Stony Brook University

BROOKHAVEN NATIONAL LABORATORY

Alkali Antimonide Photocathode Engineering

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Overview

A little bit about accelerators
Brief intro to 3-step model as it applies to semiconductors
Where do we need to be? What is limiting us now?
In situ materials analysis during cathode formation
How to grow smoother cathodes (and why you might want to)
Toward single crystals and heterojunctions

Reference Material

Some of this talk comes from a course on Cathode Physics Matt Poelker and I taught at the US Particle Accelerator School

http://uspas.fnal.gov/materials/12UTA/UTA-Cathode.shtml

https://science.energy.gov/~/media/bes/pdf/reports/2017/Future_Electron_Source_Worskhop_Report.pdf

Modern Theory and Applications of Photocathodes
W.E. Spicer & A. Herrera-Gómez
SAC-PUB-6306 (1993)

Great Surface Science Resource:
http://www.philiphofmann.net/surflec3/index.html

Does the particle source matter?... Sometimes

- The electron beam properties determine the photon beam properties
  - Pulse duration, degree of coherence, flux
- In all light sources through 3rd generation, the phase space is determined by the ring

- In X-ray free electron lasers (LCLS II, XFEL, MaRIE), this will change – the electron source will determine the beam properties
- The highest brightness sources available are photoinjectors, which use a laser on a photocathode to control the spatial and temporal profile of the emitted electron beam

Applications at the State of the Art

Electron cooling of ion machines

Requires high current with long operational life, other requirements are modest (~50 mA with 5µm emittance)

