Influence of Substrates on the Nucleation of Se-Te Films

Lorenzo X. Van Munoz

Co-Mentors: Nathan Lewis and Ethan Simonoff

Lewis Group

10/19/2019

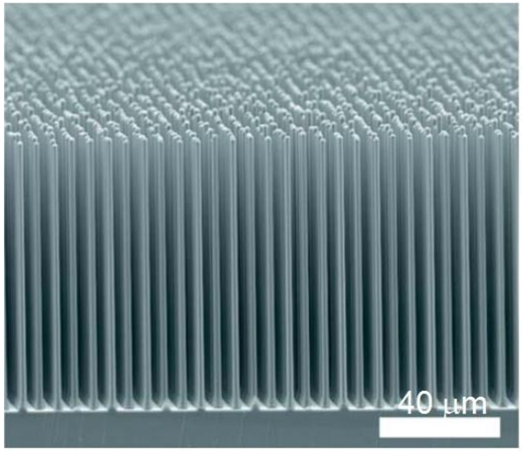
Caltech

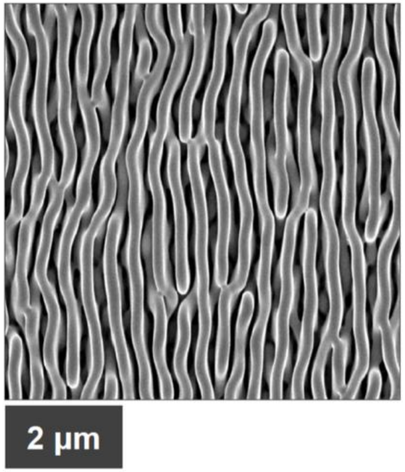
Overview

- Structures
- Inorganic phototropic growth of semiconductor films
- Selenium-Tellurium (Se-Te) films
- Substrate effects on pattern morphology
- Higher nucleation densities improve pattern morphology

Structures

- Benefits
  - Maximize light absorption
  - Maximize surface area
  - Improve catalyst placement
- Manufacturing Goals
  - Spontaneous/Self-assembling
  - Wide area structures

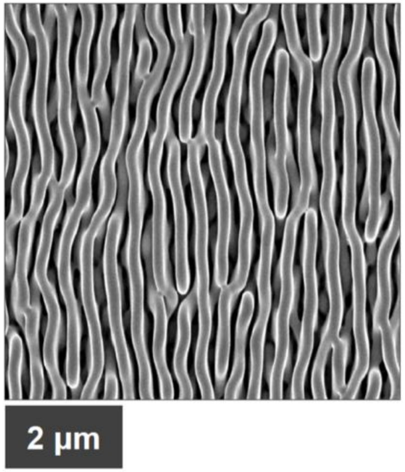




Caltech

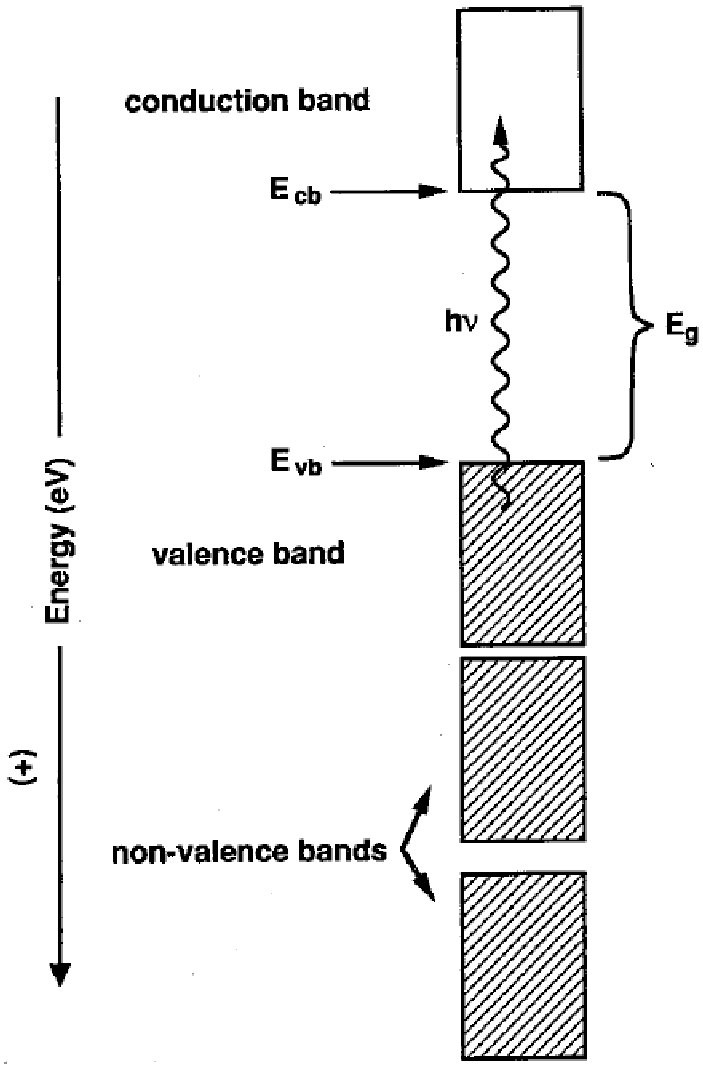
Structures

- Benefits
  - Maximize light absorption
  - Maximize surface area
  - Improve catalyst placement
- Manufacturing Goals
  - Spontaneous/Self-assembling
  - Wide area structures
  - Inspired by phototropic growth



Caltech

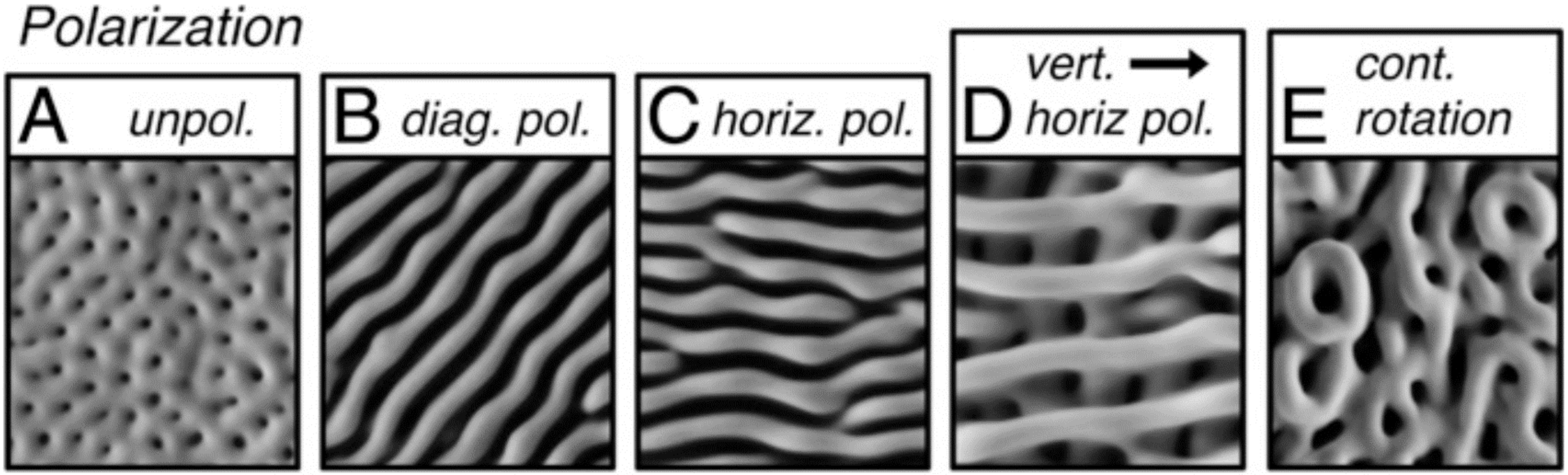
Semiconductors



- Their electronic structure allows them to store (light) energy
- Their optical properties make them candidates for structures

Caltech

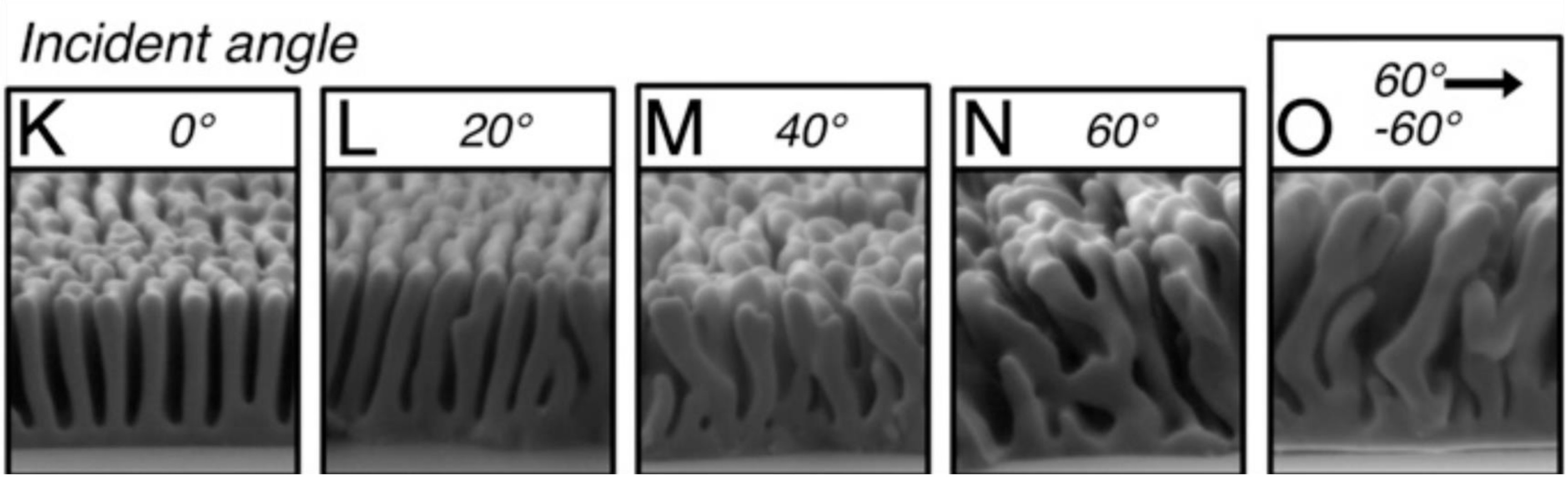
Se-Te film morphology responds to polarization of illumination source



Sadtler et al. *PNAS* **2013**, 110 (49), 19707-19712

Caltech

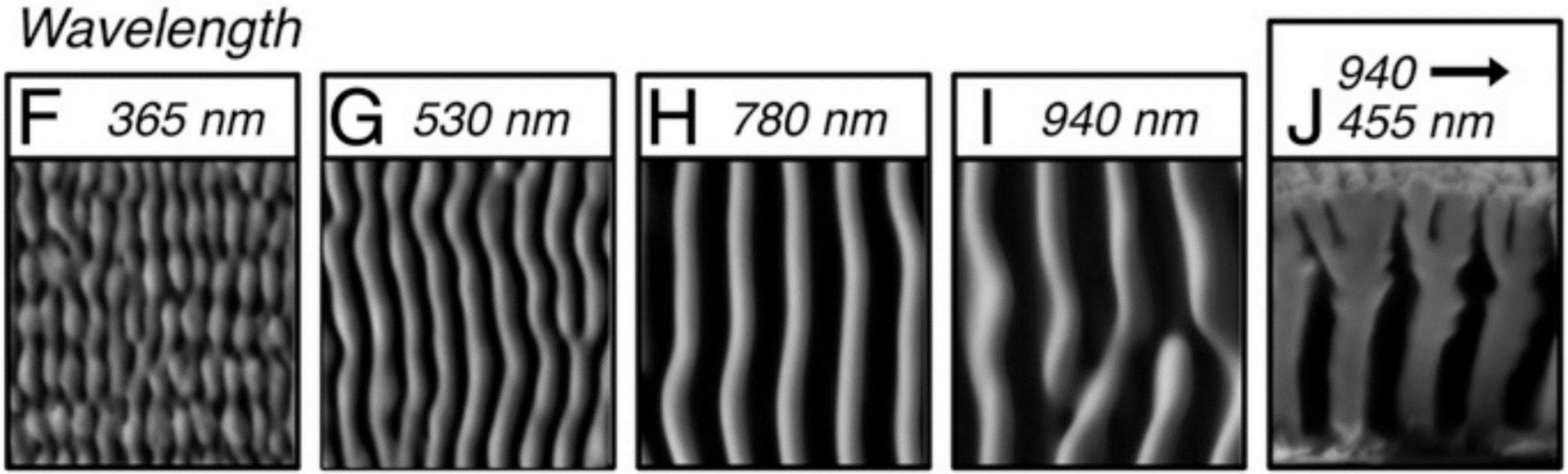
Se-Te film morphology responds to angle of illumination source



Sadtler et al. *PNAS* **2013**, 110 (49), 19707-19712

Caltech

Inorganic analogue to phototropic growth

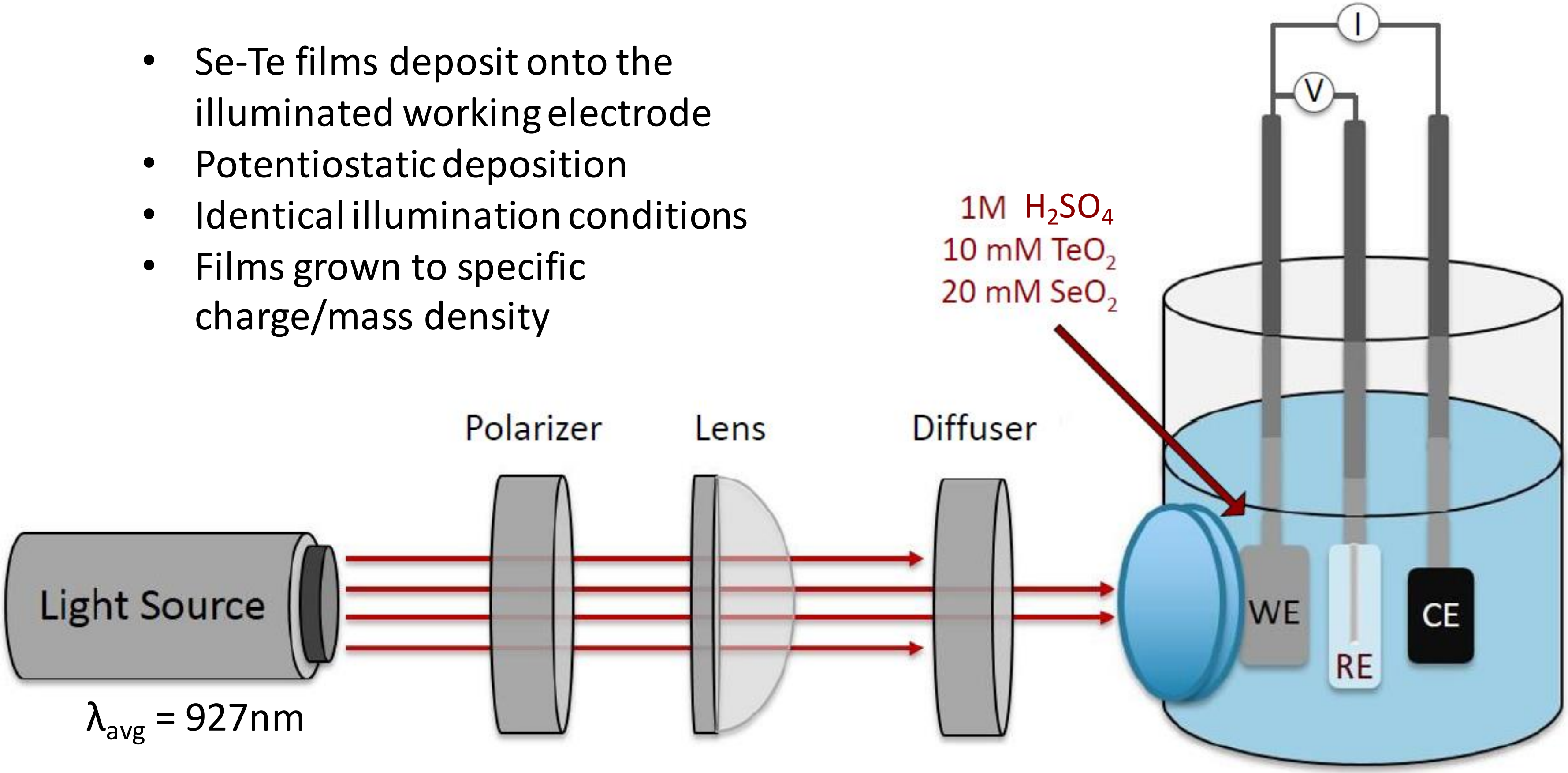


Sadtler et al. *PNAS* **2013**, 110 (49), 19707-19712

Caltech

Experimental Setup

- Se-Te films deposit onto the illuminated working electrode
- Potentiostatic deposition
- Identical illumination conditions
- Films grown to specific charge/mass density



