The Center for BRIGHT BEAMS
A National Science Foundation Science & Technology Center

# Molecular beam epitaxy of Cs-Sb thin films: structure-oriented growth of high efficiency photocathodes

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# People

The Center for BRIGHTBEAMS
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PARADIM
AN NSF MATERIALS INNOVATION PLATFORM

## Maxson group


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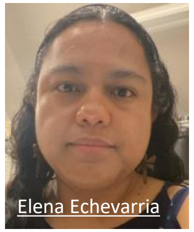
Alice Galdi


Chad Pennington


Elena Echevarria

## Arias group


Tomàs Arias


J. Kevin Nangoi

## Shen group

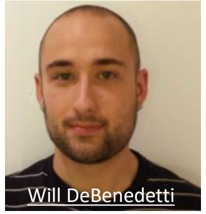

Kyle Shen


Chris Parzyck


Vivek Anil

## Hines group


Mellissa Hines


Will DeBenedetti


Jan Balajka


Hanjong Paik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https://cbb.cornell.edu/ https://www.paradim.org/

CORNELL UNIVERSITY FOUNDED A.D. 1865

# Outline

- Motivation:
  - $Cs_3Sb$ for brighter electron beams
  - Surface disorder and emittance degradation
- Methods:
  - RHEED monitored molecular beam epitaxy
- Results: epitaxy of $Cs_3Sb$ phase! (first time!)
  - First band structure measurements of $Cs_3Sb$ thin films
- Results: new phase!
  - Atomically smooth CsSb films: a visible light photoemitter with enhanced oxygen robustness
- Future work and conclusions

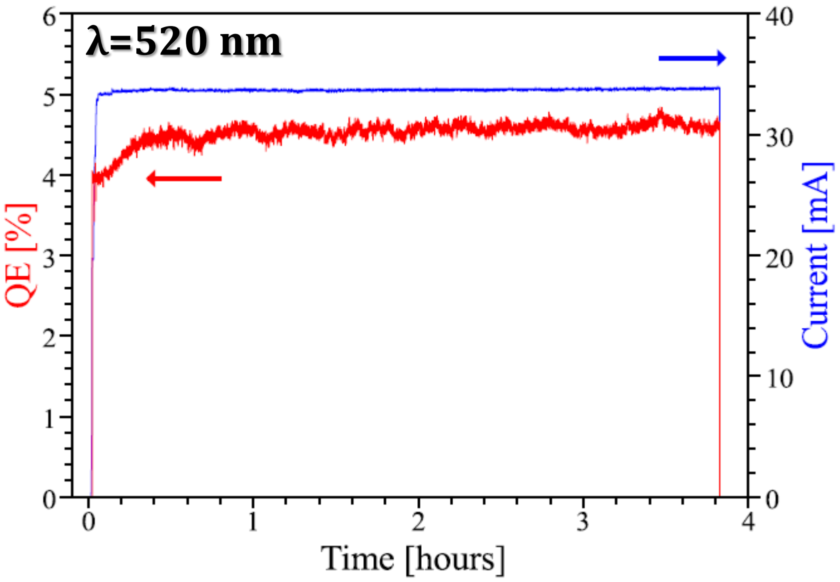
# $Cs_3Sb$ for low emittance, high current

$$B_n = \frac{2 m_e c^2 I}{\sigma_x^2 MTE}$$

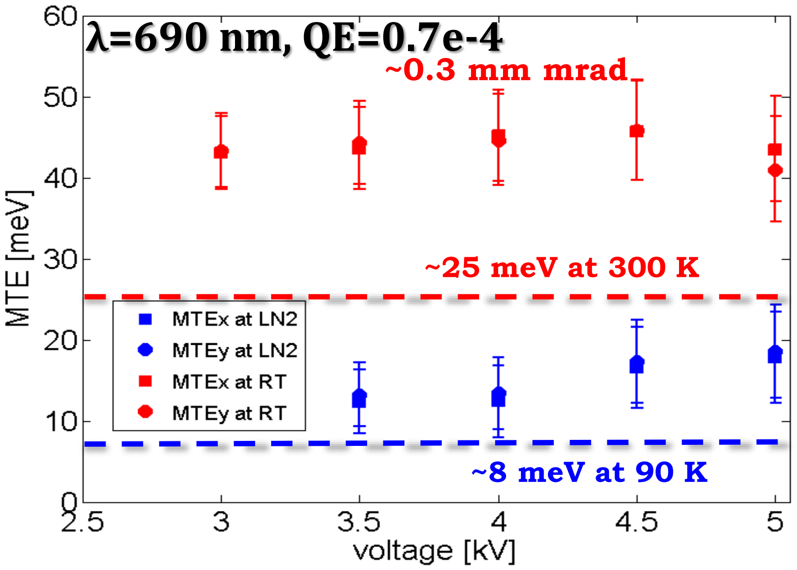
Beam current: quantum efficiency, laser fluence, lifetime

Mean transverse energy: Intrinsic momentum spread + roughness + laser heating + …

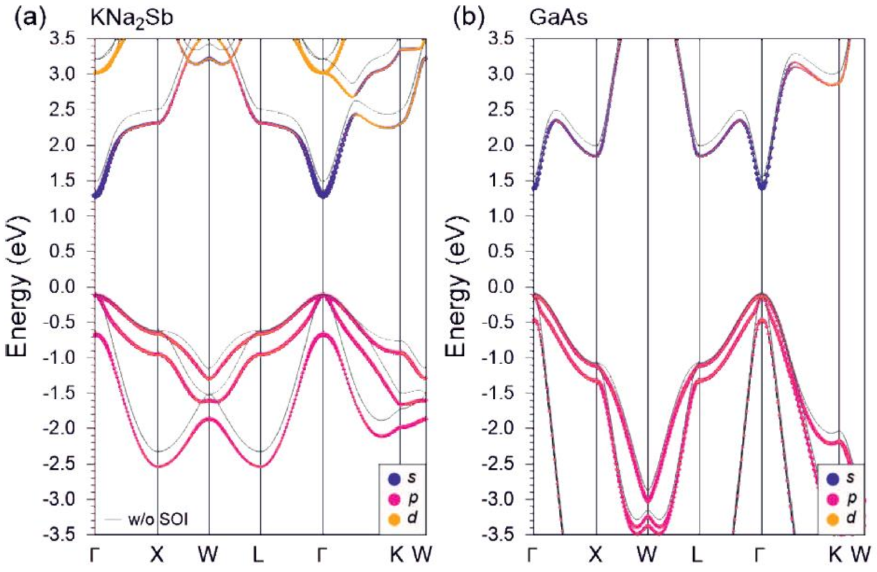
$Cs_3Sb/Na_2KSb$: next generation spin polarized photocathode?




B. Dunham et al. APL **102**, 034105 (2013)

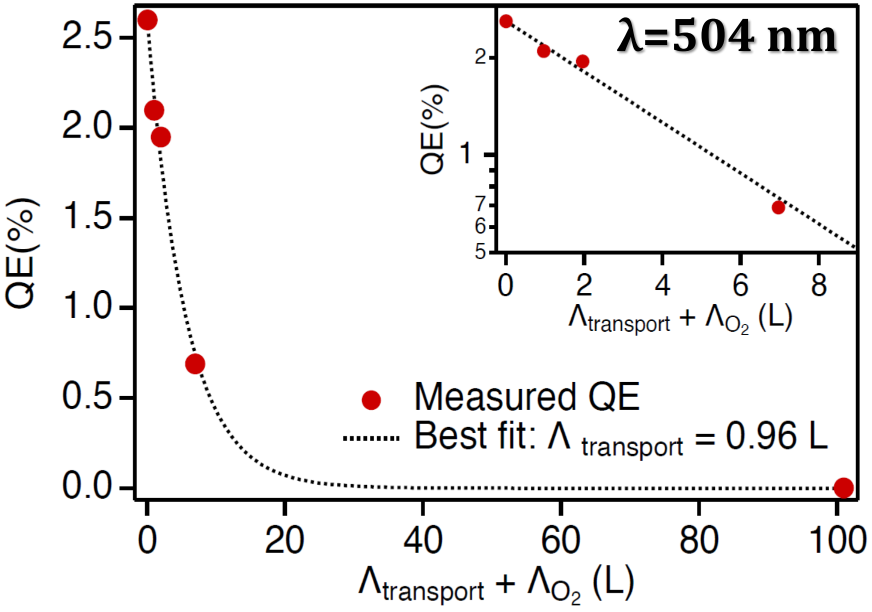


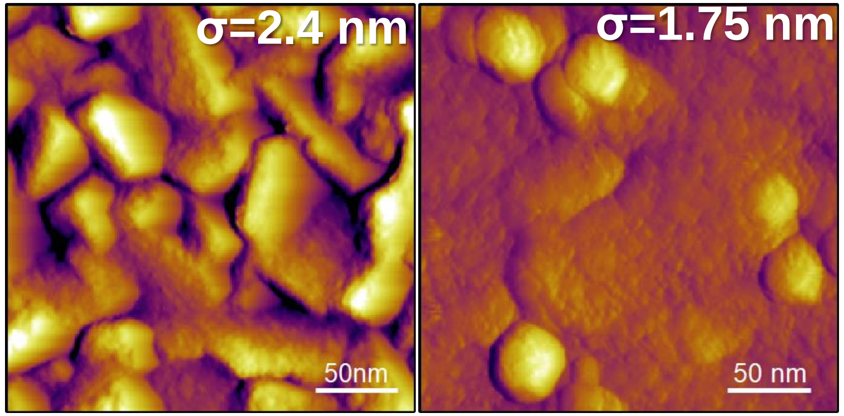

L. Cultrera et al., Phys. Rev. STAB **18** (2015) 113401




V.S. Rusetsky et al, arXiv:2205.03693 [cond-mat.mtrl-sci]

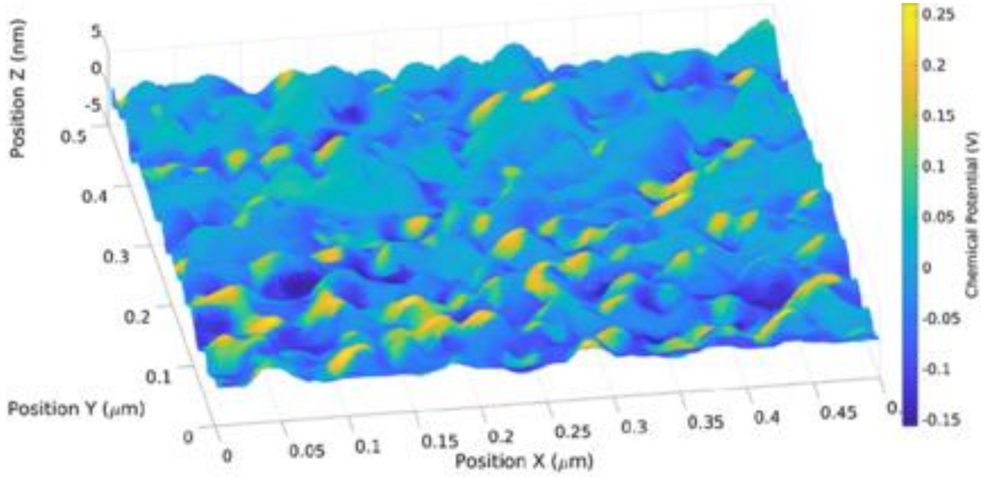
# Drawbacks: reactive, disordered




A. Galdi, *et al.* The Journal of Chemical Physics 153,144705 (2020)
A Galdi, *et al.* Applied Physics Letters 118 (24), 244101

Why does this matter for applications?
Because both heterogeneity enhaced by oxidation and roughness degrade MTE (besides QE degradation in poor vacuum)




$\Delta MTE = 25\ meV$
$@\ 10\ MV/m$
compare to measured:
$42\ meV@300K$
$15meV@90K$

Measured surface and surface potential of a $Cs_3Sb$ photocathode

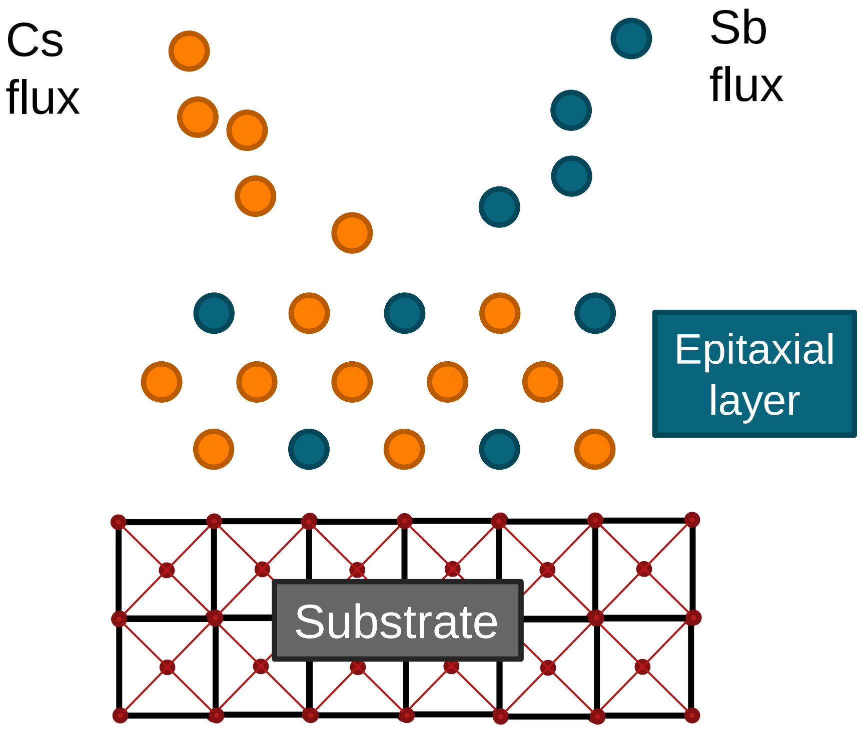
G. S. Gevorkyan, PRAB **21**, 093401 (2018)

