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

Molecular beam epitaxy of Cs_3Sb: a single crystalline visible light photocathode

Alice Galdi

Department of Industrial Engineering
Università degli Studi di Salerno (Italy)

CLASSE, Cornell University

People

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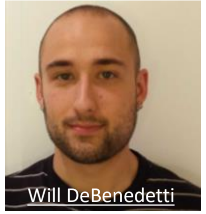
PARADIM
AN NSF MATERIALS INNOVATION PLATFORM

Maxson group

Shen group

Arias group

Hines group



Outline

- Background & Motivation
  - –Why study Cs_3Sb?
  - –Deficits of Cs_3Sb thin films
  - –Motivation for epitaxial films
- Growth of Epitaxial Cs_3Sb
  - –*In operando* characterization (RHEED)
  - –Sample growth: solid phase epitaxy
- *In situ* Characterization
  - –XPS
  - –Quantum Efficiency
  - –ARPES
- Conclusions and Future Directions

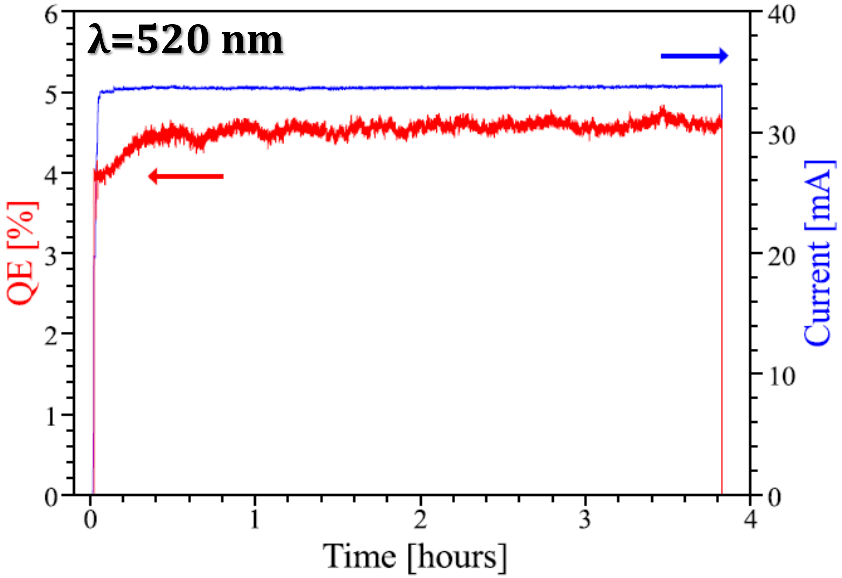
Cs_3Sb for low emittance, high current

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

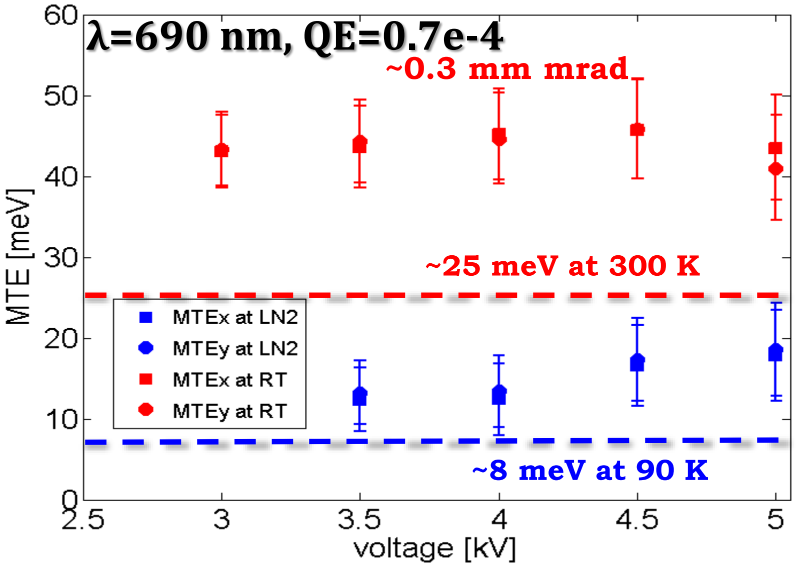
Beam current: quantum efficiency, laser fluence

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

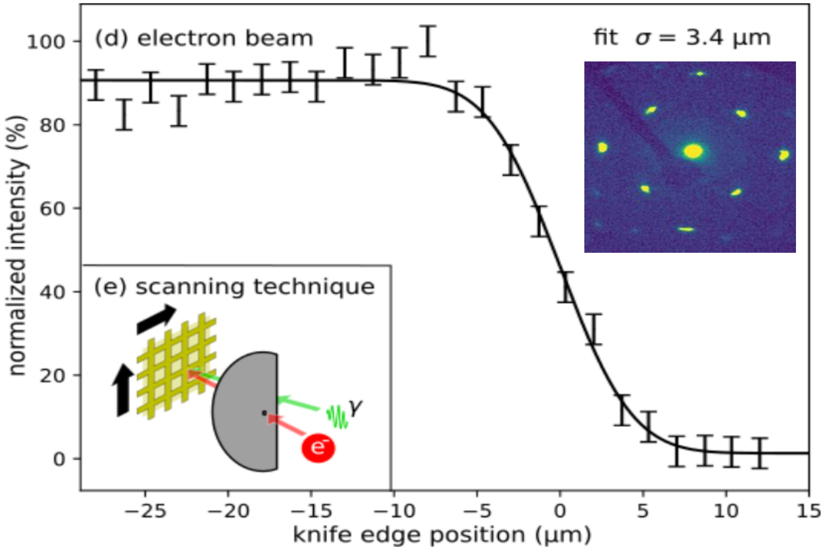
Alkali antimonide (Cs_3Sb-related) photocathodes are crucial to achieve excellent performances in the MEDUSA UED instrument



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

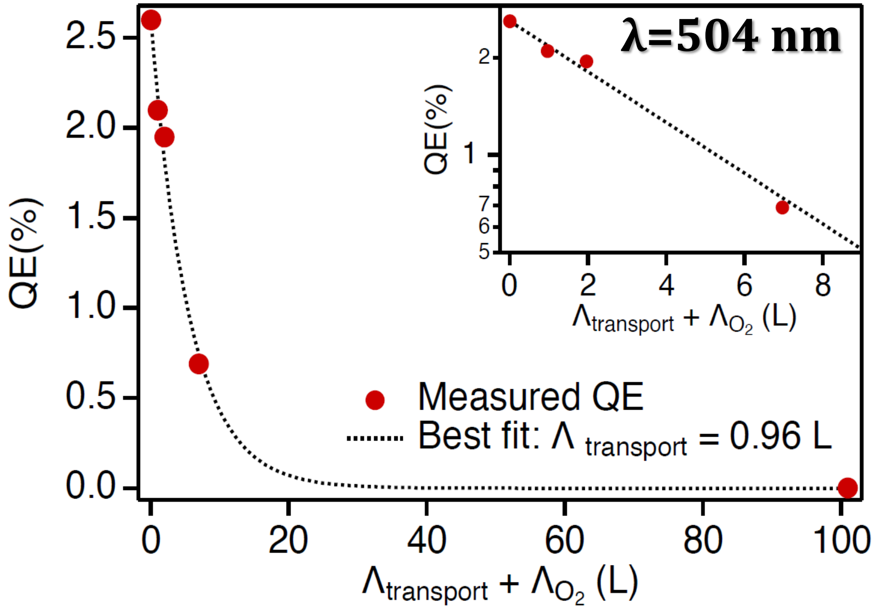


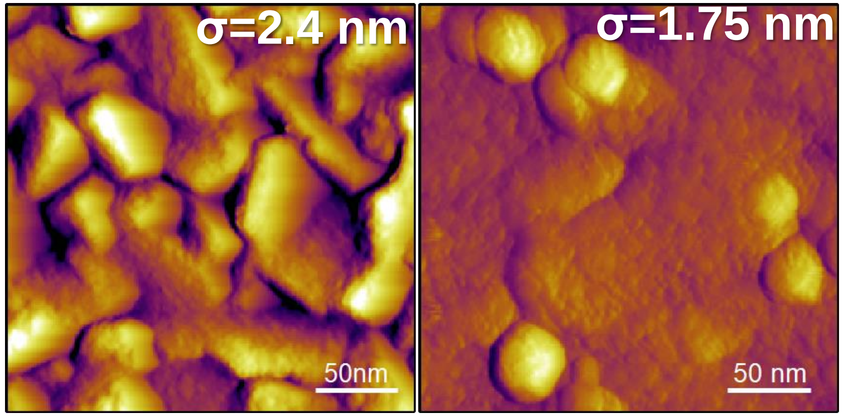
L. Cultrera et al., Phys. Rev. STAB **18** (2015) 113401



See Duncan/Li presentation in session E

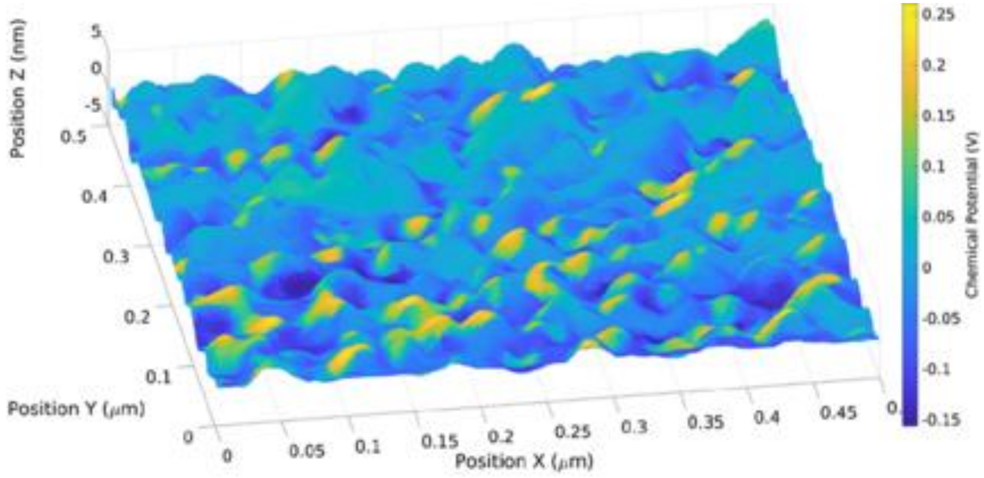
Drawbacks: reactive, disordered





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)



Measured surface and surface potential of a Cs_3Sb photocathode

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

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

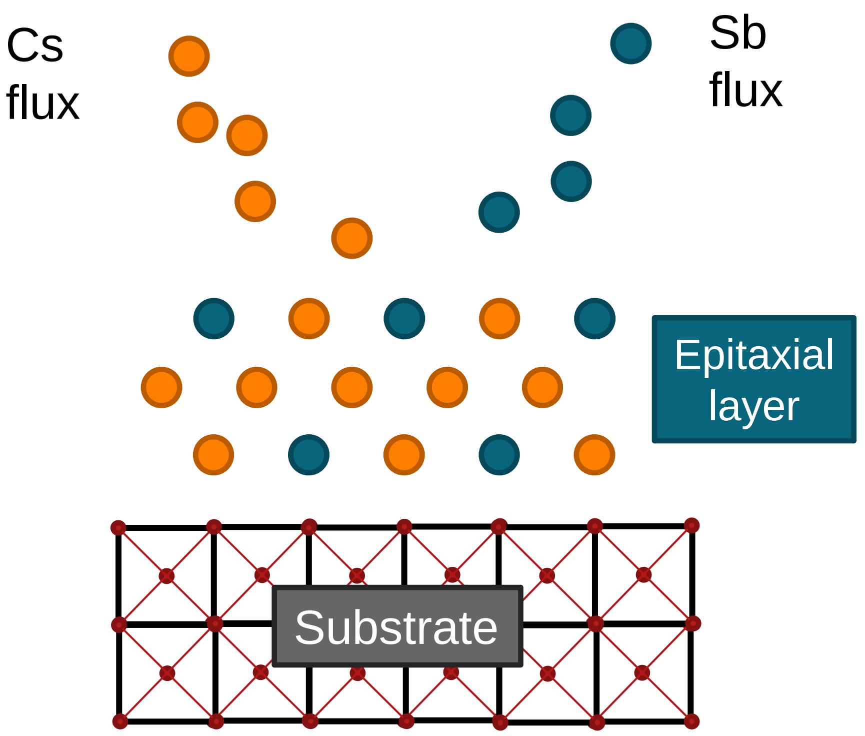
Single crystalline photocathodes: epitaxy

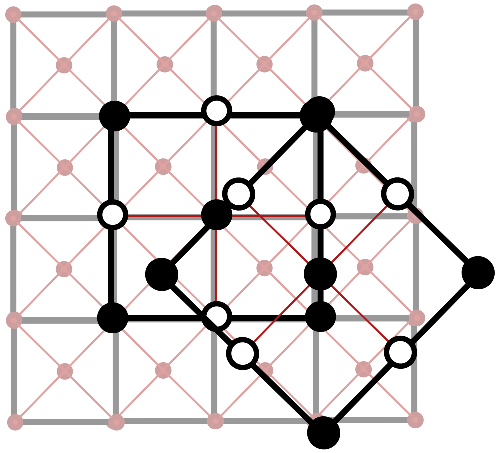
Epitaxy is the growth of a crystal layer with one or more well-defined orientations with respect to an underlying crystal seed layer (usually a single crystal substrate)

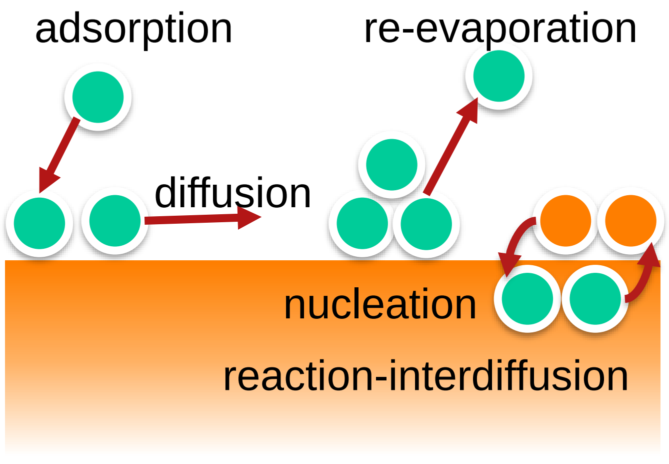
Single domain films would allow:

- 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



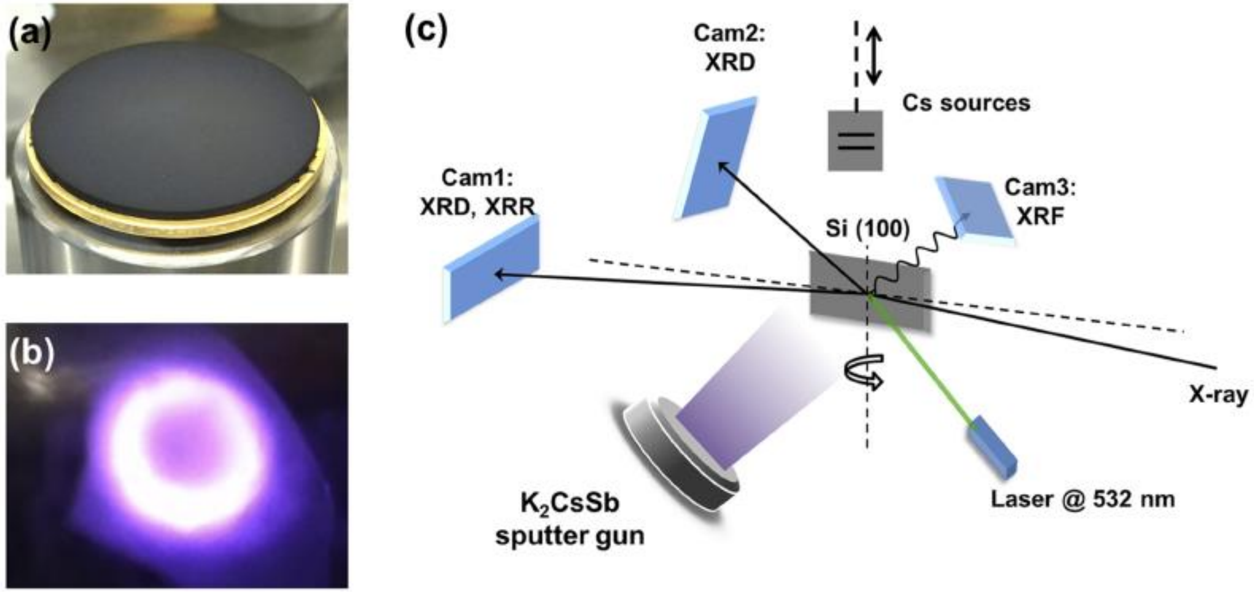


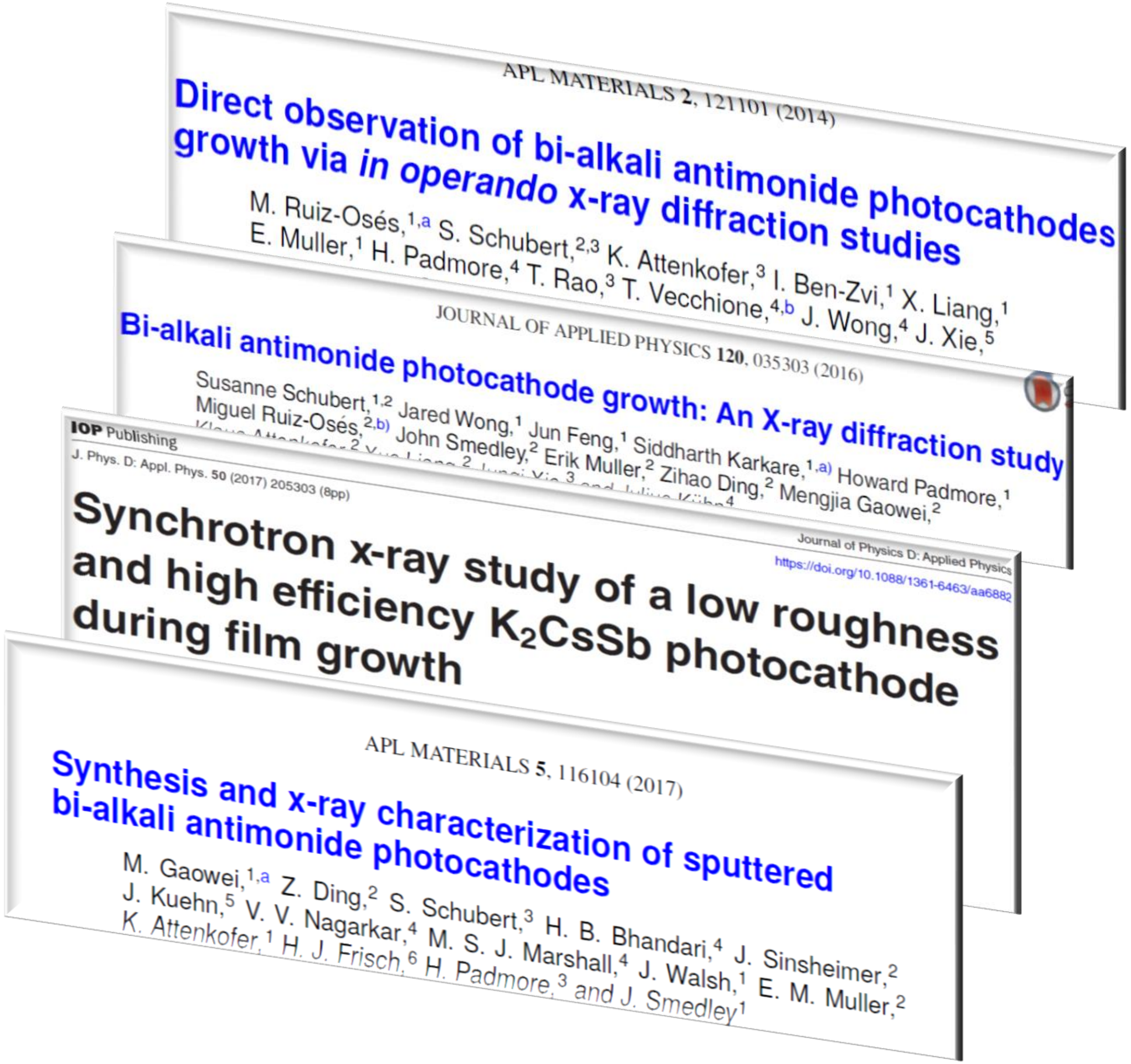


geometric similarity+chemistry+dynamics

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)

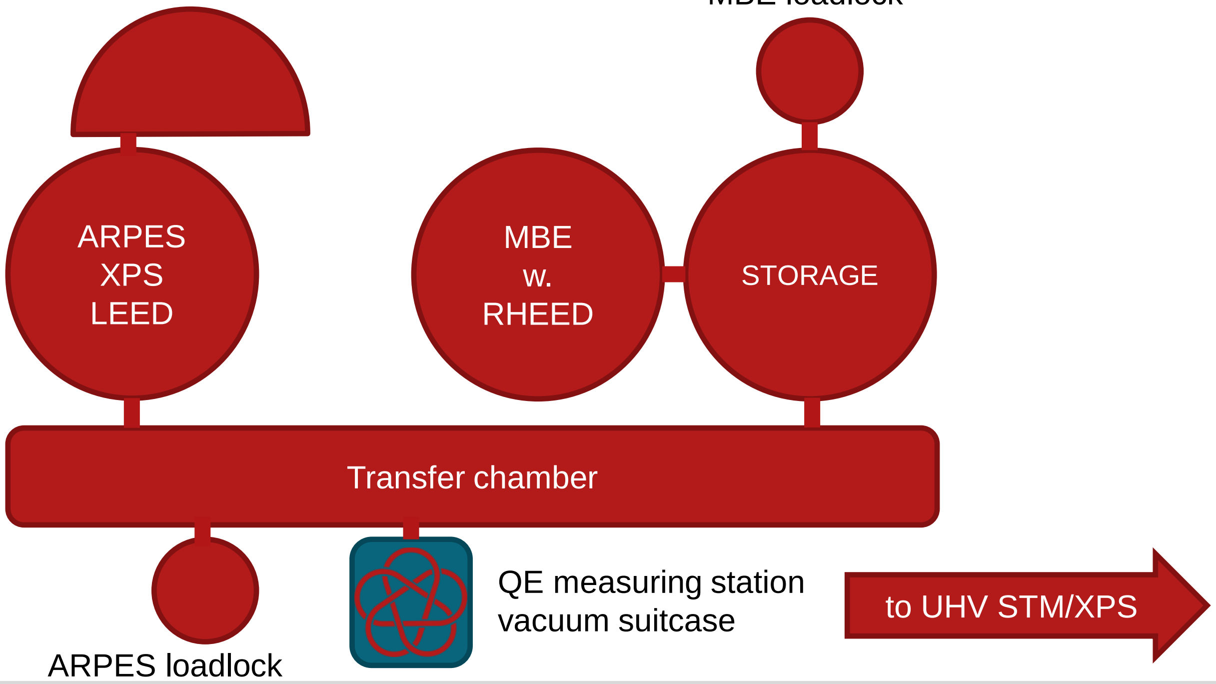
Synthesis and x-ray characterization of sputtered bi-alkali antimonide photocathodes

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]

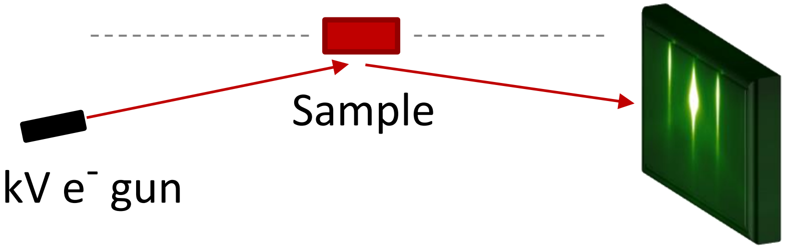
RHEED assisted MBE @ PARADIM

PARADIM Thin Film User Facility

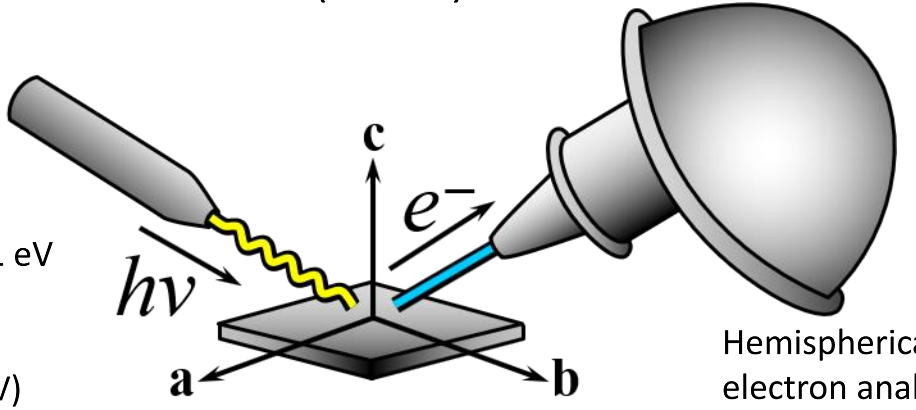
- Molecular Beam Epitaxy System
  - *In Operando* high energy electron diffraction (RHEED)
  - P_{base} = 2x10^{-9} torr
- Sample Transfer System
  - *In Situ* Quantum Efficiency Station (biased pickup coil)
  - P_{base} = 1x10^{-9} torr
- ARPES/XPS System
  - Scientia DA30 electron analyzer
  - Fermi 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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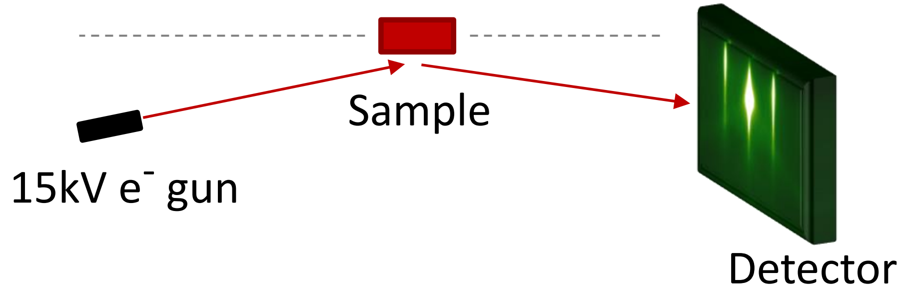
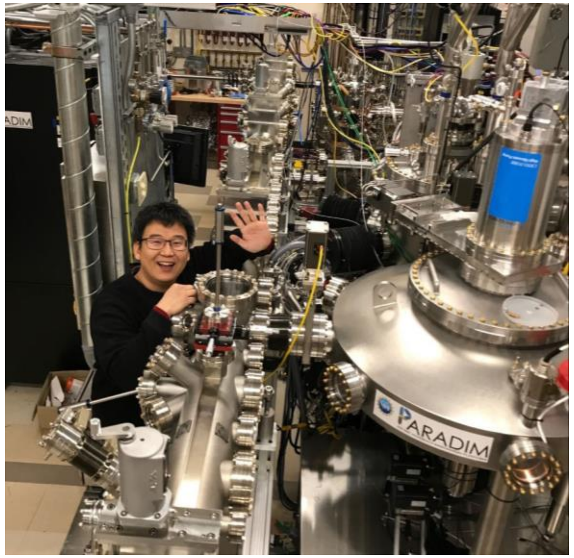
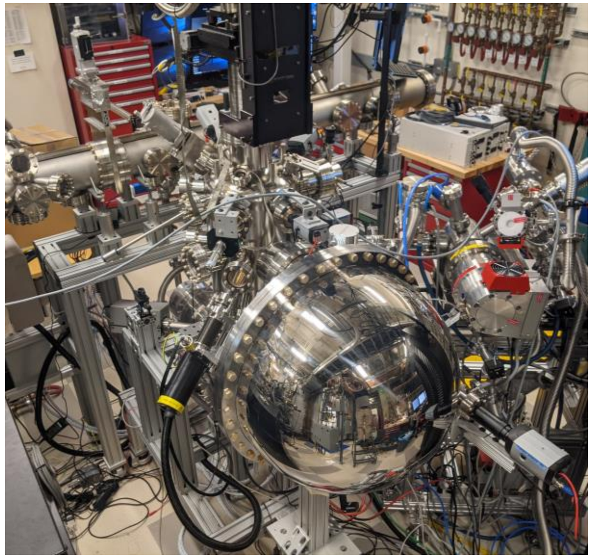
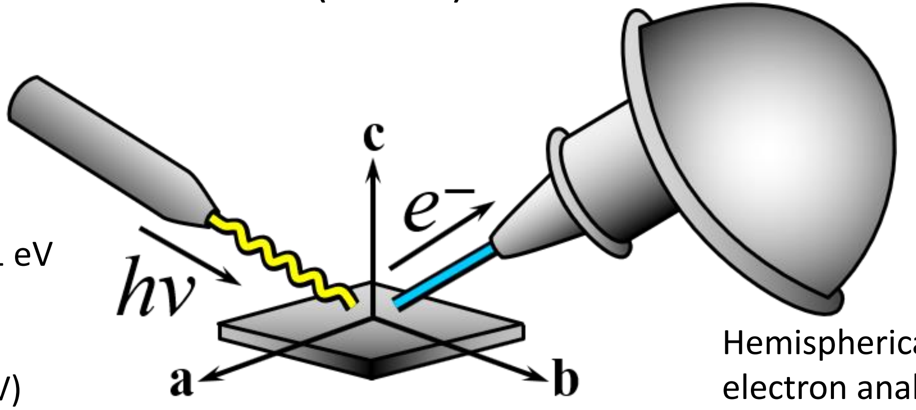






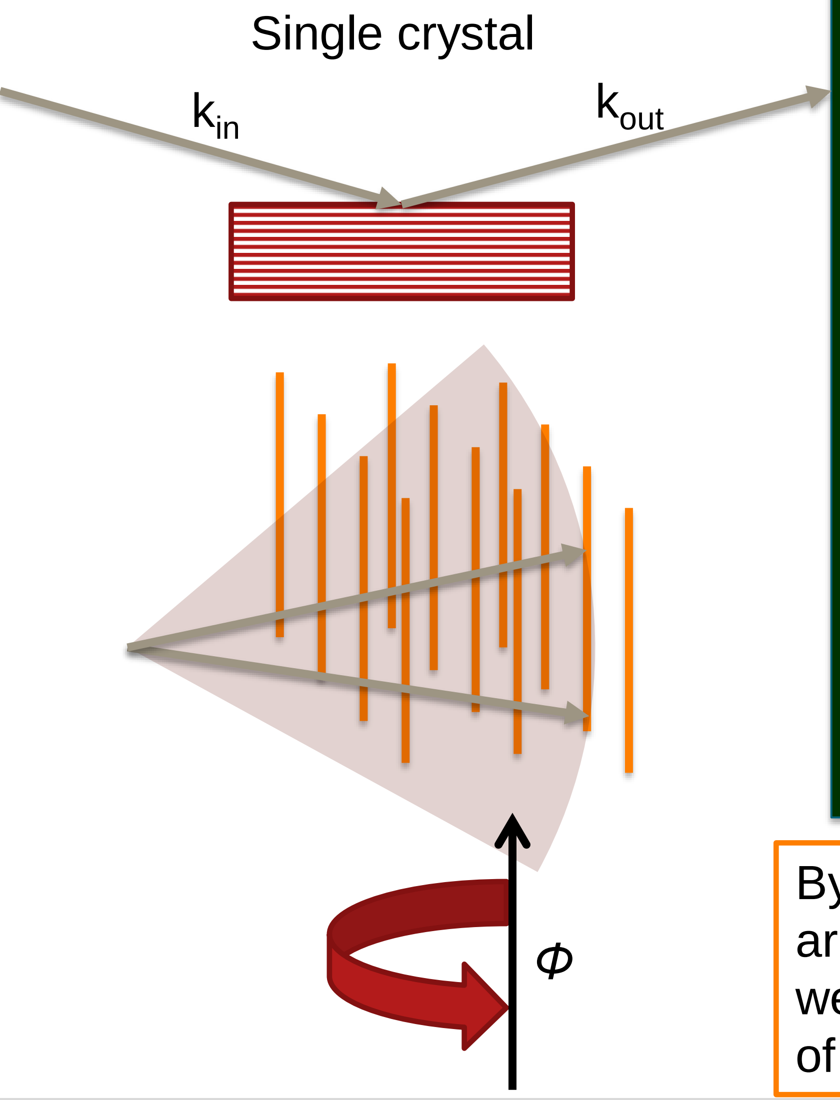
Angle Resolved Photoemission Spectroscopy (ARPES)