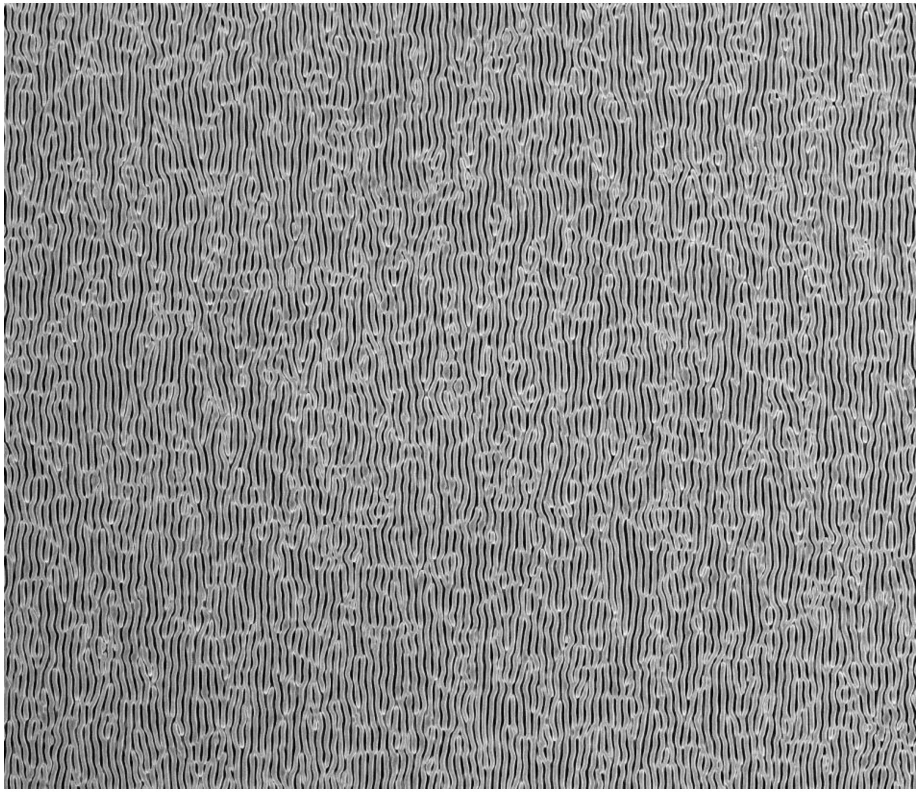
λ_{avg} = 927nm

Simonoff et al. *Nano Letters* **2019,** *19* (2), 1295-1300

Caltech

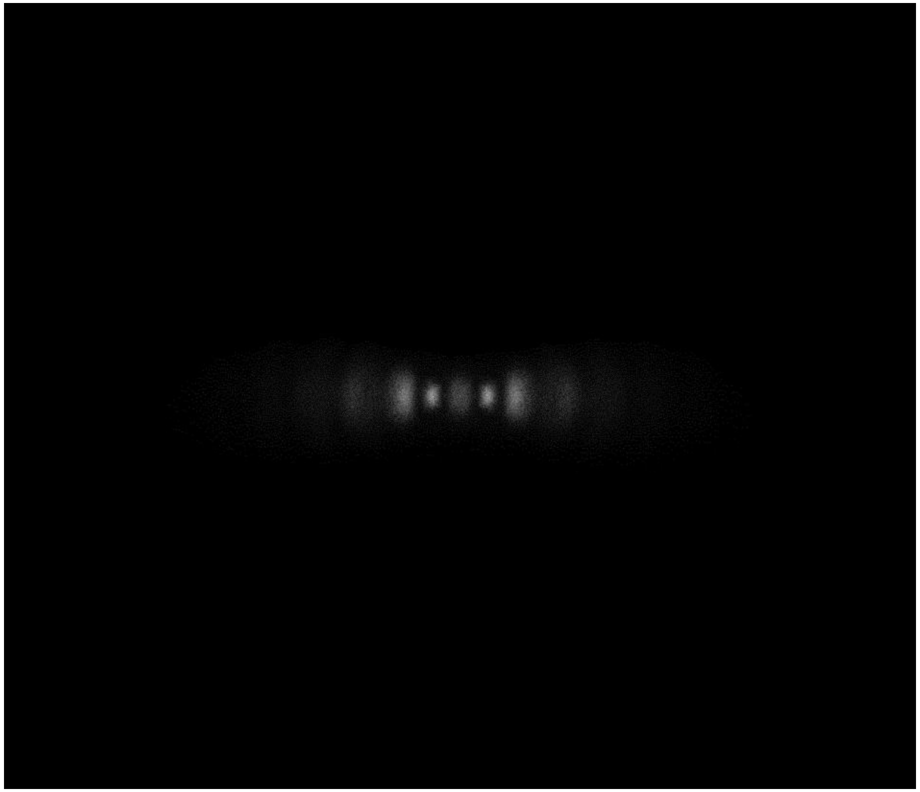
How to understand and analyze Fourier transforms (FT) of these structures

20 μm



SEM image obtained at 6500X, 4096px wide

20 μm[-1]

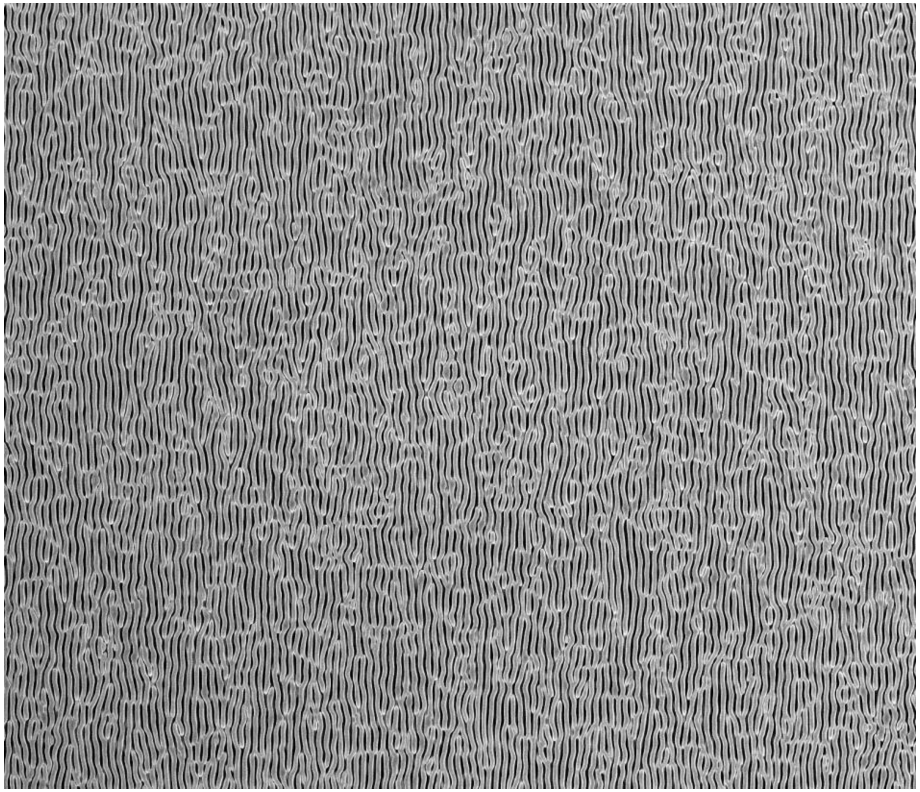


2DFT performed in Gwyddion

Caltech

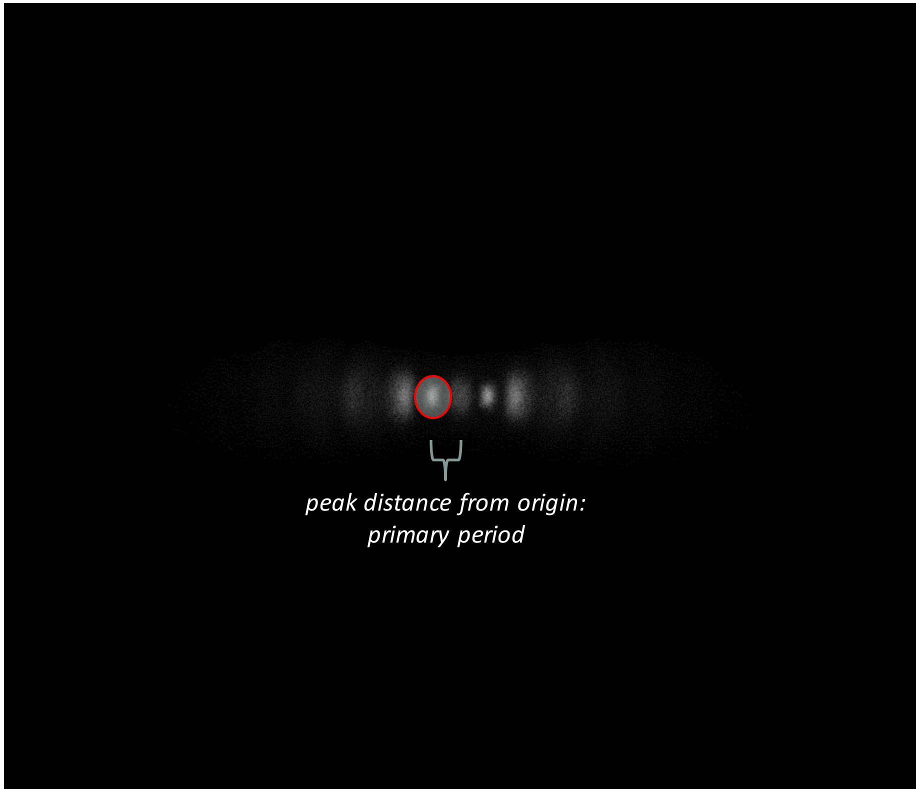
How to understand and analyze Fourier transforms (FT) of these structures

20 µm



SEM image obtained at 6500X, 4096px wide

20 µm^{-1}

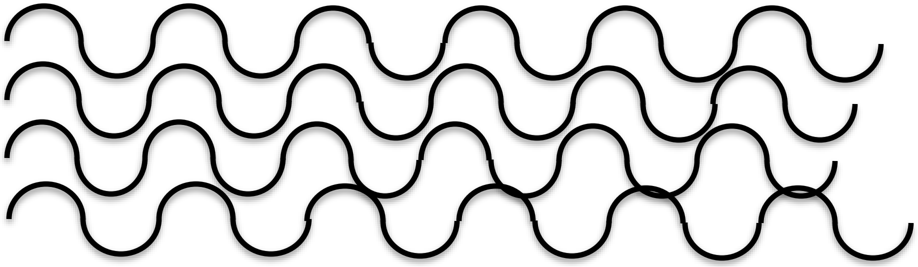


2DFT performed in Gwyddion

Caltech

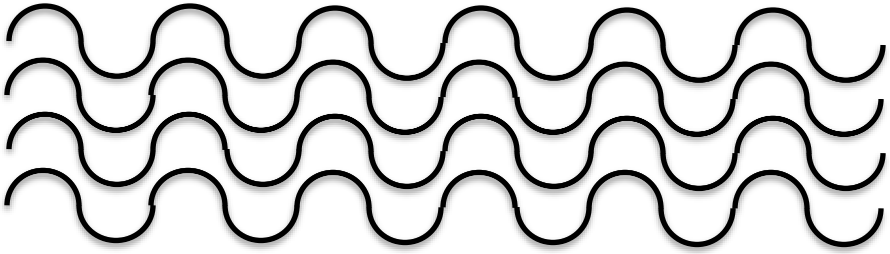
Horizontal width of FT band gives spectral width (frequency space) of pattern period

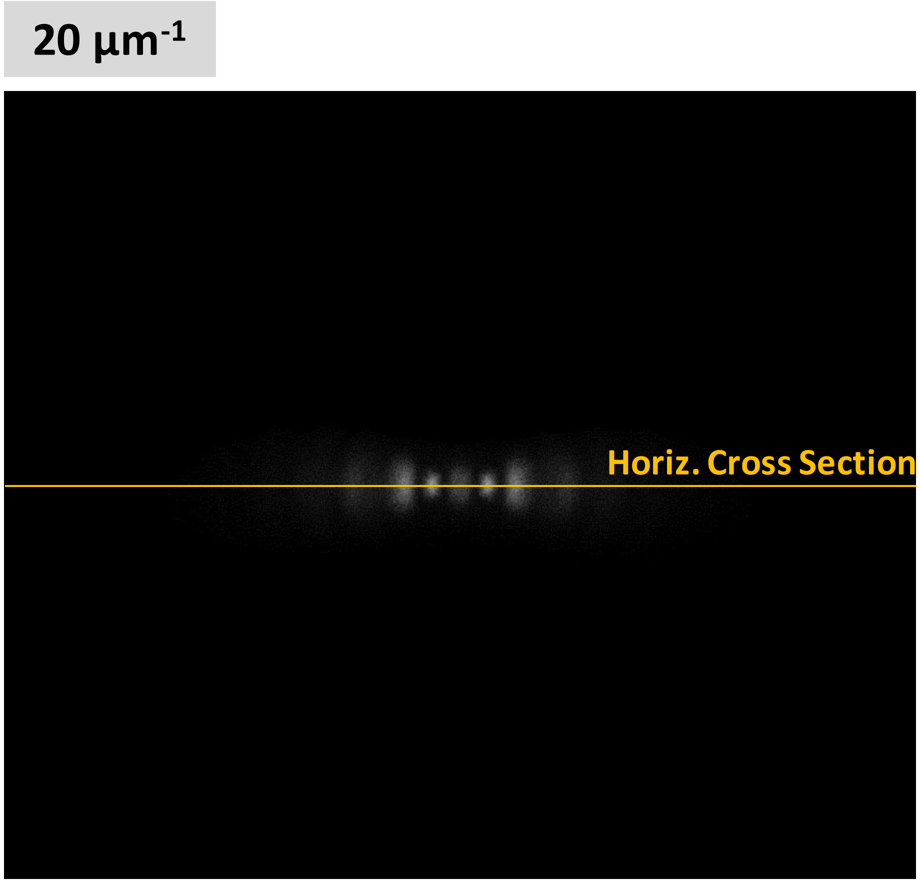
Wide



vs.