# Single crystalline photocathodes: epitaxy

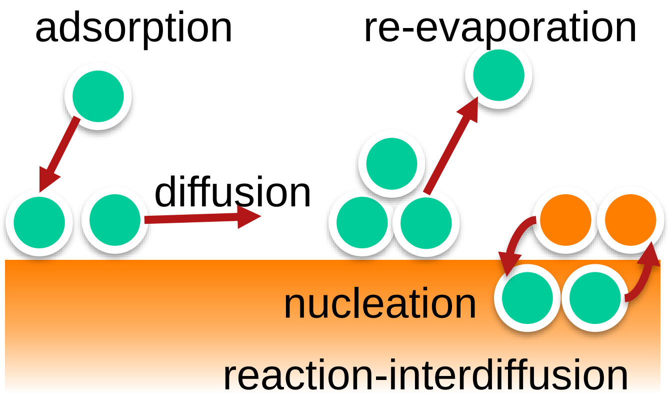
Epitaxy is the growth of a crystal layer with one or more well-defined orientations with respect to an underlying crystal seed layer (usually a single crystal substrate)

Epitaxial single-oriented films would allow:

- Roughness control
- Orientation control → surface potential control
- Measurements of intrinsic properties (optical constants, band structure, intrinsic MTE…)

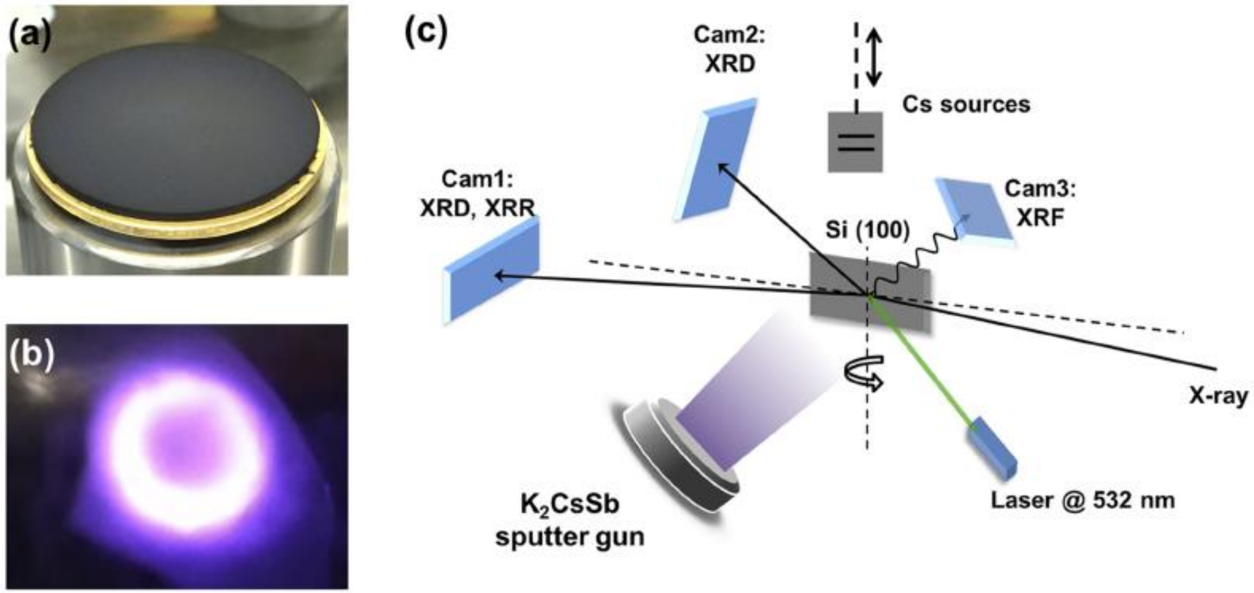


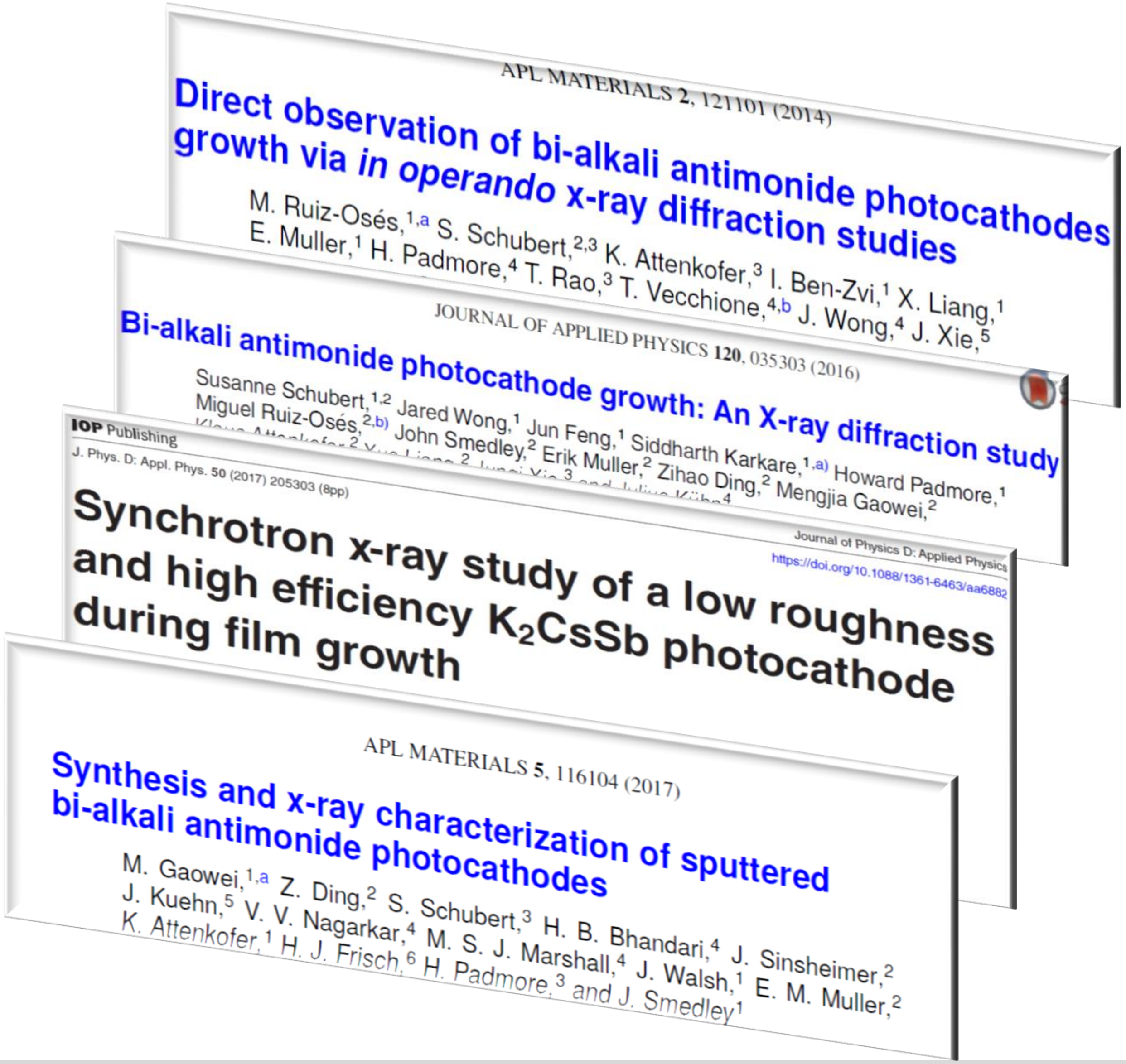

1) Choose the method: MBE
2) Select suitable substrates
3) Identify suitable growth conditions



# Previous results

Our work builds on many experimental results obtained via *in-operando* characterization of the growth of alkali antimonide thin films with different techniques.





APL MATERIALS 2, 121101 (2014)

Direct observation of bi-alkali antimonide photocathodes growth via *in operando* x-ray diffraction studies

M. Ruiz-Osés,[1,a] S. Schubert,[2,3] K. Attenkofer,[3] I. Ben-Zvi,[1] X. Liang,[1] E. Muller,[1] H. Padmore,[4] T. Rao,[3] T. Vecchione,[4,b] J. Wong,[4] J. Xie,[5]

JOURNAL OF APPLIED PHYSICS 120, 035303 (2016)

Bi-alkali antimonide photocathode growth: An X-ray diffraction study

Susanne Schubert,[1,2] Jared Wong,[1] Jun Feng,[1] Siddharth Karkare,[1,a)] Howard Padmore,[1] Miguel Ruiz-Osés,[2,b)] John Smedley,[2] Erik Muller,[2] Zihao Ding,[2] Mengjia Gaowei,[2]

IOP Publishing

J. Phys. D: Appl. Phys. 50 (2017) 205303 (8pp)

Journal of Physics D: Applied Physics

https://doi.org/10.1088/1361-6463/aa6882

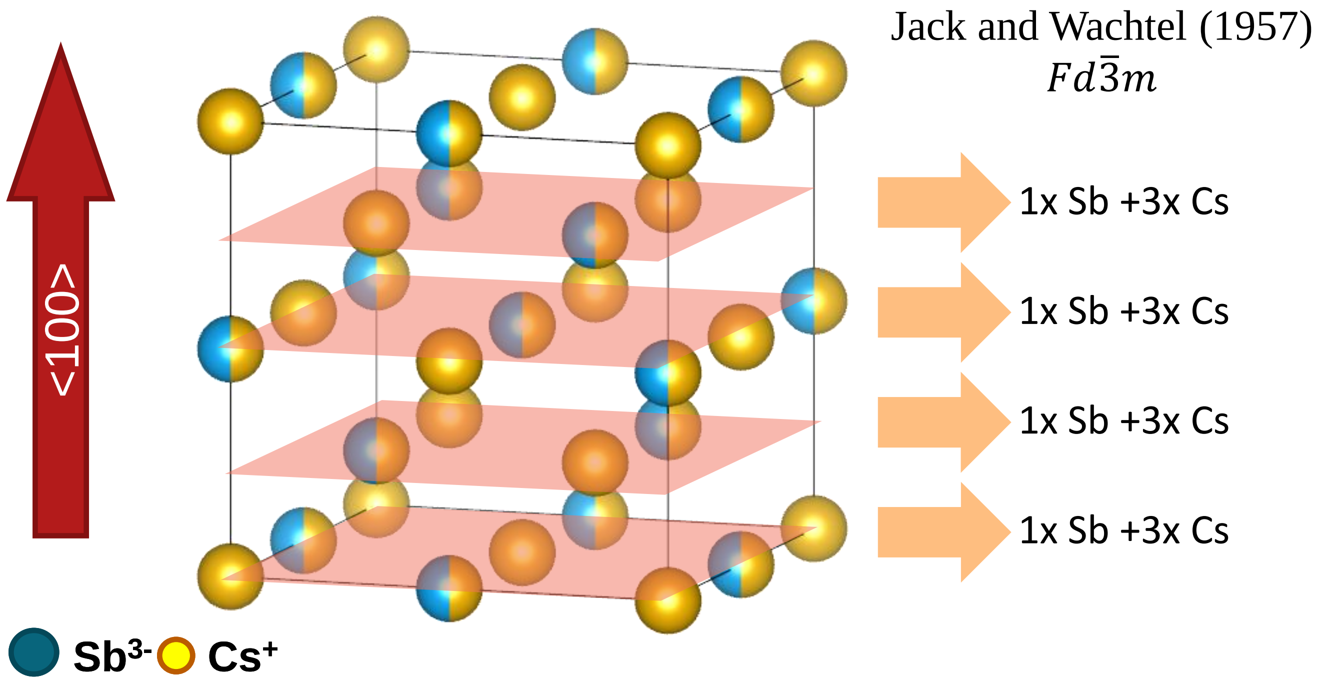
Synchrotron x-ray study of a low roughness and high efficiency $K_2CsSb$ photocathode during film growth

APL MATERIALS 5, 116104 (2017)

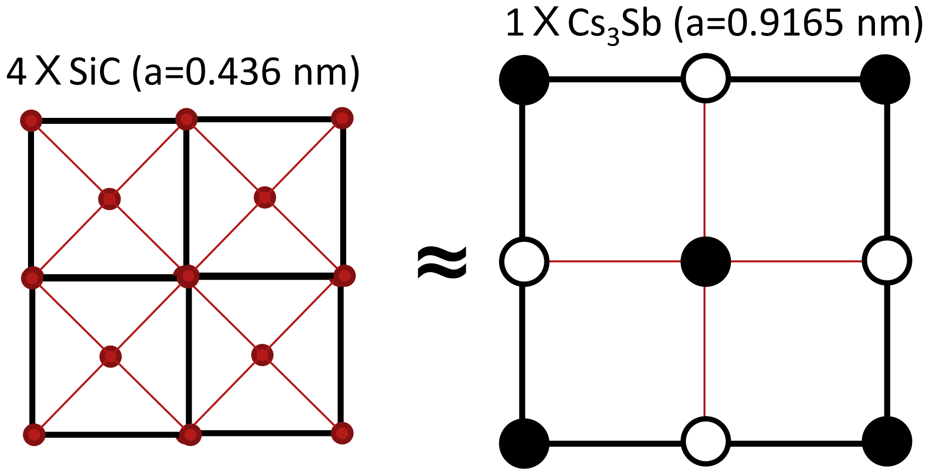
Synthesis and x-ray characterization of sputtered bi-alkali antimonide photocathodes