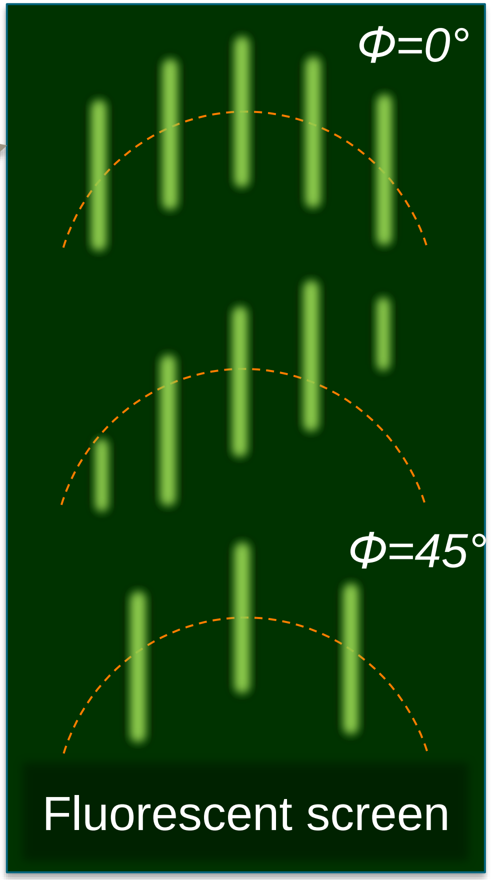
Helium plasma discharge lamp
hv=21.22, 40.81 eV
(+X-ray tube Mg/Al anode 1.254/1.487 keV)



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

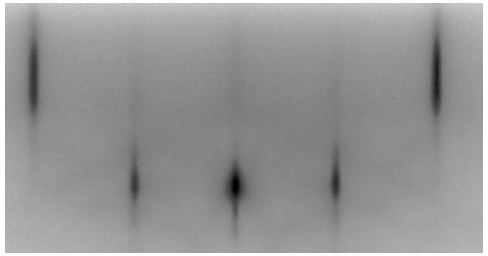
Information provided by RHEED



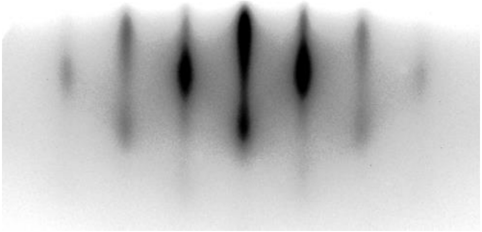


By rotating the sample around its surface normal, we intersect different sets of reciprocal space rods

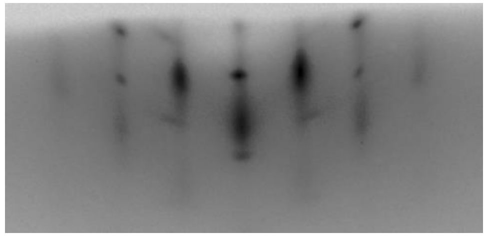
- Real-time
- Sub-ML sensitivity
- Qualitative probe of surface roughness and crystallinity



Single crystal
High coherence



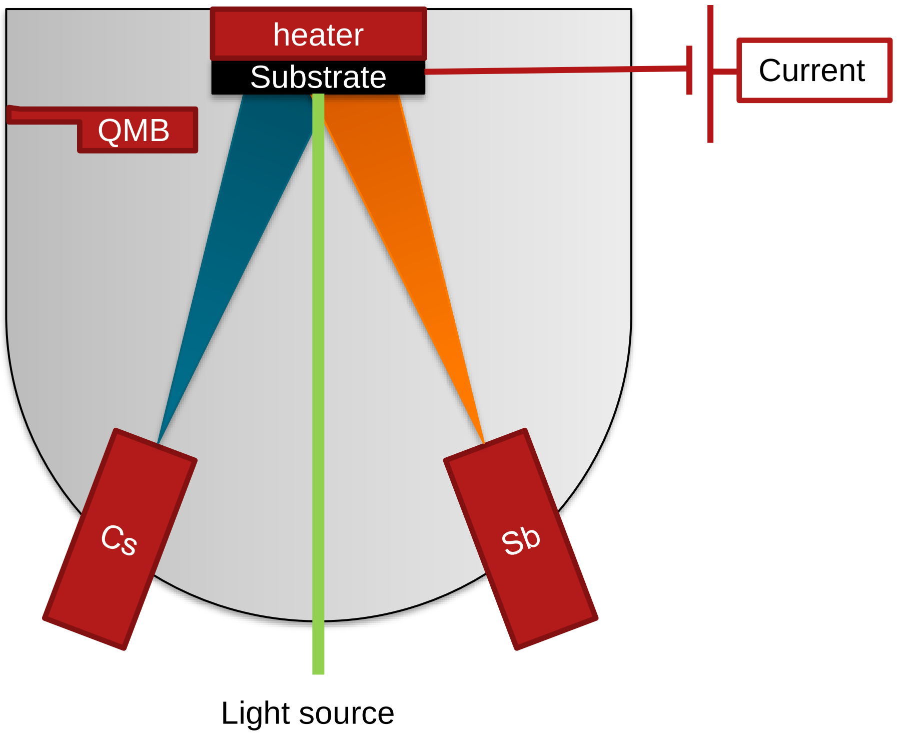
Film
Reduced coherence
Roughened surface



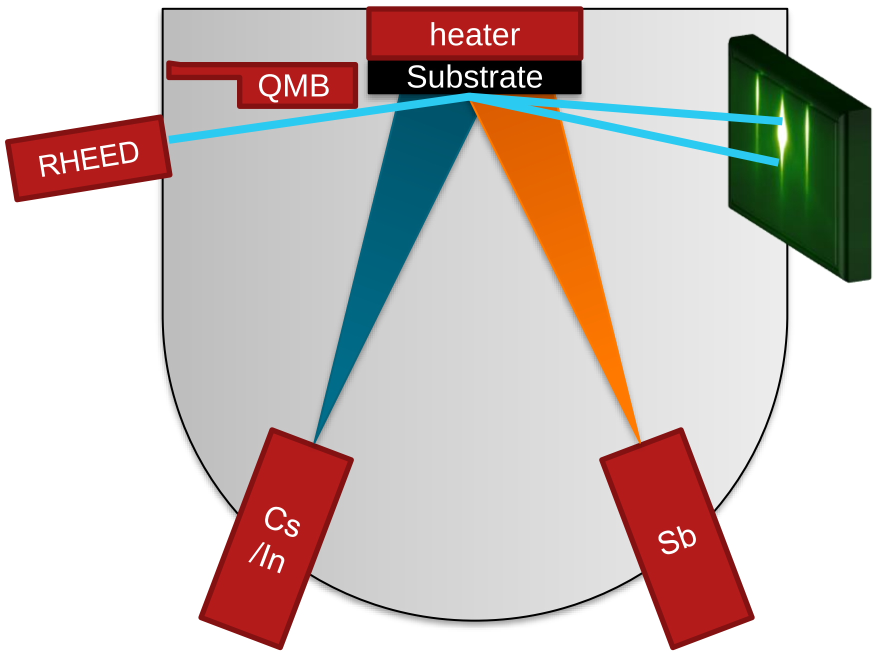
Film
Polycrystalline
domains/impurities

The experiment

Typical photocathode growth:
Photocurrent monitored
Quantum efficiency oriented

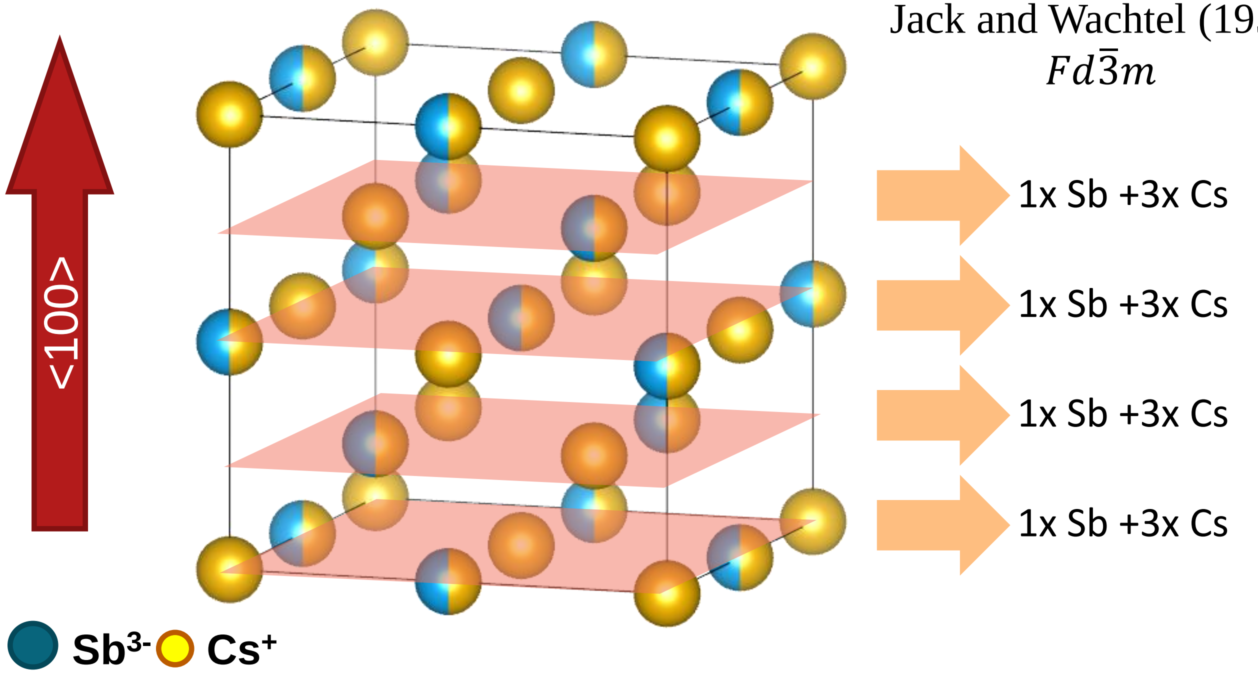


Our growth method:
RHEED monitored
Structure oriented

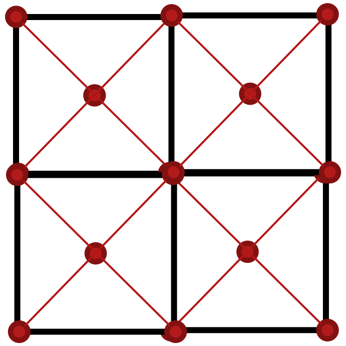


Growing with structure in mind

Jack and Wachtel (1957)
$Fd\bar{3}m$

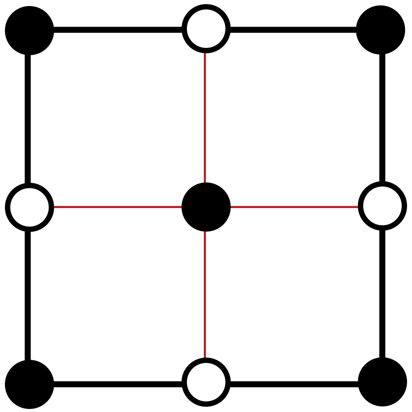


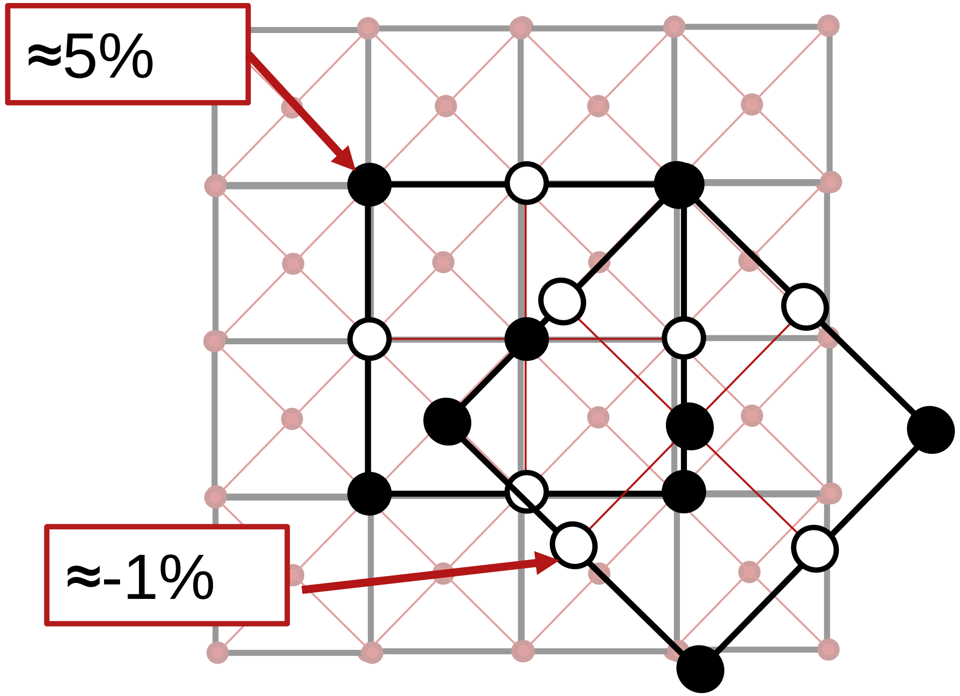
4 X SiC (a=0.436 nm)



≈

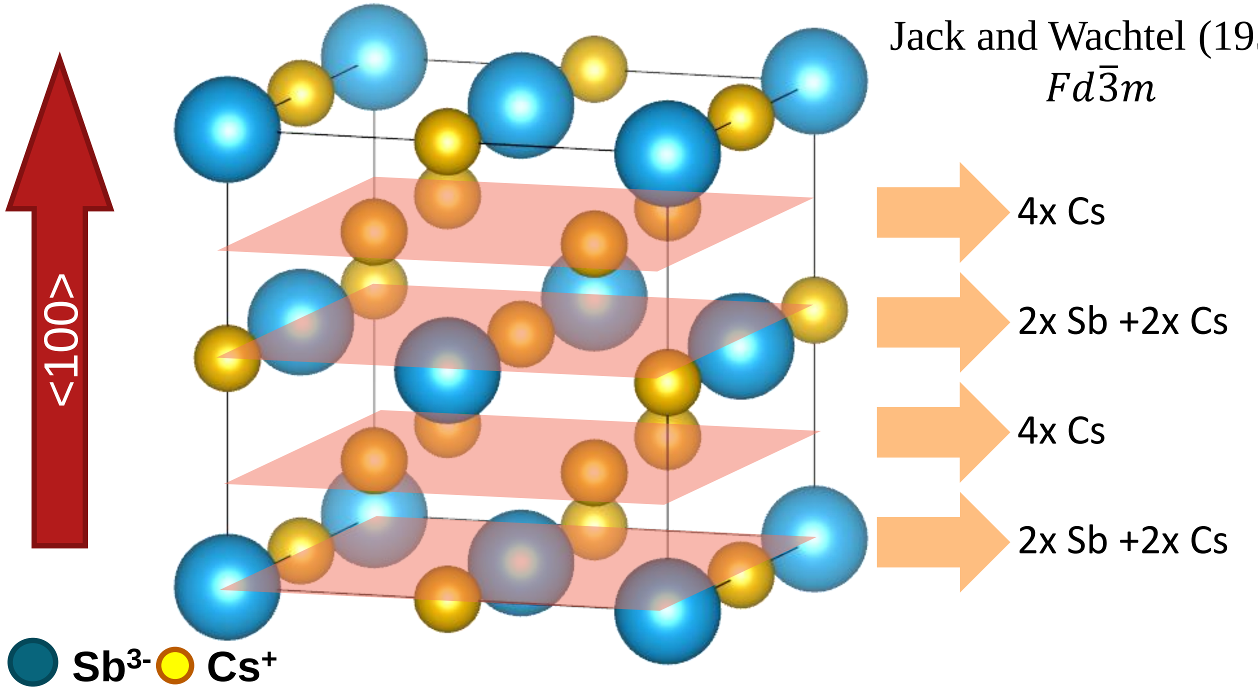
1 X Cs_3Sb (a=0.9165 nm)