Narrow

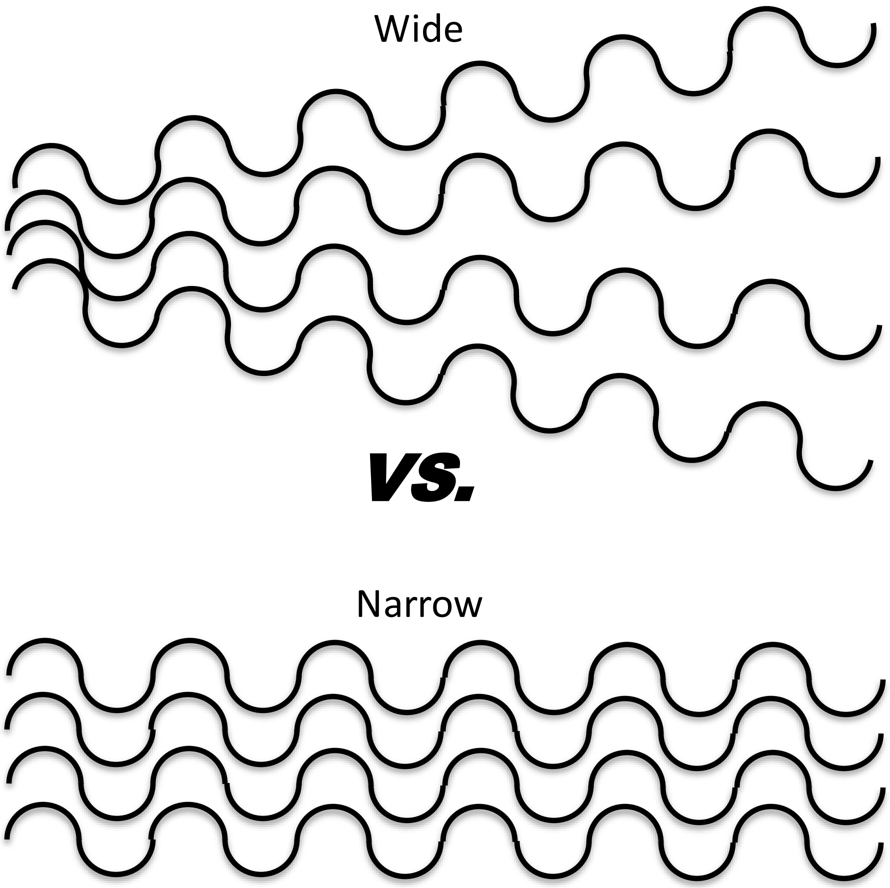


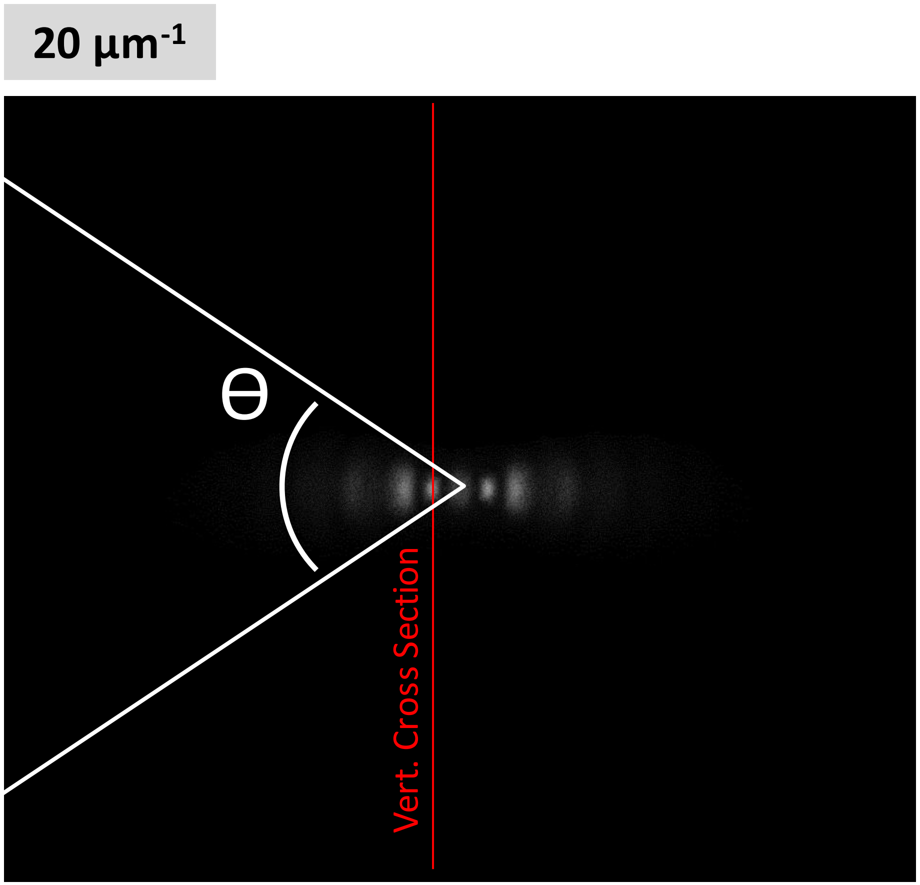


2DFT performed in Gwyddion

Caltech

Vertical width of FT band gives degree of angular-spread of a pattern of given period



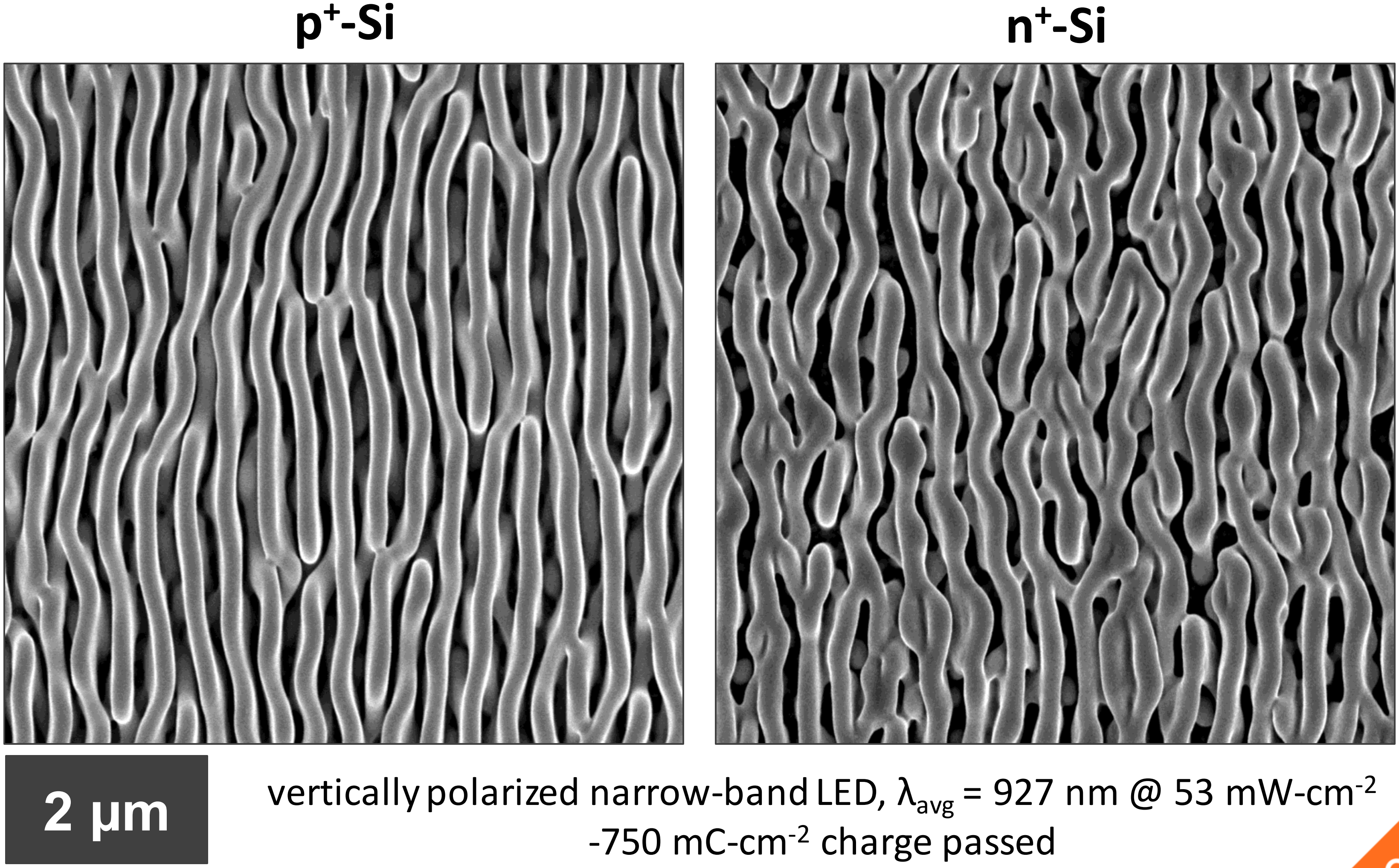


2DFT performed in Gwyddion

Vertical cross-section converted to polar coordinates and FWHM reported in angular units

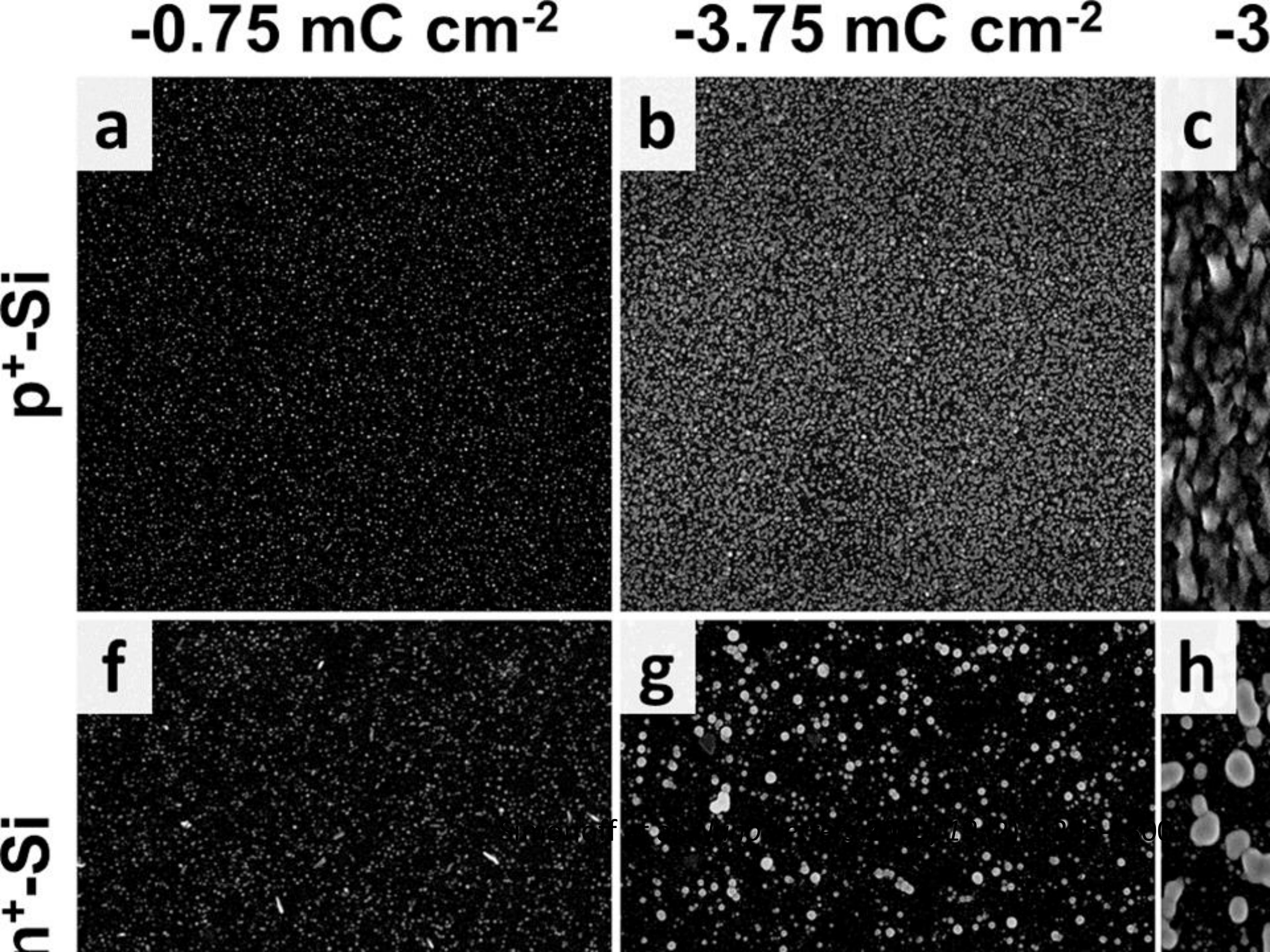
Caltech

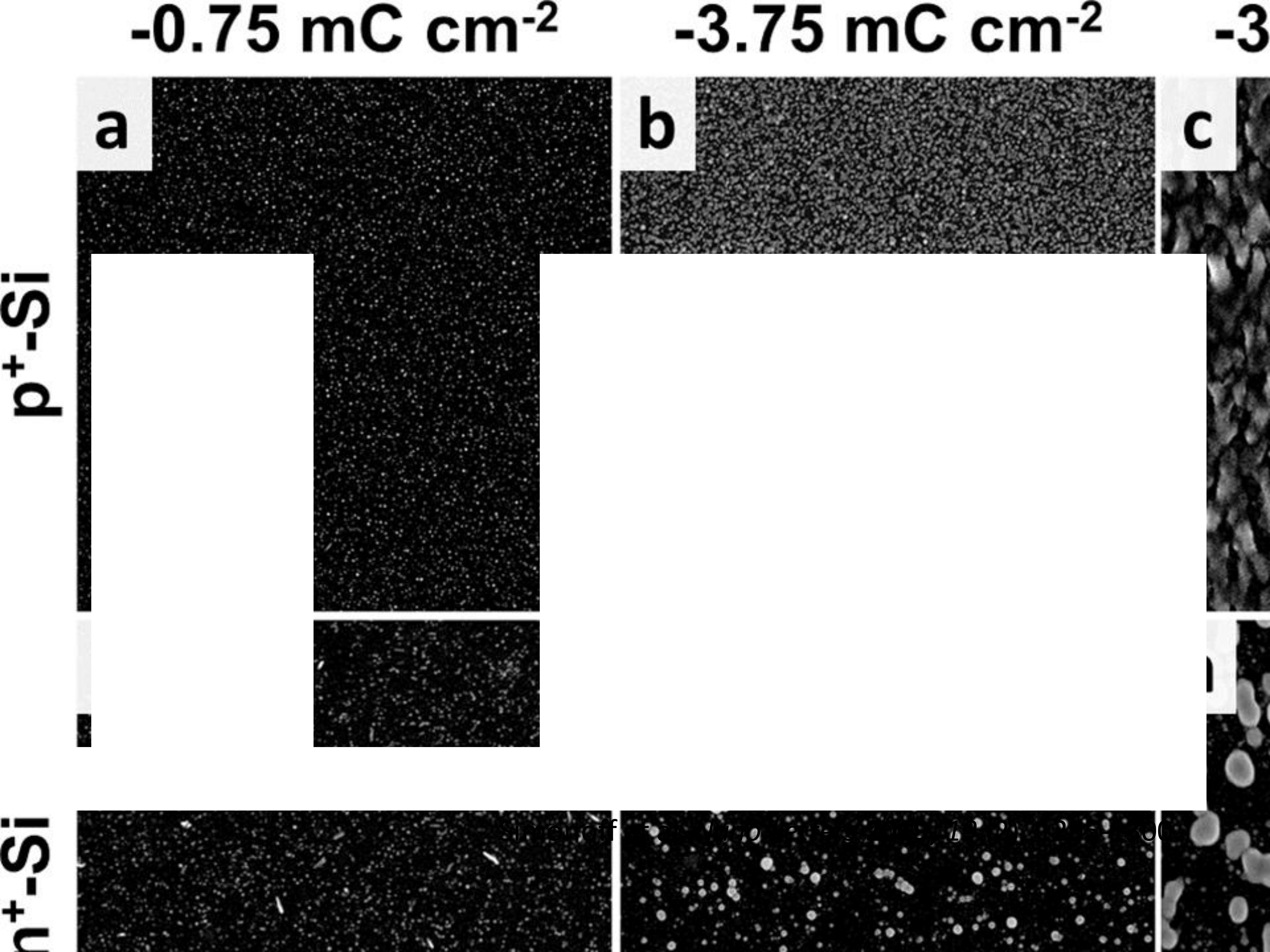
Films grown potentiostatically under identical illumination conditions are observed to be less defective on p^+-Si vs. n^+-Si.



vertically polarized narrow-band LED, λ_{avg} = 927 nm @ 53 mW-cm^{-2}
-750 mC-cm^{-2} charge passed

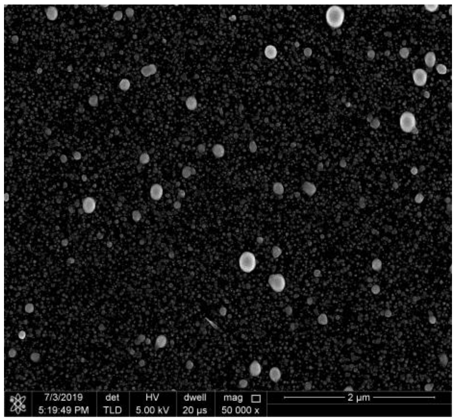
Caltech


-0.75 mC cm-2
-3.75 mC cm-2
-3
a
b
c
f
g
h
p+-Si
n+-Si

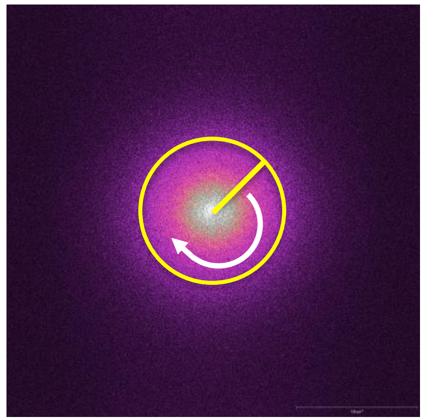

-0.75 mC cm-2
-3.75 mC cm-2
-3
a
b
c
p+-Si
n+-Si
Simonoff

Radially integrated FT spectra measure nucleation density (particle spacing)