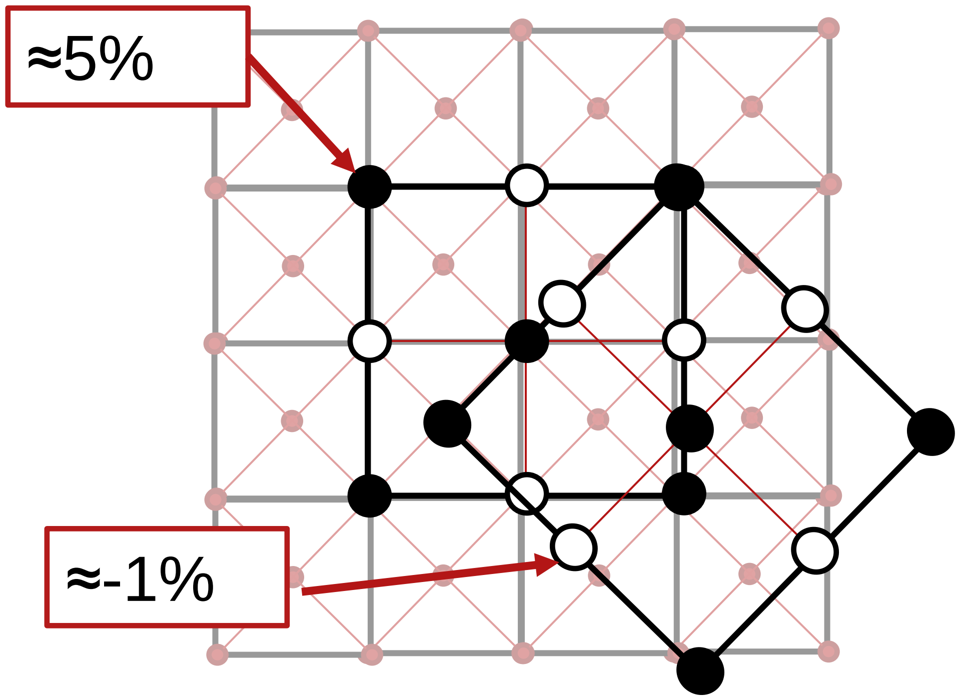
M. Gaowei,[1,a] Z. Ding,[2] S. Schubert,[3] H. B. Bhandari,[4] J. Sinsheimer,[2] J. Kuehn,[5] V. V. Nagarkar,[4] M. S. J. Marshall,[4] J. Walsh,[1] E. M. Muller,[2] K. Attenkofer,[1] H. J. Frisch,[6] H. Padmore,[3] and J. Smedley[1]

# $Cs_3Sb$ structure and possible epitaxial relations




Based on previous studies, we selected 3C-SiC as substrate
(but also tested: $TiO_2$ , $MgF_2$)
A Galdi, *et al.* Applied Physics Letters 118 (24), 244101

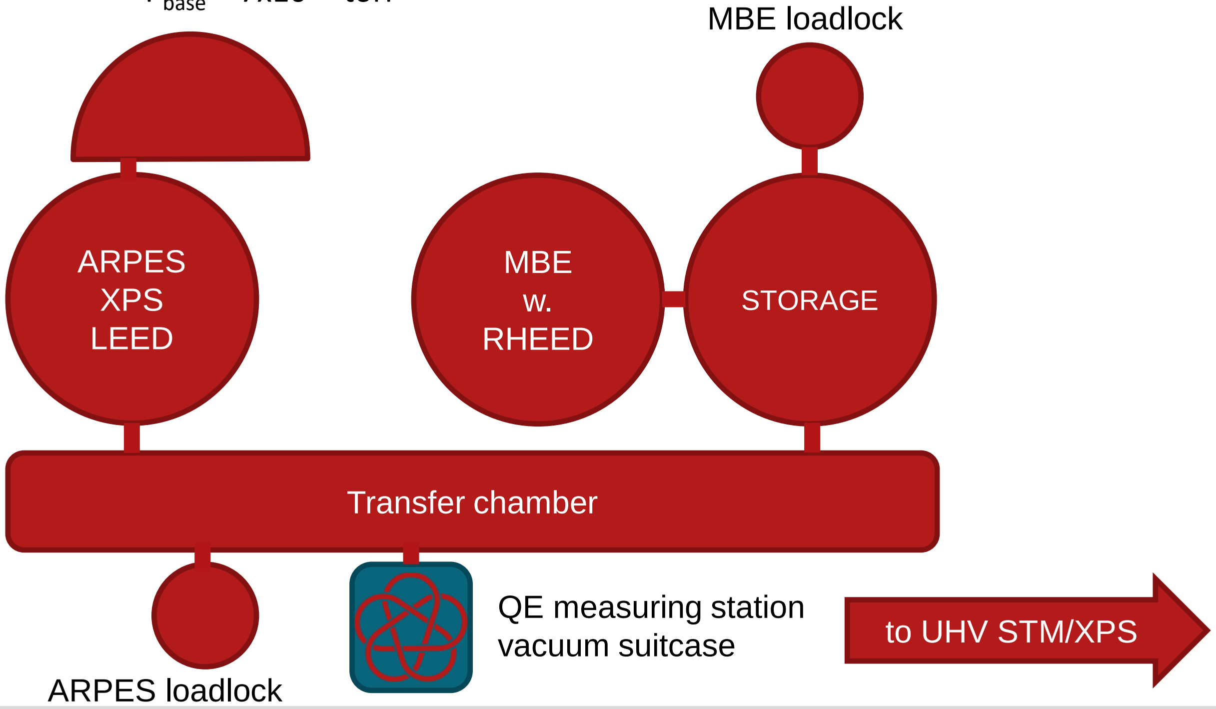


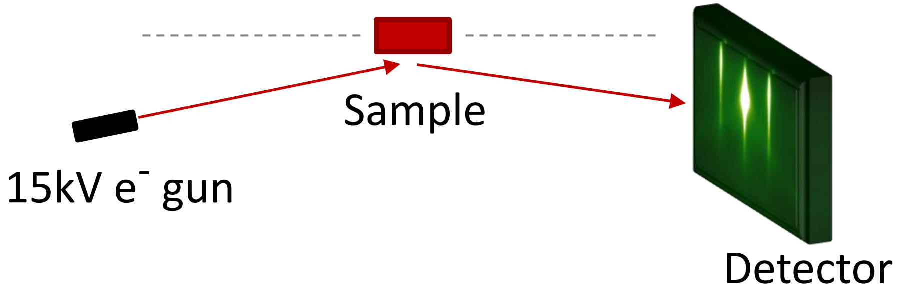
# RHEED assisted MBE @ PARADIM

## PARADIM Thin Film User Facility

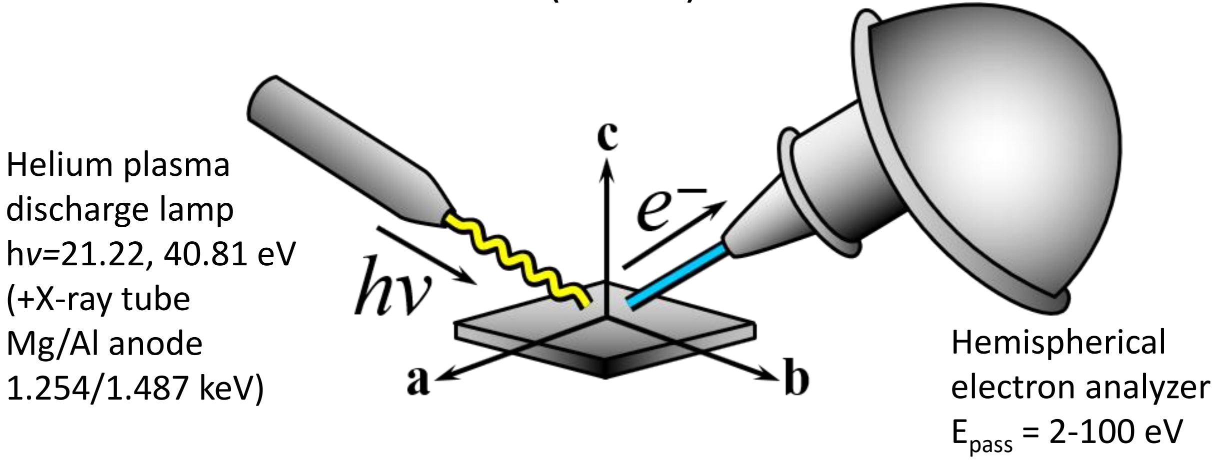
- Molecular Beam Epitaxy System
  - *In Operando* high energy electron diffraction (RHEED)
  - $P_{base} = 2x10^{-9}$ torr
- Sample Transfer System
  - *In Situ* Quantum Efficiency Station (biased pickup coil)
  - $P_{base} = 1x10^{-9}$ torr
- ARPES/XPS System
  - Scientia DA30 electron analyzer
  - Fermi Helium Plasma discharge lamp
  - Specs XR50 Al/Mg X-ray source
  - $P_{base} = 7x10^{-11}$ torr




Reflection High Energy Electron Diffraction (RHEED)




Angle Resolved Photoemission Spectroscopy (ARPES)



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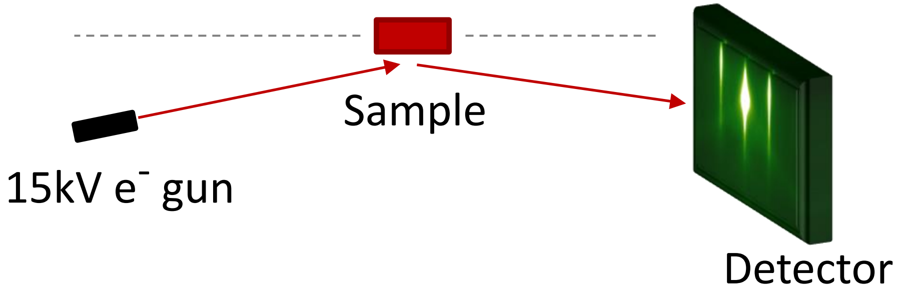
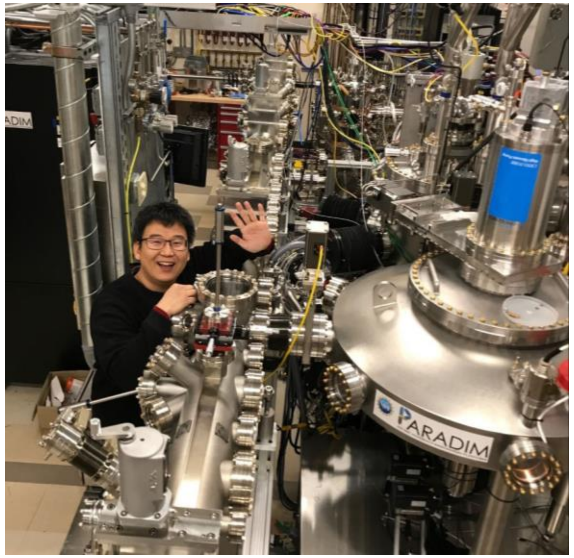
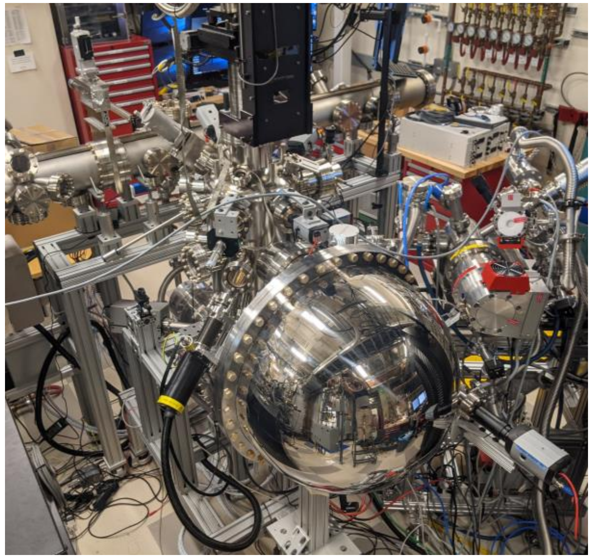
Reflection High Energy Electron Diffraction (RHEED)

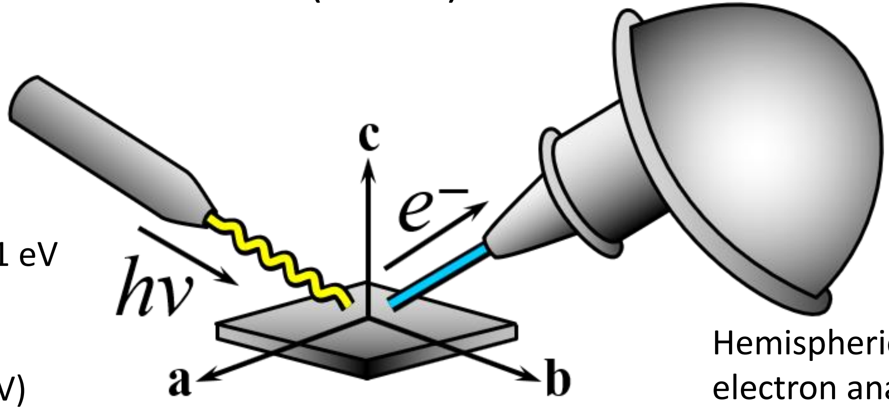


Angle Resolved Photoemission Spectroscopy (ARPES)

