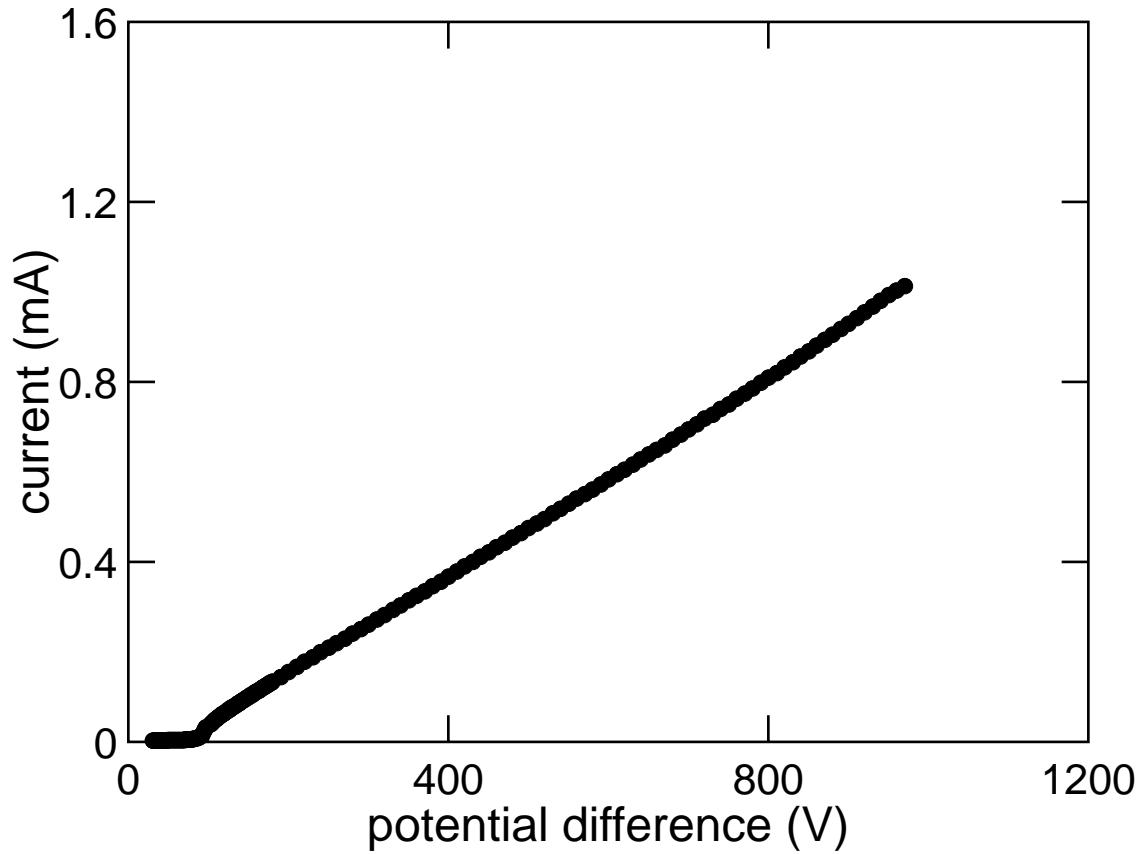
Results



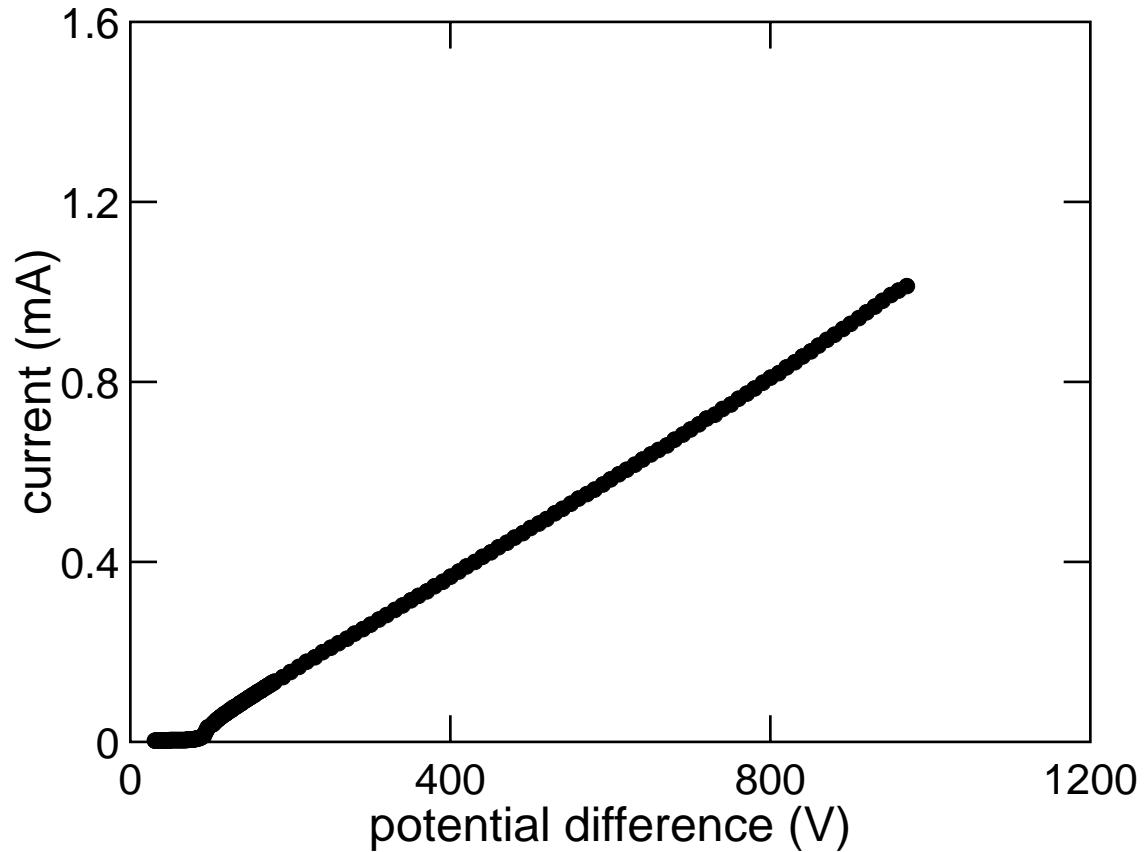
Results



Results