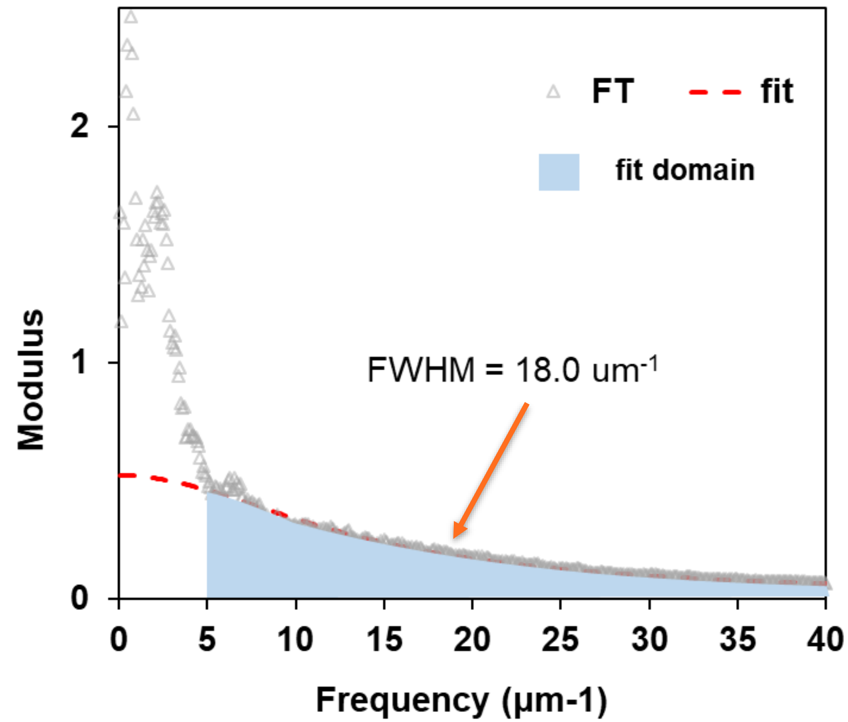
eds174-15, n$^+$-Si substrate, 3.75 mC/cm2, -280mV vs Ag/AgCl



50kx SEM image | 2 μm



2DFT, Gwyddion | 100μm^{-1}



Larger FWHM span higher frequencies

Lorentzian fit to observed particle-to-particle spacings of 200 nm to 10 nm

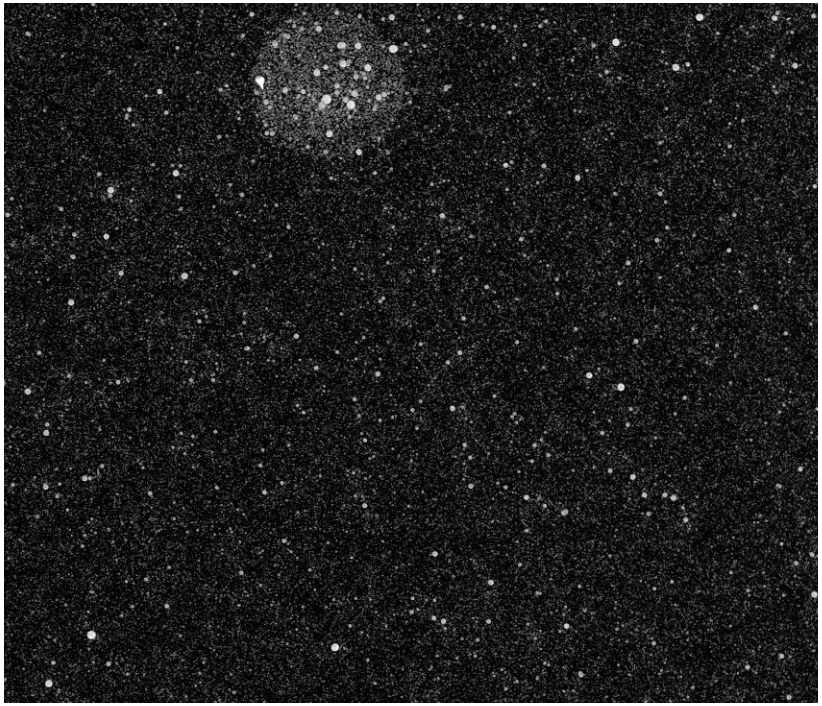
Caltech

Higher nucleation density is observed on n^+-Si substrates at more negative applied potentials.

4 µm

-3.75 mC cm^{-2} charge passed on n^+-Si

-200 mV vs Ag/AgCl



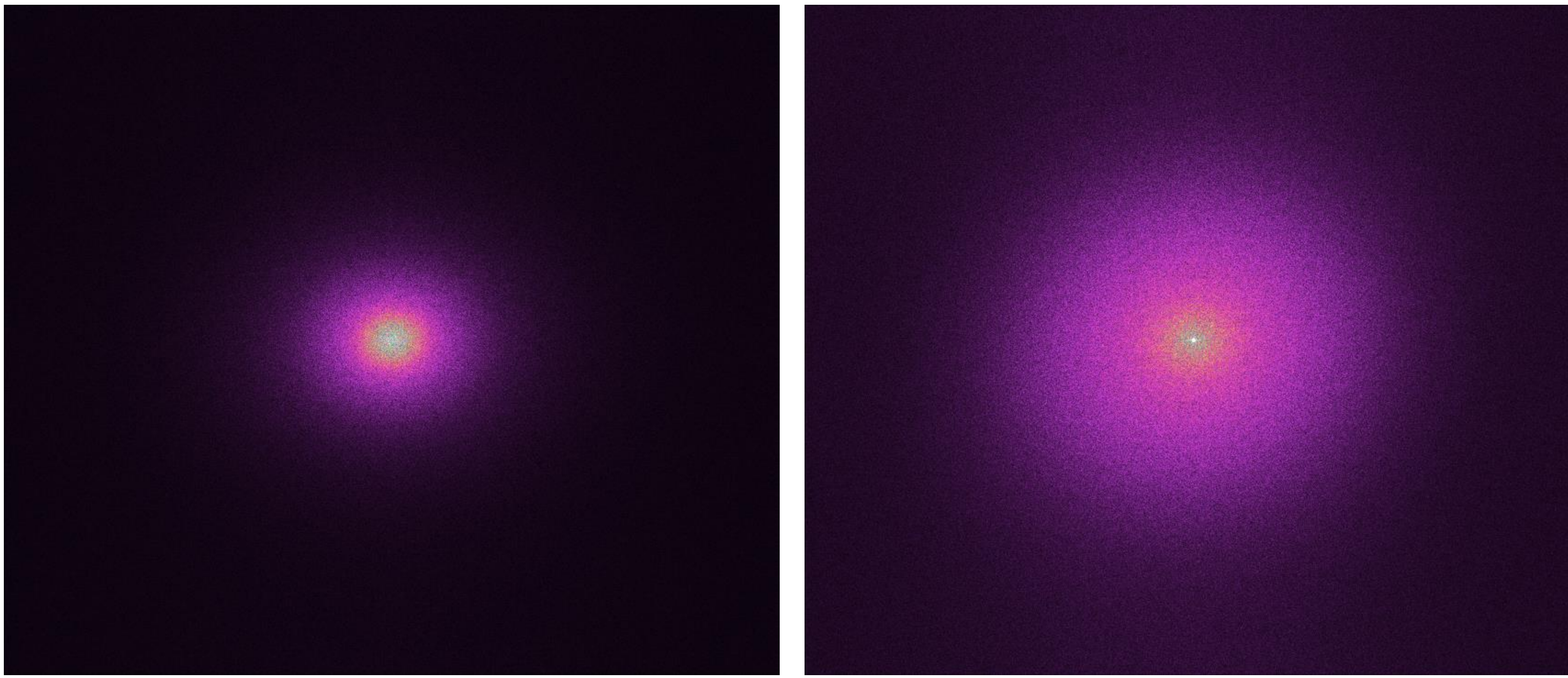
-300 mV vs Ag/AgCl

Caltech

Higher frequency intensity is observed in 2D FTs of Se-Te nucleation on n^+-Si substrates at more negative applied potentials.

80 μm^{-1}

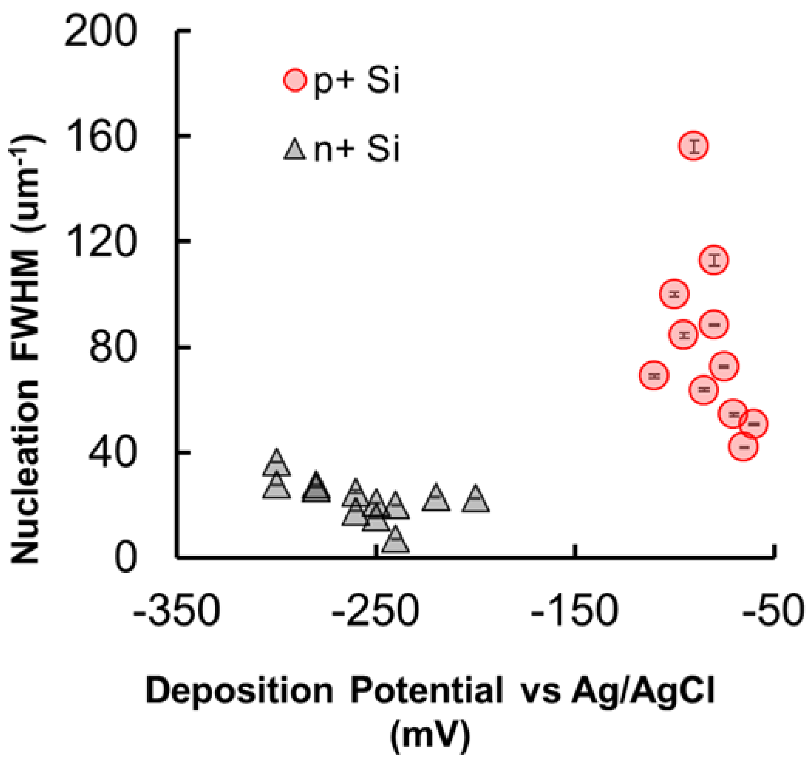
2D FT (-3.75 mC cm^{-2} charge passed on n^+-Si)



-200 mV vs Ag/AgCl **-300 mV vs Ag/AgCl**

Similar nucleation density trend is observed on p^+-Si substrates across working potential range.

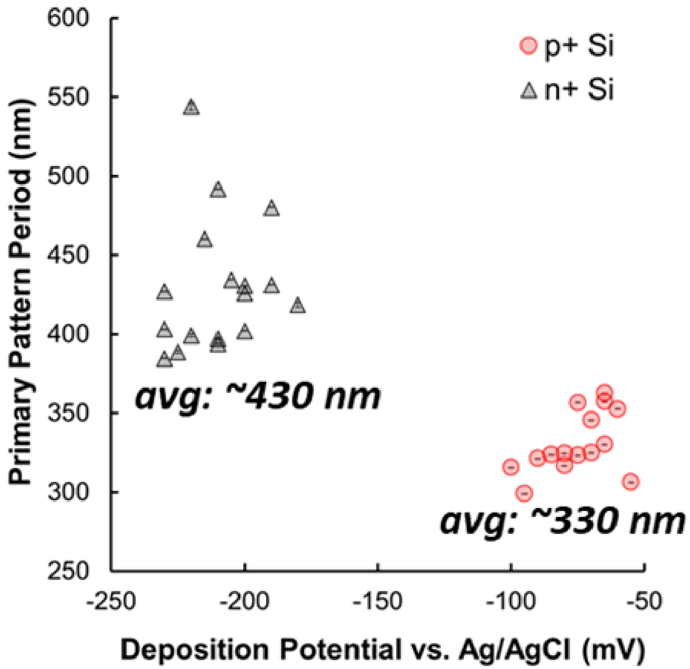
Nucleation density measurements

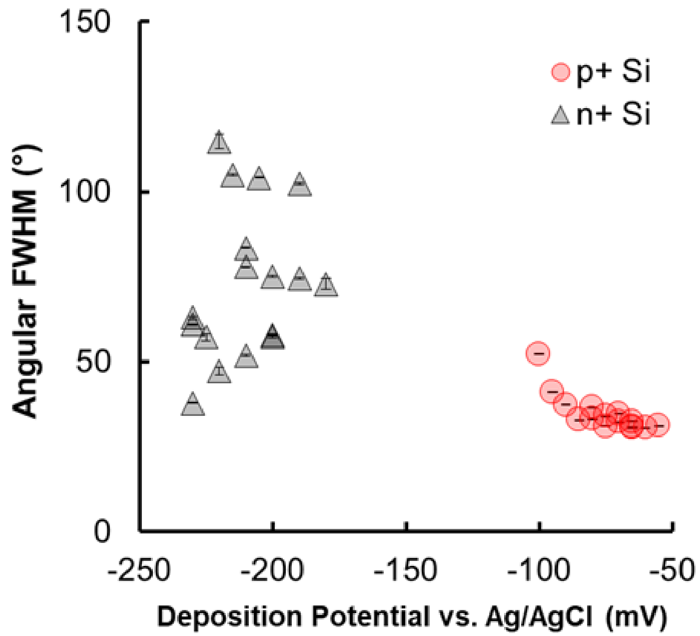


- Nucleation density is larger on p+-Si vs. n+-Si
- Both substrates demonstrate larger nucleation densities at more negative potentials

Pattern period and fidelity measurements

Simonoff et al. Nano Letters 2019, 19 (2), 1295-1300





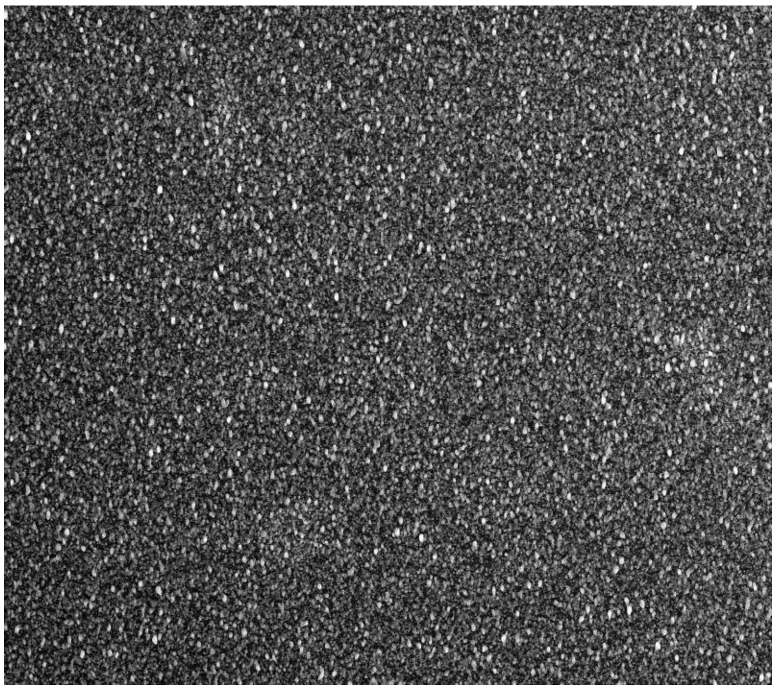
- p^+-Si displays lower period and higher fidelity than n^+-Si
- n+-Si shows improved packing and fidelity at more negative potentials
- Potential trend is less pronounced in p+-Si
- This follows nucleation density

Caltech

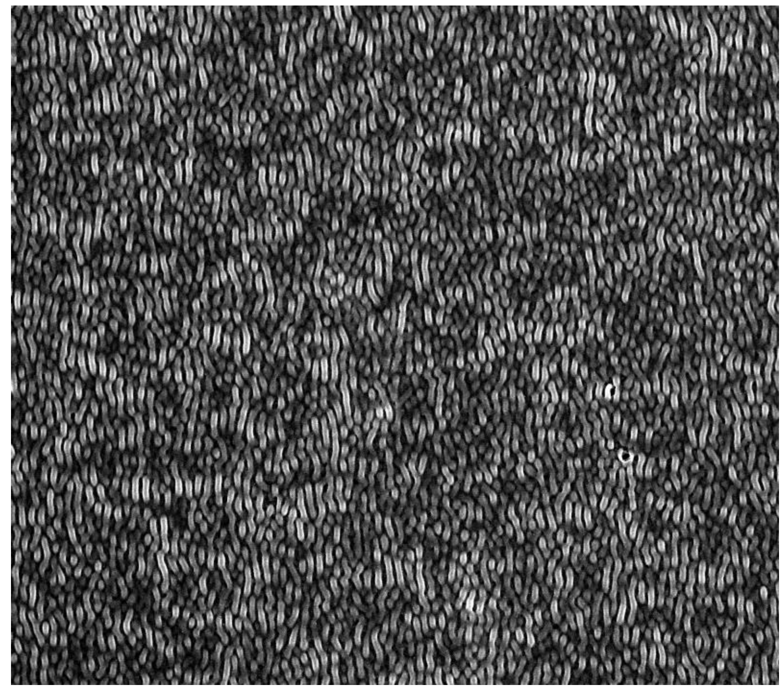
High nucleation density of Se-Te on p^+-Si results in more direct crossover between thin film and lamellar pattern.