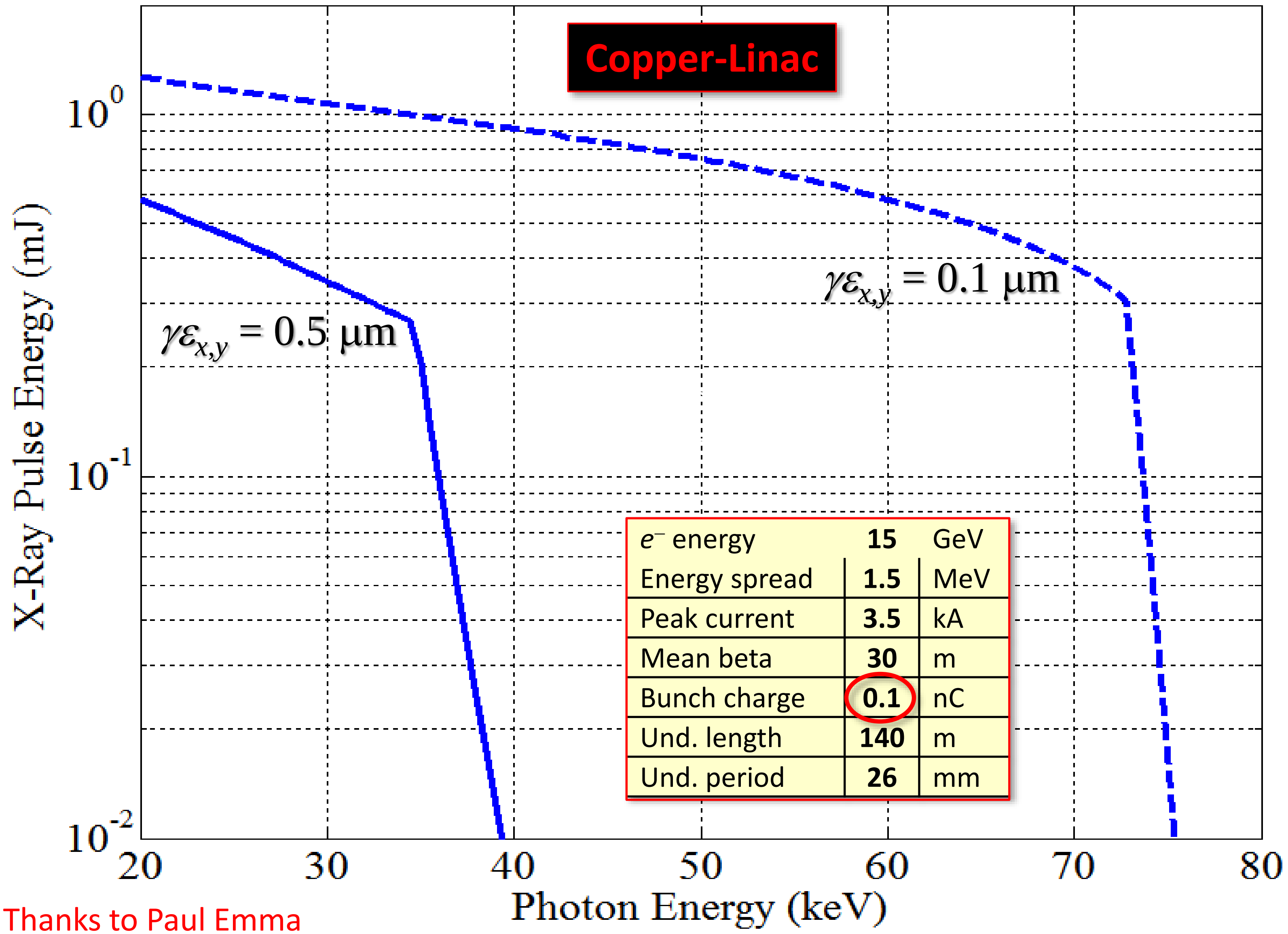
FEL sources

Going to moderate currents (still under 1 mA); emittance improvement is a big deal (ideally 0.1 µm)

Ultrafast Electron Diffraction/Microscopy

High brightness! Ideally a factor of 100 from current photoinjectors. Very low current. Short pulse duration (100 fs at sample, less for some applications)

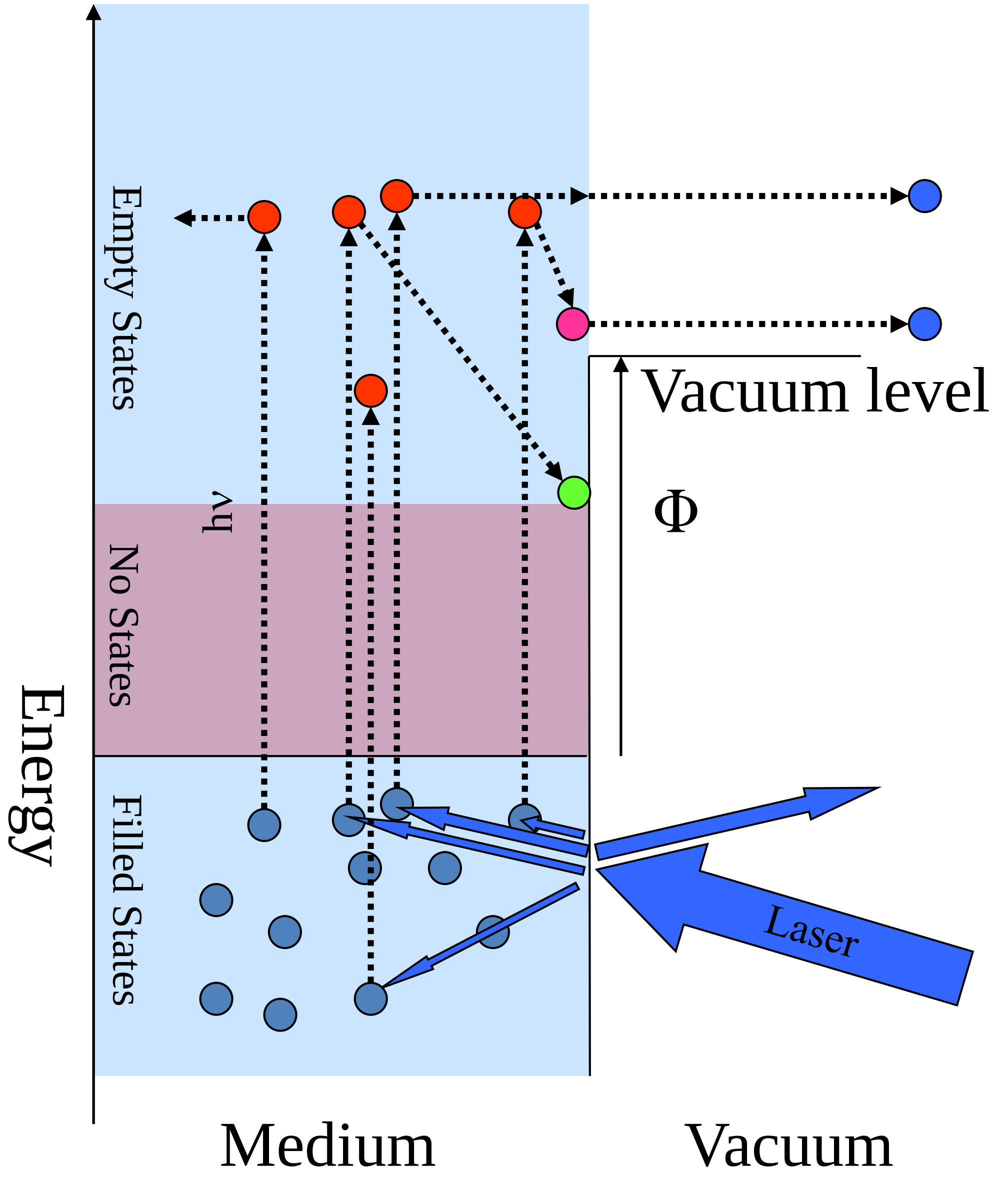
Emittance Leverage at LCLS-II/HXR (15 GeV, 120 Hz)



e^- energy	**15**	GeV
Energy spread	**1.5**	MeV
Peak current	**3.5**	kA
Mean beta	**30**	m
Bunch charge	**0.1**	nC
Und. length	**140**	m
Und. period	**26**	mm