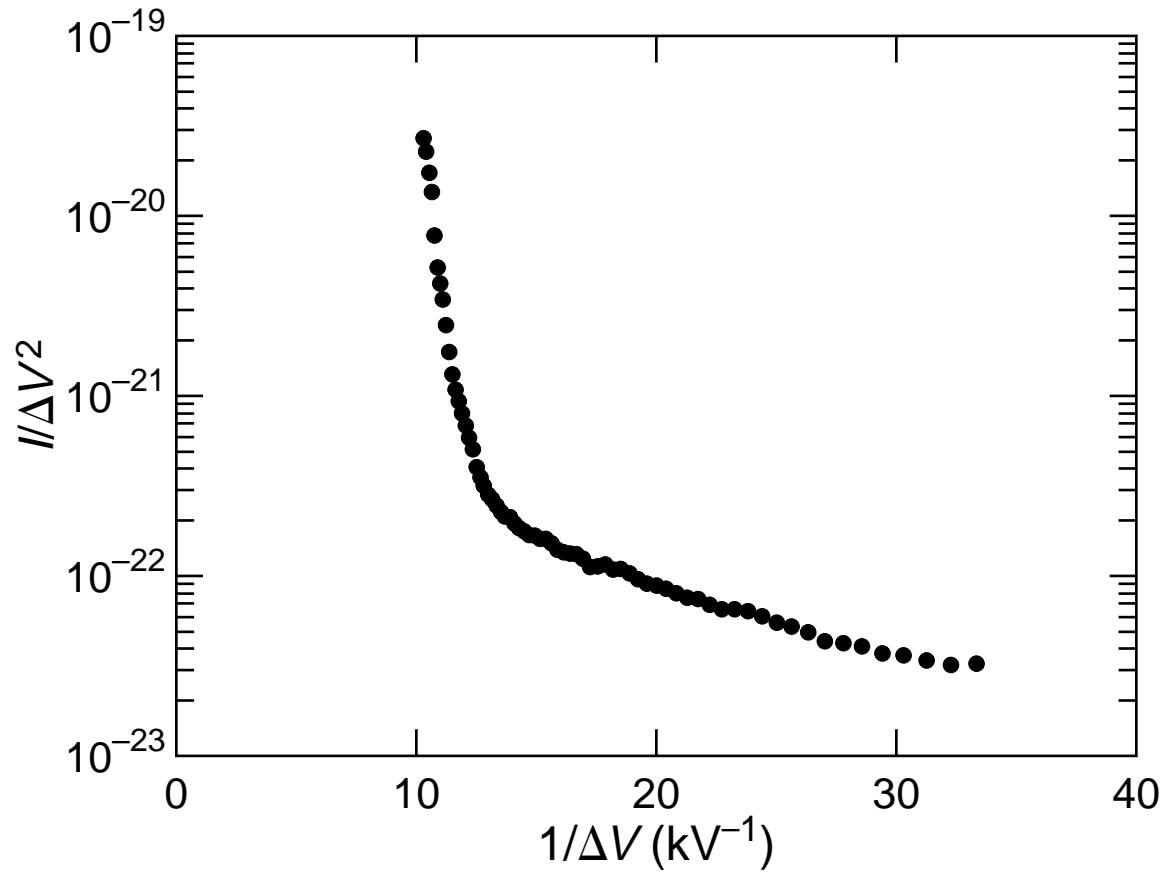


Results

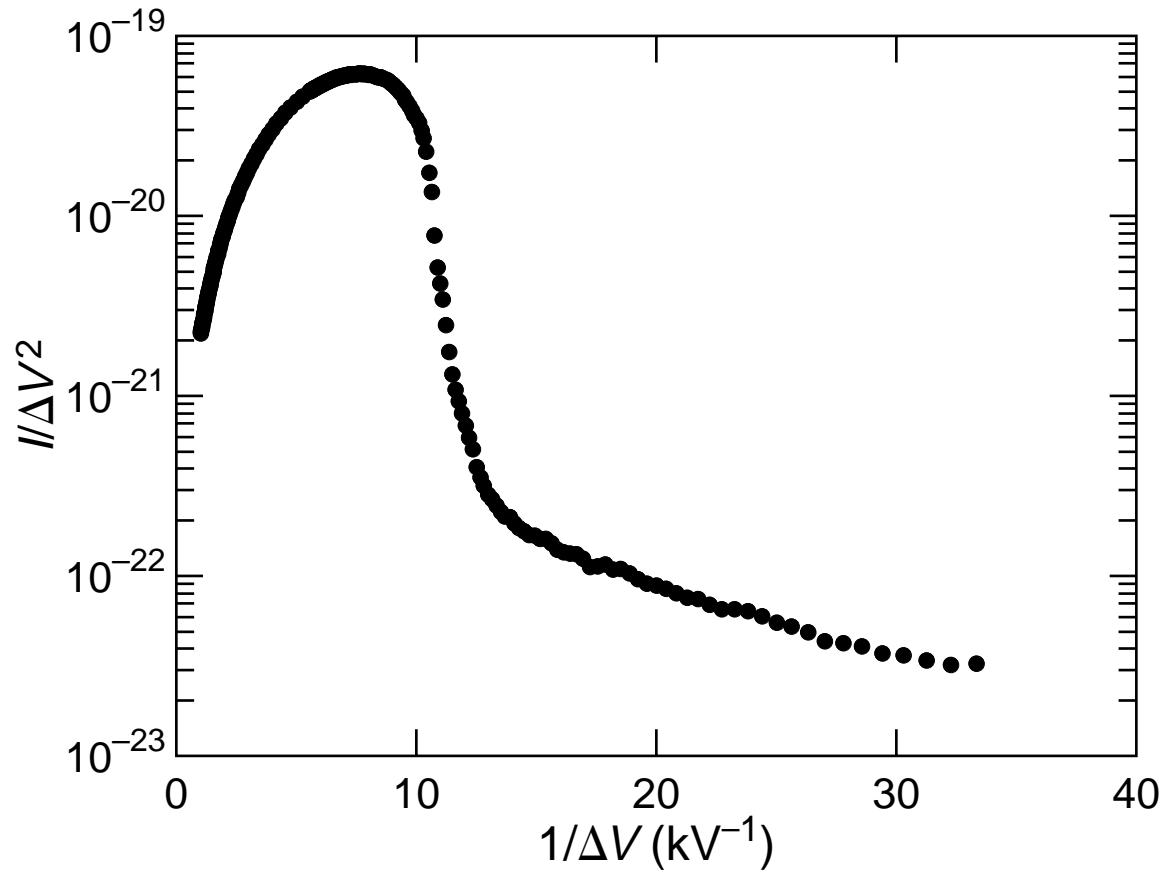


maximum current: 2 mA (4 mm² sample)