5 µm

-80 mV vs Ag/AgCl on p^+-Si



-37.5 mC cm^{-2} charge passed

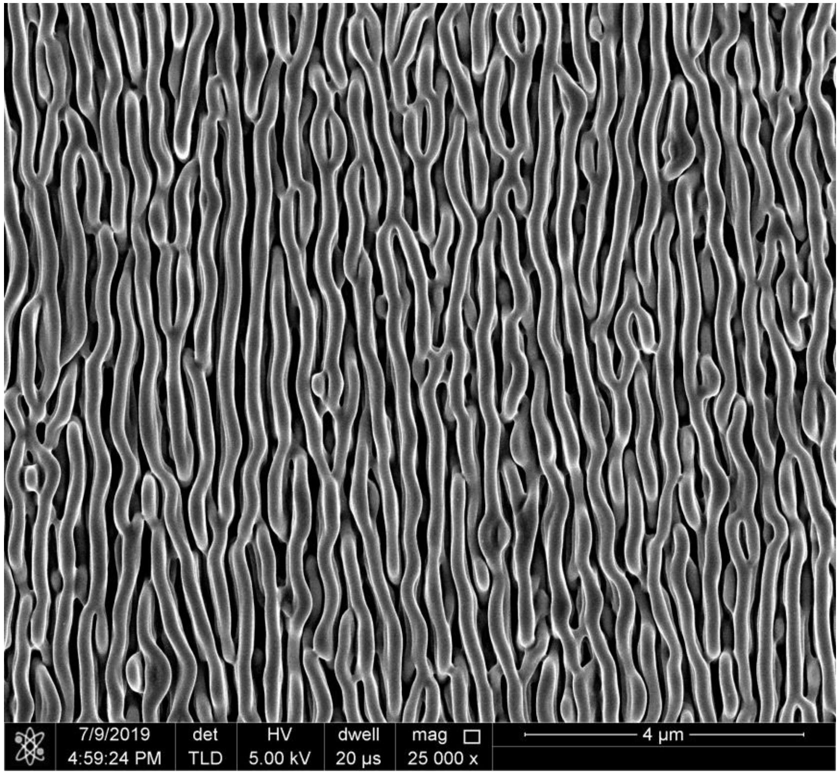


-75 mC cm^{-2} charge passed

Caltech

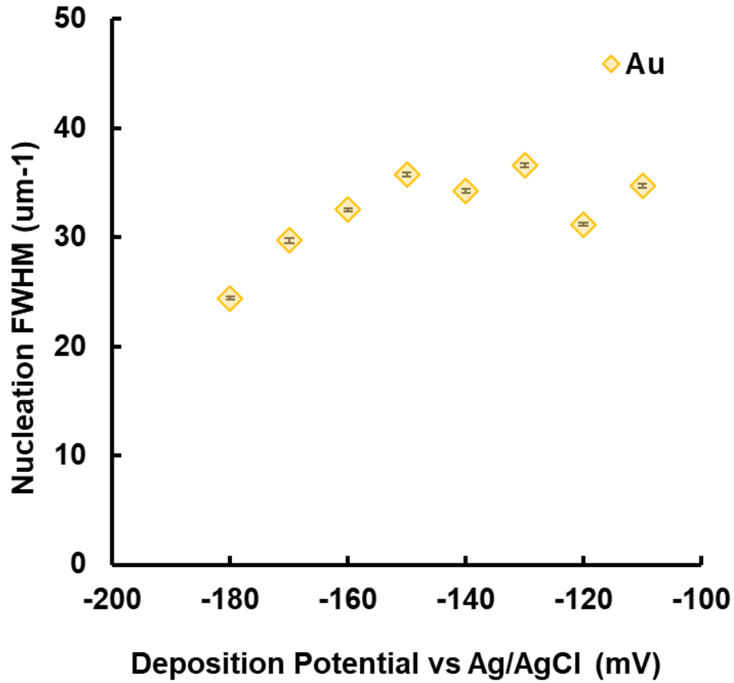
Pattern analysis for Se-Te films deposited on Au substrates

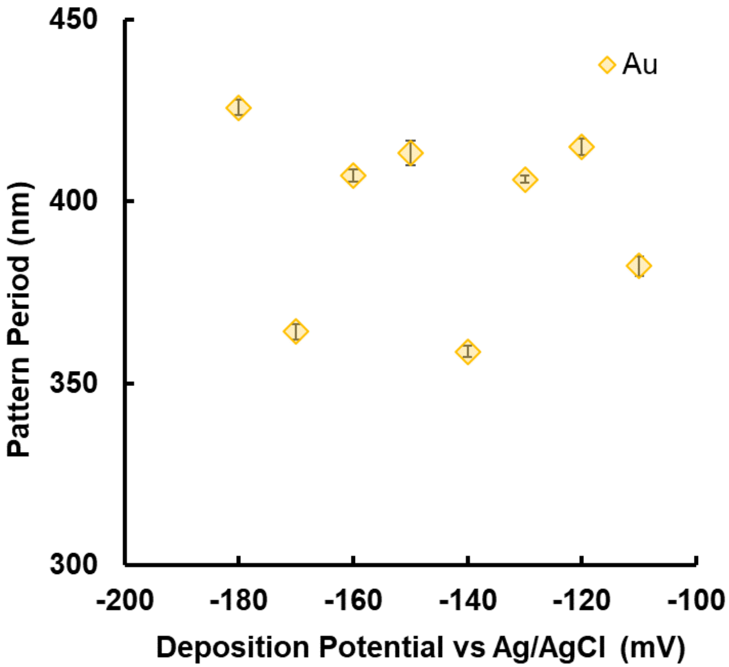
eds 176-14, Au substrate, -750 mC/cm2, -150mV vs Ag/AgCl



4 µm

Se-Te film morphology on Au responds to potential unlike on p⁺-Si and on n⁺-Si



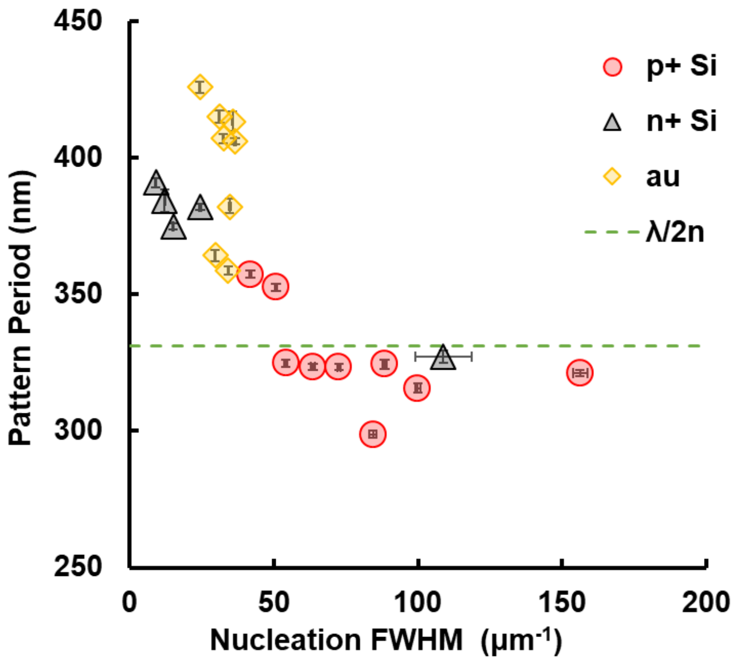


At *more negative potentials:*

- Nucleating structures have fewer high frequencies
- Pattern packing worsens (period increases relative to optical simulations)

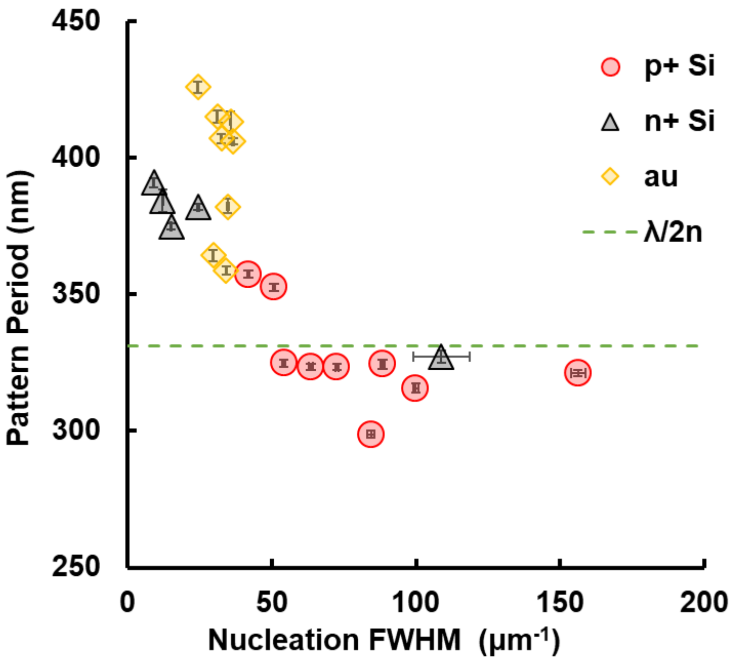
Caltech

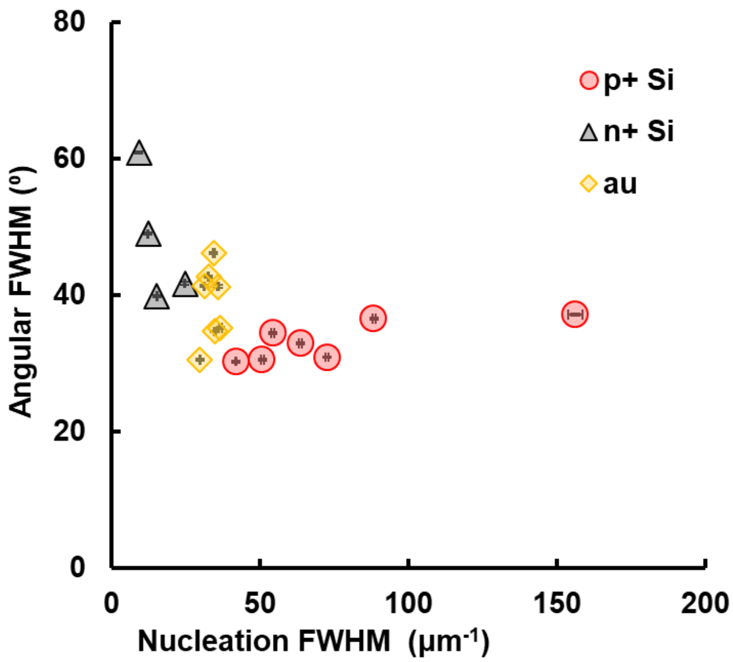
Nucleation density influences pattern period and fidelity independent of substrate



Caltech

Nucleation density influences pattern period and fidelity independent of substrate





Higher nucleation density gives better pattern packing and fidelity independent of potential-dependent substrate behavior

Caltech

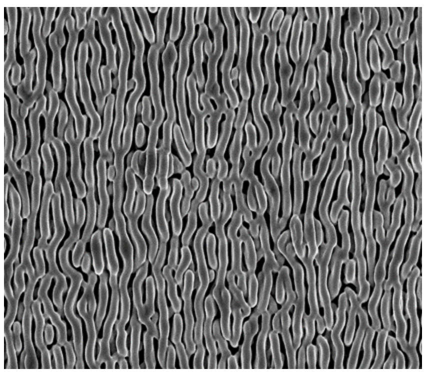
Striking potential for initial 0.5% deposition influences pattern

Step 1: -3.75 mC cm^{-2} @ ***XXX*** mV vs. Ag/AgCl

Step 2: -746.25 mC cm^{-2} @ -200 mV vs. Ag/AgCl

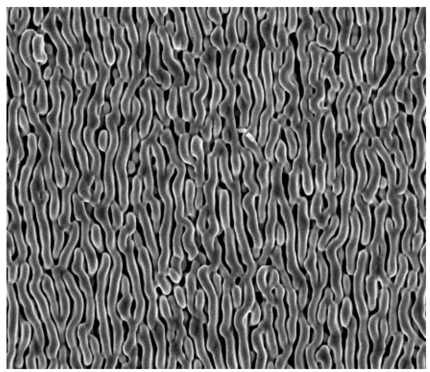
Total: -750 mC cm^{-2}

4 µm *Control (n^+-Si)*



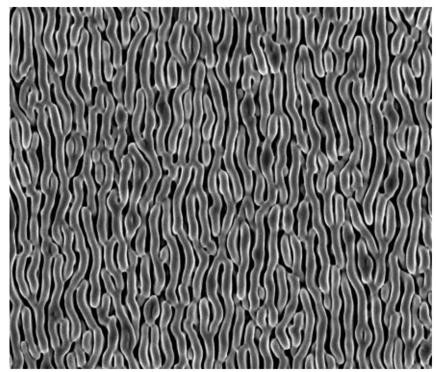
-200 mV

$\lambda_{pattern}$ = 391 nm



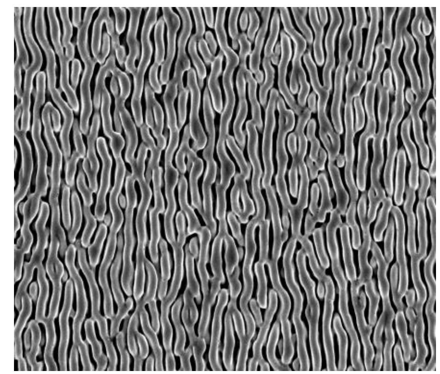
-250 mV

$\lambda_{pattern}$ = 384 nm



-300 mV

$\lambda_{pattern}$ = 376 nm



-350 mV

$\lambda_{pattern}$ = 374 nm

Increasing nucleation density, pattern packing, fidelity

Conclusions

- Inorganic phototropic growth creates a wide array of structures
- Nucleation density is negatively correlated with pattern period and angular FWHM
  - Larger nucleation density makes better patterns
- This is despite the substrate-dependent potential response of Se-Te films
- Nucleation density can be induced

Caltech

Next Steps

- Understand how nucleation morphology changes final pattern via optical pathway
  - Simulate the scattering intensity with Lumerical model for nucleation densities and polarizations
- Design and build an optical device with Se-Te films

Caltech

Acknowledgements

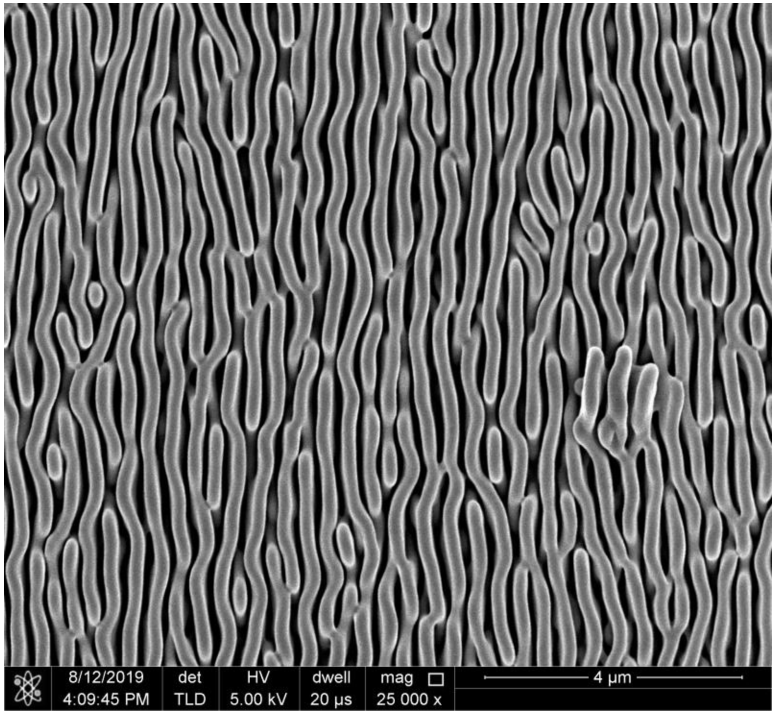
- Ethan
- Lewis Group
- SURF Program
- SFP Office
- Richard H. Cox

Electrochemical Set-up

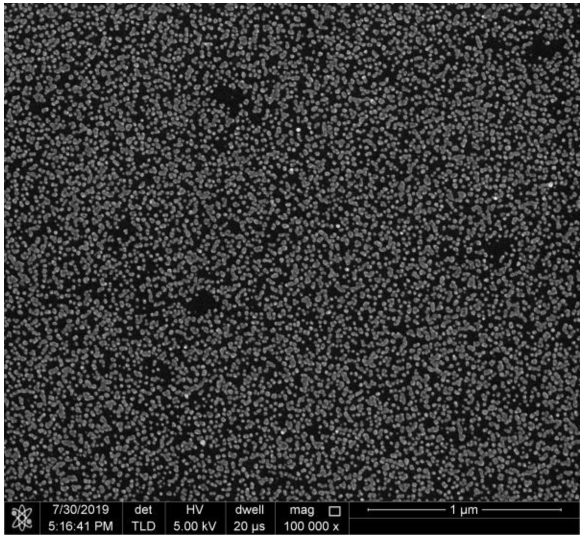
- Se-Te solution
  - 1M H_2SO_4
  - 20mM SeO_2
  - 10mM TeO_2
- Selenious Acid
  - $H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se(s) + 3H_2O$; E = .739
- Tellurious Acid
  - $TeO_3^{2-} + 3H_2O + 4e^- \rightarrow Te(s) + 6OH^-$; E = -.47