Thanks to Paul Emma

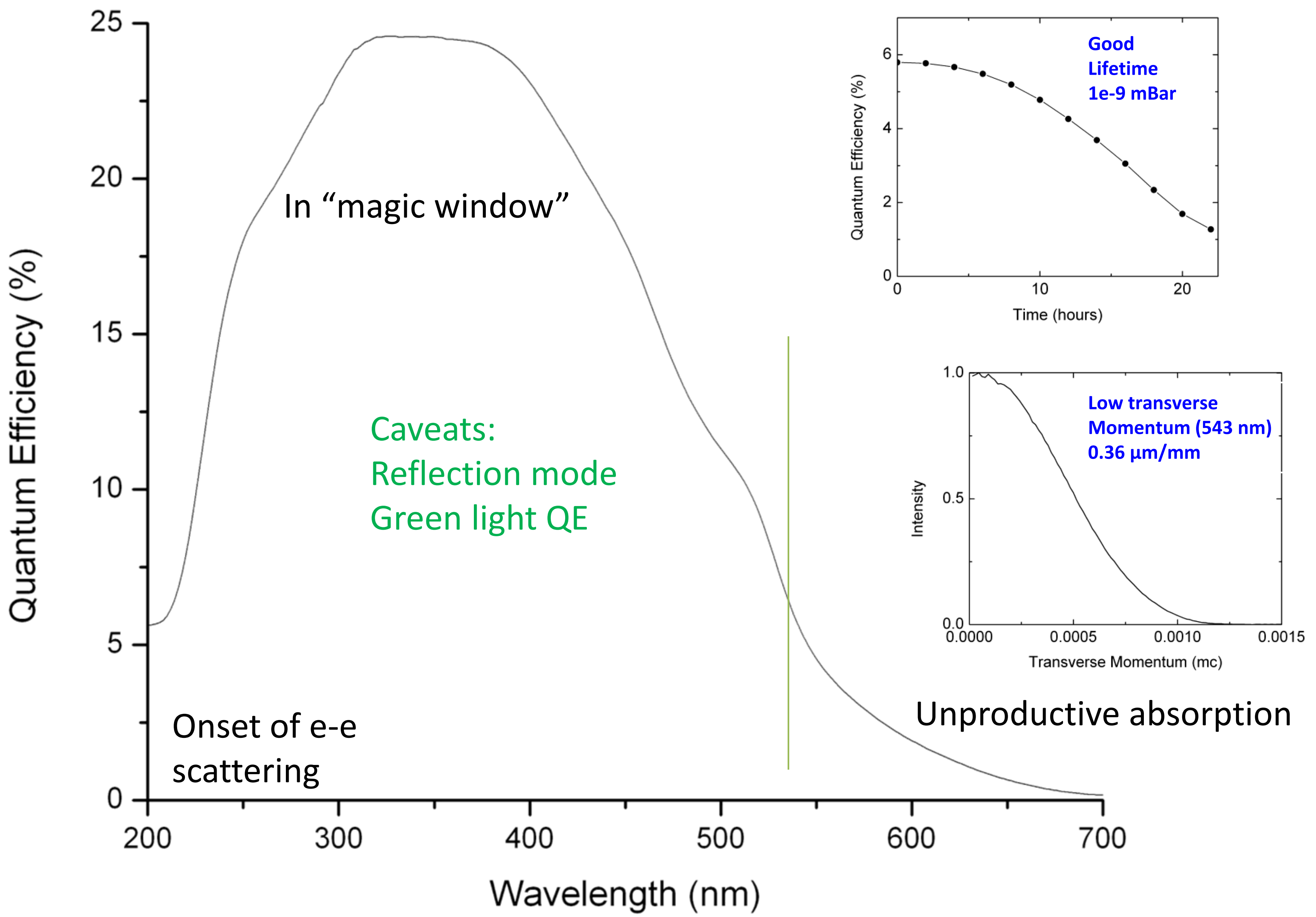
Three Step Model of Photoemission - Semiconductors



1) Excitation of e^-
   - Reflection, Transmission
   - Energy distribution of excited e^-
2) Transit to the Surface
   - e^--phonon scattering
   - e^--defect scattering
   - e^--e^- scattering
   - Random Walk
3) Escape surface
   - Overcome Workfunction
   - Multiple tries

Need to account for Random Walk in cathode suggests Monte Carlo modeling

K_2CsSb: A Good Candidate



In “magic window”