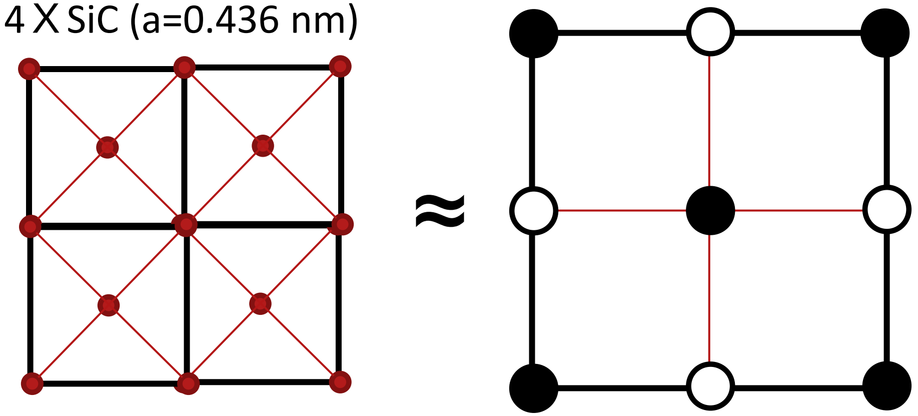


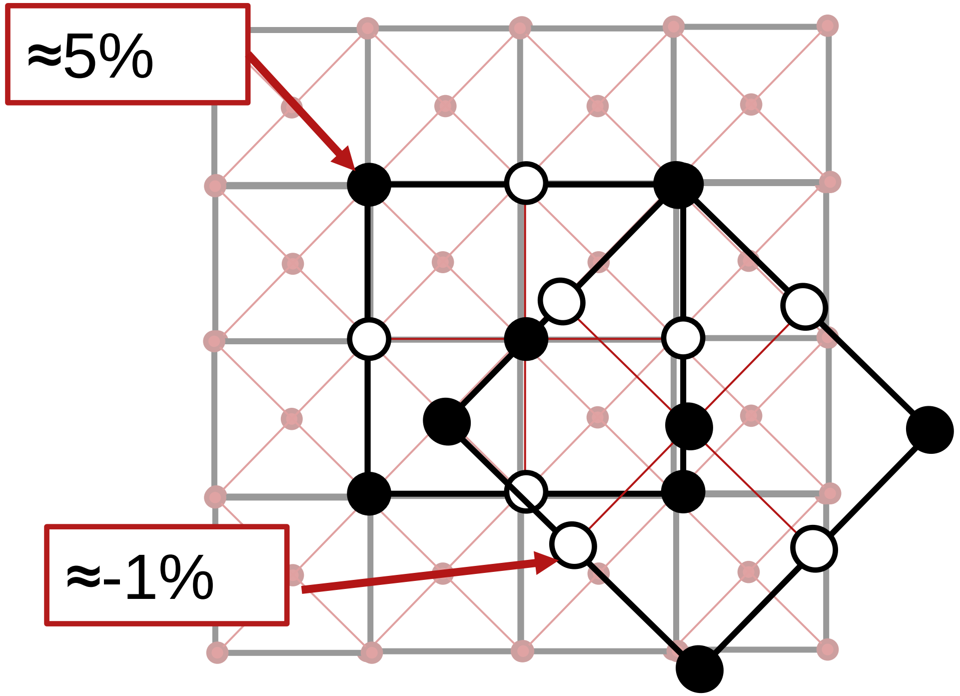
Growing with structure in mind

Jack and Wachtel (1957)
$Fd\bar{3}m$

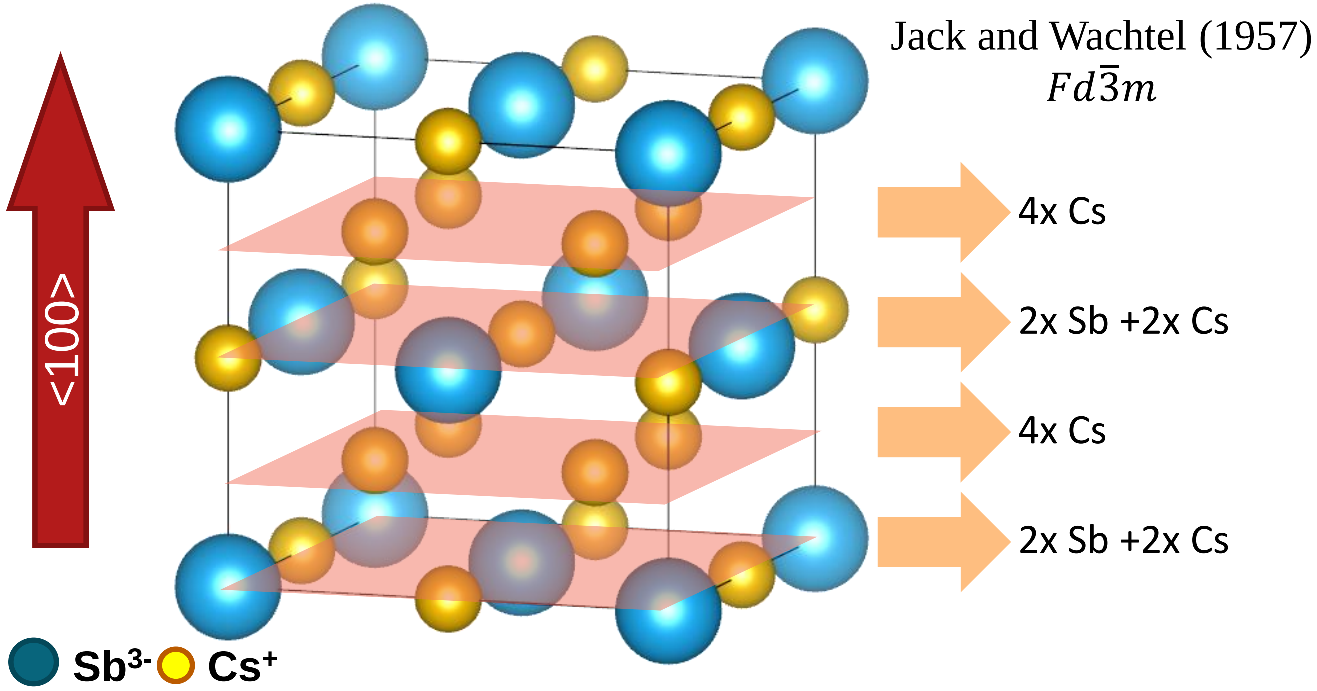


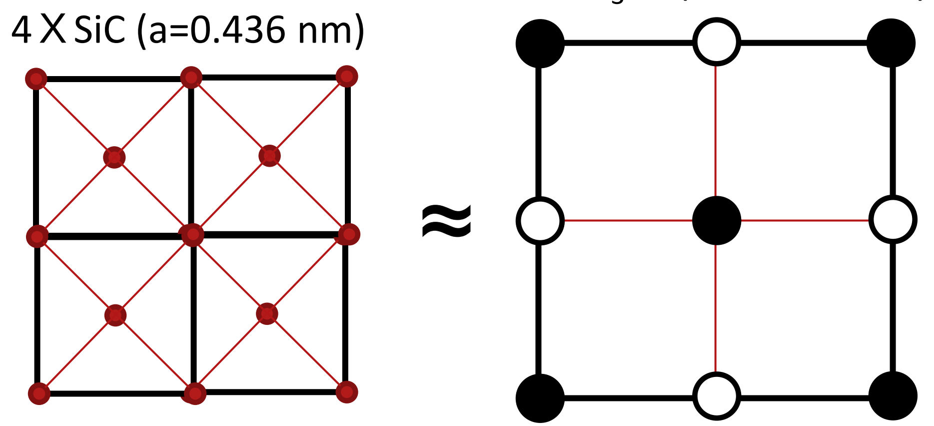
4 X SiC (a=0.436 nm) ≈ 1 X Cs_3Sb (a=0.9165 nm)





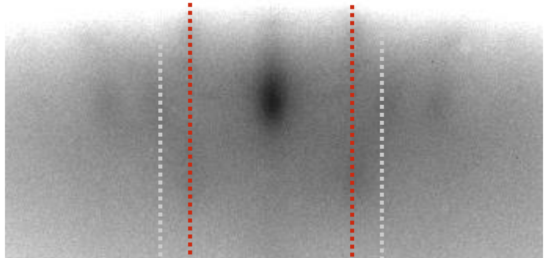
Growing with structure in mind





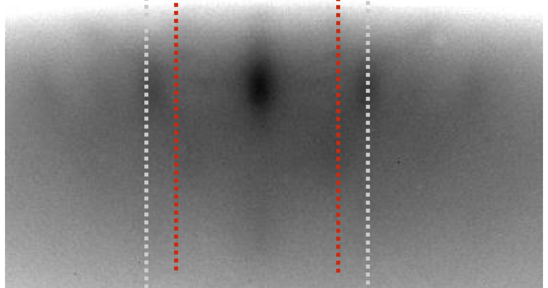
T=40°C
40 ML of Sb deposited
QE=6-7% @532nm
Low Crystallinity

Deposit ½ ML of antimony on SiC in shuttered intervals
Cs provided continuously



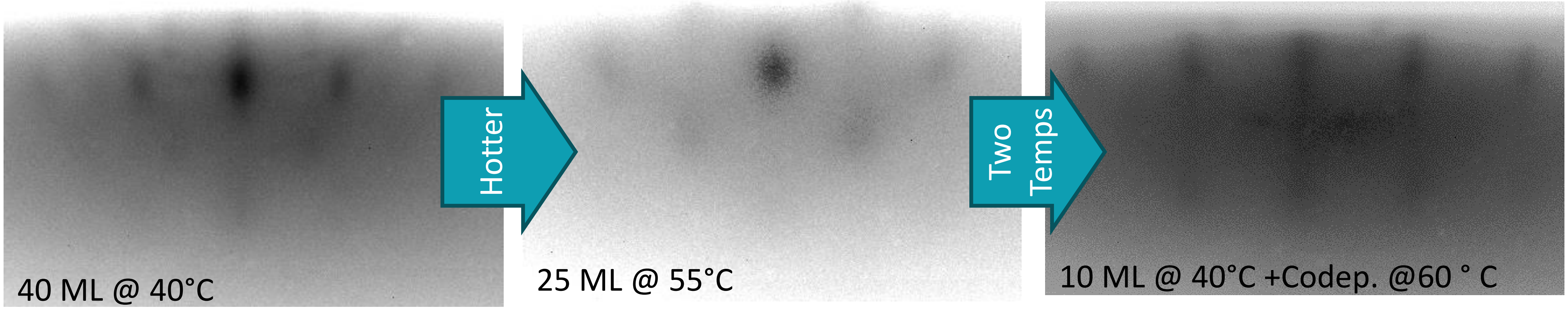
Img 07: Θ=109.5° //$(100)_{SiC}$

An oriented structure emerges:
$(001)_{Cs3Sb}//(001)_{SiC}$
But, some in-plane disorder

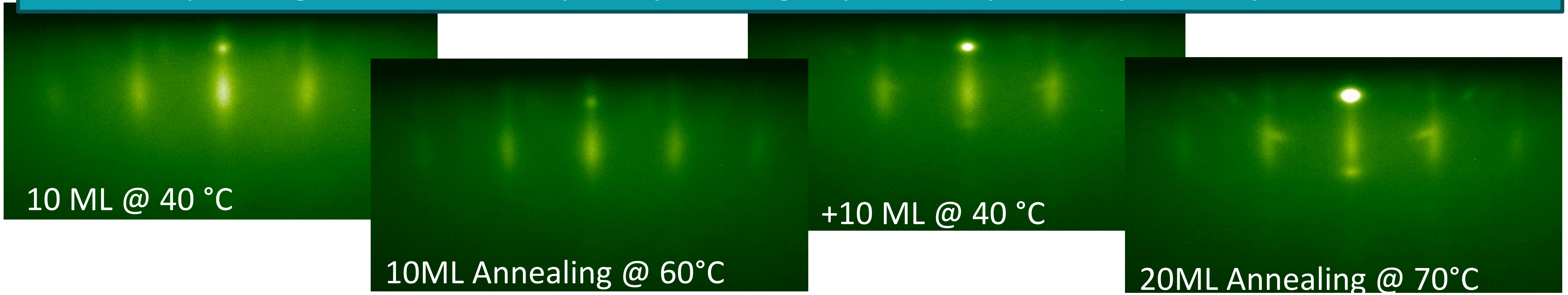


Img 08: Θ=154.5° //$(110)_{SiC}$

Temperature study

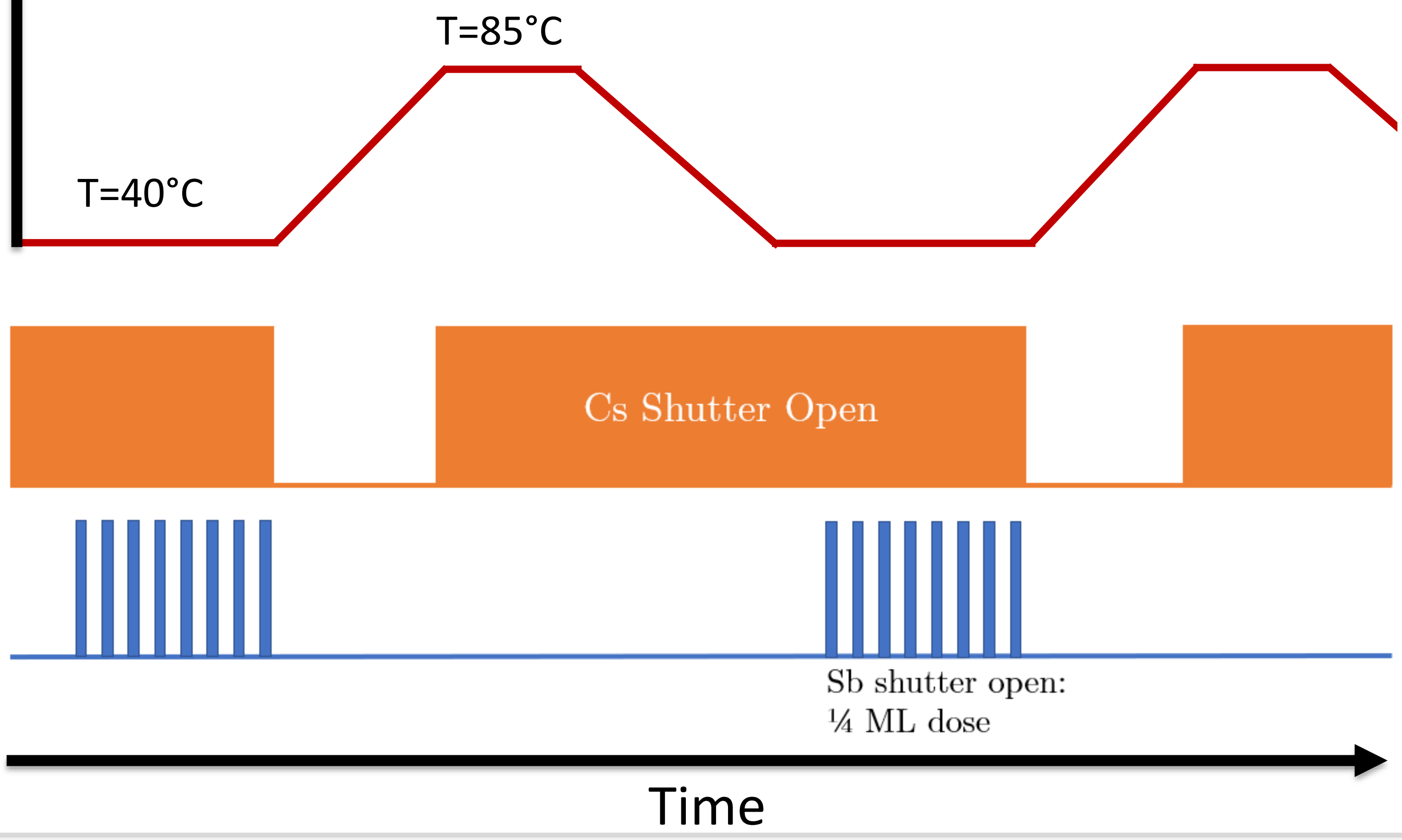


Depositing at higher temperature does not help
Depositing cold and subsequently heating improves crystallinity and in-plane order.