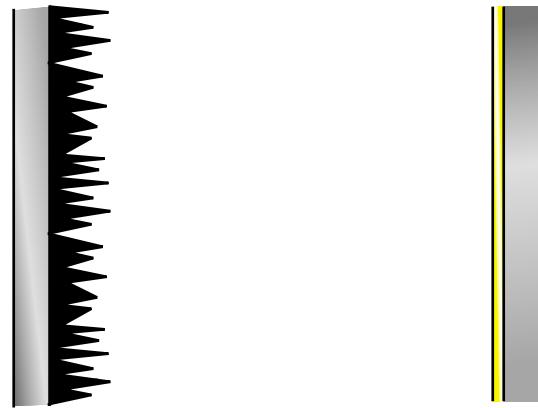
Results



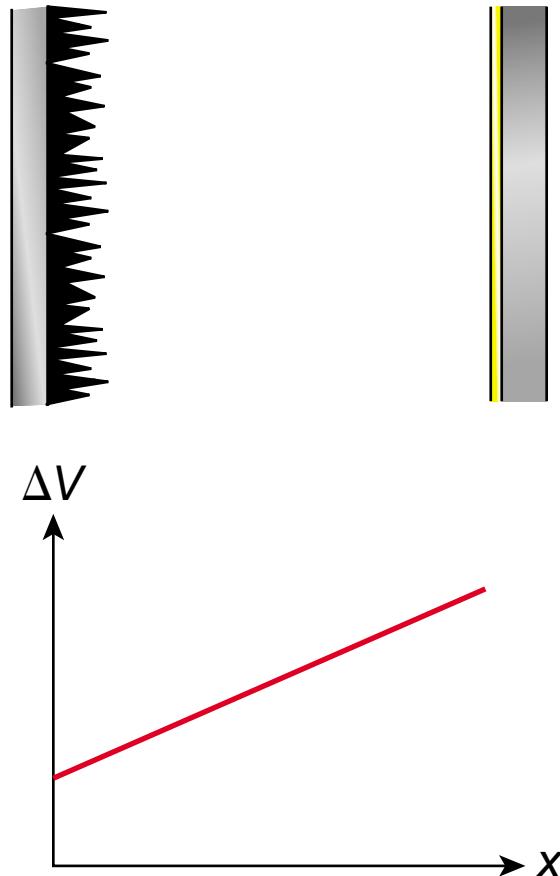
Results



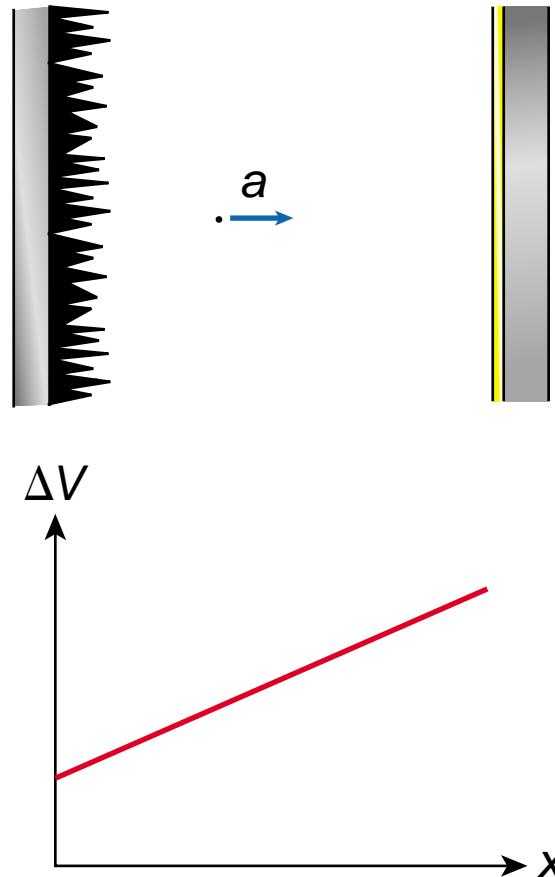
Space charge effect



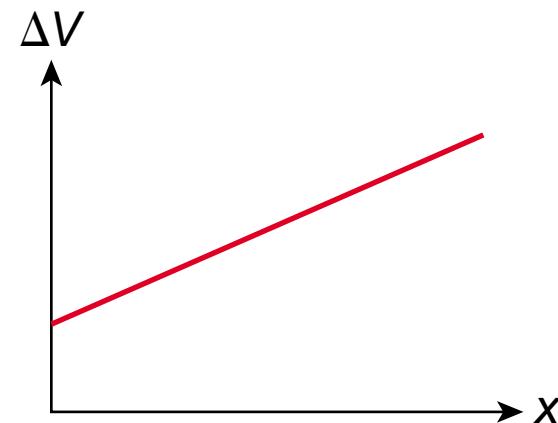
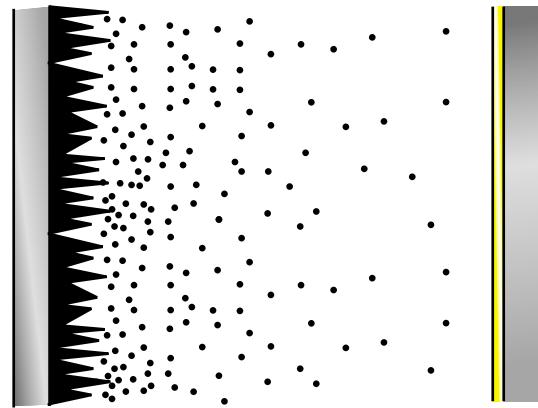
Space charge effect



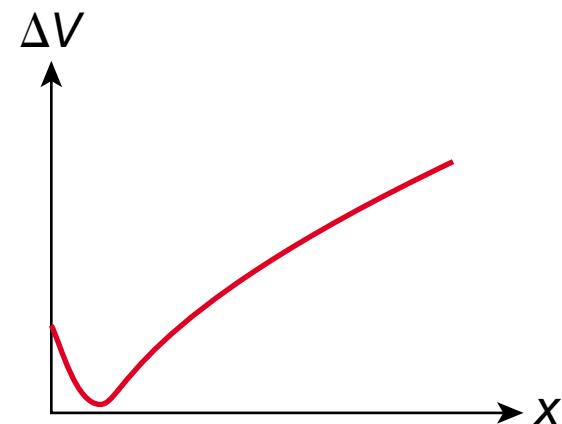
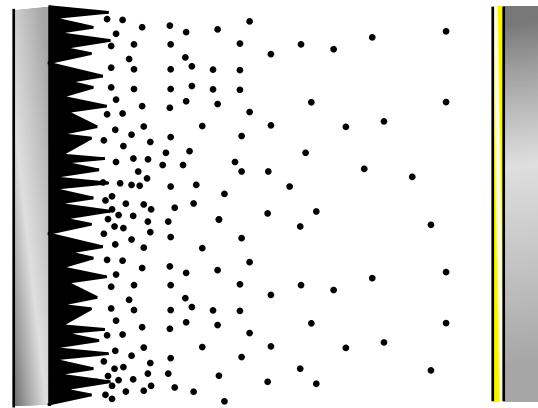
Space charge effect