Caveats:
Reflection mode
Green light QE

Onset of e-e scattering

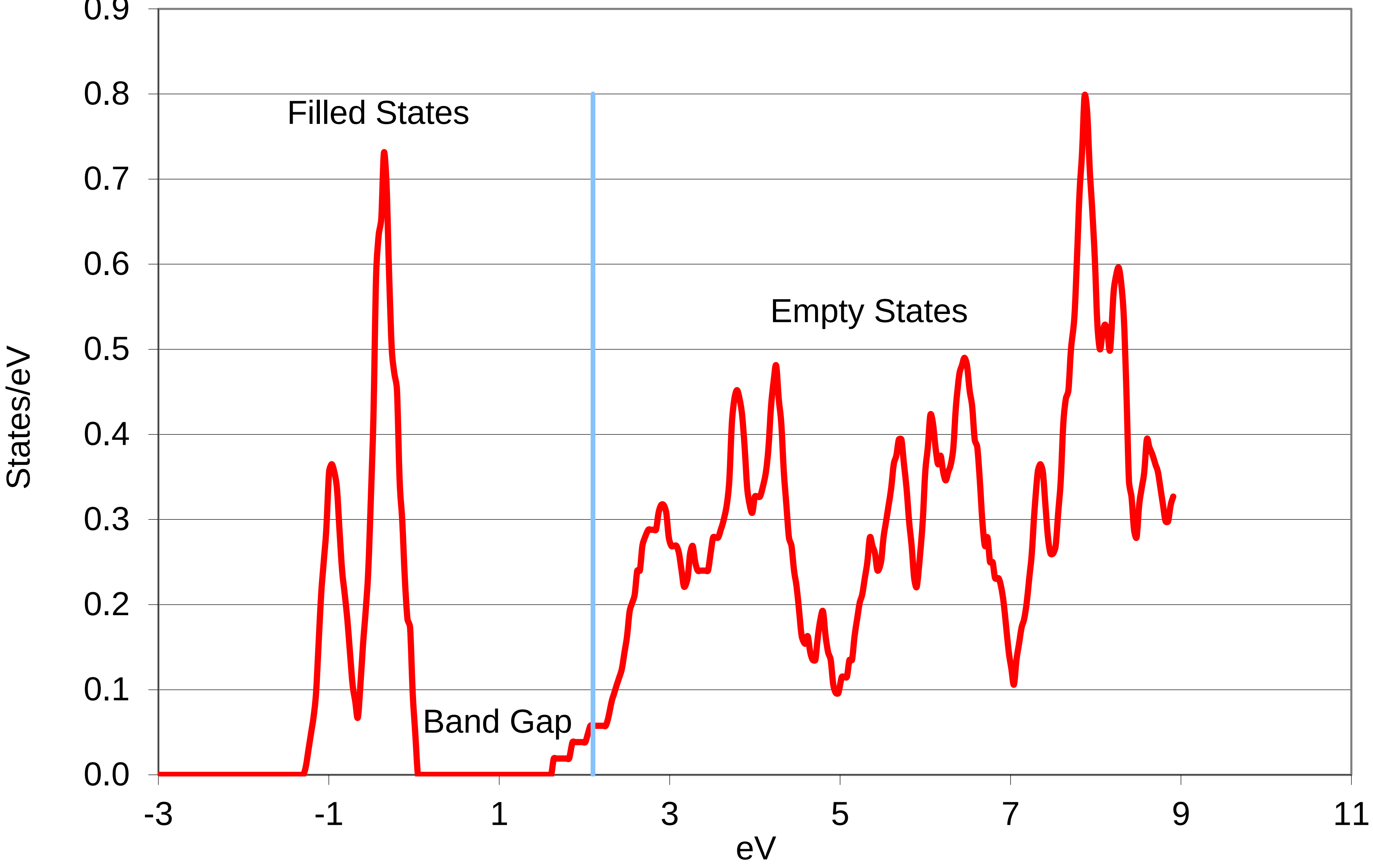
Unproductive absorption

Good Lifetime 1e-9 mBar

Low transverse Momentum (543 nm) 0.36 μm/mm

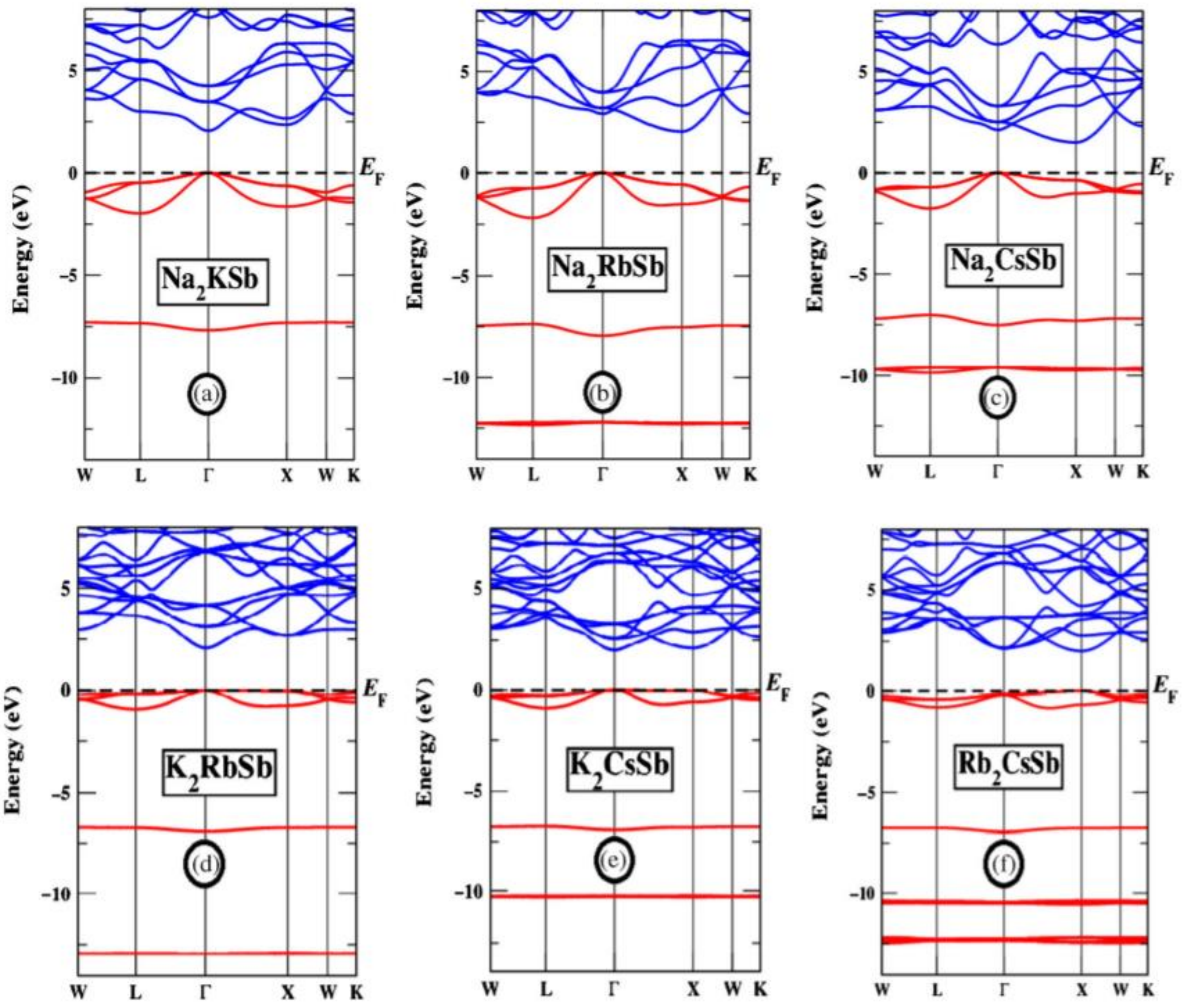
T. Vecchione et al., *Appl. Phys. Lett.* **99**, 034103 (2011)

K_2CsSb DOS



A.R.H.F. Ettema and R.A. de Groot, Phys. Rev. B **66**, 115102 (2002)

Alkali Antimonide Family



Bull. Mater. Sci. Indian Academy of Sciences. DOI 10.1007/s12034-016-1300-1

Parameters, and how to affect them

Increasing the electron MFP will improve the QE. Phonon scattering cannot be removed, but a more perfect crystal can reduce defect and impurity scattering:

$$\frac{1}{\lambda_{MFP}} = \frac{1}{\lambda_{el-el}} + \frac{1}{\lambda_{ap}} + \frac{1}{\lambda_{op,ems}} + \frac{1}{\lambda_{op,abs}} + \frac{1}{\lambda_{impurity}} + \frac{1}{\lambda_{defect}} + \frac{1}{\lambda_{boundary}}$$

Control of surface roughness is critical to minimizing the intrinsic emittance – epitaxial growth?

A question to consider: Why can CsI (another ionic crystal, PEA cathode) achieve QE>80%?