Solid Phase (Molecular Beam) Epitaxy

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

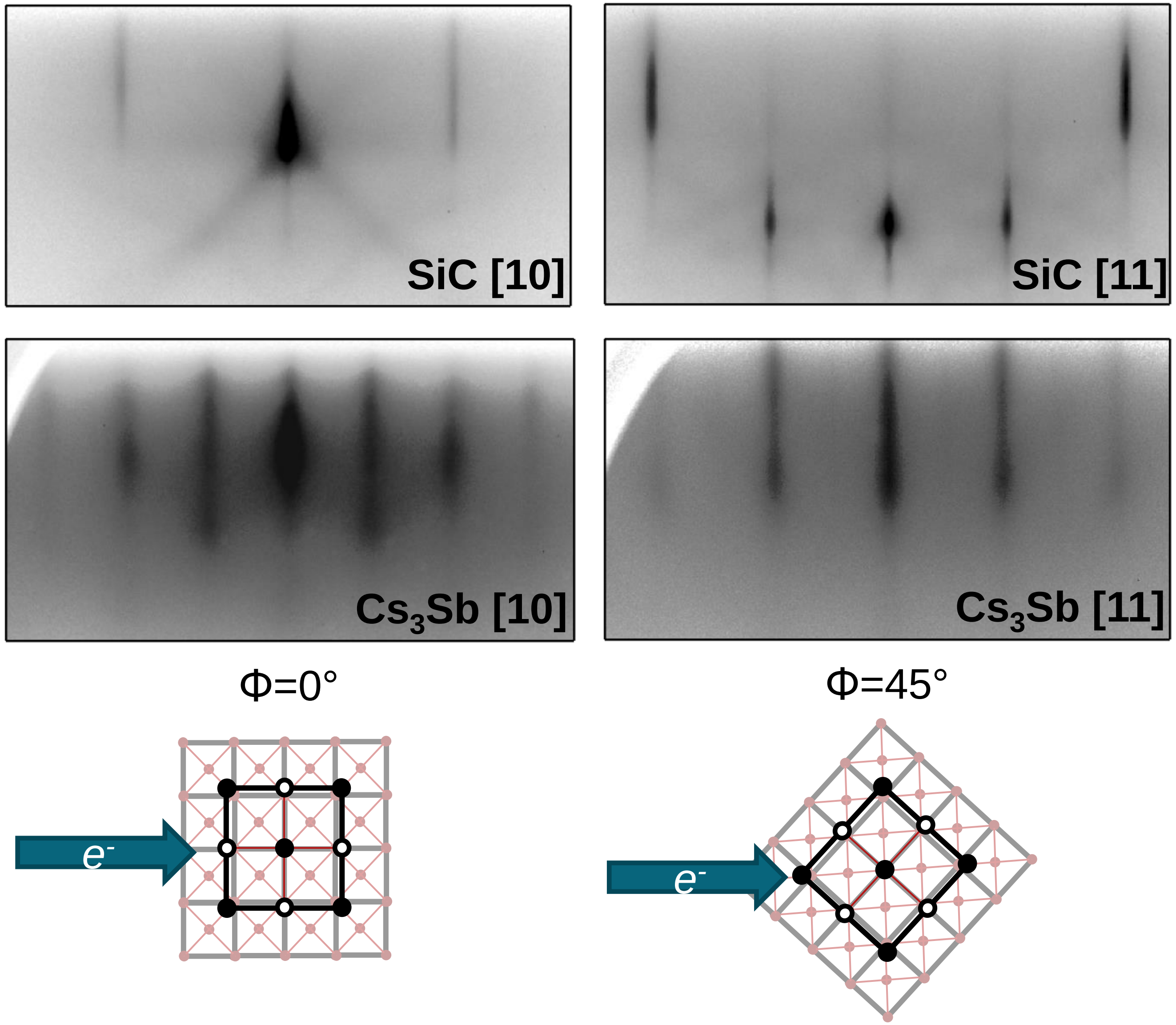


This trick is well known in both semiconductor and oxide thin film growth, for example:

- Ge doping of Silicon films (reduced interdiffusion)
- Low Temp GaAs (reduced Arsenic precipitation)
- $BaTiO_3$ / $SrTiO_3$ on Silicon (oxides on oxygen sensitive substrates)

M. Twigg et al. APL **63** (1993)
C. Hwang et al. JAP **77** (1995)
F. Niu, B. Wessels, JVST B, **25** (2007)
Meier et al. J. Crystal Growth **294** (2006)

It is epitaxial



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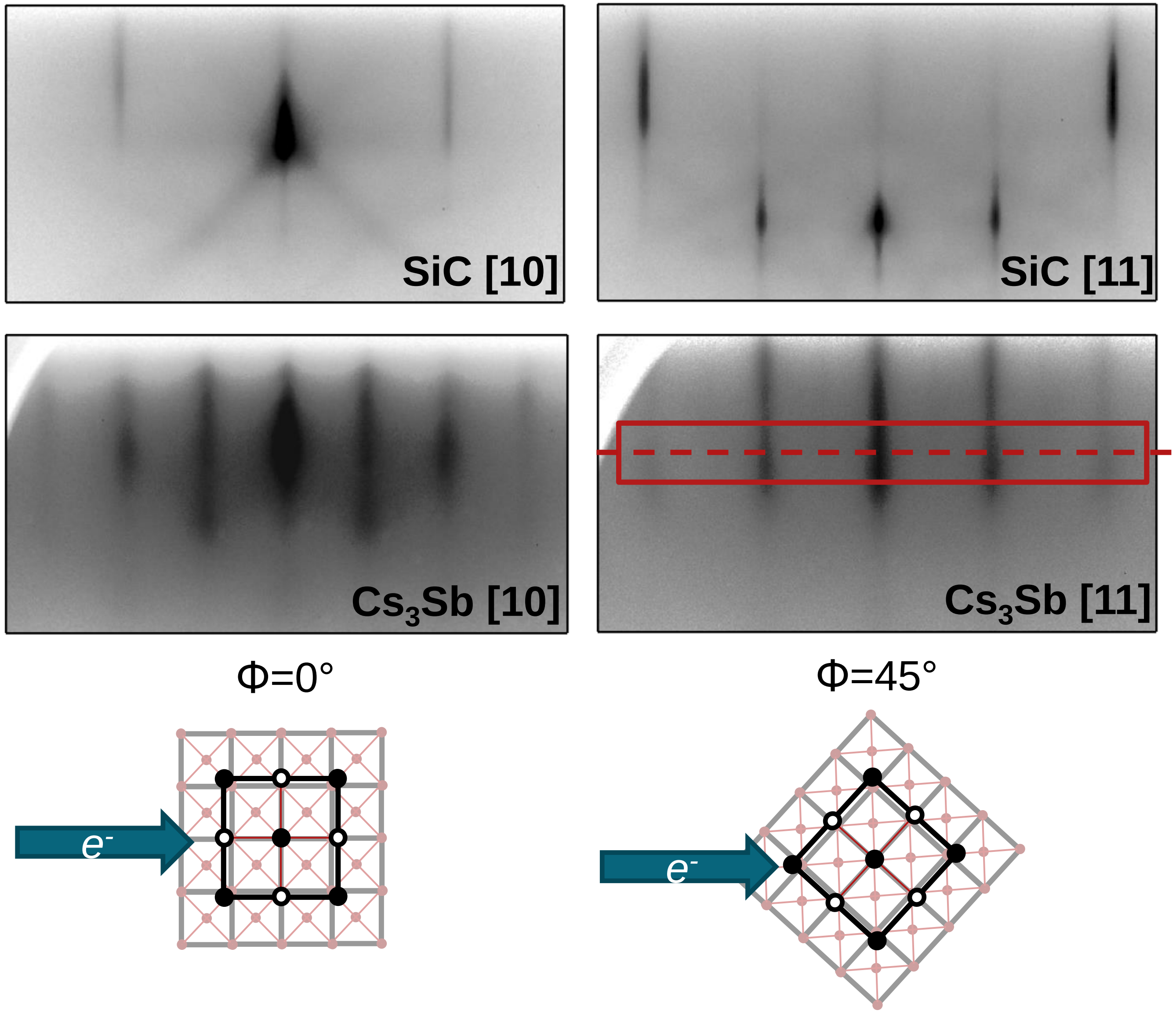

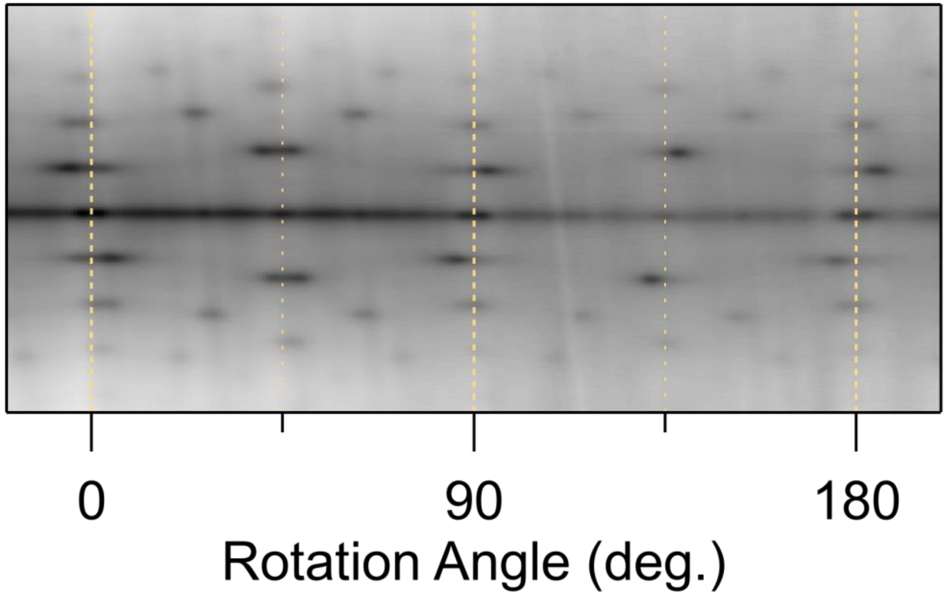

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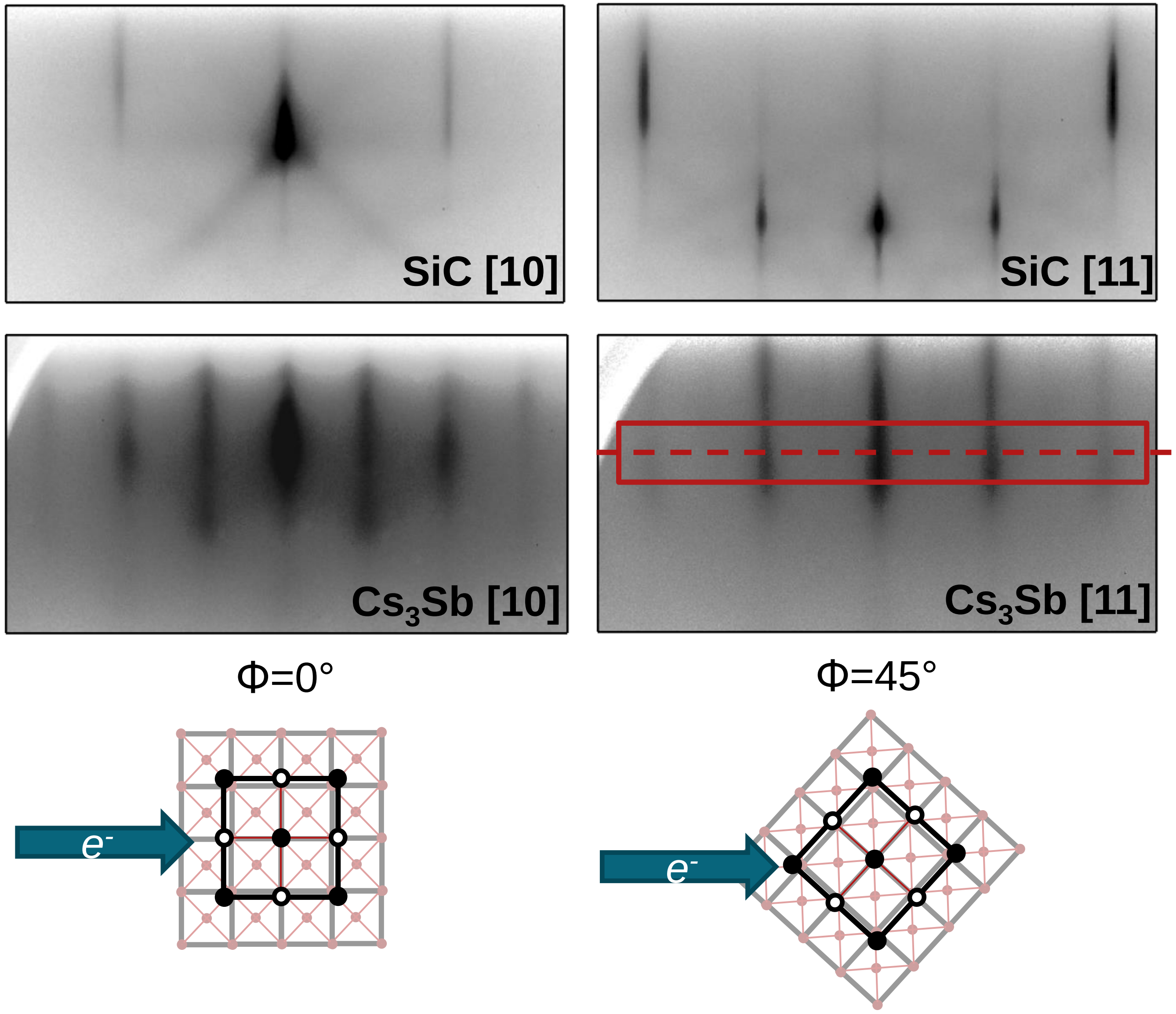
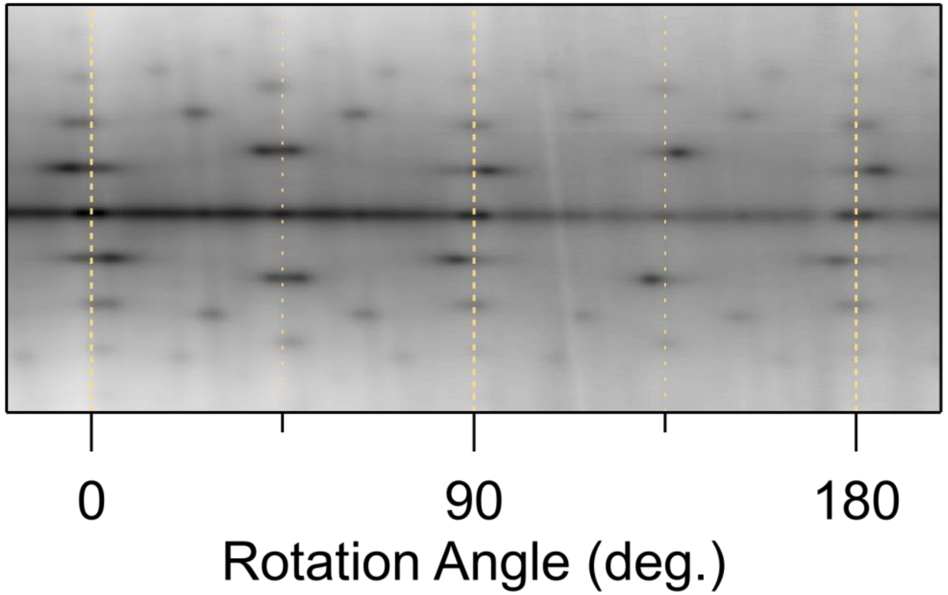
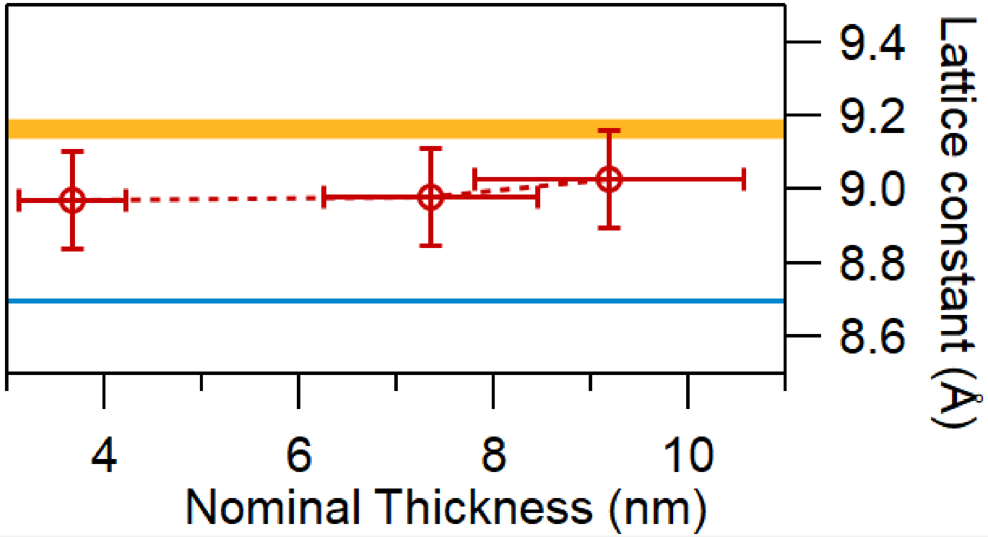
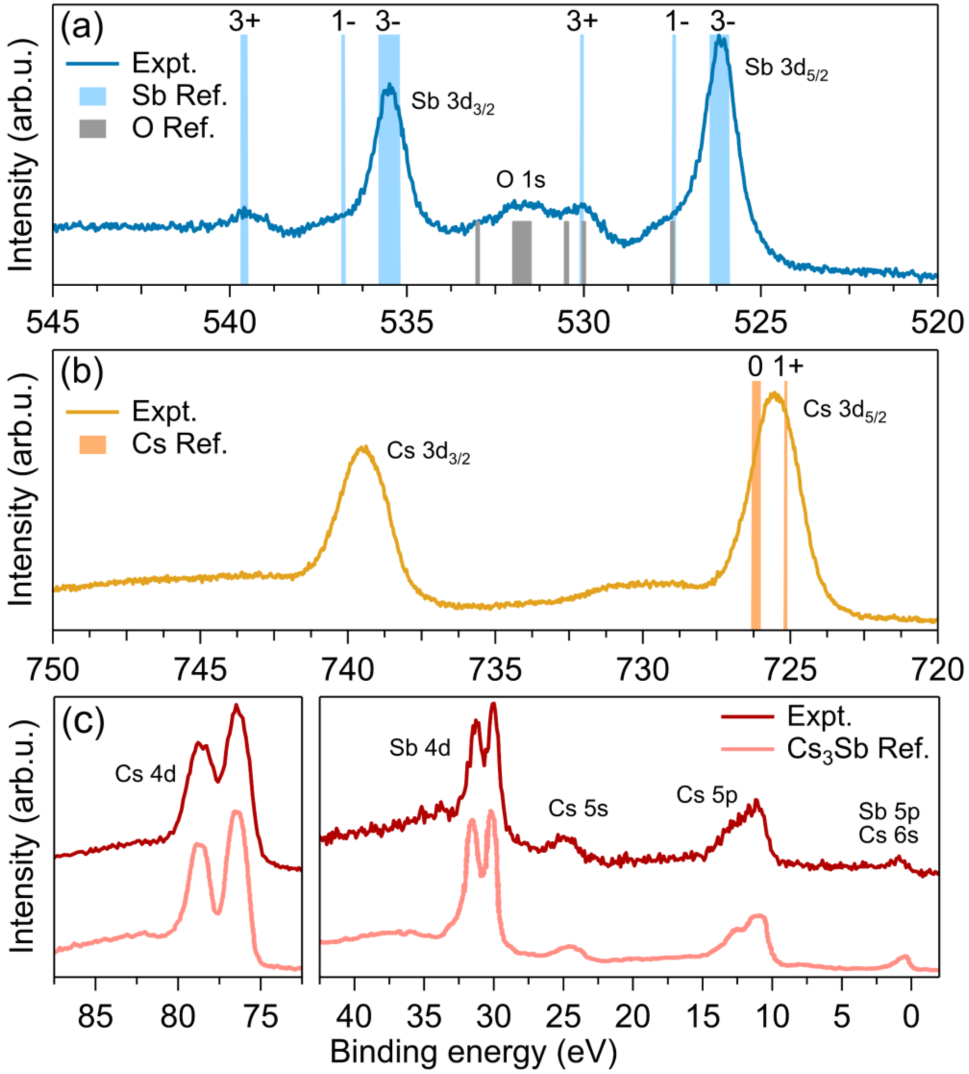