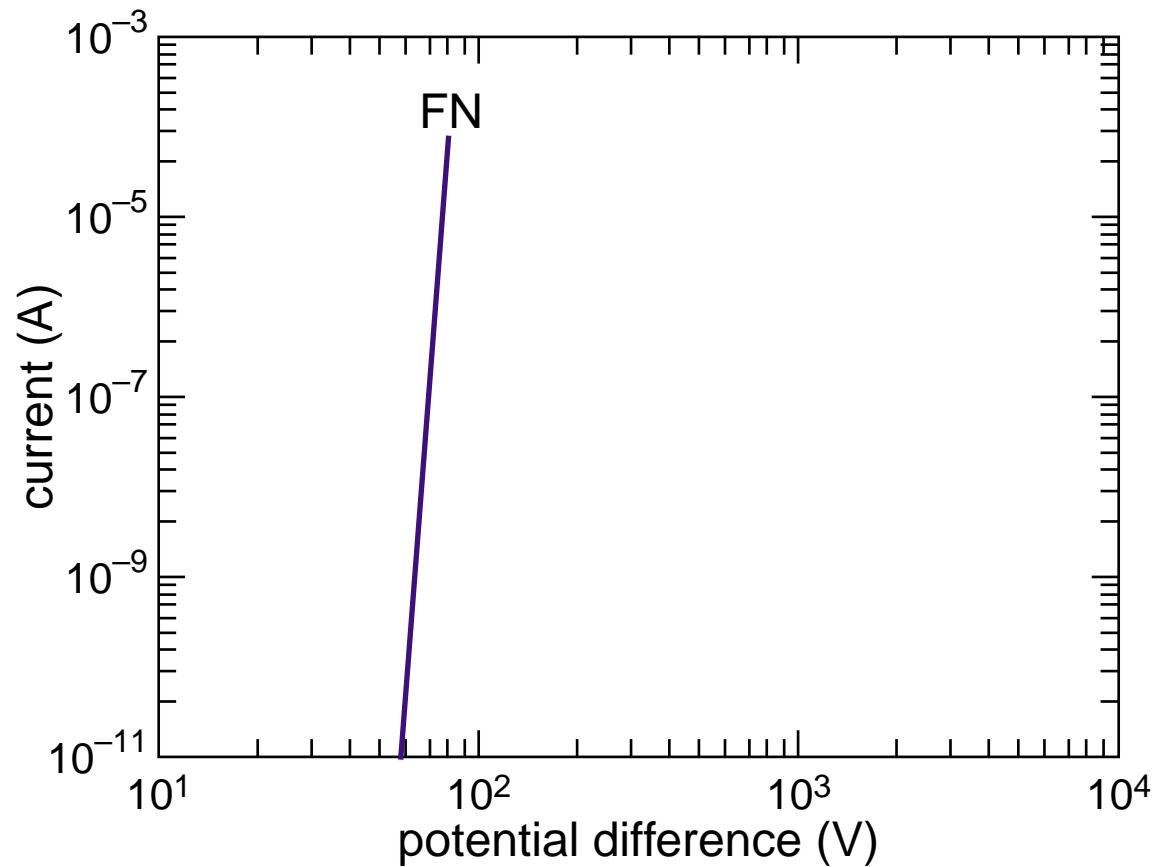
Space charge effect



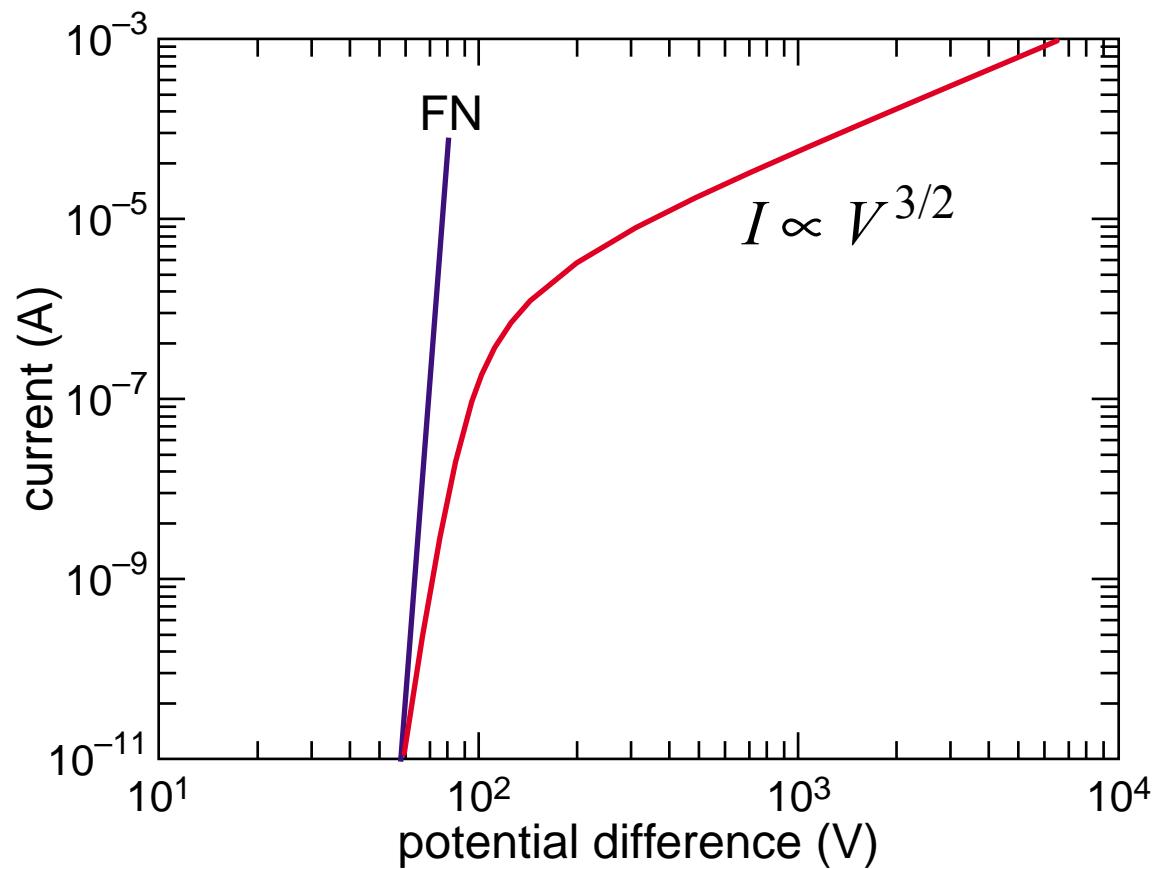
Space charge effect



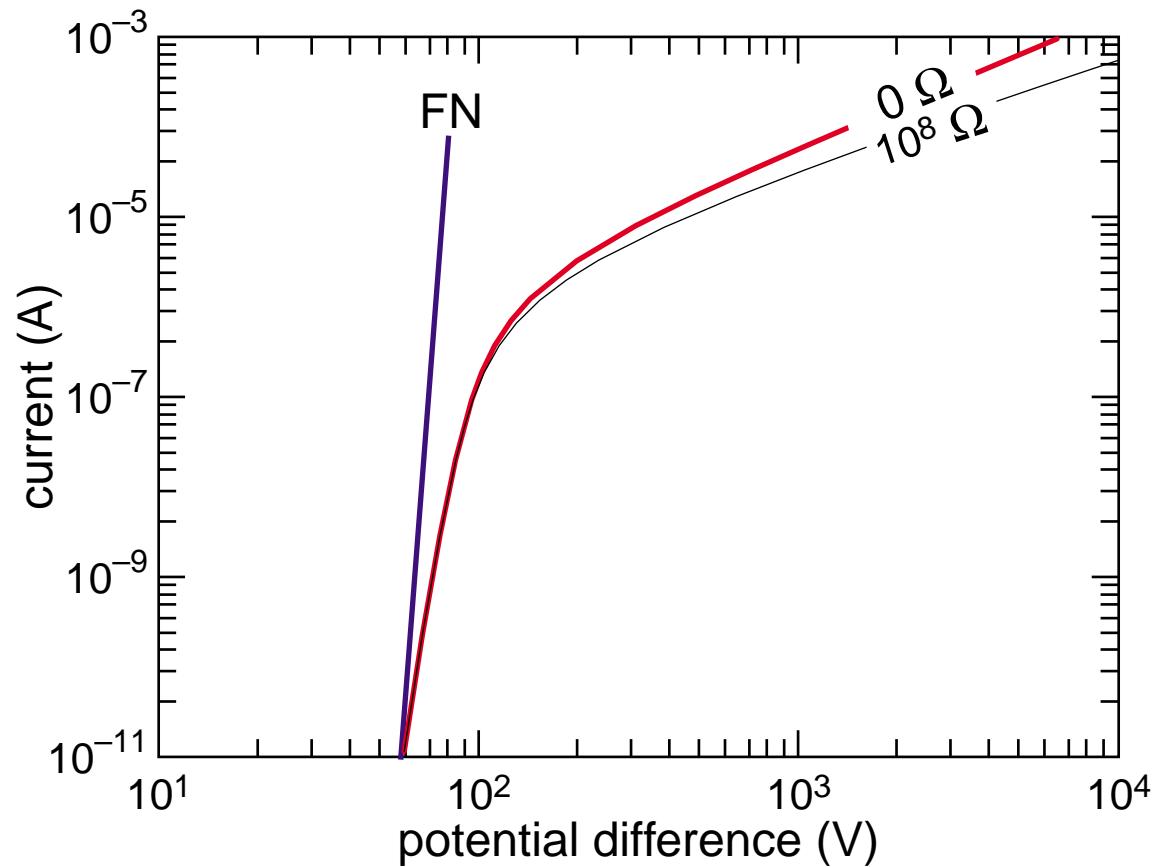
Space charge effect



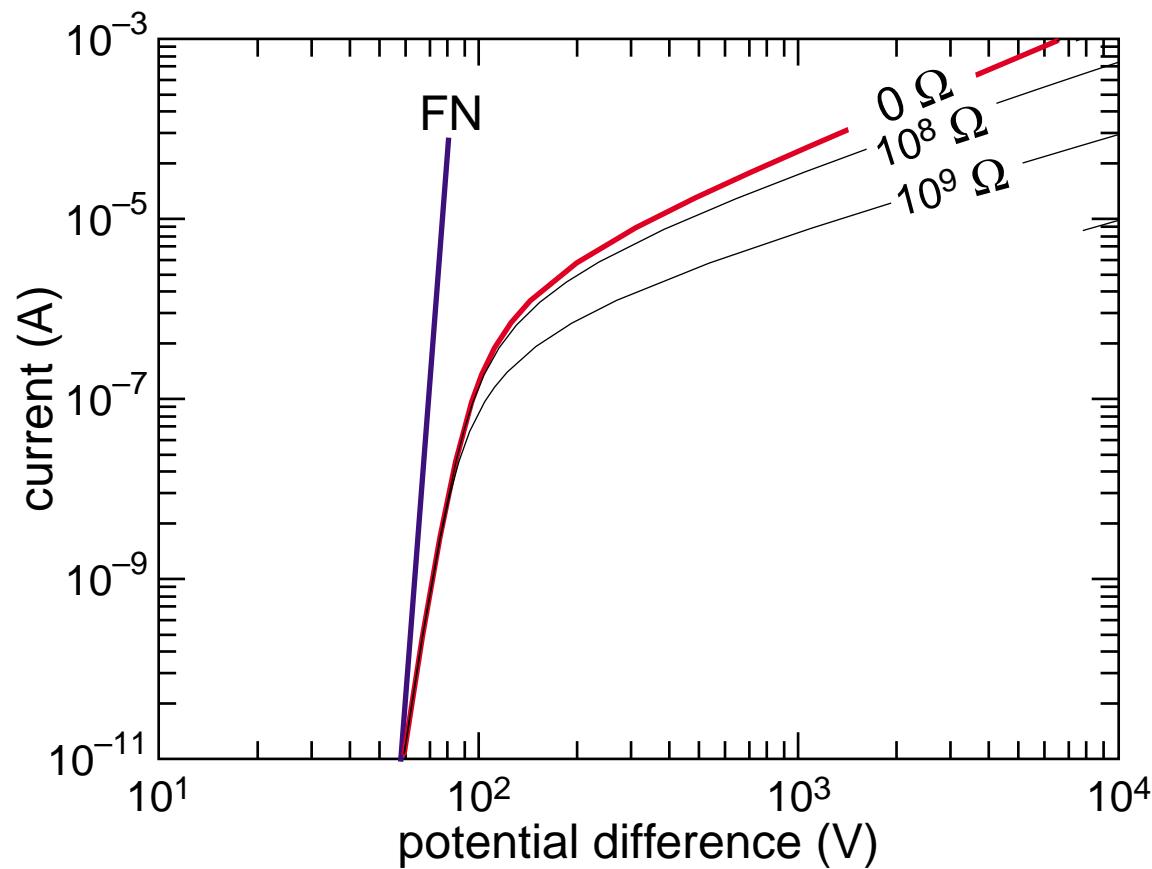
Space charge effect