P Si films

- Hypothetically denser nucleation due to deposition by photoactive substrate led to high fidelity pattern



4 µm

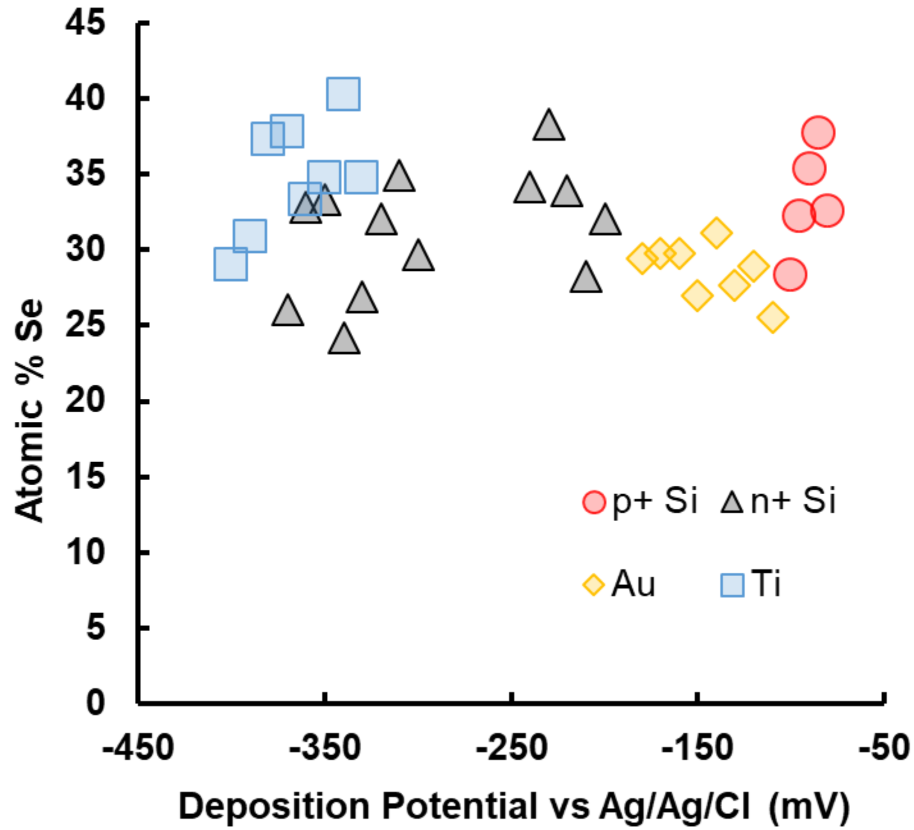


1 µm

Caltech

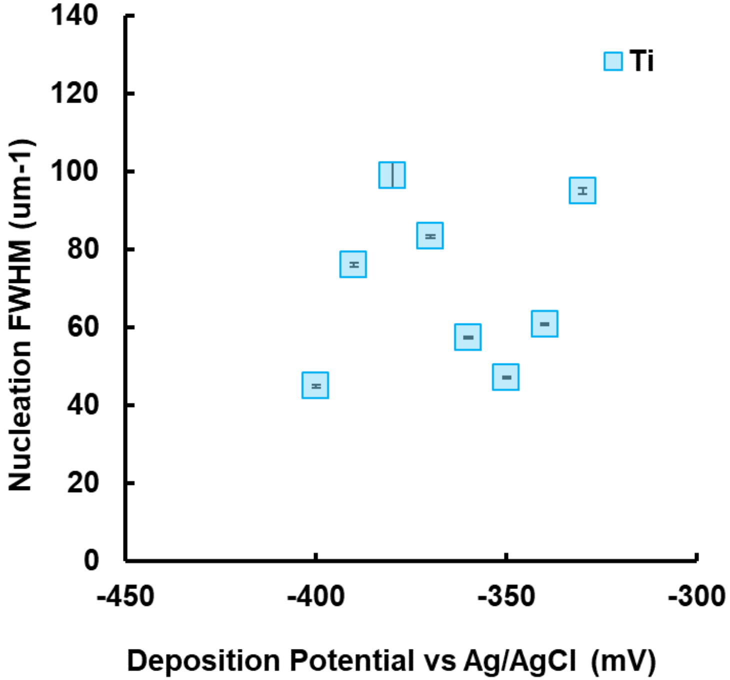
Se-Te Stoichiometry

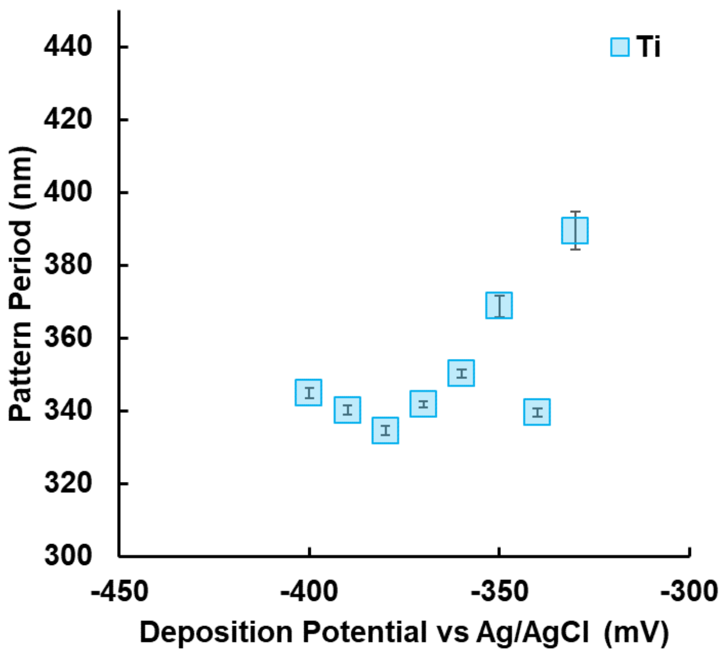
- Similar film stoichiometry on different substrates determines similar Se-Te work function



Caltech

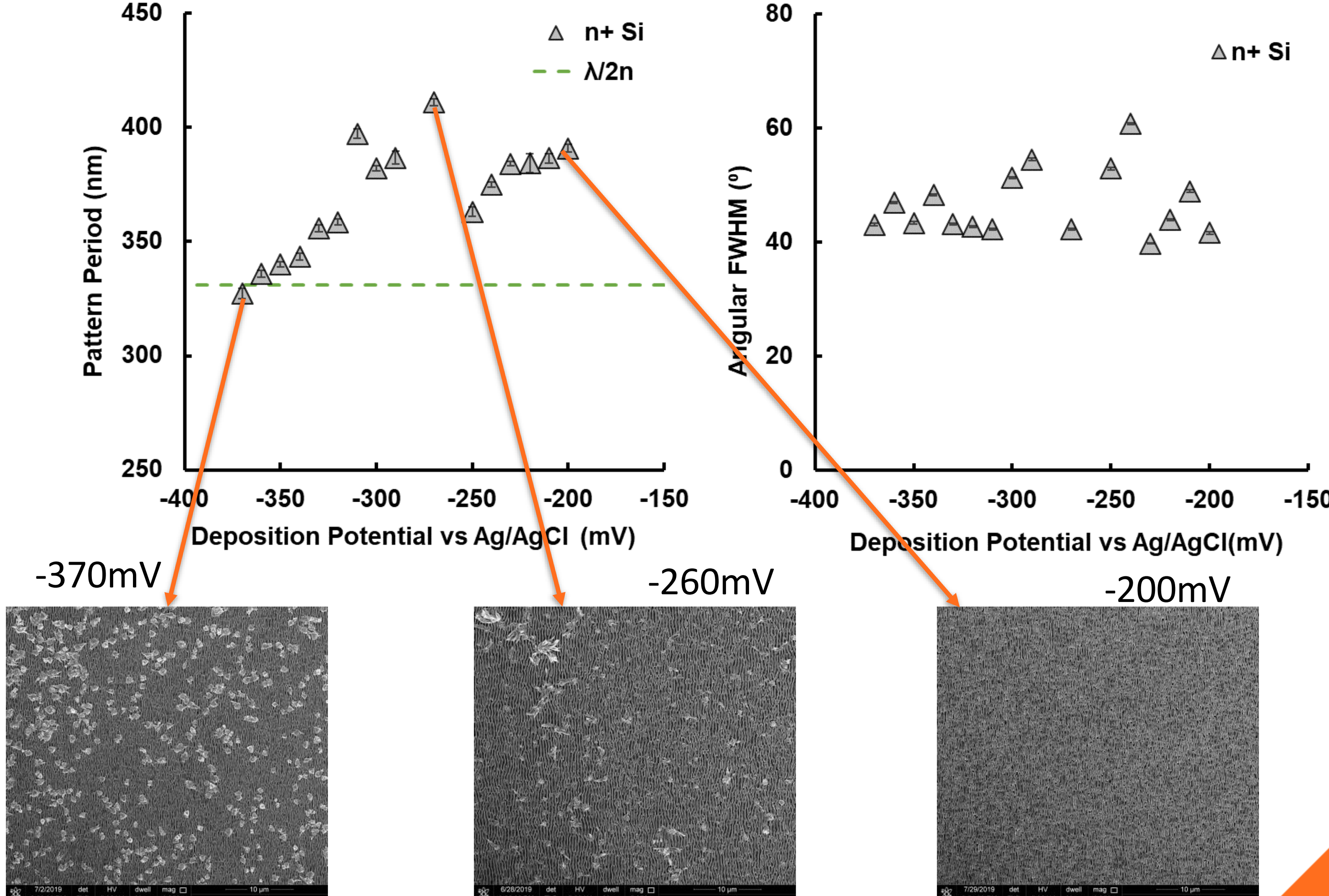
Se-Te films deposited on Ti display oscillatory behaviors



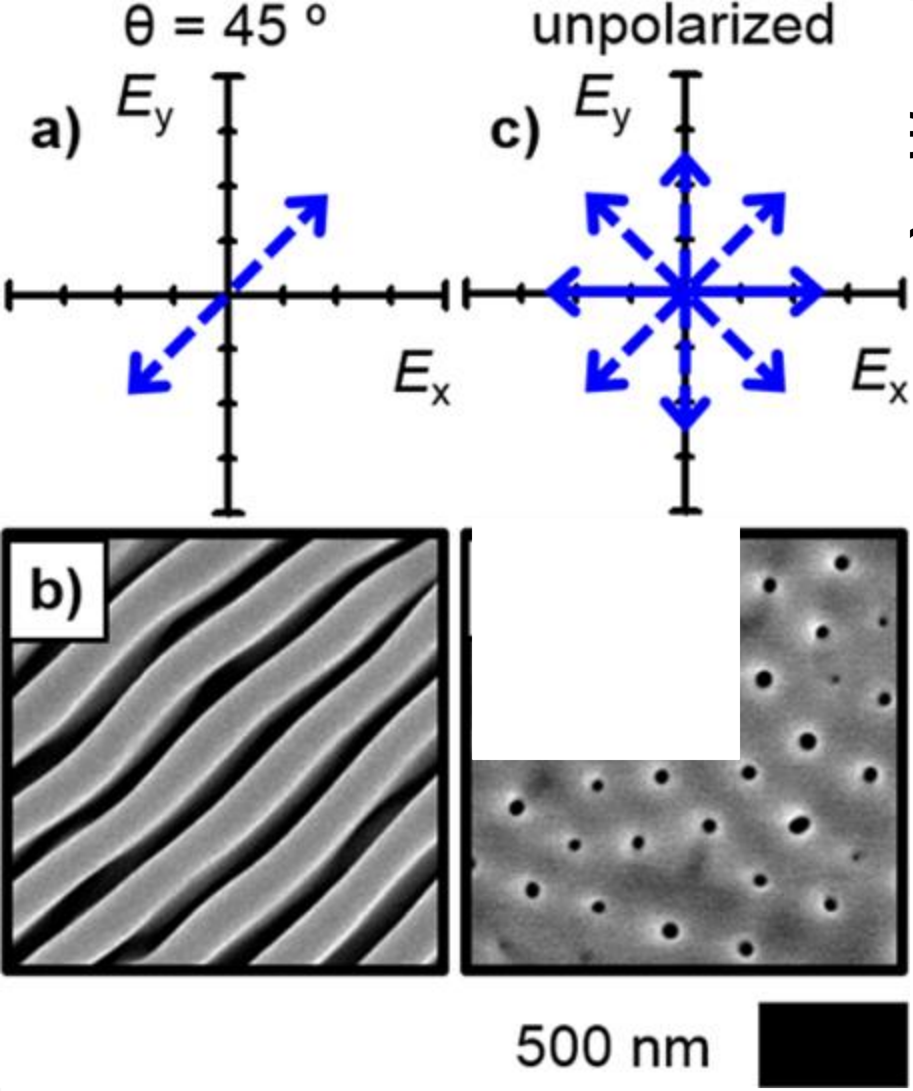


Caltech

Fidelity artefacting

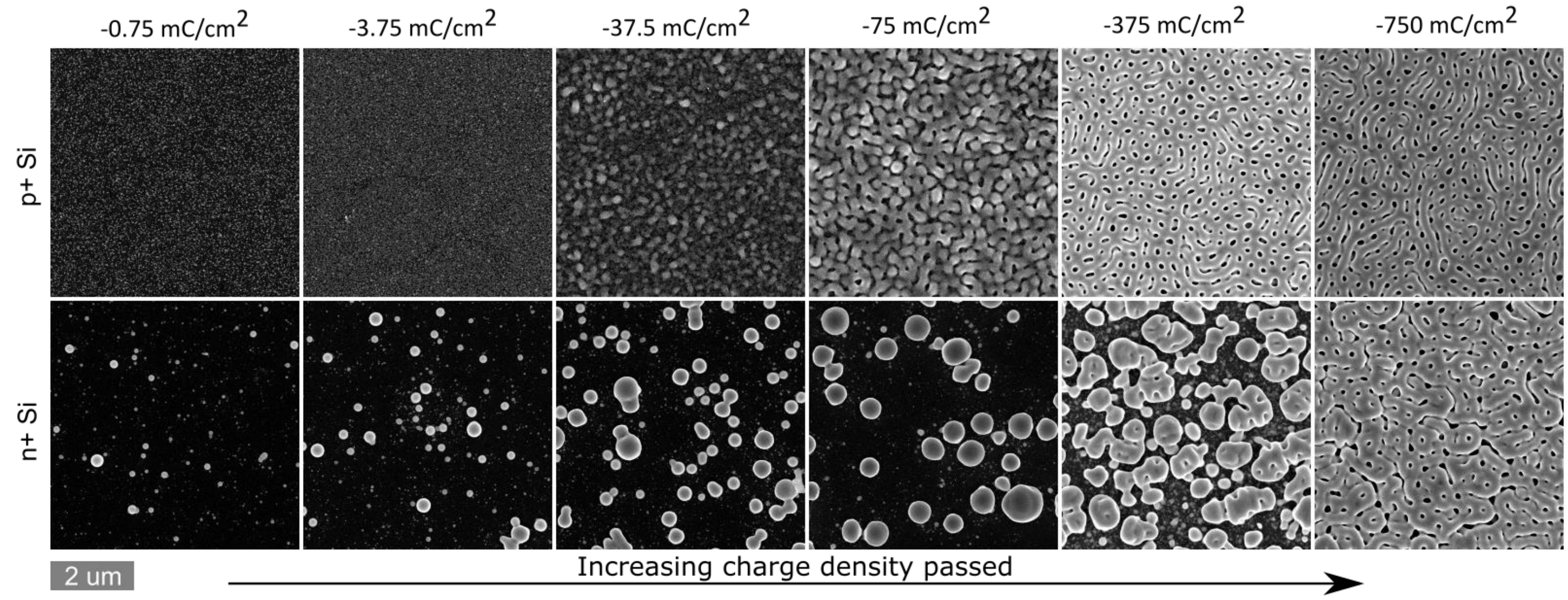


e-Te films grown on n+-Si
r unpolarized light



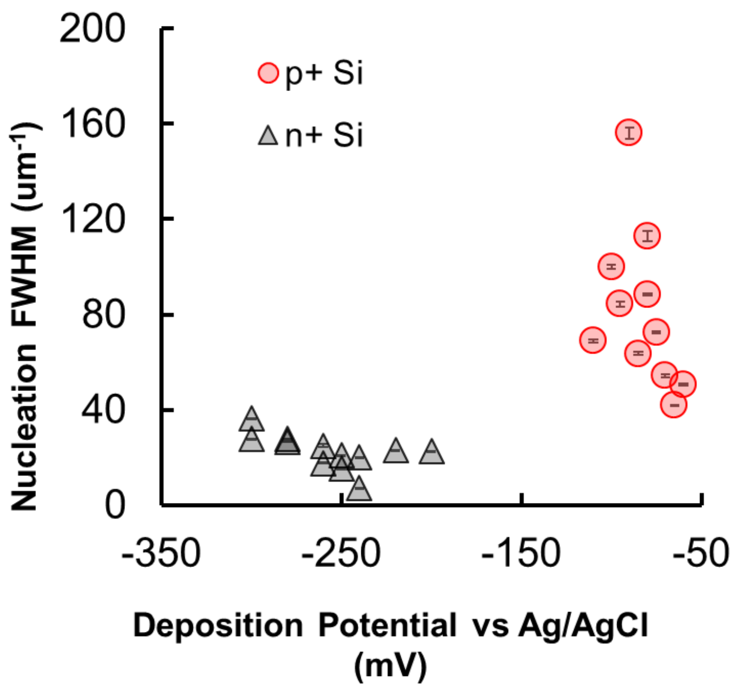
Carim et al. *Nano Letters* **2016,** *16* (5), 2963-2968