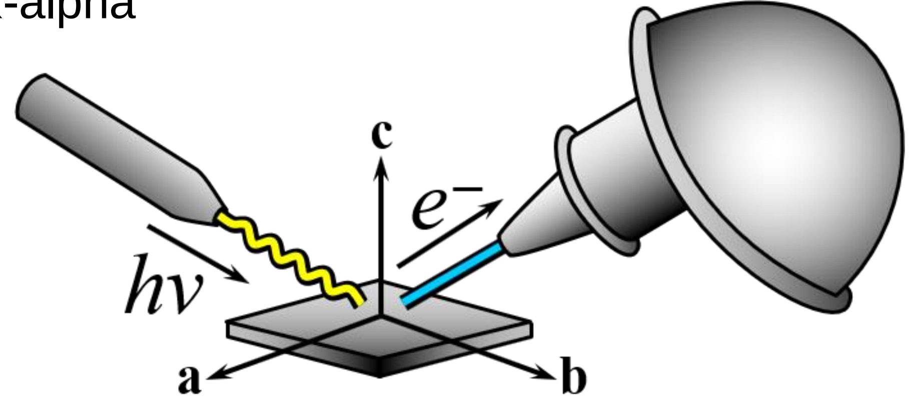
It really is Cs_3Sb



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

In-situ XPS analysis

Mg K-alpha



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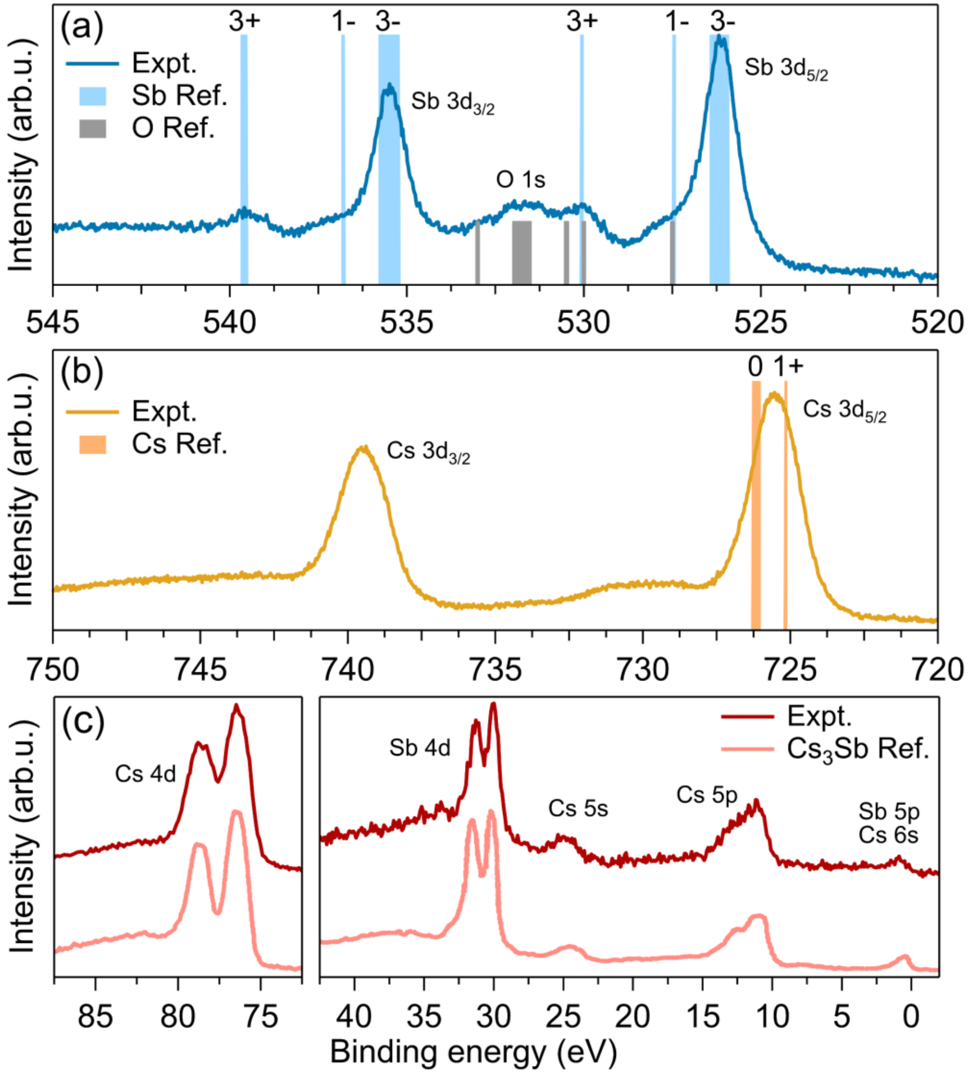

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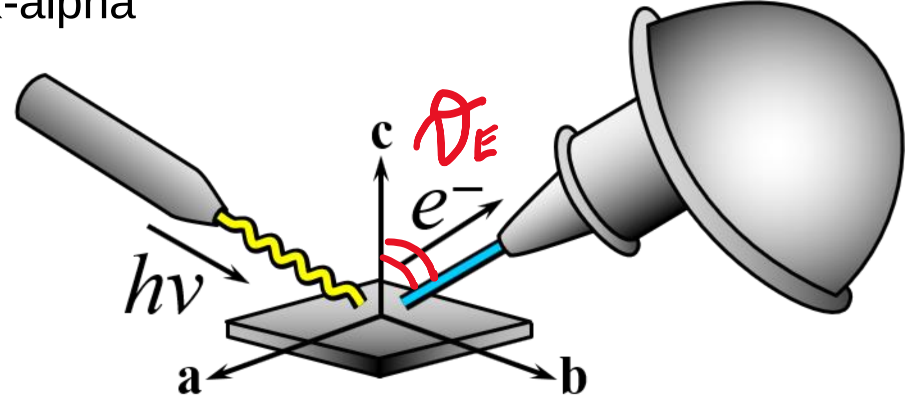
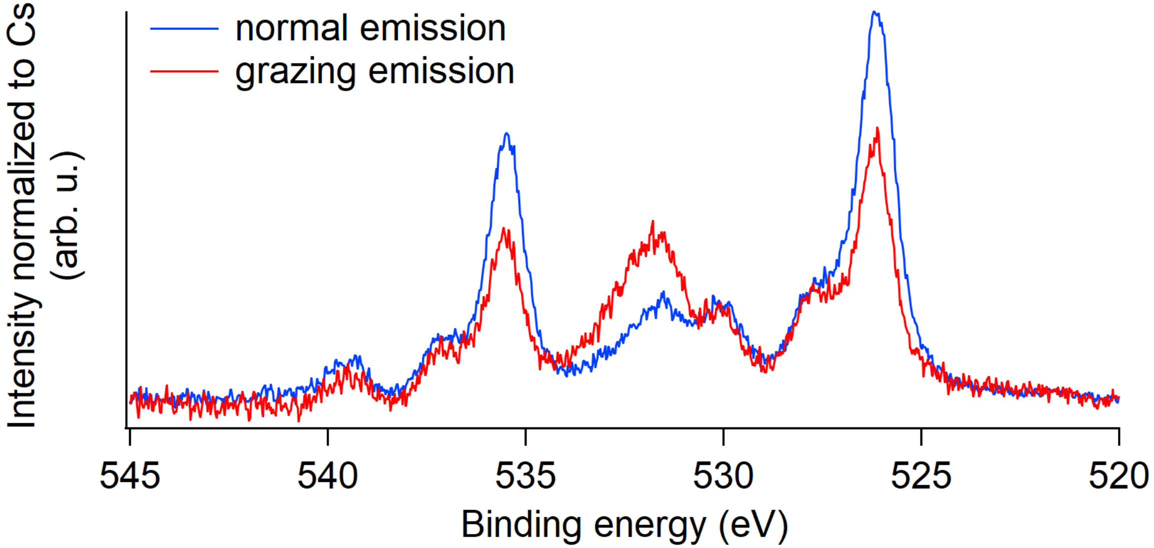
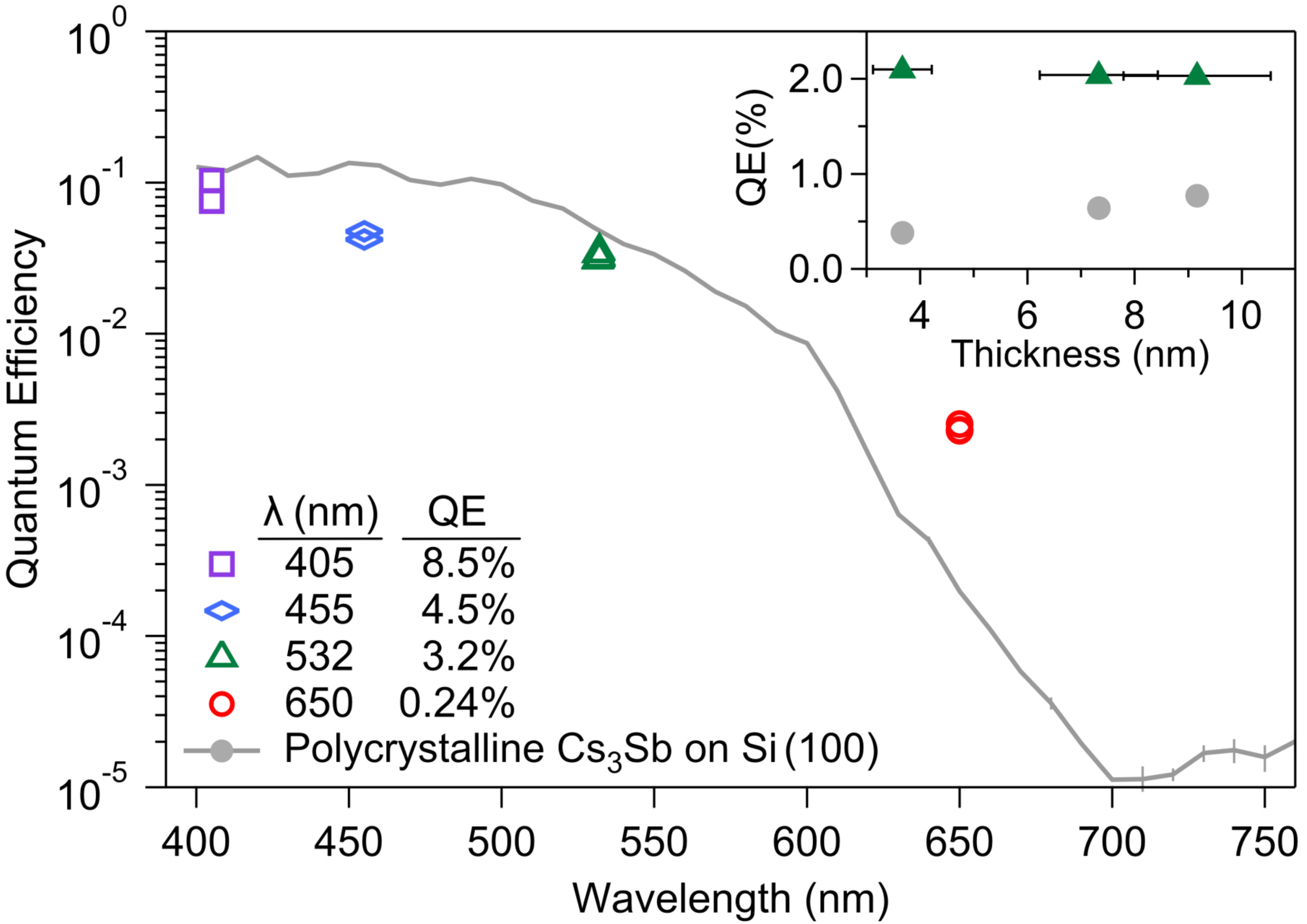