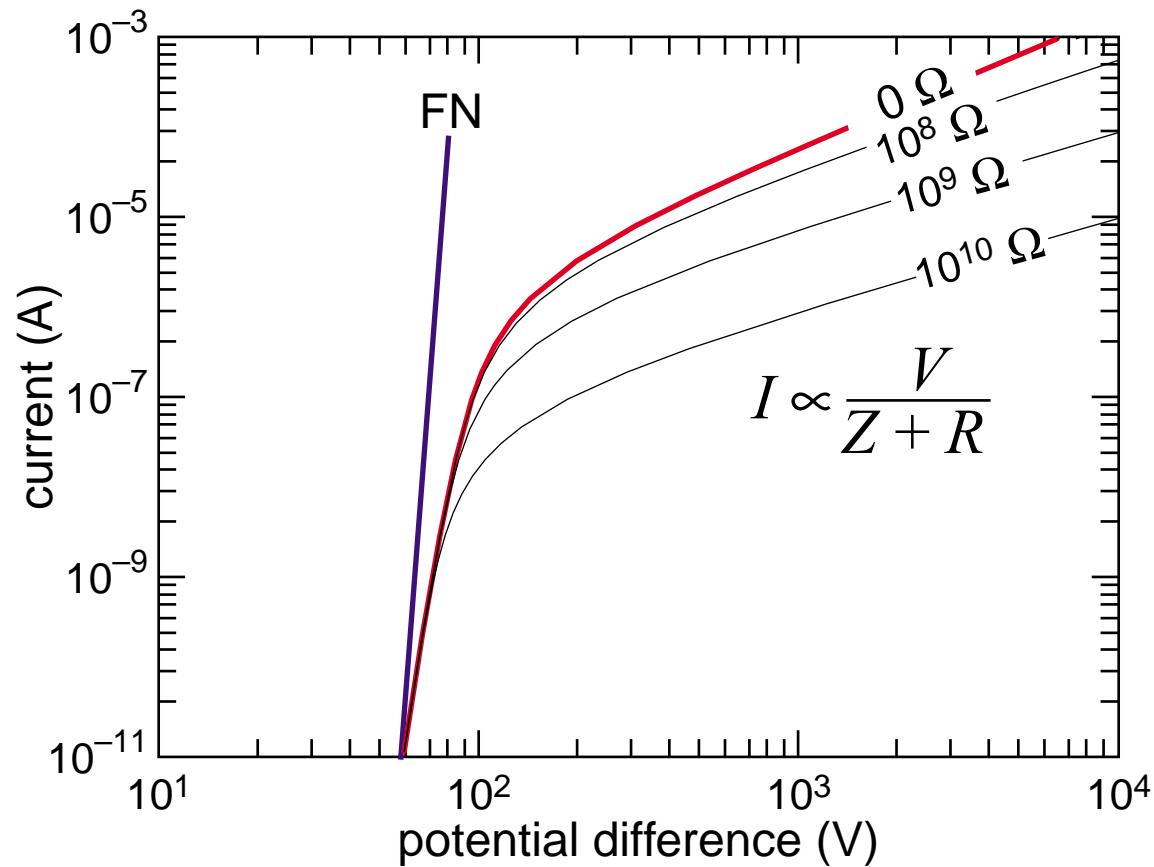
Space charge effect



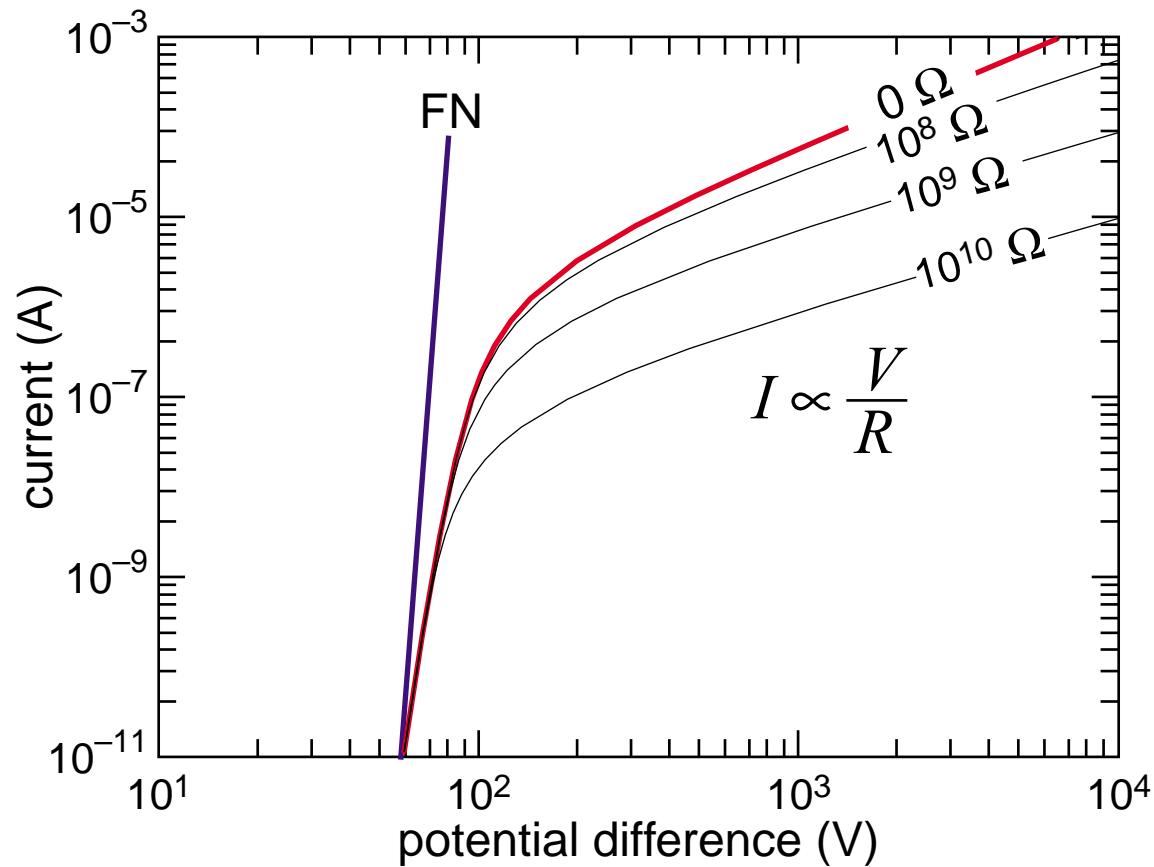
Space charge effect



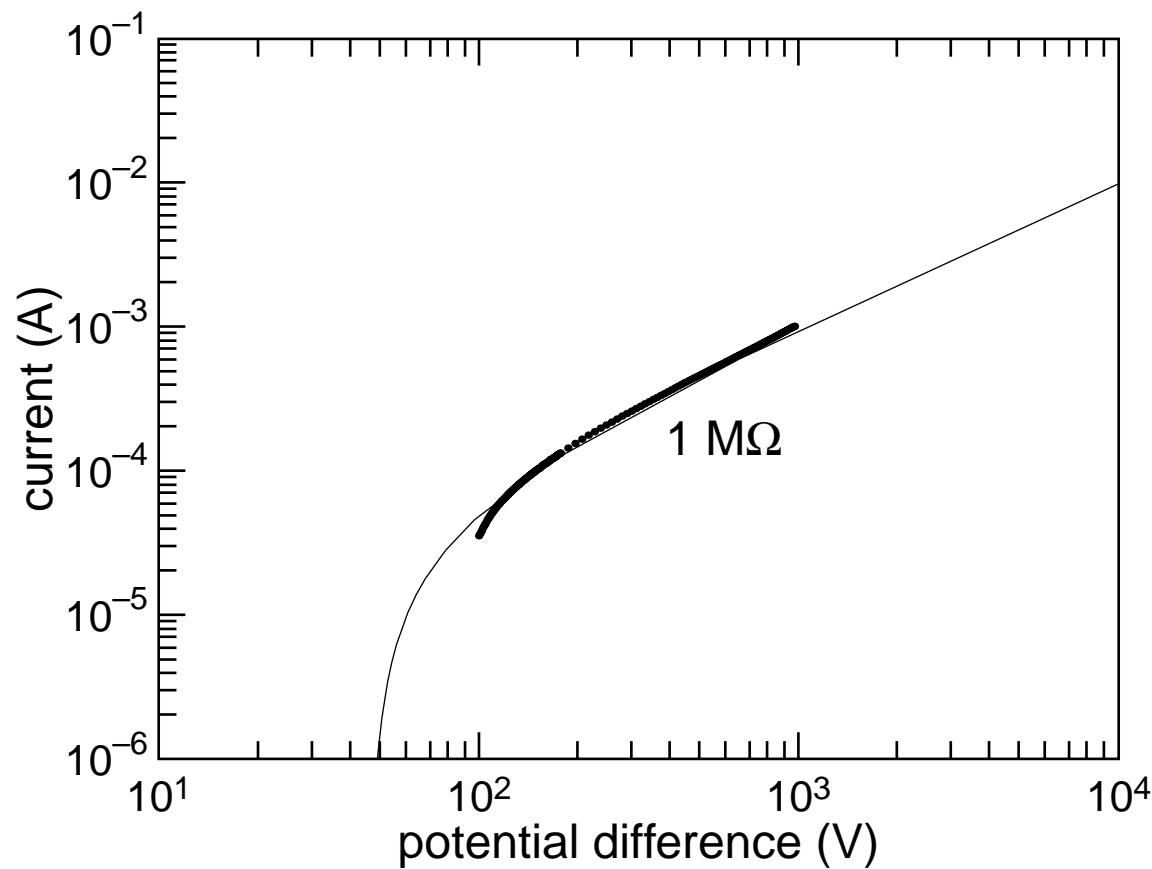
Space charge effect



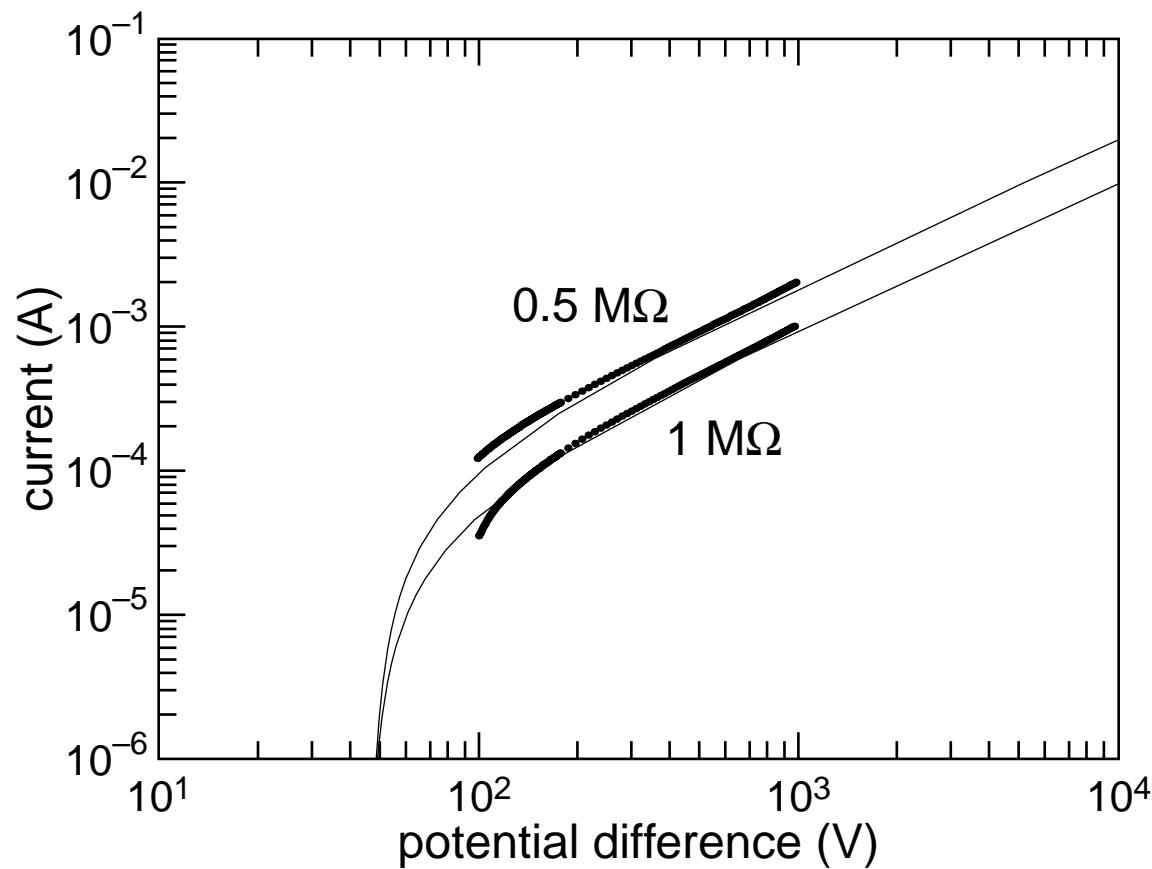
Space charge effect



Space charge effect



Space charge effect



Outline

- ▶ **Background**
- ▶ **Results**
- ▶ **Discussion**

Discussion

Ion channeling and electron backscattering

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

Discussion

Secondary ion mass spectrometry:

- ▶ 10^{20} cm^{-3} sulfur

- ▶ 10^{17} cm^{-3} fluorine

Discussion

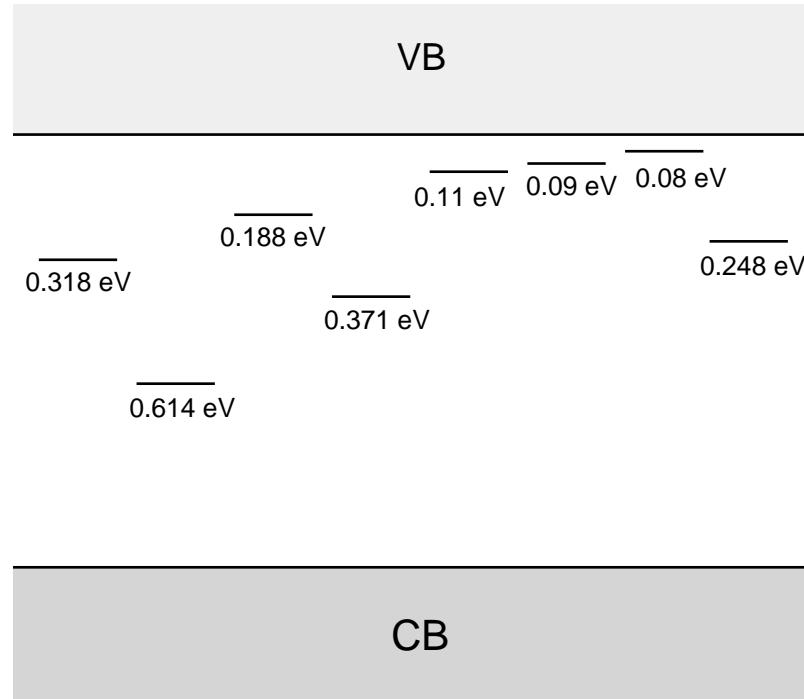
sulfur introduces states in the gap

VB

CB

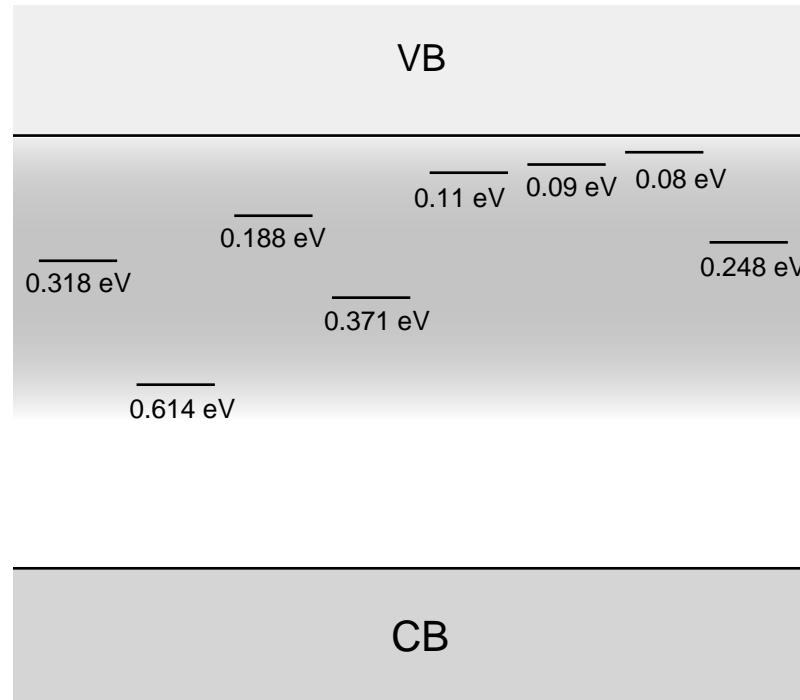
Discussion

sulfur introduces states in the gap

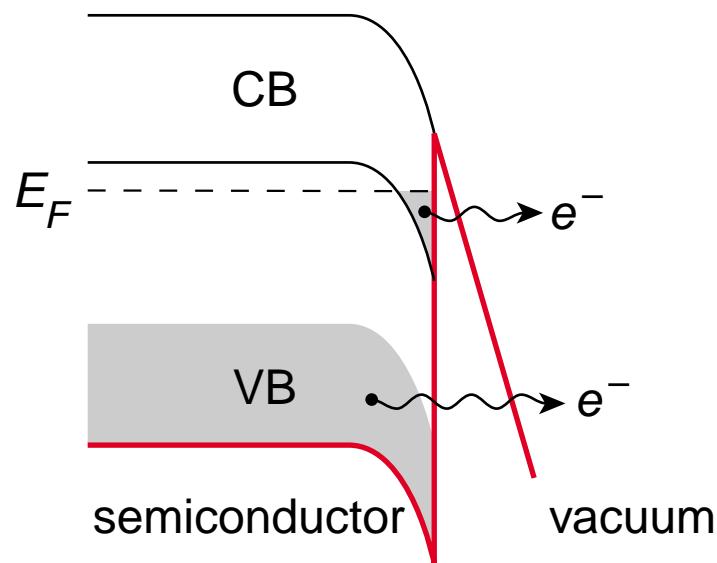


Discussion

states broaden into a band

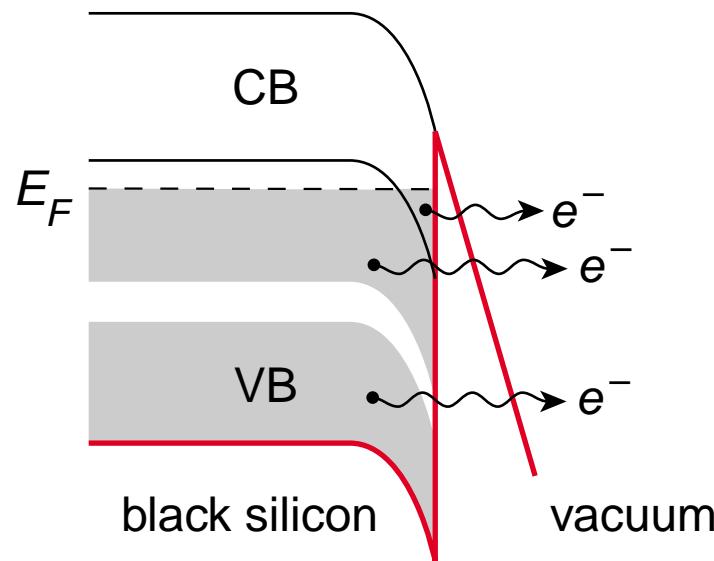


Discussion



Discussion

sulfur band provides additional electrons



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**
- ▶ **provides stable, high field-emission current**

Summary

Microstructured silicon

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

Summary

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-up Petri dish 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 of times brighter than the Sun.

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. Hydrogen fluoride is used to etch silicon. I thought maybe the SF₆ would decompose and then the fluorine would decompose the silicon." Mazur would soon

Applications

- ▶ **display technology**
- ▶ **detector technology**
- ▶ **solar cells**

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 know stories of werewolves. The most horrific tale is when a werewolf turns into a tiny, tiny devil when he's full moon.