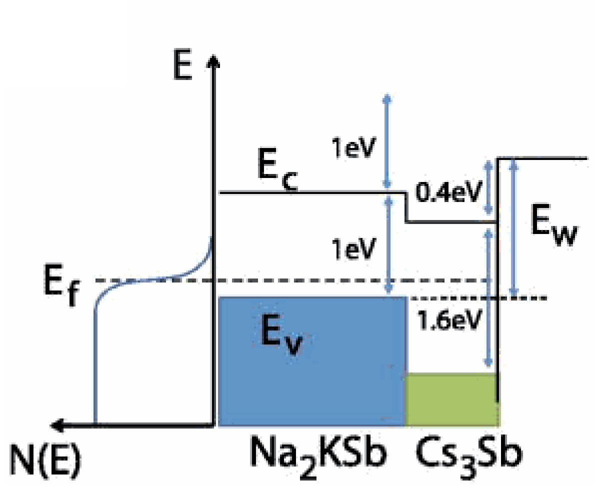
T.H. Di Stefano and W.E. Spicer, Phys. Rev. B **7**, 1554 (1973)

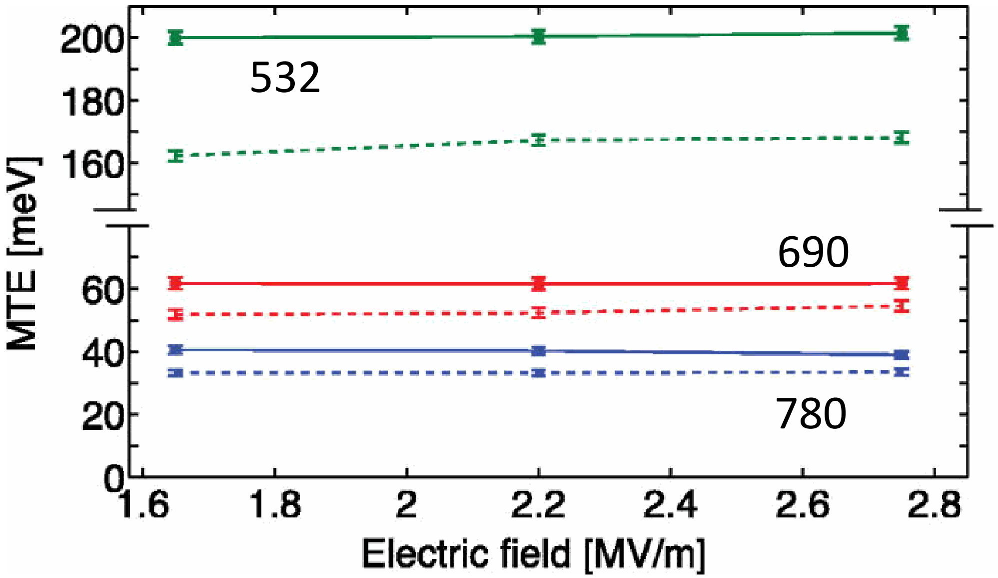
Large band gap and small electron affinity play a role, but, so does crystal quality.

Scattering

Phonon scattering can be helpful

- Well known in thermalization of electrons in GaAs and Diamond
- Luca & company recently demonstrated in PEA materials:
- 20% reduction in MTE for transmission mode operation





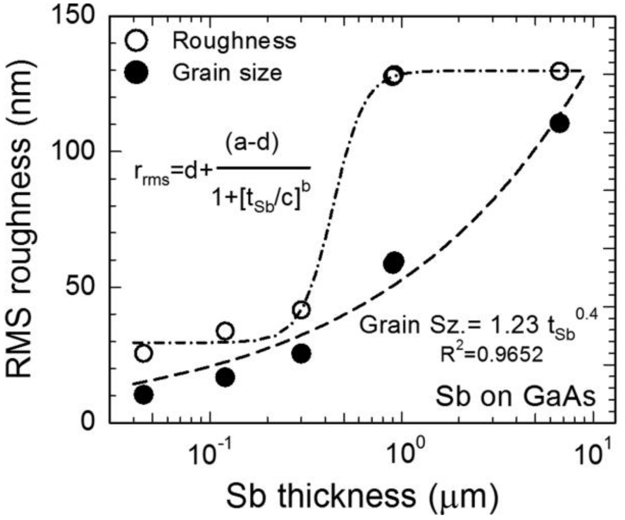
150 nm Na_2KSb (with few nm surface layer)