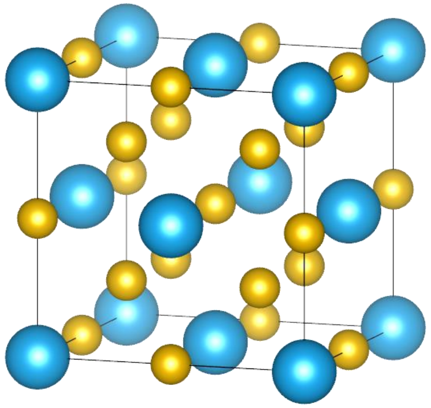


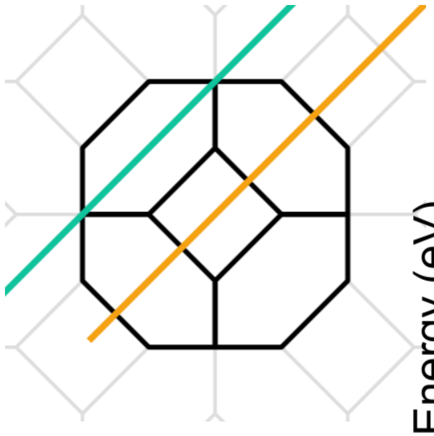
It has enhanced efficiency at 650 nm and small thickness

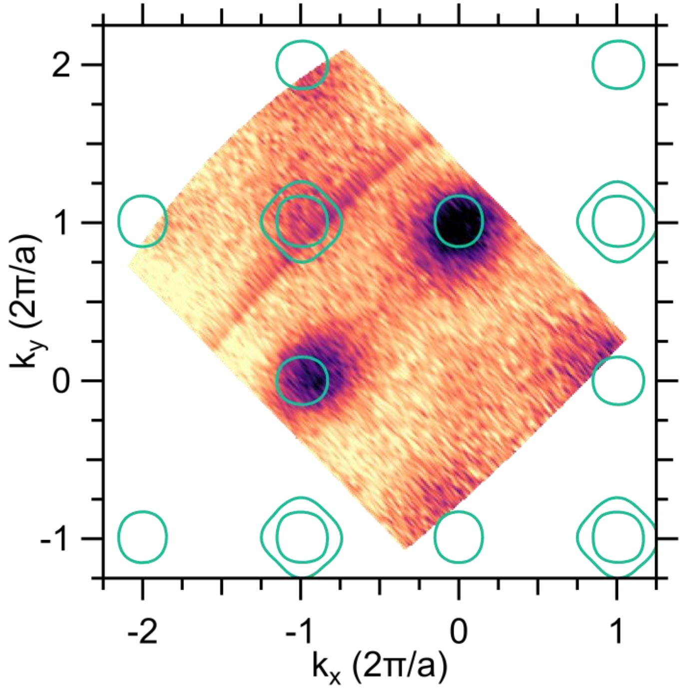


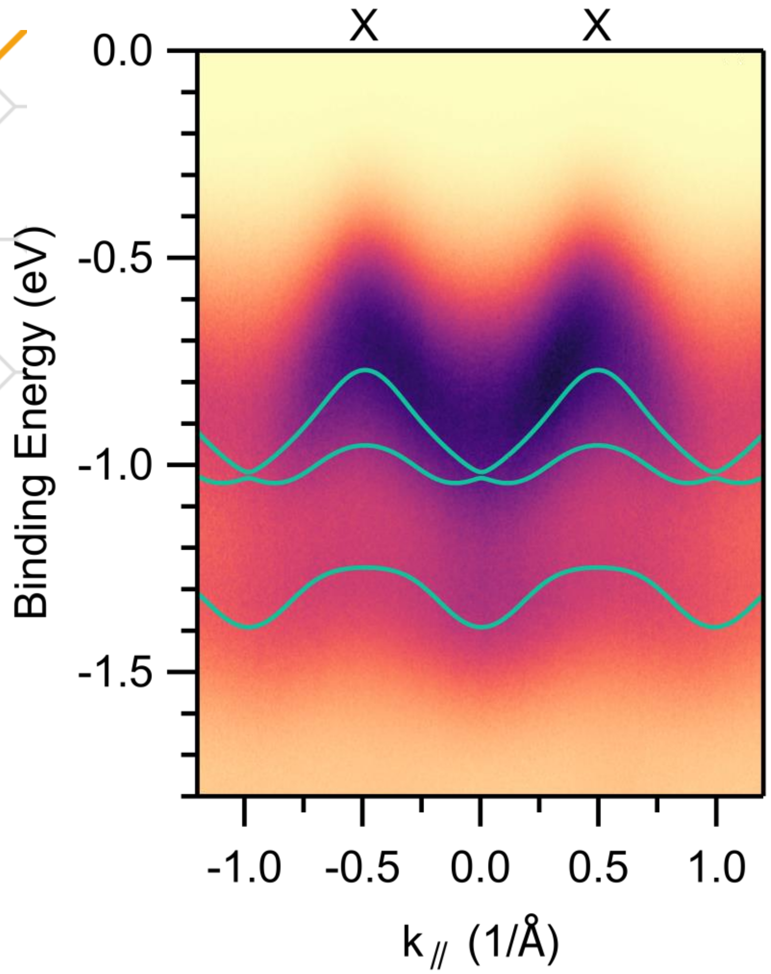
Grey line and dots represent the data from a codeposited Cs_3Sb sample grown by photocurrent-monitored codeposition in Newman laboratory. The thickness is estimated by the nominal deposited Sb thickness.

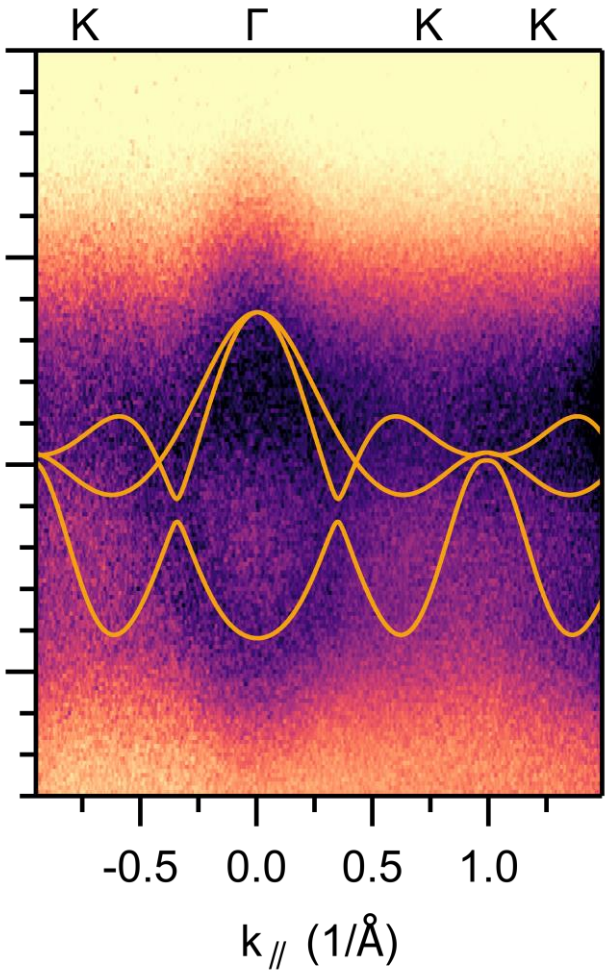
First measured ARPES on Cs_3Sb











Comparison with DFT calculations of Cs_3Sb band structure in the $Fm\bar{3}m$ symmetry.
Data show enhanced bandwidth (strain+intrinsic distortions?)

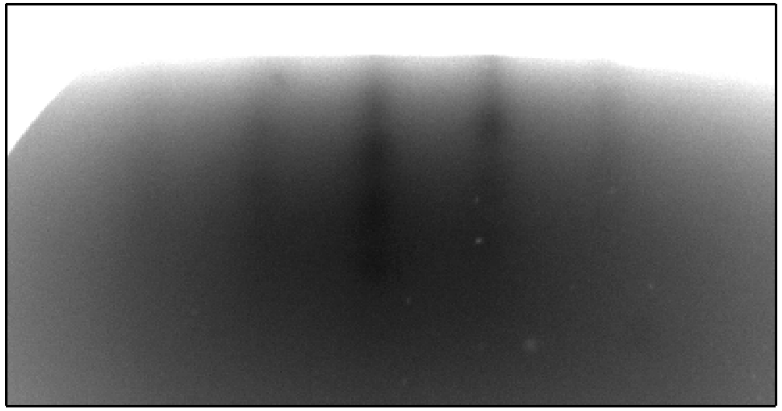
Conclusions

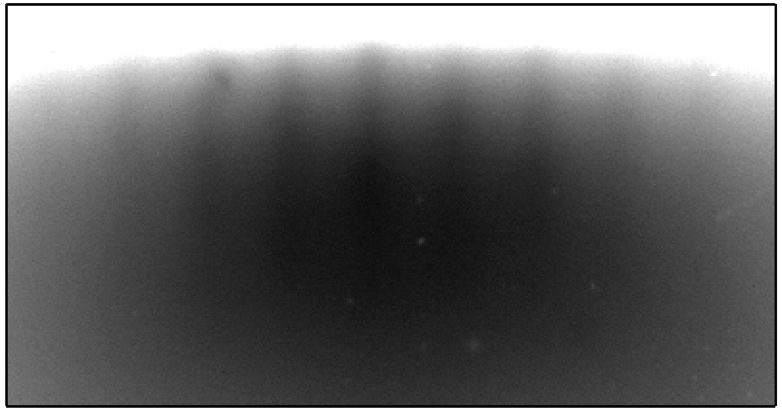
- We successfully deposited epitaxial Cs_3Sb (100) films on 3C-SiC (100) substrates
- XPS measurements well reproduce literature data on Cs_3Sb (including ours)
- Ultrathin samples (<10 nm) have >2% QE at 532 nm
- We observe enhnaced QE at 650 nm on our best epitaxial sample
- ARPES measurements unveil for the first time the Cs_3Sb band structure
- DFT band strucure calculations show good agreement with measurements, but significant bandwidth discrepancy indicates that strain and intrinsic instabilities of the Cs_3Sb structure may play a role

Future work

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

First epitaxial Cs_3Sb sample grown in **PHOEBE**-MBE



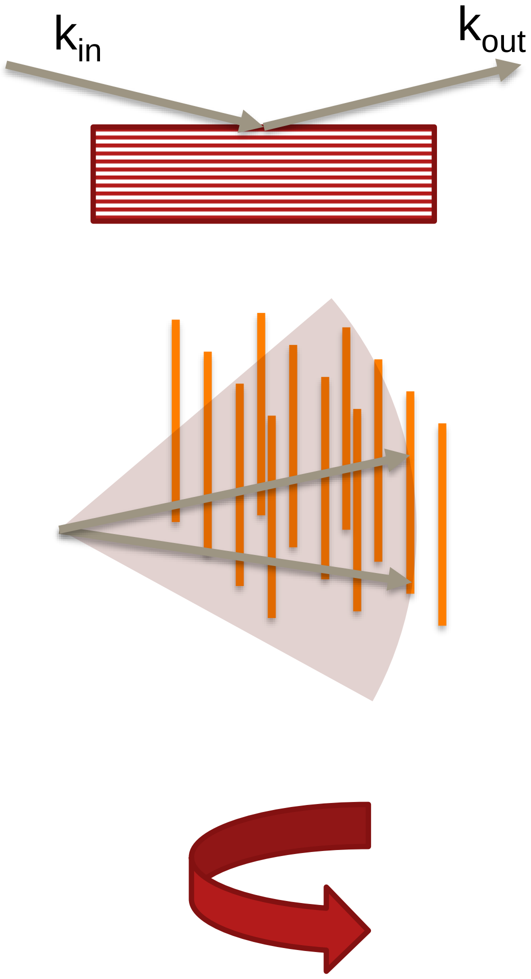


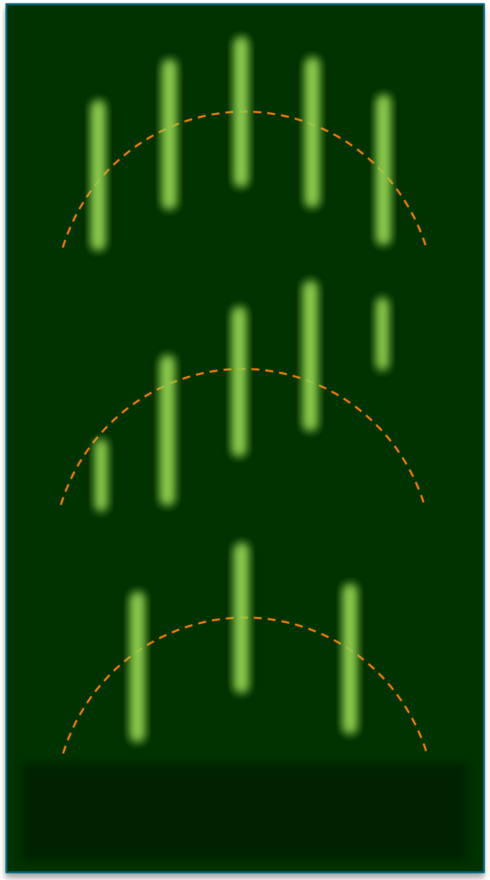
- MTE measurements on epitaxial Cs_3Sb samples
- Epitaxial growth of other alkali antimonide compounds
- Study of strain effects on different substrates
- Photocathode heterostructures