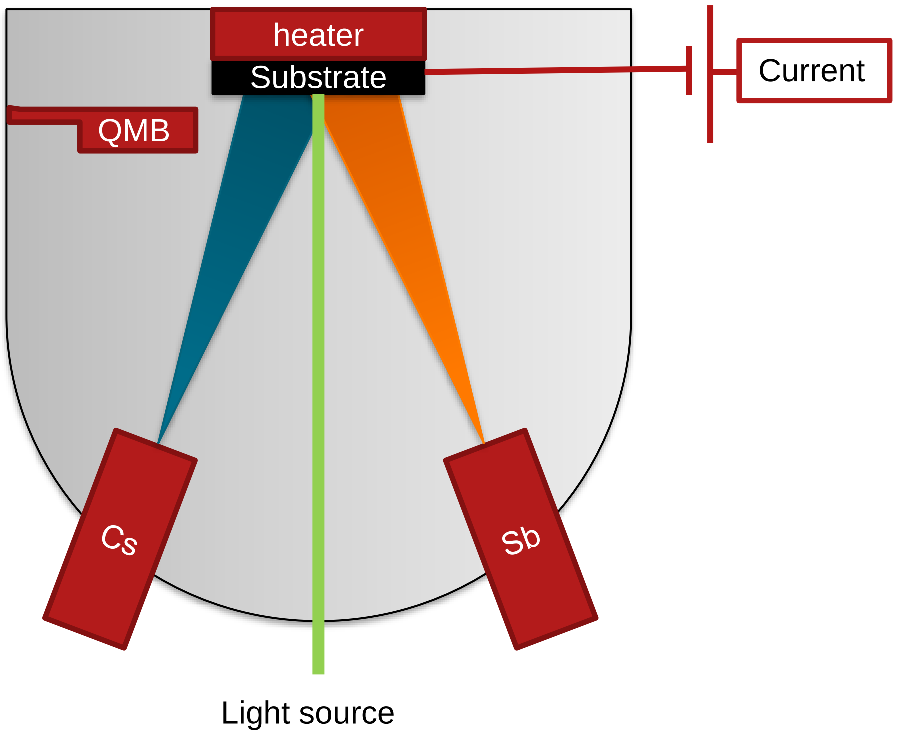
Helium plasma discharge lamp
hν=21.22, 40.81 eV
(+X-ray tube Mg/Al anode 1.254/1.487 keV)



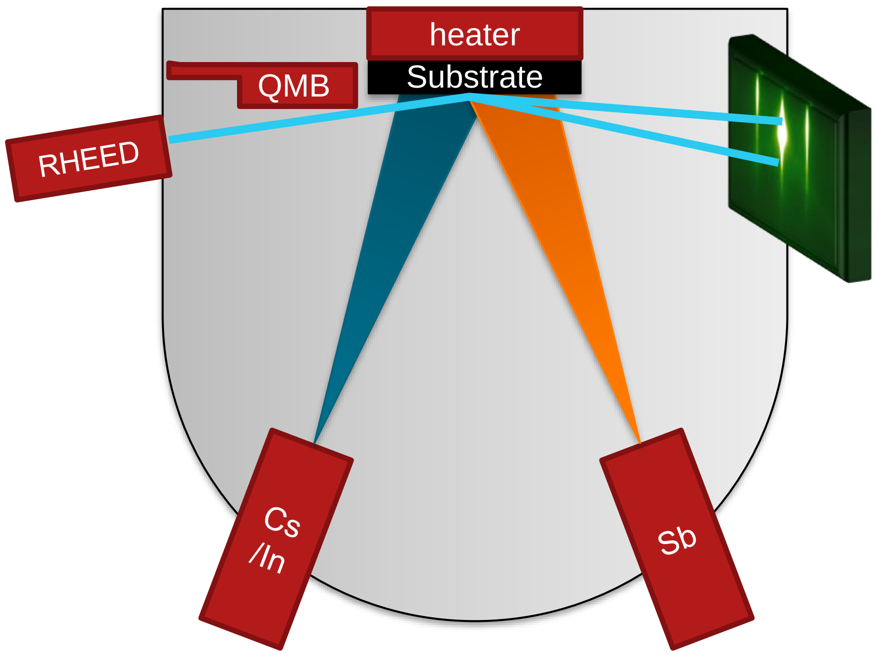

Hemispherical electron analyzer
$E_{pass}$ = 2-100 eV

# The experiment

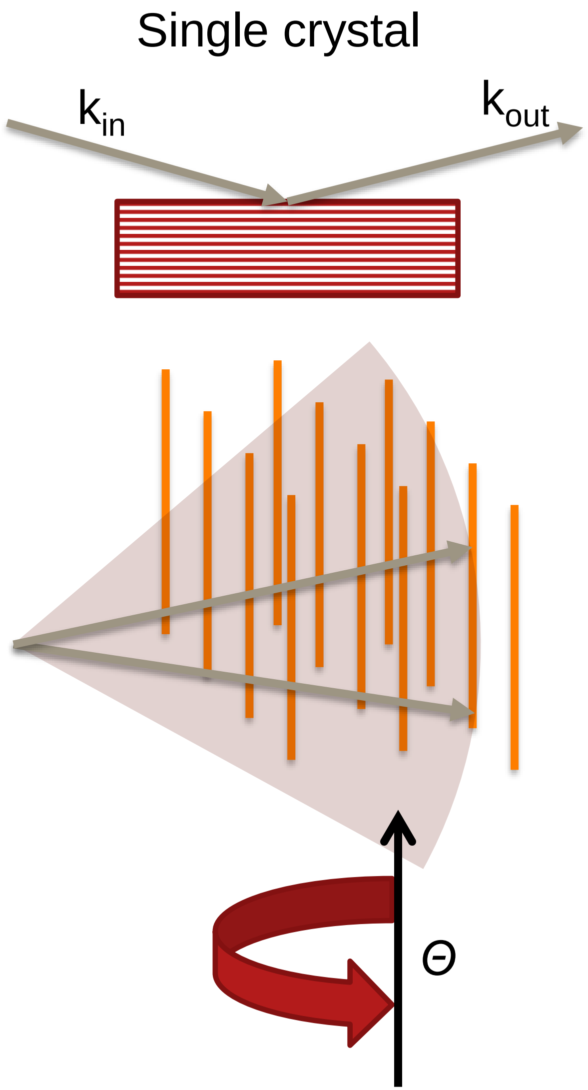
Typical photocathode growth:
Photocurrent monitored
Quantum efficiency oriented

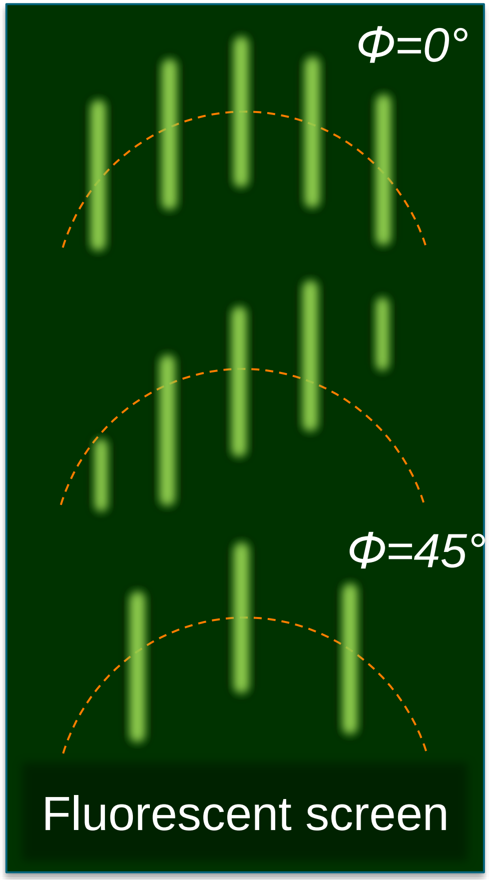



Our growth method:
RHEED monitored
Structure oriented



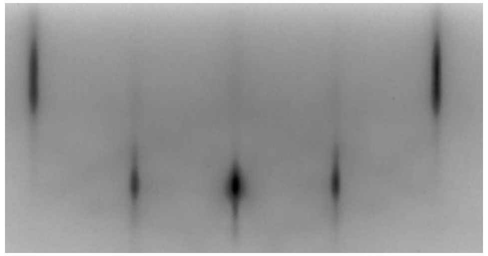
# Information provided by RHEED



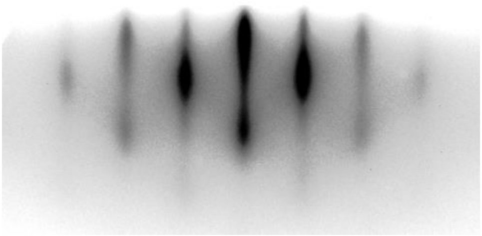




By rotating the sample around its surface normal, we intersect different sets of reciprocal space rods

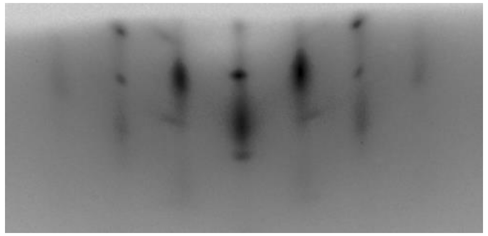
- Real-time
- Sub-ML sensitivity
- Qualitative probe of surface roughness and crystallinity



Single crystal
High coherence



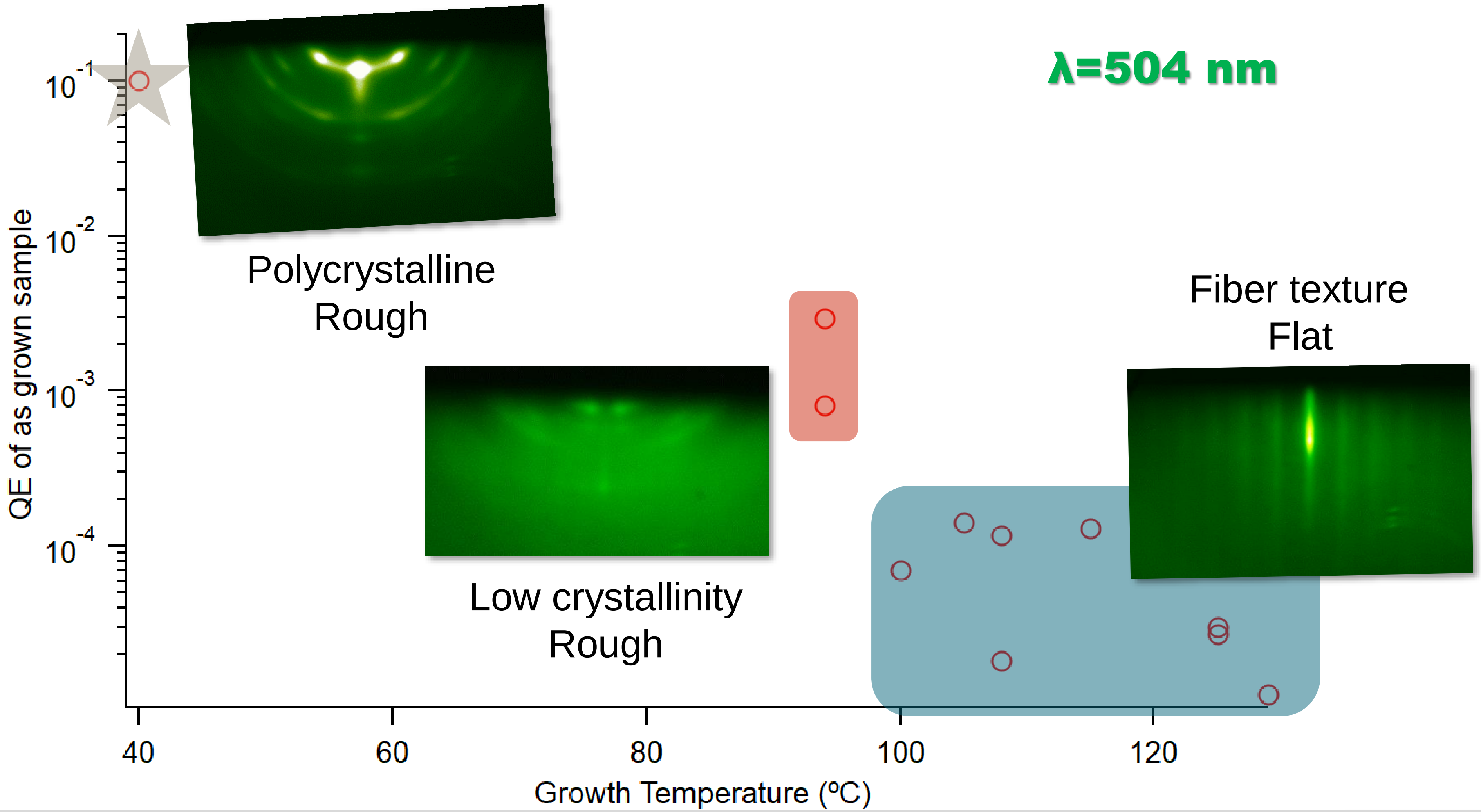
Film
Reduced coherence
Roughened surface