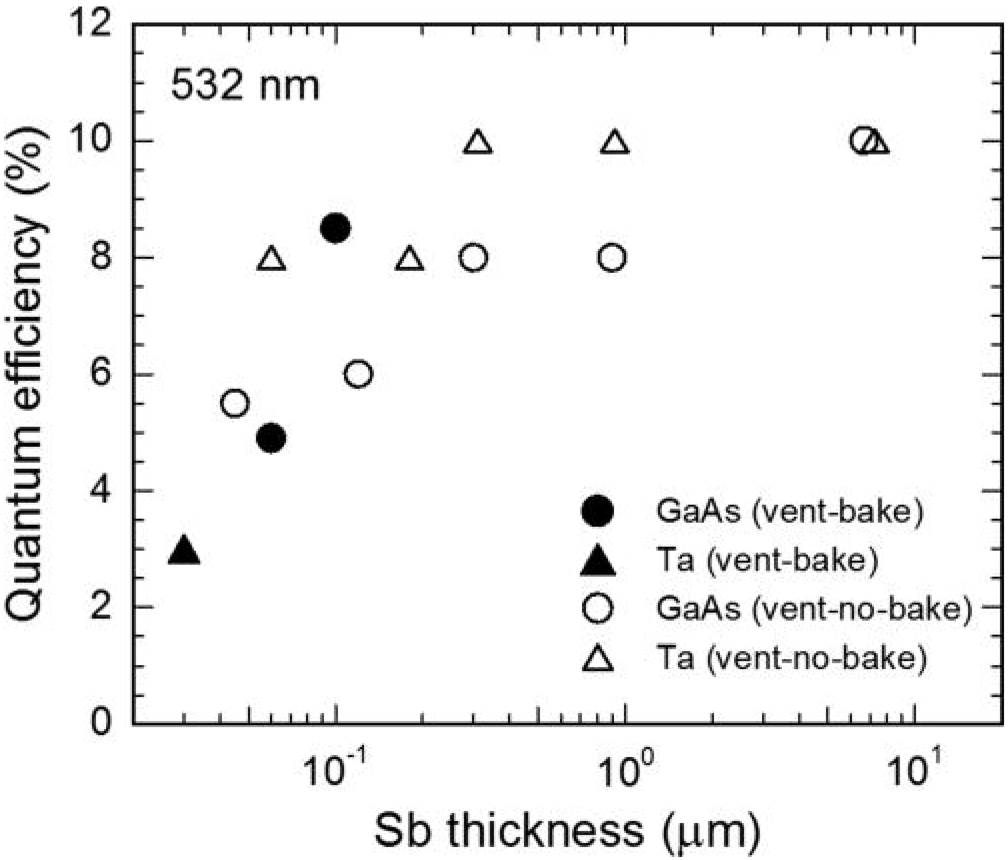
Appl. Phys. Lett. **108**, 124105 (2016)

Grain Boundaries

Grain boundary scattering: just bad

- Large grains or Epitaxy
- One solution: REALY thick cathodes (50 optical absorption lengths)
- Another: Stay tuned





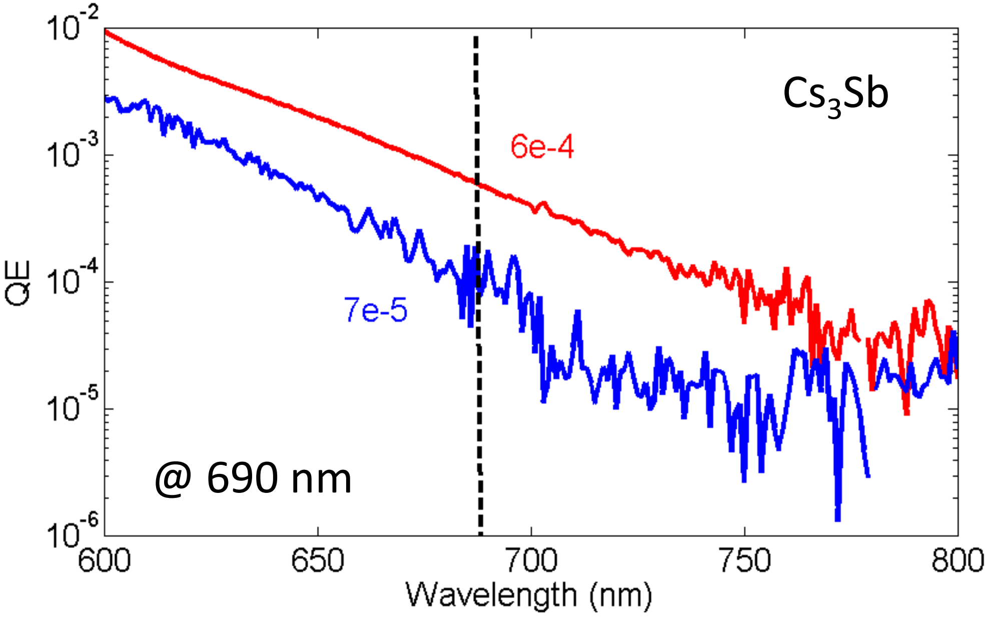
J. Vac. Sci. Technol. A **34**, 021509 (2016)