Backup slides

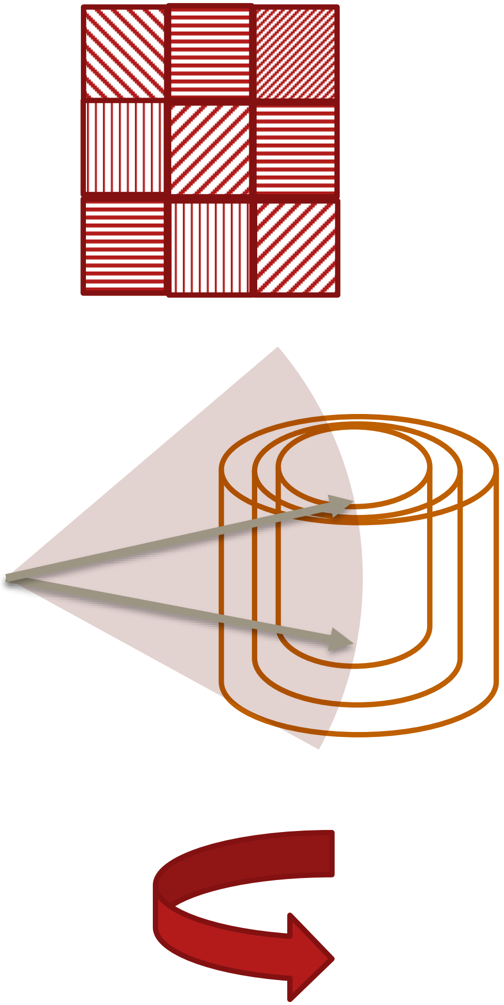
Information provided by RHEED

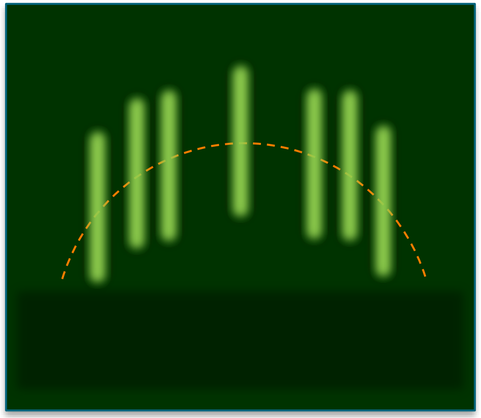
Single crystal





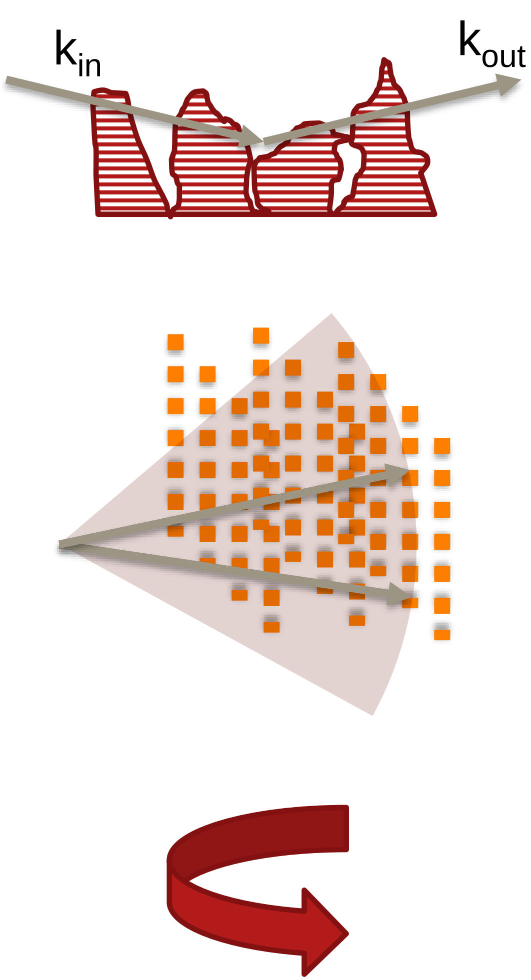
Fiber texture

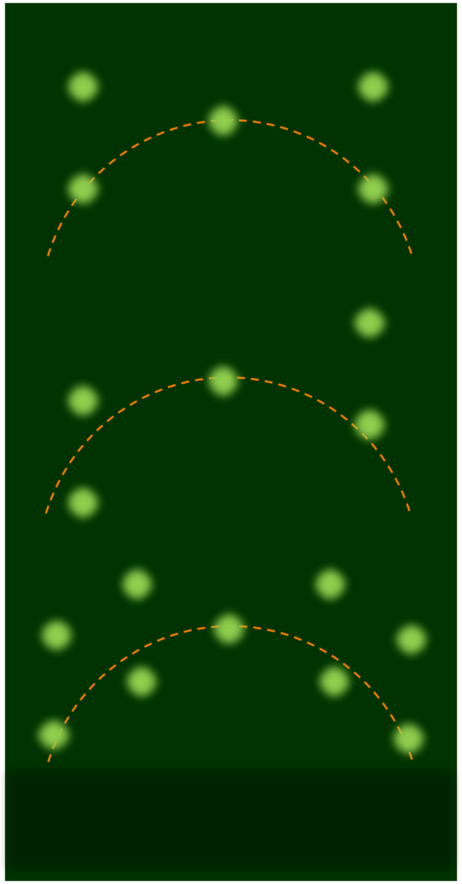




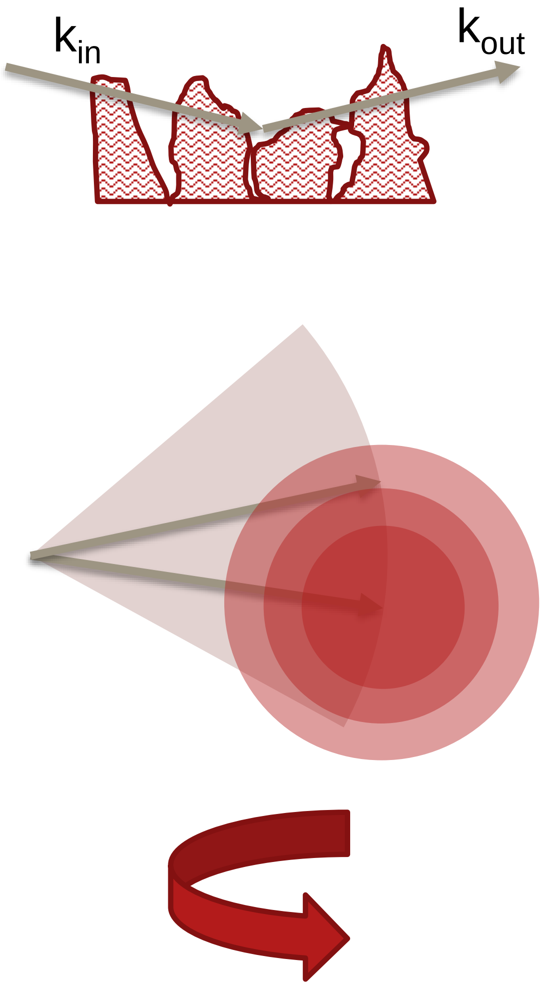
Information provided by RHEED

Single crystal islands





Polycrystalline islands



No texture

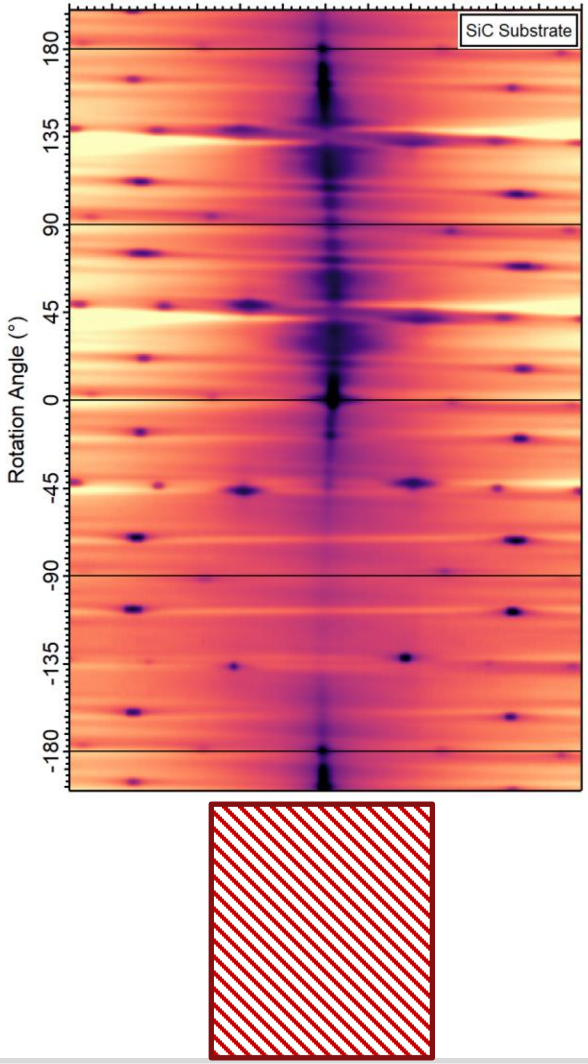
Textured film

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

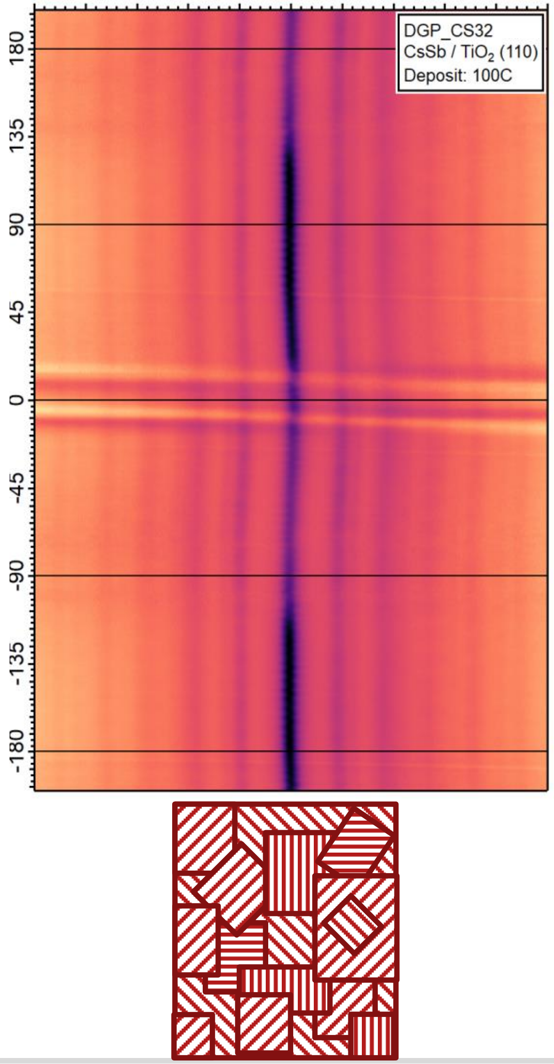
Rotation dependence if the texture axis is in-plane (biaxial)

Epitaxial Relationship

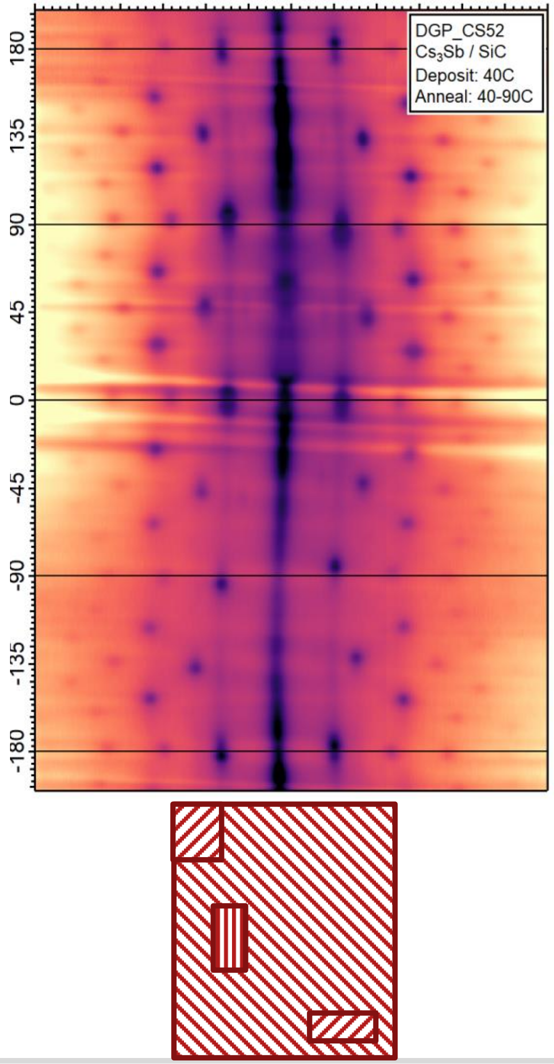
Substrate
Fully Ordered



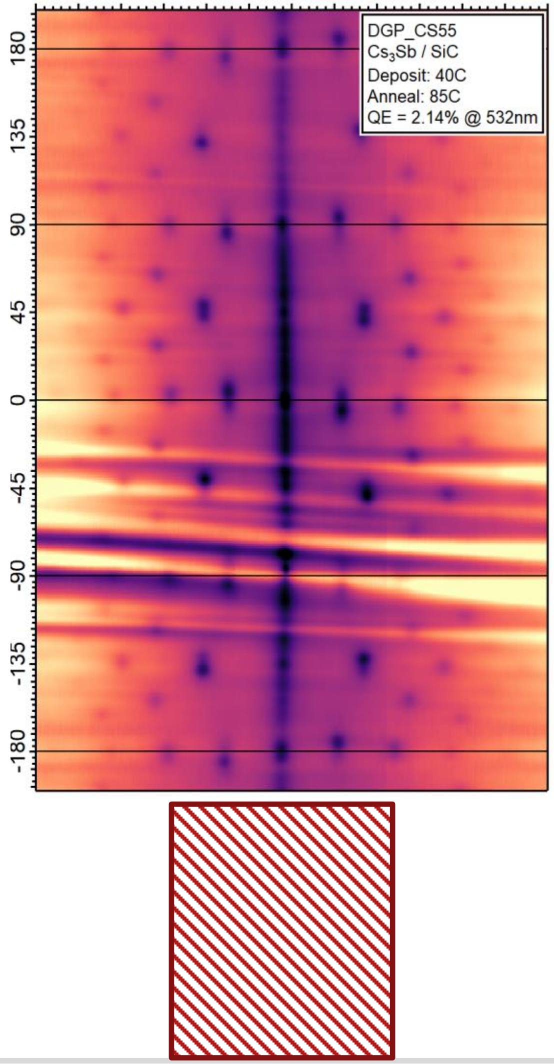
Fiber Textured Film
Only c-axis oriented



Partially Ordered Film

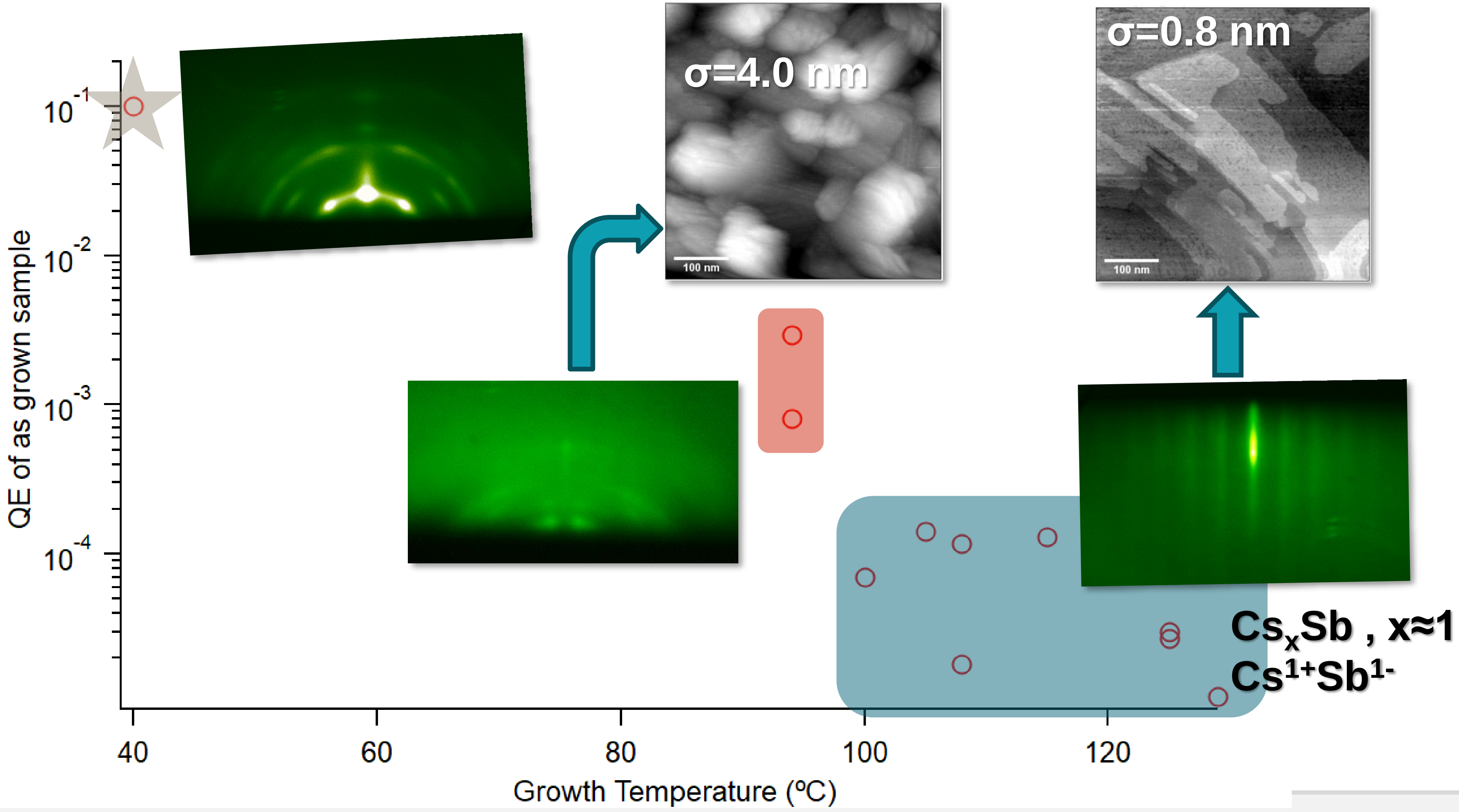


Epitaxial Film



Previous results: codeposited samples

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



Higher Growth Temperature

Improved Crystallinity
OOP Film Orientation
Reduced Surface Roughness
Reduced Quantum Efficiency

Lower Growth Temperature

Improved Quantum Efficiency
Polycrystalline Films