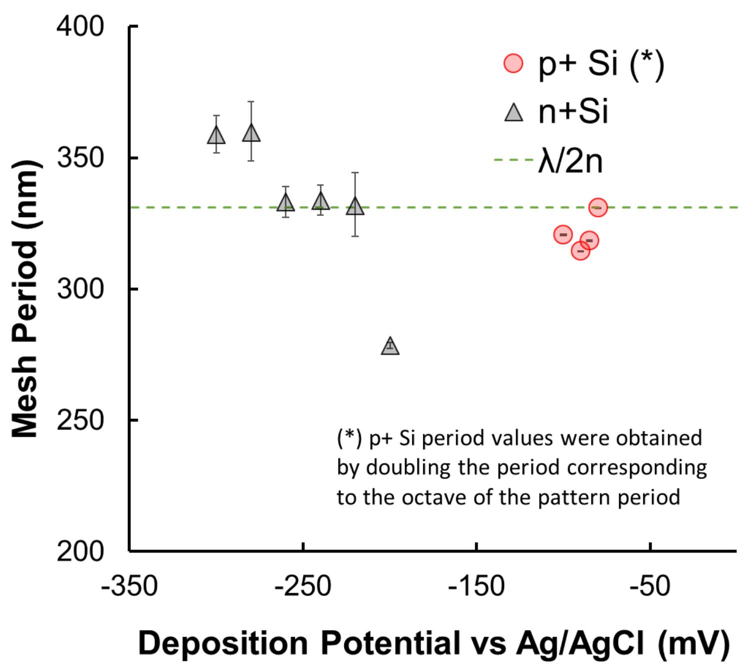
Patterns grown under unpolarized light



Caltech

Unpolarized pattern period varies less with applied potential



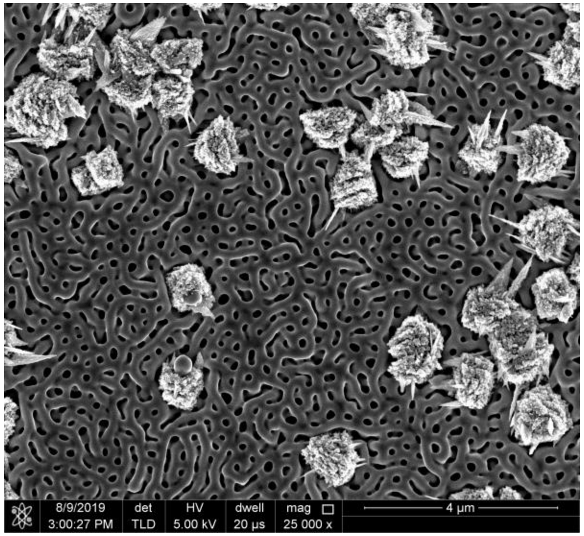


Geometrically, the scattering interference with neighboring particles is twice as likely

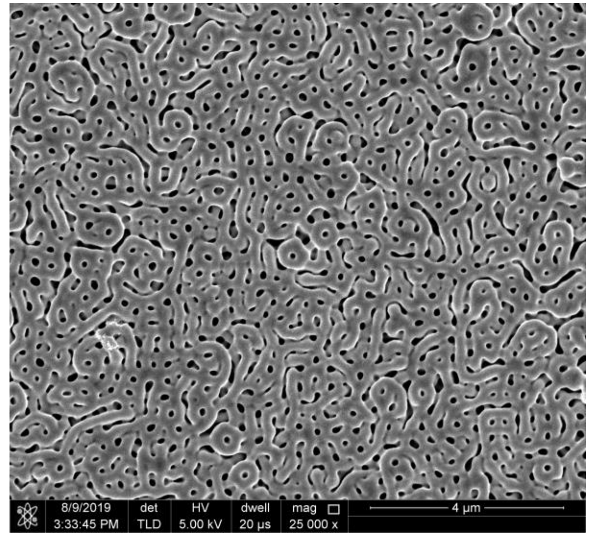
Unpolarized structures

Defected patterns show grain boundary transitions across the potential range

n+-Si, -300 mV

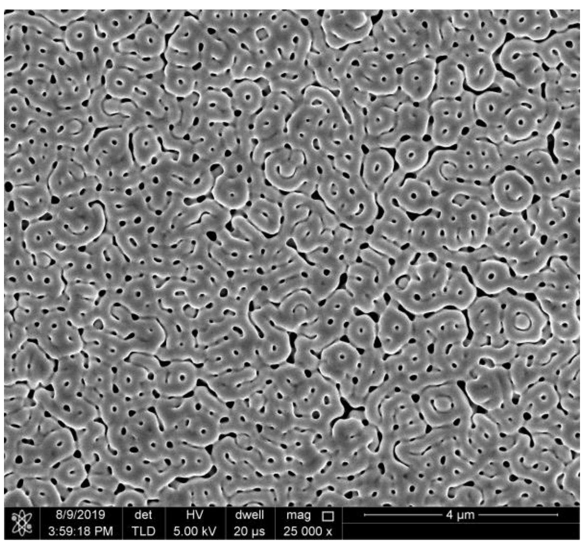


n+-Si, -240 mV

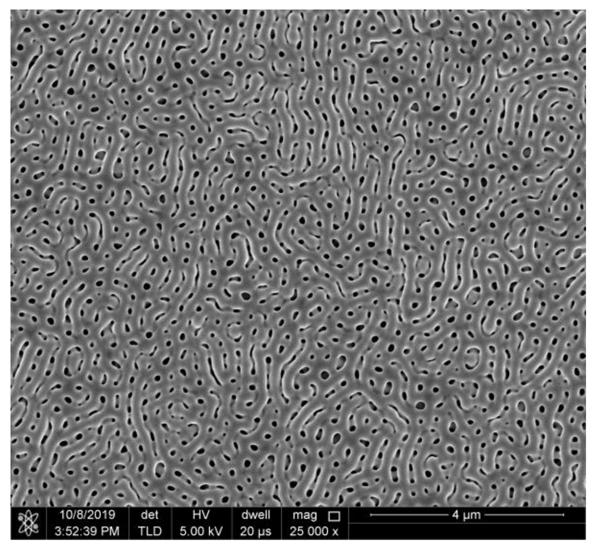


4 µm

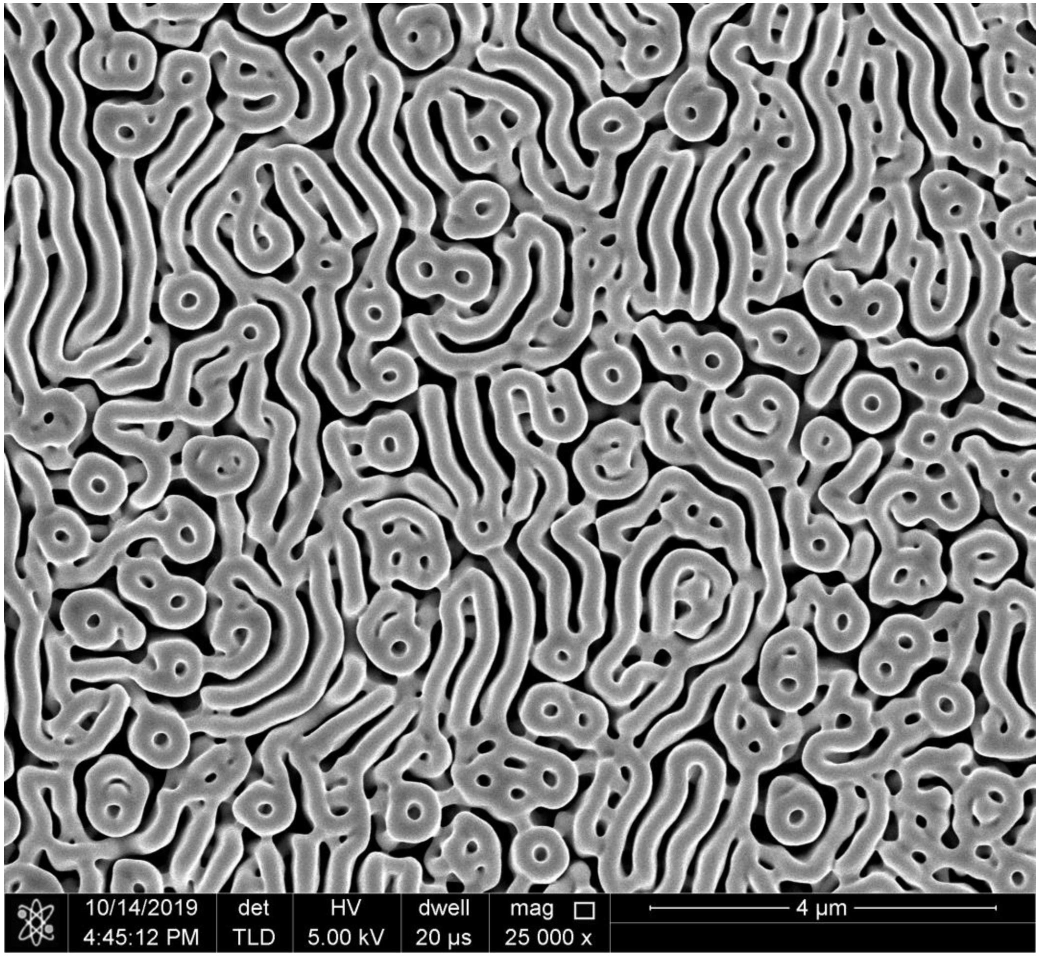
n+-Si, -200 mV



p+-Si, -80 mV



Novel morphology



4 µm

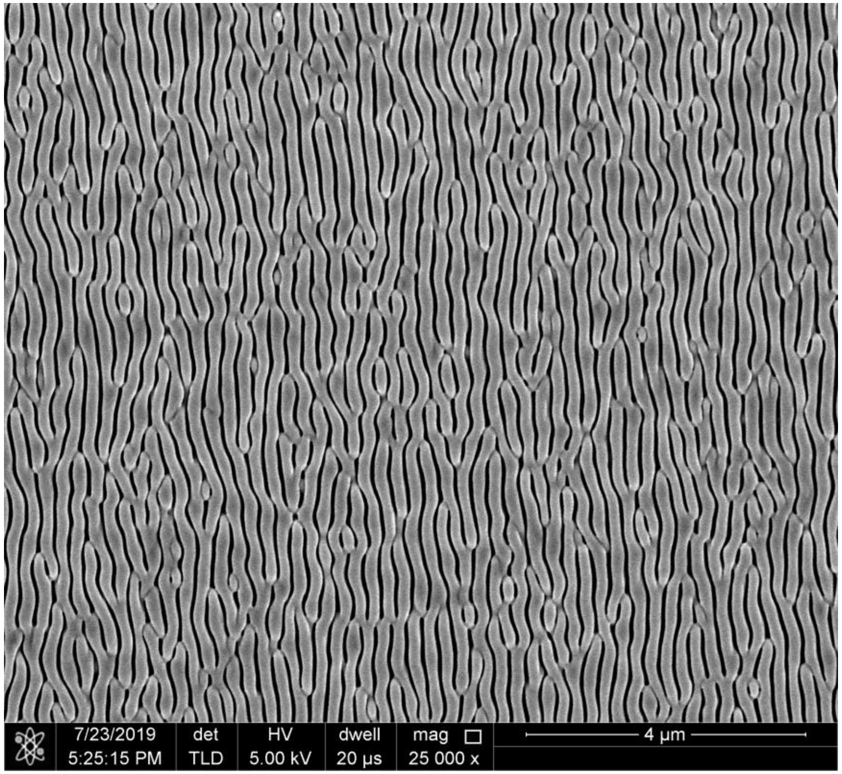
-3000 mC/cm2 deposited on p+-Si at -80 mV vs Ag/AgCl with unpolarized illumination. Its 2D FFT is isotropic.

Caltech

Solar Squiggle

- Created this summer
- Deposited on p+ Si
- Wafer ~ 33 cm^2
- Illumination: the Sun