Film
Polycrystalline domains/impurities

# Temperature study: codeposition

- Cs-Sb co-deposition on SiC substrates
  - Cs:Sb ratio = 6:1 (as measured by Quartz Crystal Microbalance)




Higher Growth Temperature

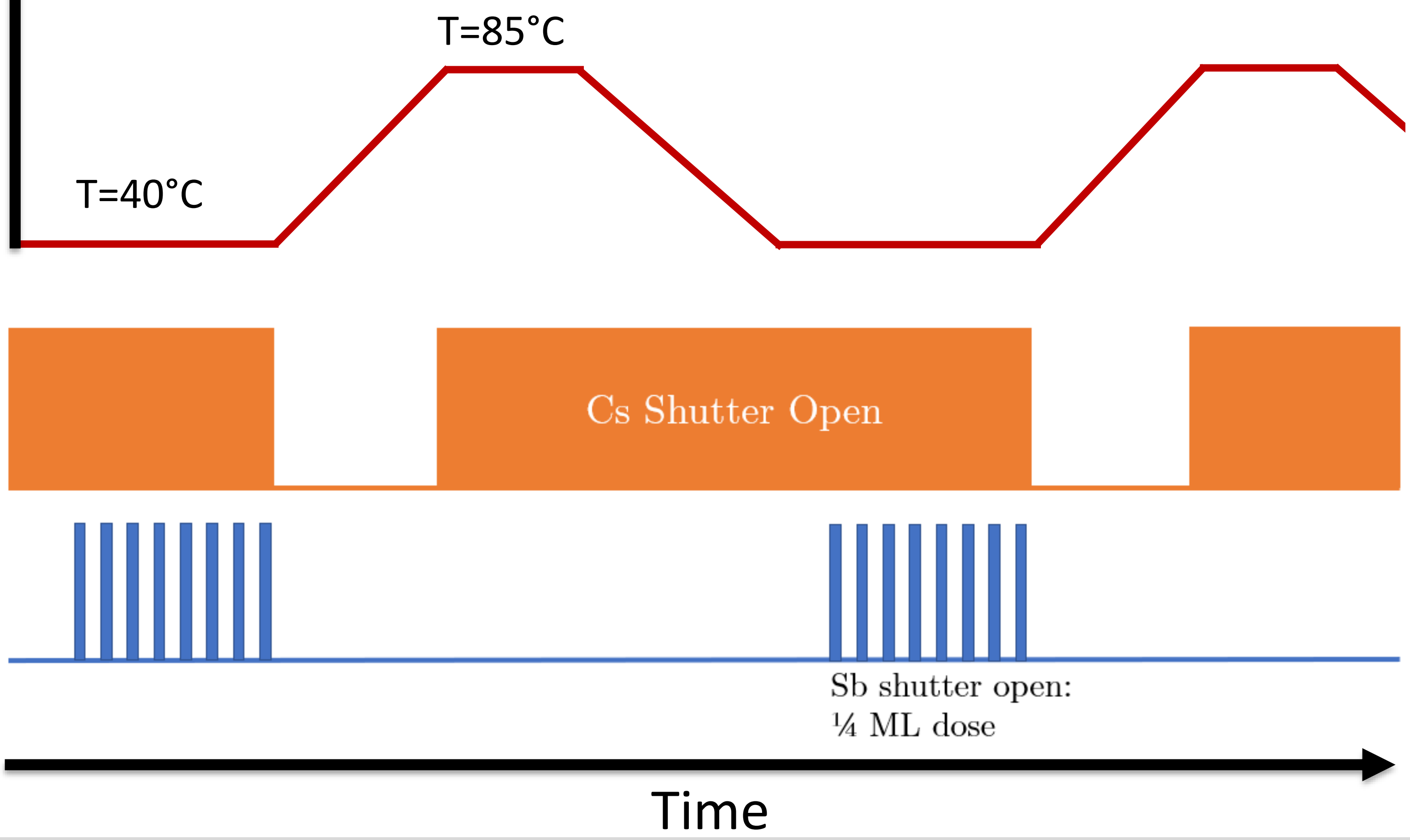
Improved Crystal Order
OOP Film Orientation
Reduced Surface Roughness
Reduced Quantum Efficiency

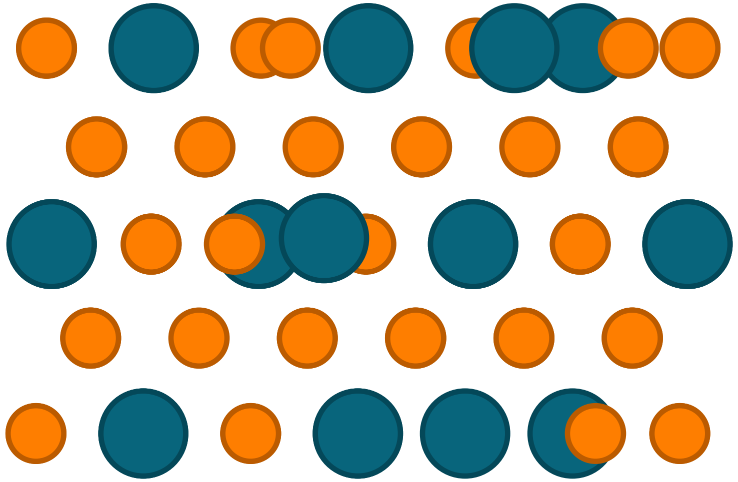
Lower Growth Temperature

Improved Quantum Efficiency
Polycrystalline Films

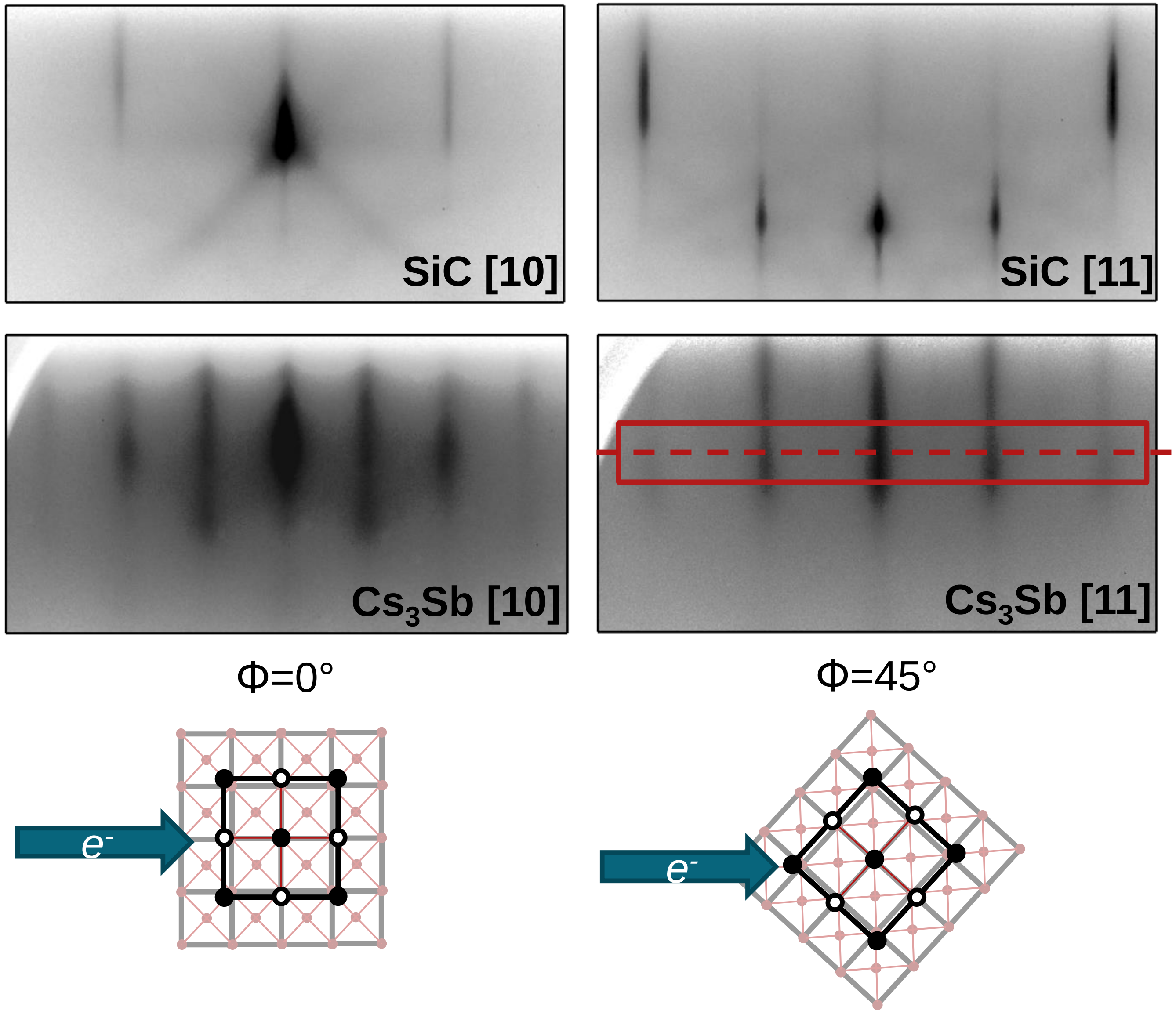
# Solid Phase (Molecular Beam) Epitaxy

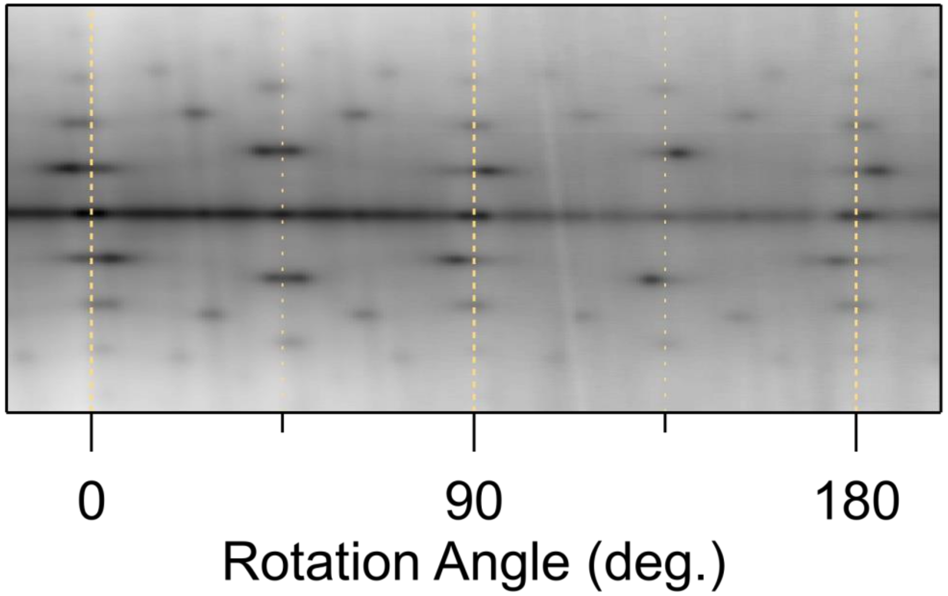
- **<u>Low</u>** Deposition temperature to take advantage of improved Cs sticking coefficient
- **<u>High</u>** temperature Cs anneal to improve crystallinity