Silicon has a powerful laser. In the early 1990s, Marantz was the first to make use of it. At 400 nm, 25% harder than a tempered glass. This device can withstand a several times more than the Sun's energy.

Marantz's new "black silicon" is extremely hard. It is the only material that can withstand the "laser attack". The same laser that attacks the entire device.

This will attack silicon substrate. When fluoride is used to etch silicon, it

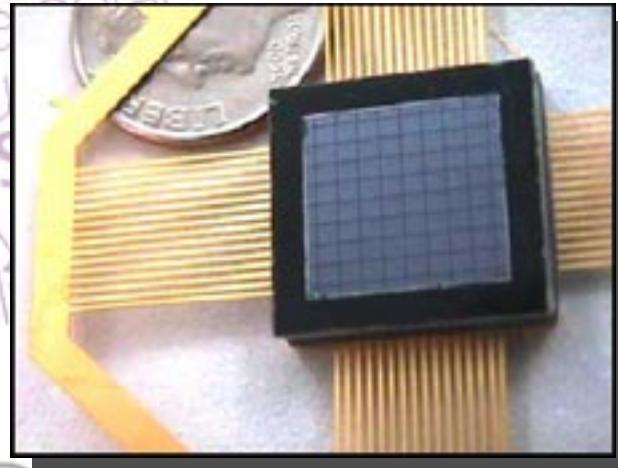
isn't enough to do the job. The acid

and then the fluorine will do

the job. Marantz es-

Applications

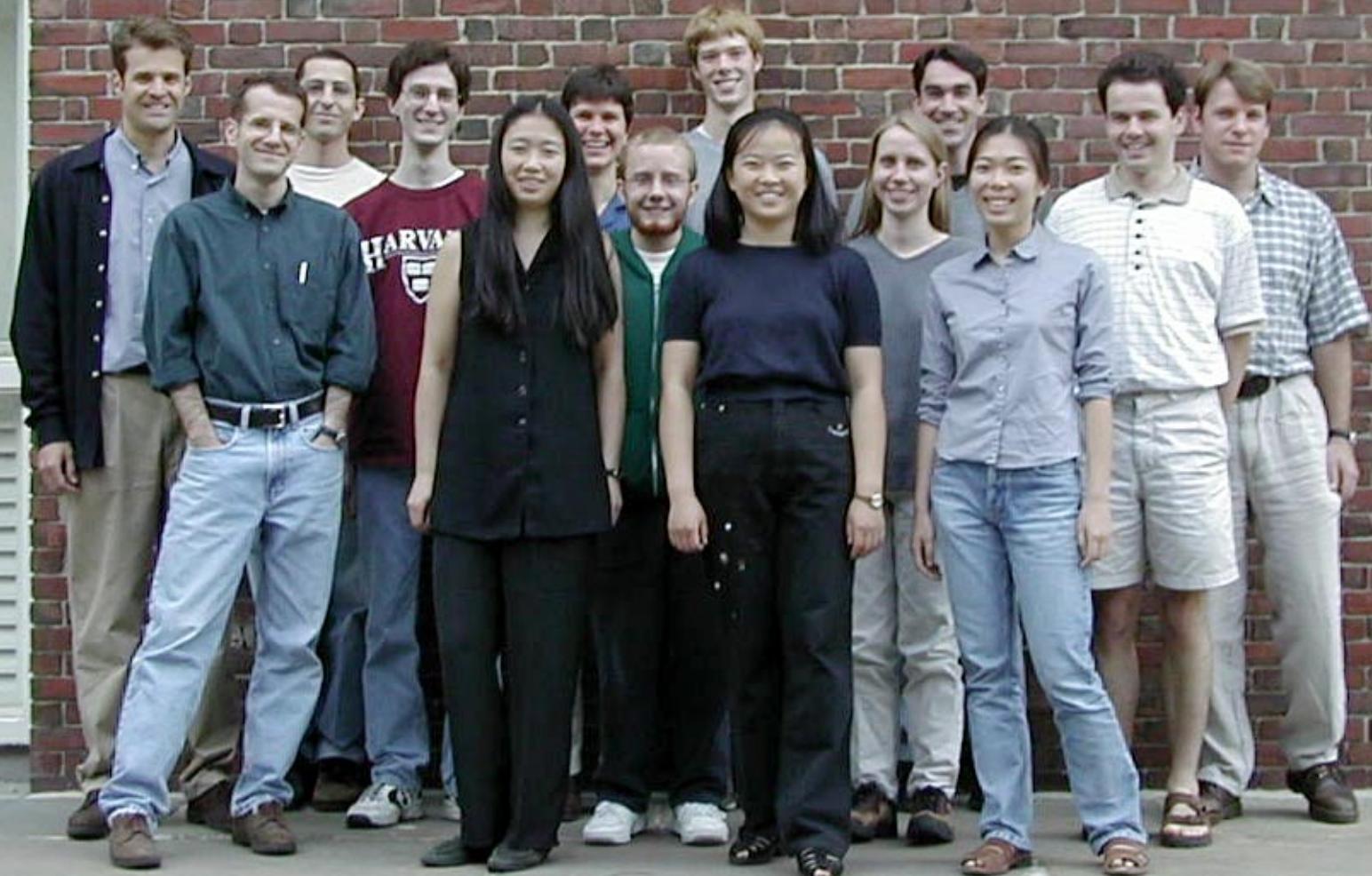
- ▶ **display technology**
- ▶ **detector technology**
- ▶ **solar cells**



TALL, DARK AND STRANGER

We all have stories of encounters with tall, dark figures who seem to know more than they should. Stories of a different kind don't usually come from the world of silicon. But when we look at the latest developments in solar-cell technology, it's hard not to feel like we're in the middle of one such story. The latest generation of solar cells, known as "thin-film" or "concentrator" cells, are being developed by companies like Sharp, Matsushita and others. These cells are made by depositing thin layers of semiconductor material onto a substrate. The most common material used is cadmium telluride, which is a type of compound semiconductor. This material has a bandgap of about 1.4 eV, which is higher than the sun's energy level (about 1.24 eV) and extremely low compared to traditional silicon cells (which have a bandgap of about 1.1 eV). As a result, these cells can convert more sunlight into electricity than traditional silicon cells. In fact, some thin-film cells have already achieved efficiencies of up to 15%, which is comparable to the best silicon cells. However, there are still some challenges to overcome before these cells can compete with traditional silicon cells on a large scale. One challenge is the cost of production. While the initial investment for a thin-film cell line is relatively low, the ongoing costs of materials and equipment can be quite high. Another challenge is the stability of the cells over time. While they are currently very efficient, they may not be able to withstand harsh environmental conditions like extreme heat or cold. Finally, there is the issue of recycling. Unlike traditional silicon cells, which can be easily melted down and reused, thin-film cells contain toxic materials like cadmium and tellurium, which must be disposed of carefully to prevent environmental contamination. Despite these challenges, the potential for thin-film cells is enormous. They could revolutionize the way we generate electricity, making it more efficient, less expensive and more sustainable. And who knows? Maybe one day we'll even have a "tall, dark and stranger" encounter with a solar cell that's better than anything we've seen before.

GORDON MCKAY
LABORATORY OF
APPLIED SCIENCE



A photograph of a group of approximately 15 people, mostly men, standing in two rows in front of a red brick wall. Some faint, large letters are visible on the wall, including 'JABCO' and 'APPL'.

Funding: Army Research Office

Acknowledgments:
Prof. Li Zhao (Fudan University)
Prof. Mike Aziz (Harvard University)

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

<http://mazur-www.harvard.edu>