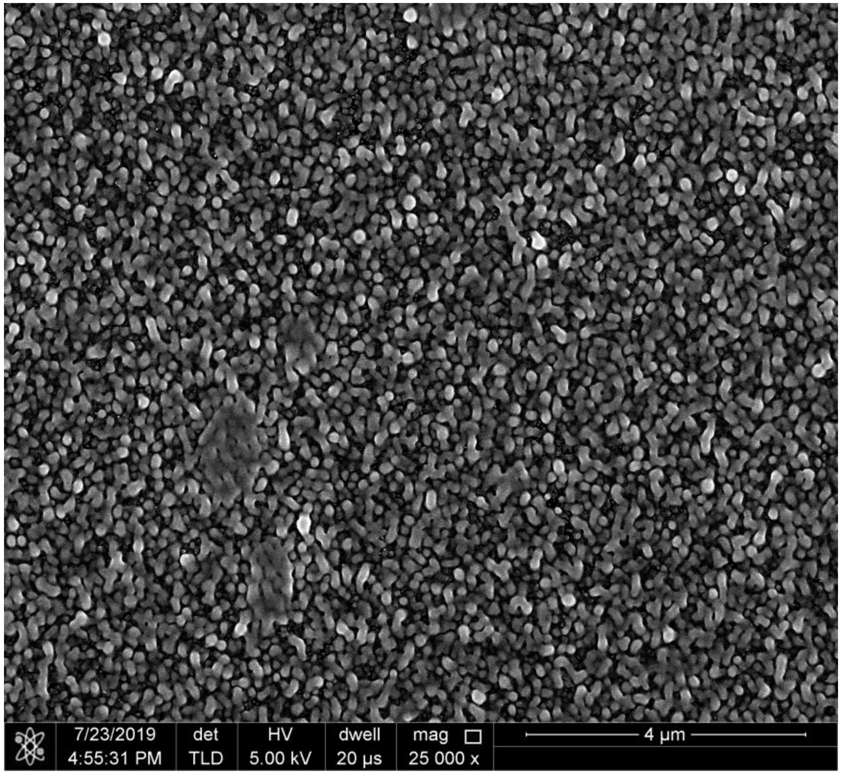
Solar Squiggle



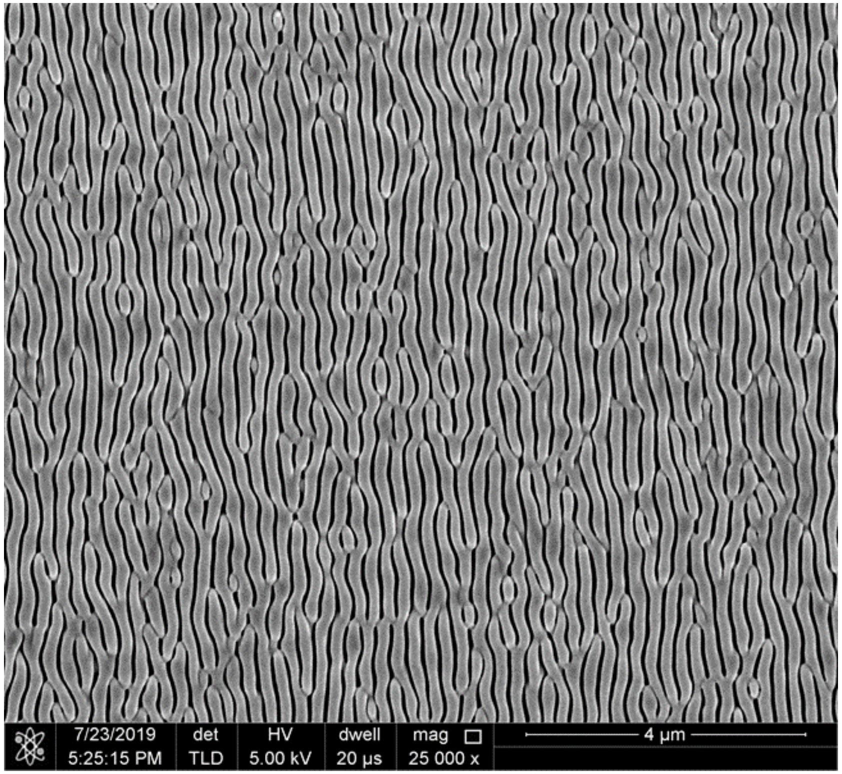
4 µm^{-1}

Background: 2D FFT Analysis

Nucleation: Density



Lamellar Pattern: Period, Fidelity



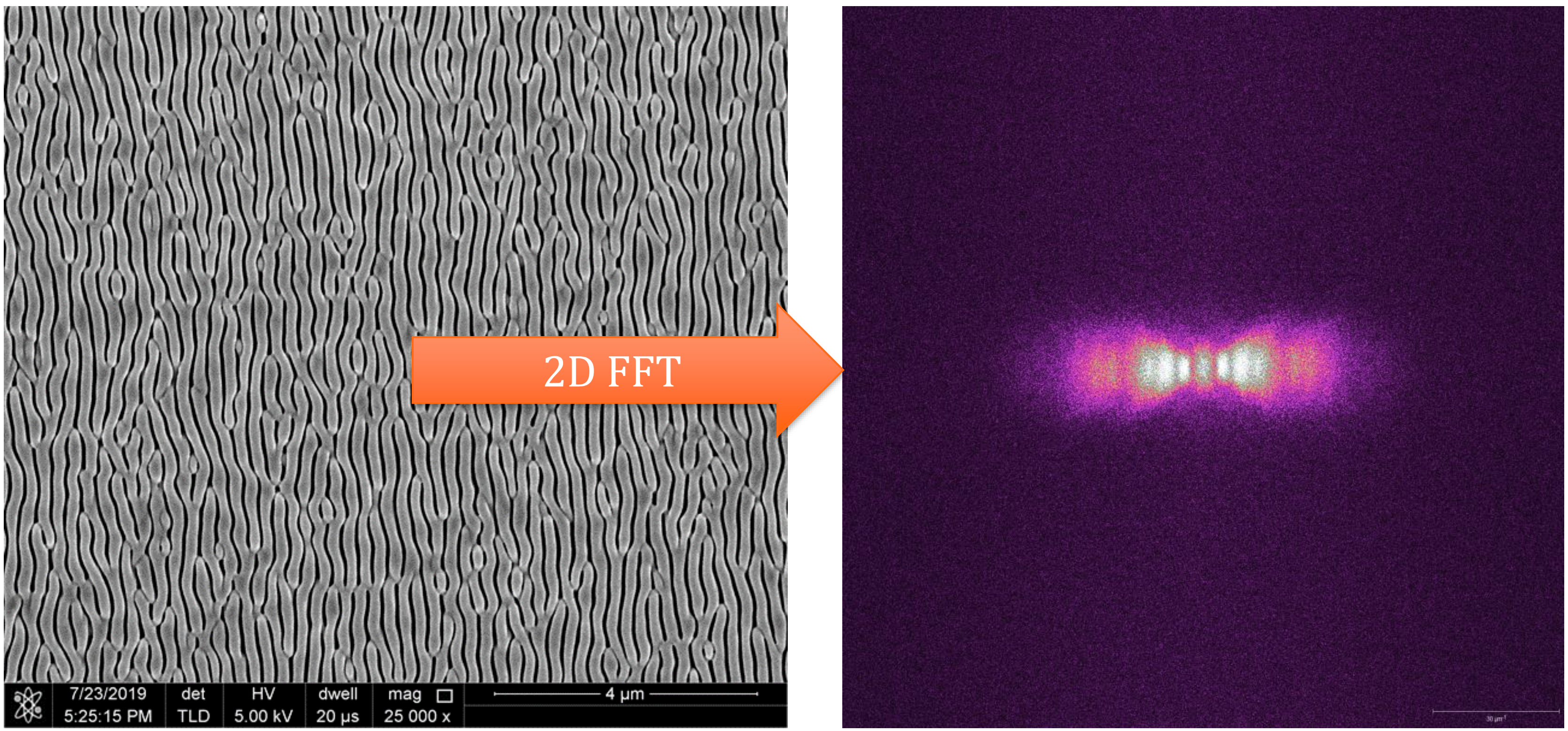
4 µm

Caltech

Background: 2D FFT converts periodic spacings to frequencies

- Mention light growth phase

Frequency = 1/Period

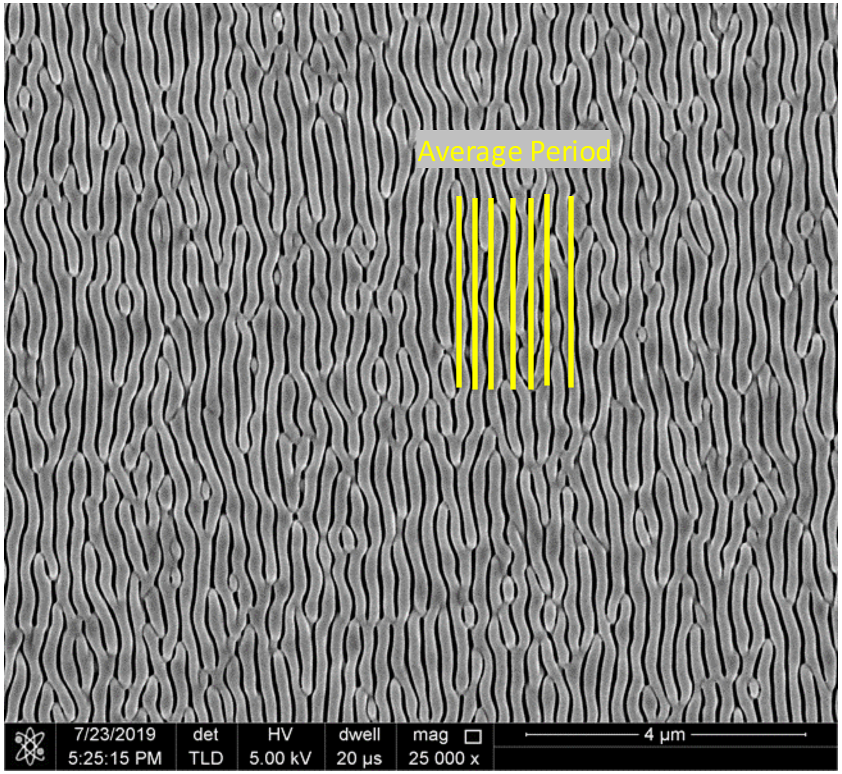


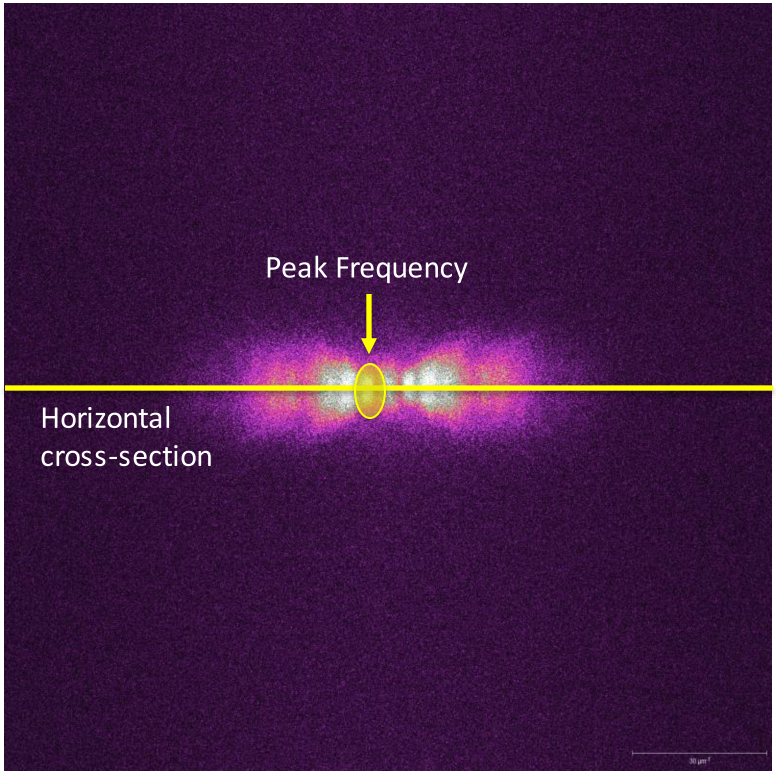
4 µm

30 μm^{-1}

Background: Horizontal

- Mention light growth phase





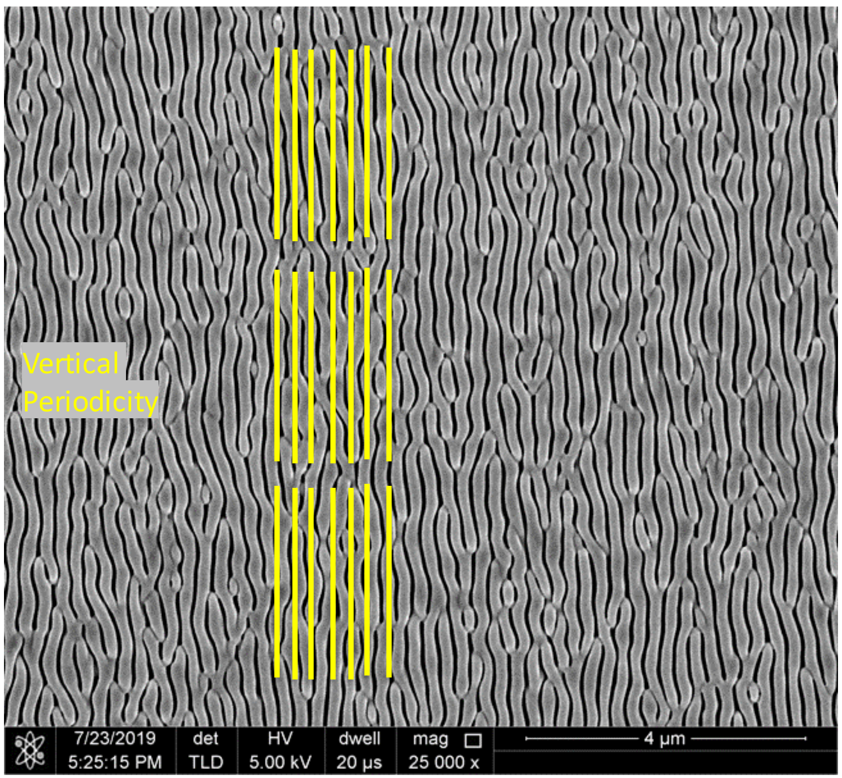
4 µm

30 μm^{-1}

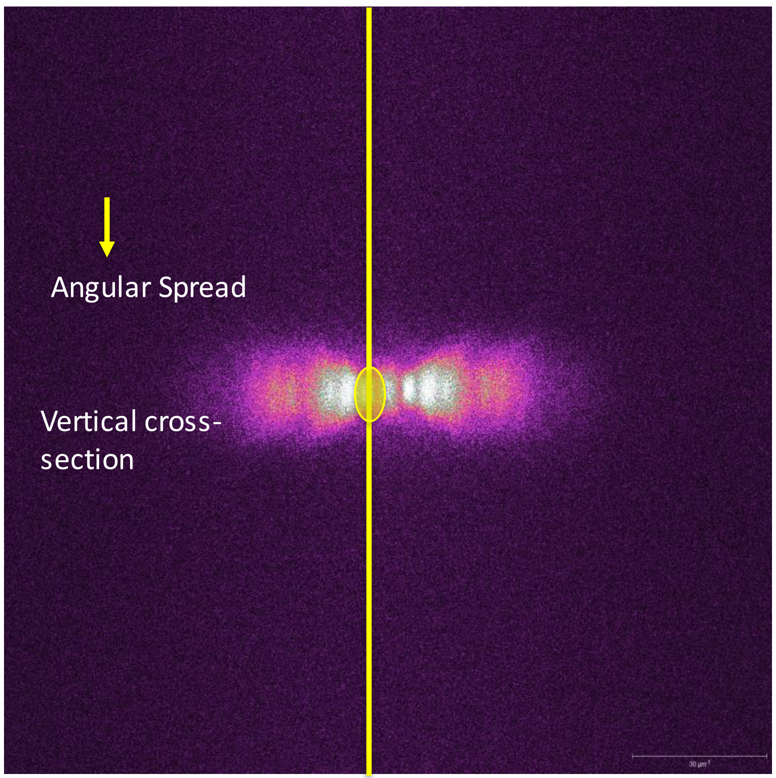
Caltech

Background: Vertical

- Mention light growth phase

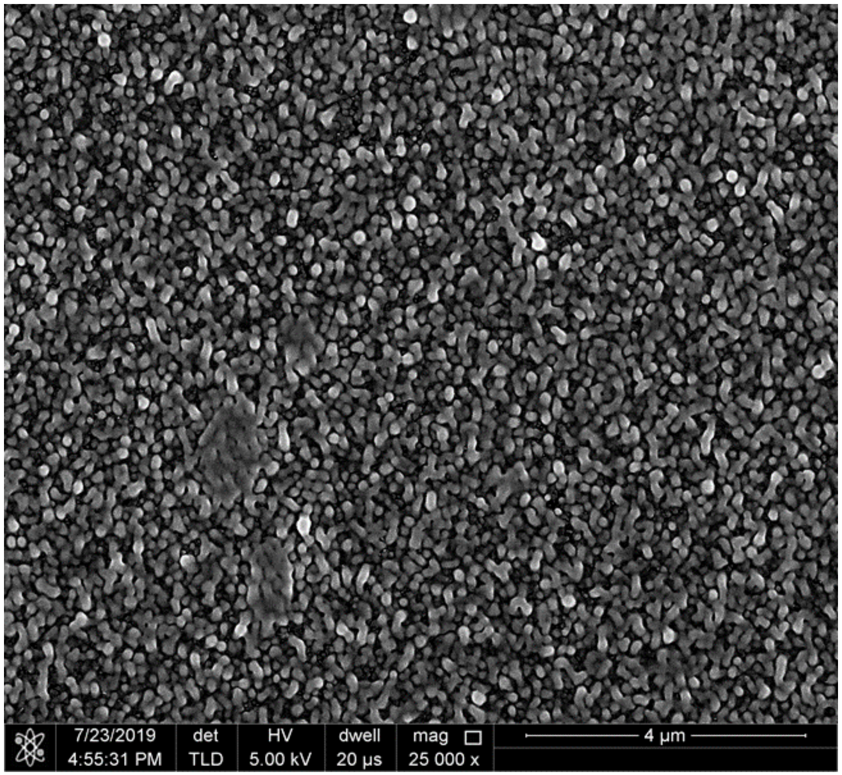


4 µm

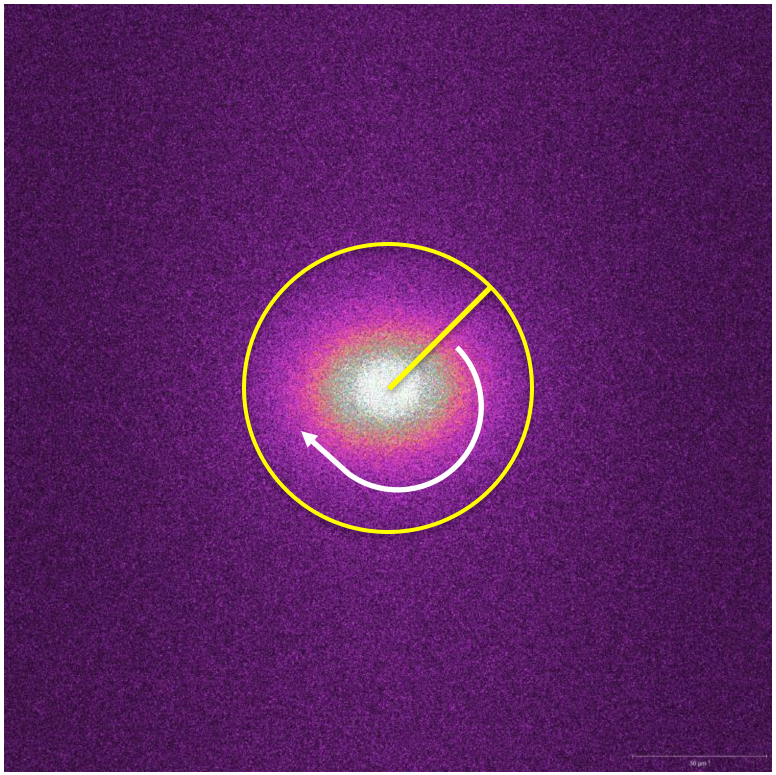


30 μm^{-1}

Background: Radially integrated FT measures isotropic nucleation morphology



4 µm



30 μm^{-1}

Caltech