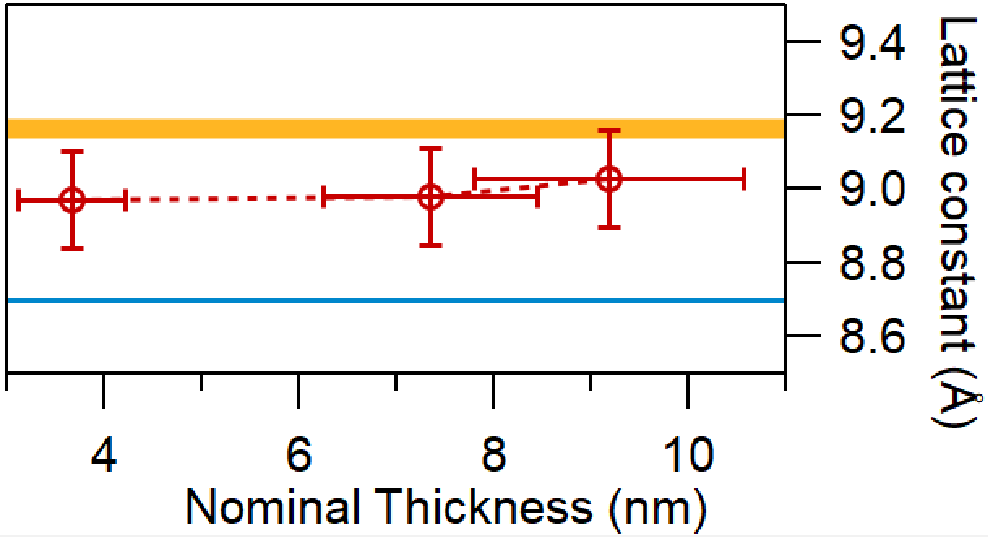


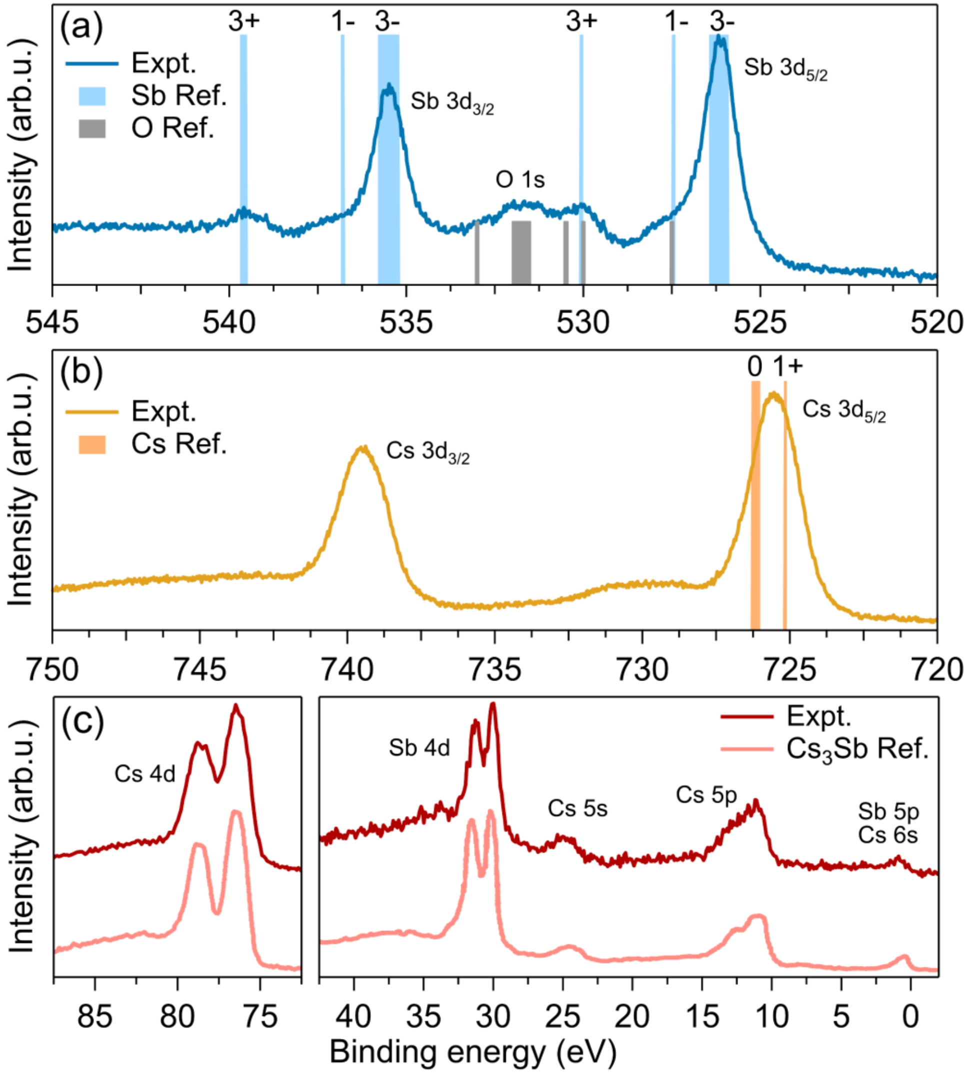
# It is epitaxial!



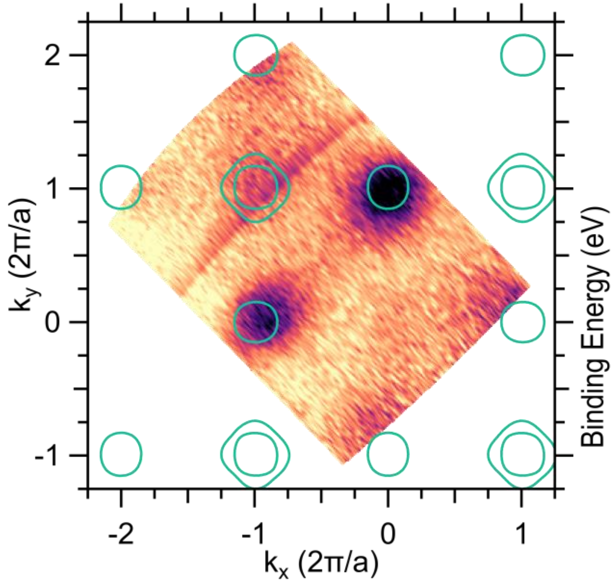



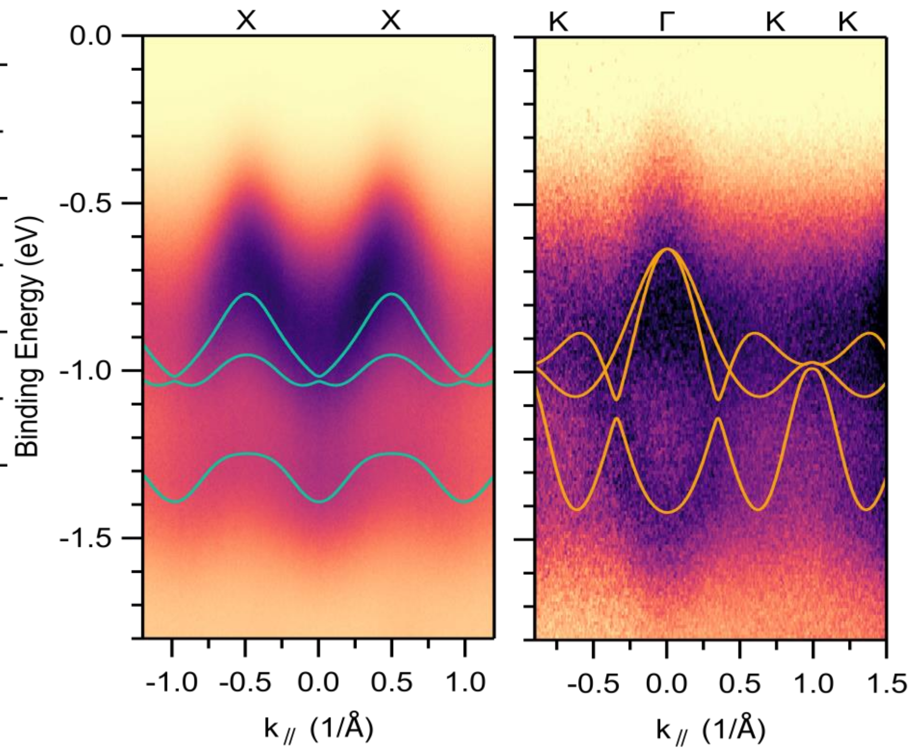



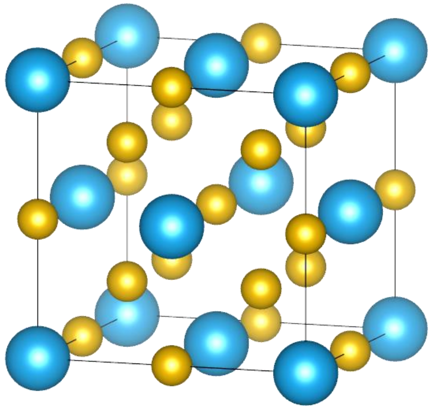
# It really is $Cs_3Sb$: XPS and ARPES




C. W. Bates, *et al.* Thin Solid Films 69, 175 (1980)

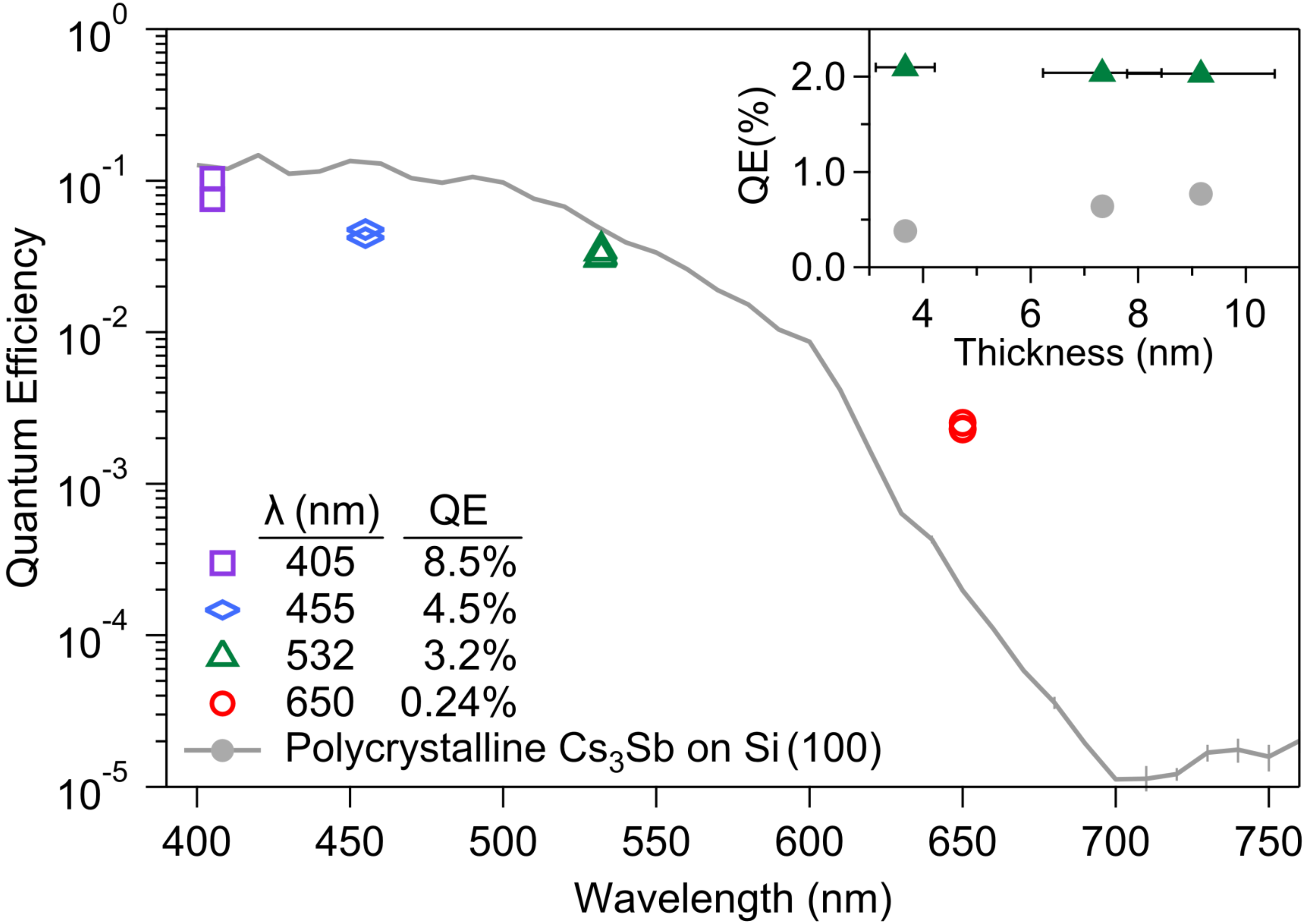


XPS: perfect agreement
ARPES: larger bandwidth (Strain? Structure distortion?)

# High efficiency in the ultrathin limit




Grey line and dots represent the data from a codeposited $Cs_3Sb$ sample grown by photocurrent-monitored codeposition.

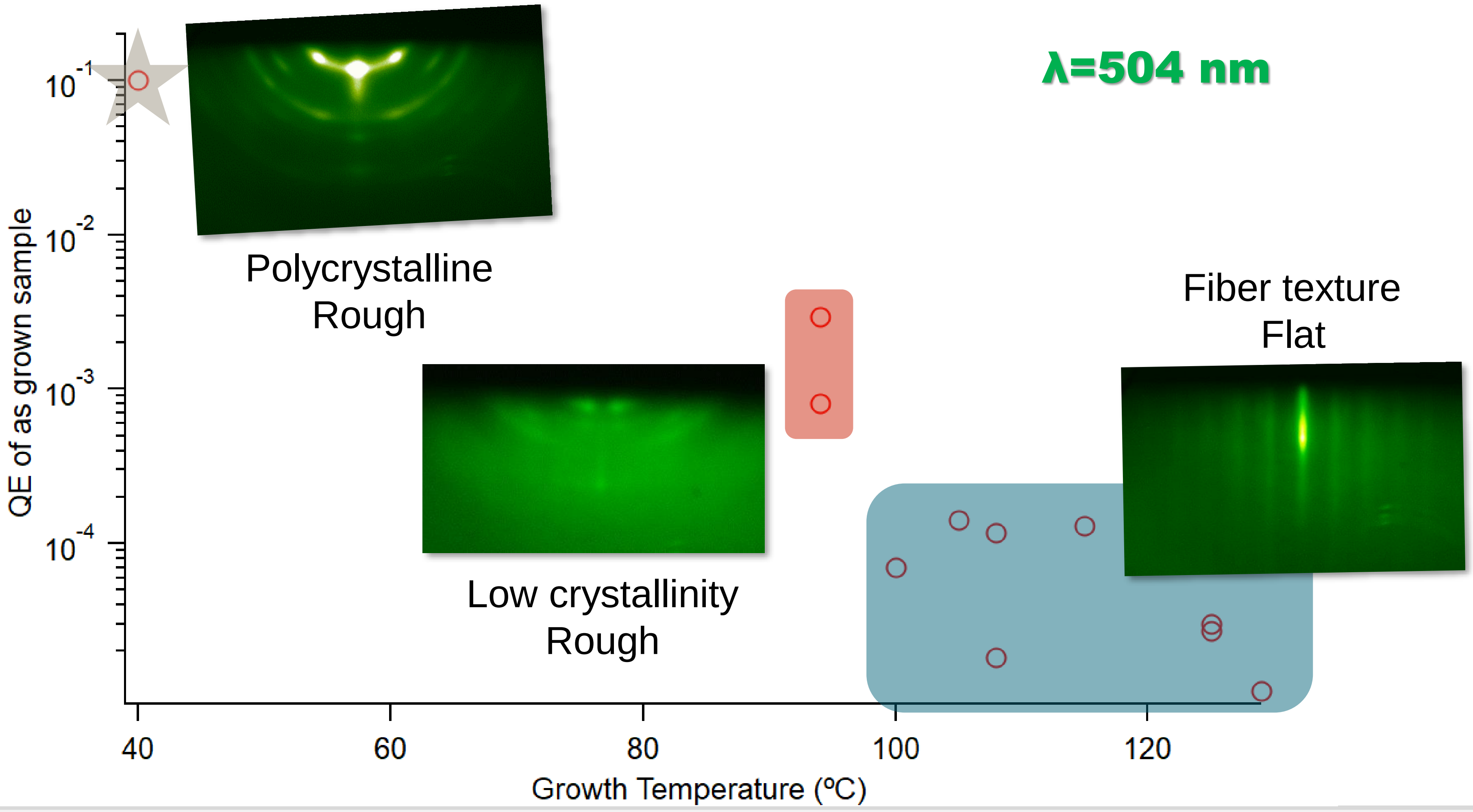
Enhanced QE:

- At the photoemission threshold
- At small thickness

C.T. Parzyck, A. Galdi *et al.*
Physical Review Letters 128, 114801

# Temperature study: codeposition

- Cs-Sb co-deposition on SiC substrates
  - Cs:Sb ratio = 6:1 (as measured by Quartz Crystal Microbalance)




Higher Growth Temperature

↓

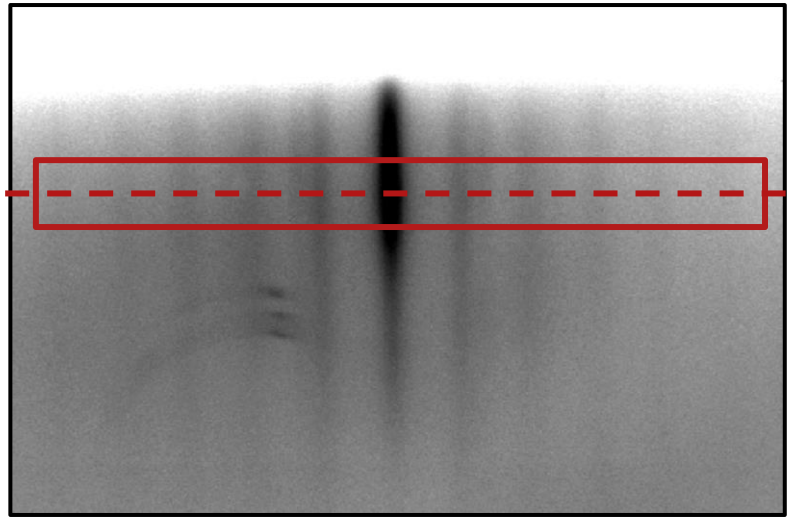
**Improved Crystal Order**
**OOP Film Orientation**
**Reduced Surface Roughness**
**Reduced Quantum Efficiency**

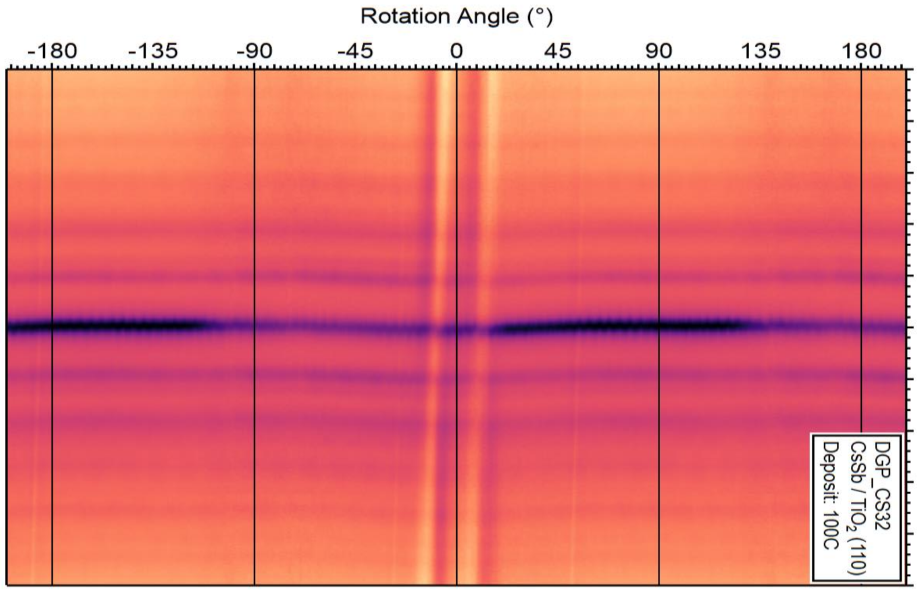
Lower Growth Temperature

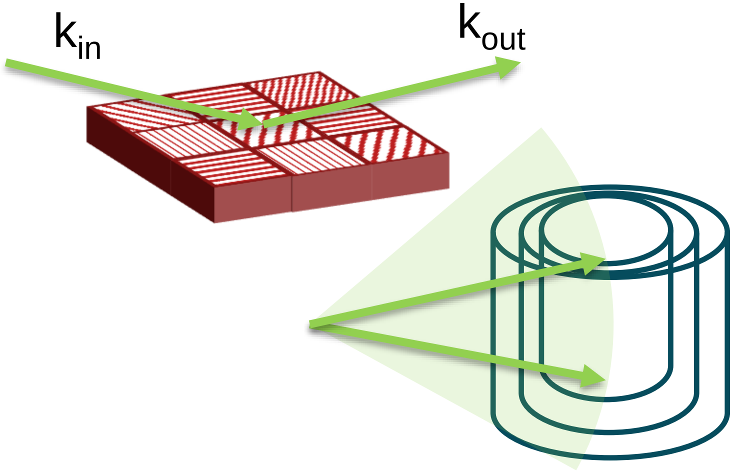
↓

**Improved Quantum Efficiency**
**Polycrystalline Films**

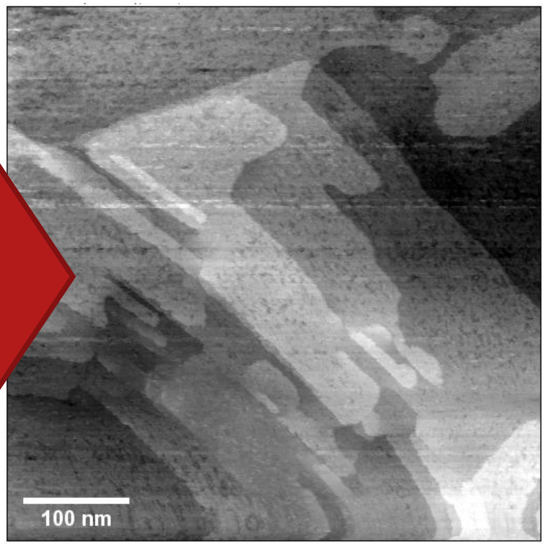
# Flat co-deposited samples

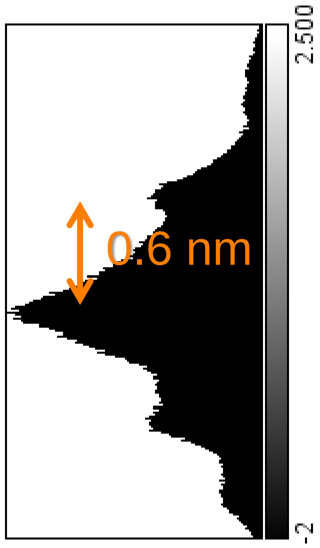


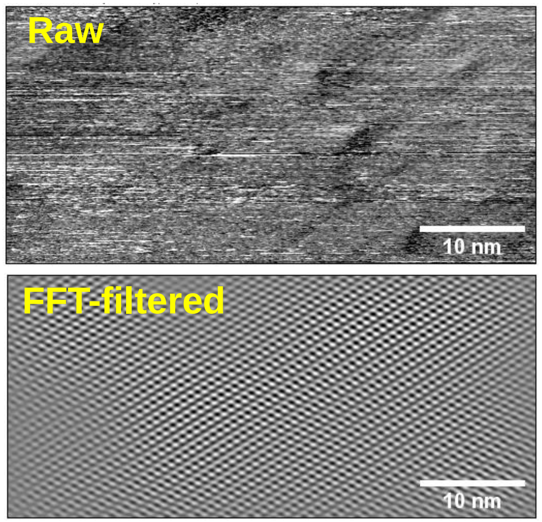


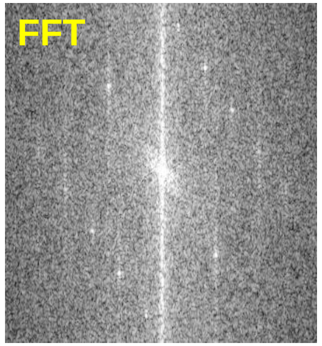




In vacuum transfer to STM



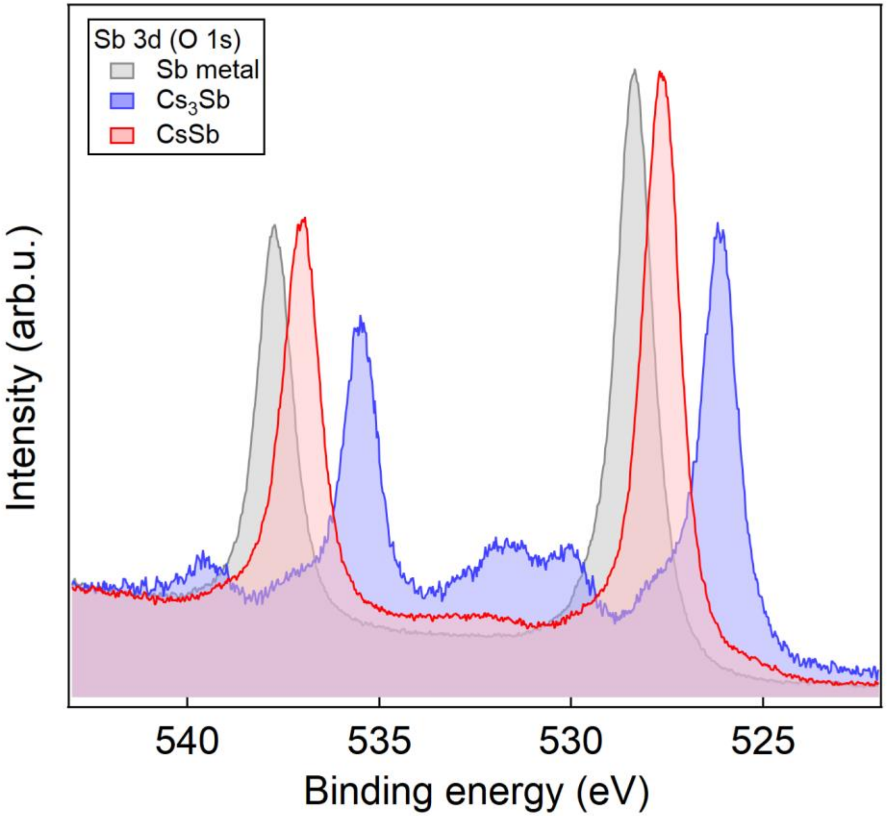



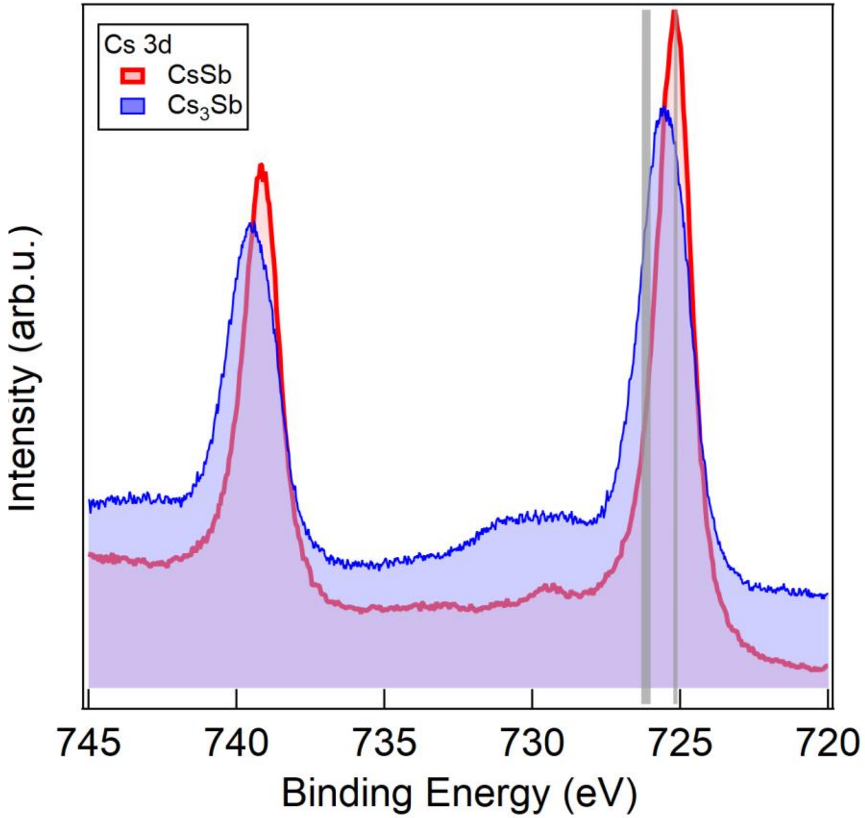

~~$Cs_3Sb$~~

Lattice:

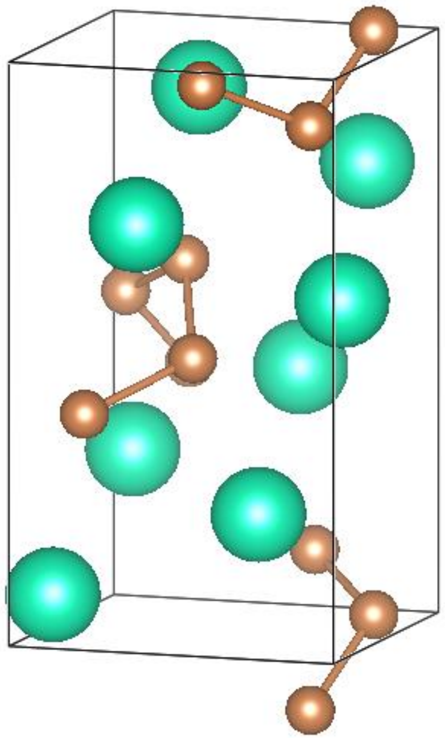
0.76 nm x 1.42 nm

# Flat co-deposited samples




CsSb parameters:
a = 7.34 Å
b = 7.57 Å
c =13.27 Å
P1 structure



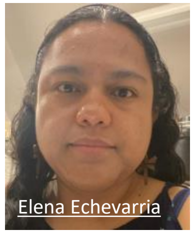
$$Cs{:}Sb \approx 1{:}1$$

Structure and composition data suggest that the compound we are forming is closely related to CsSb

# Current work in PHOEBE @ Cornell U.

**PHOEBE**: **PHO**tocathode **E**pitaxy and **B**eam **E**xperiments laboratory


- Study of epitaxial $Cs_3Sb$ and CsSb samples: spectral response, lifetime, oxygen resistance, mean transverse energy

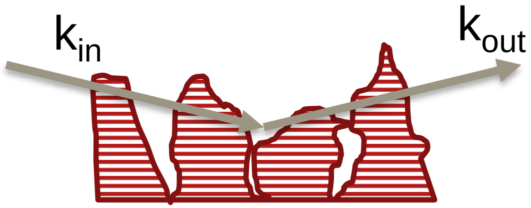



# Conclusions

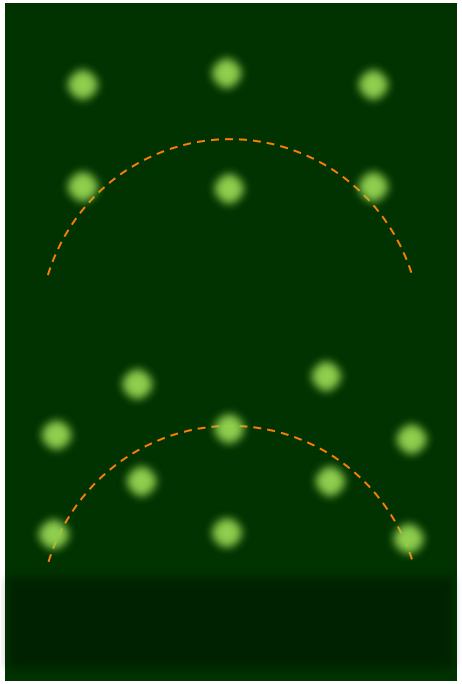
- Epitaxy of $Cs_3Sb$ is achieved using molecular beam epitaxy via monitoring the sample structure with RHEED
- State-of-the-art MBE machines and in-situ RHEED allow to explore various growth regimes and efficient optimization of the samples beyond quantum efficiency
- High throughput:
  - PARADIM experiments: 59 samples grown in 27 days (24h per day)
  - PHOEBE: 75 Cs-Sb samples grown between 09/2021 and 08/2022
- Structure-oriented growth identifies an interesting phase: CsSb
  - Atomically smooth
  - Easily achievable via codeposition
  - QE ~1% at 400 nm
  - Robust against oxidation

# Information provided by RHEED

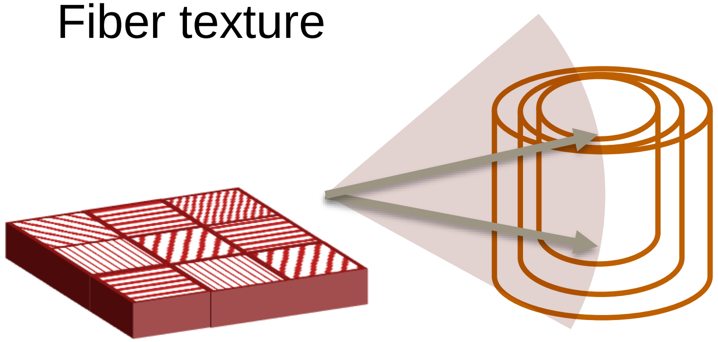
Epitaxial island growth

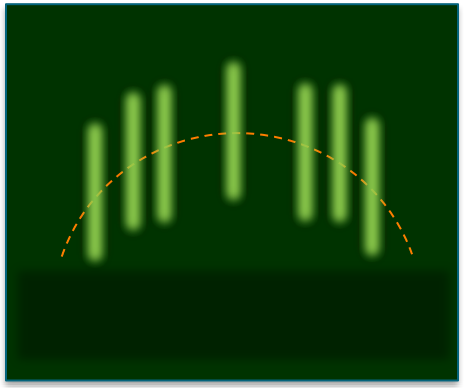



Transmission pattern:
Streaks turn into spots

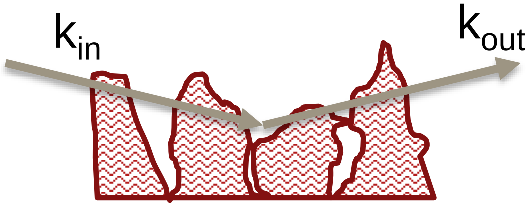


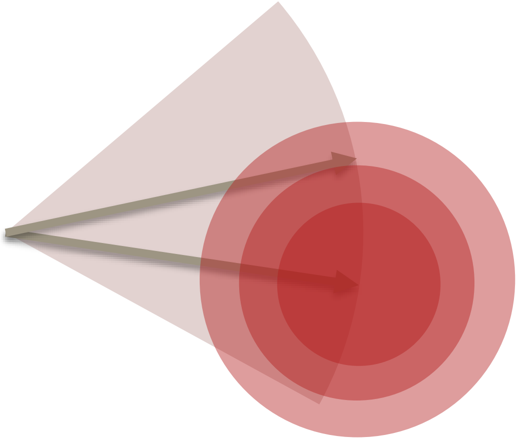
Fiber texture

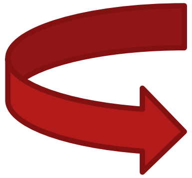




Polycrystalline islands





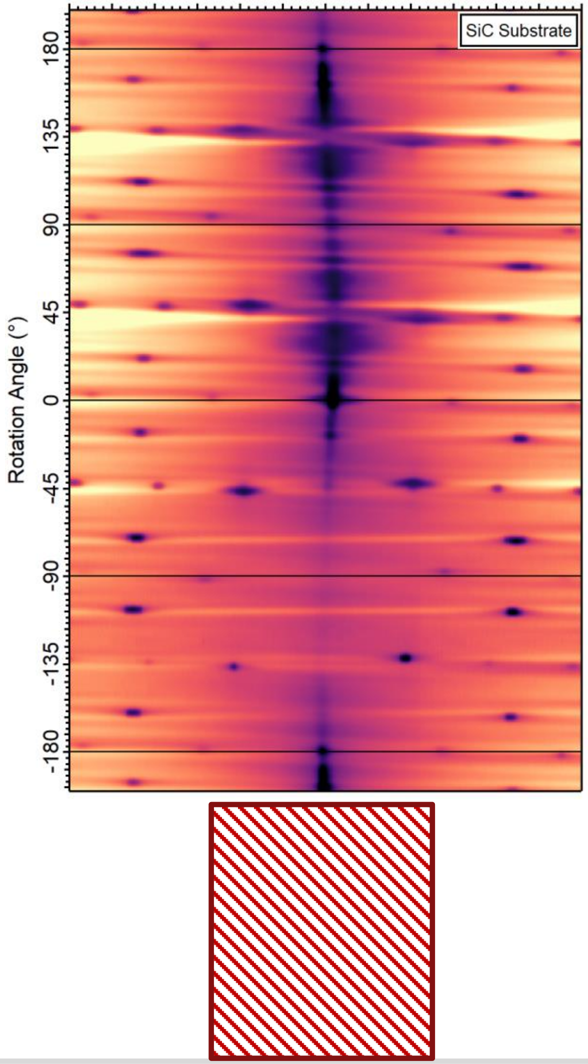
No texture

Textured film

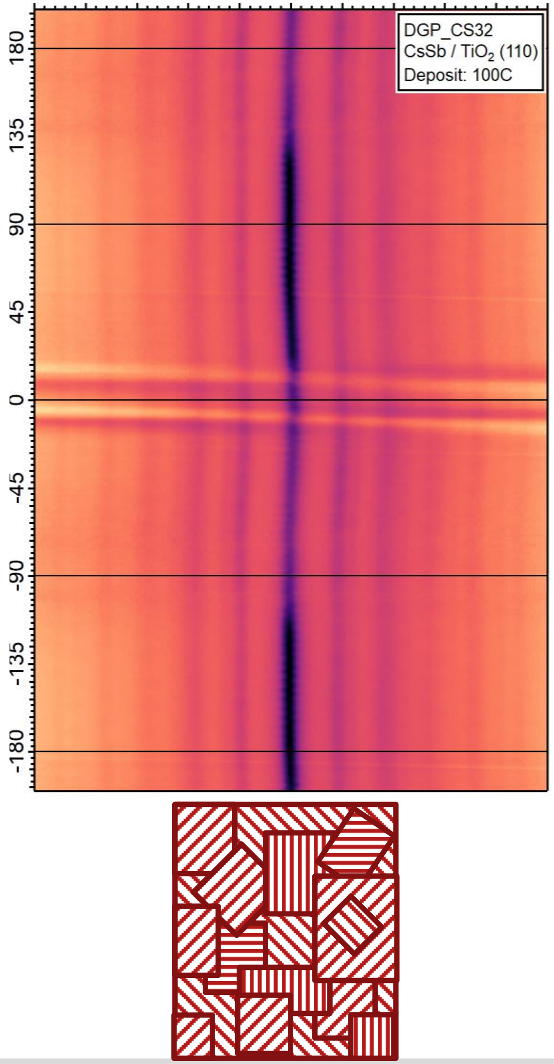
No rotation dependence if the texture axis is out-of-plane (uniaxial)
Rotation dependence if the texture axis is in-plane (biaxial)

# Epitaxial Relationship

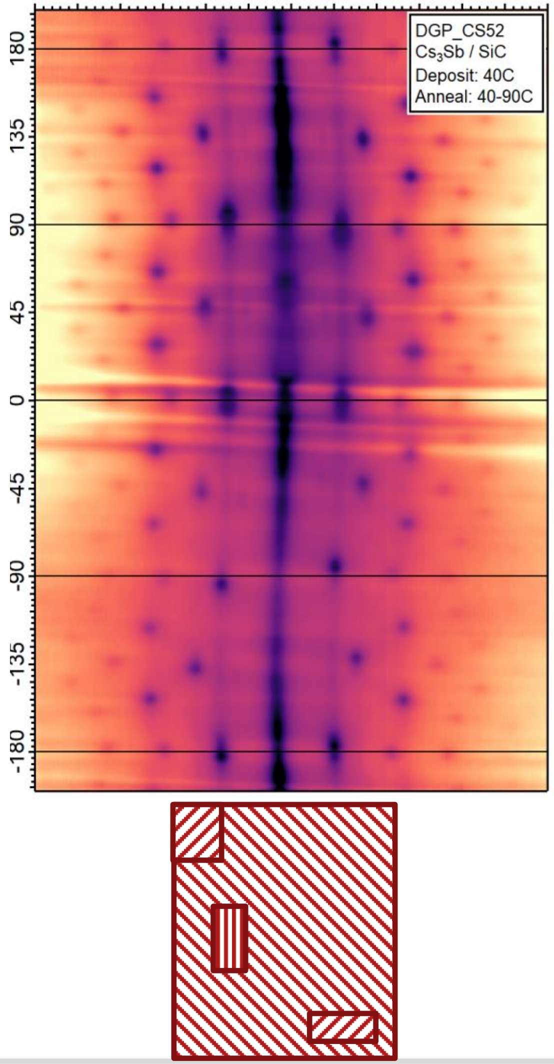
Substrate
Fully Ordered




Fiber Textured Film
Only c-axis oriented




Partially Ordered Film




Epitaxial Film