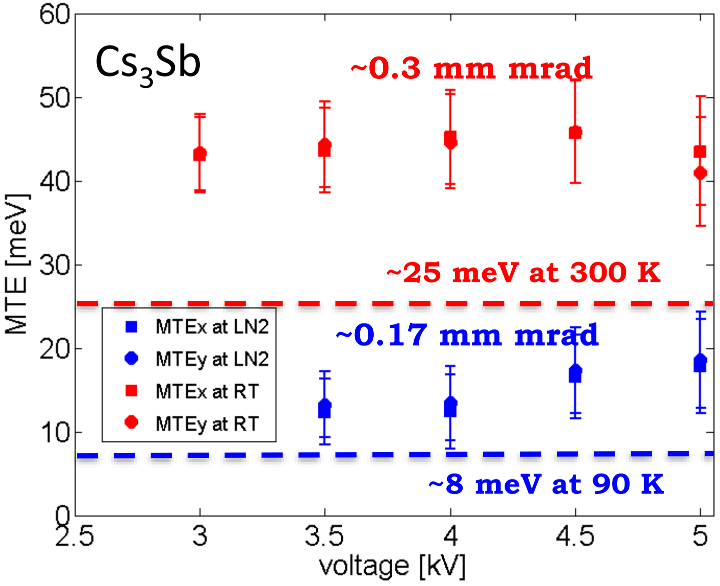
Lattice Temperature

For E_{excess}<0, MTE=kT, and lattice temperature becomes important

Photoemission in this domain relies on defect states

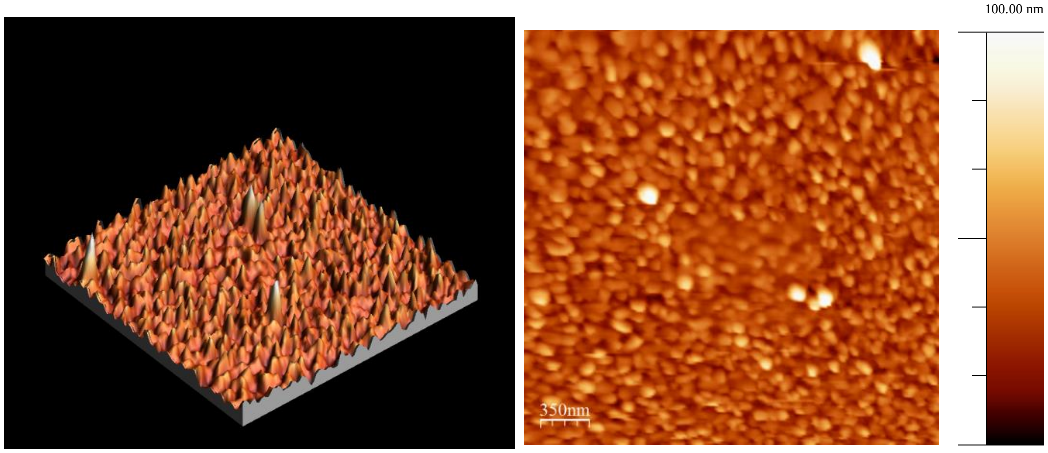
- May depend on crystal quality
- Material conductivity will as well





Phys. Rev. ST Accel. Beams **18**, 113401

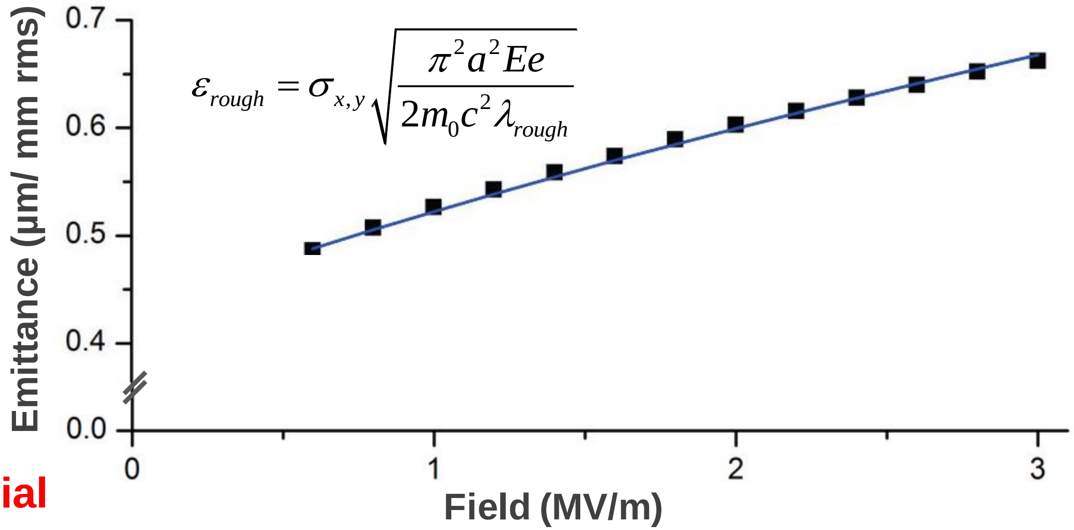
Roughness and Emittance



S. Schubert et al., APL Materials 1, 032119 (2013)

**25 nm roughness,
100 nm spatial period**

**Emittance vs field
measured with
Momentatron, 532 nm light**



$$\varepsilon_{rough} = \sigma_{x,y}\sqrt{\frac{\pi^2 a^2 E e}{2 m_0 c^2 \lambda_{rough}}}$$

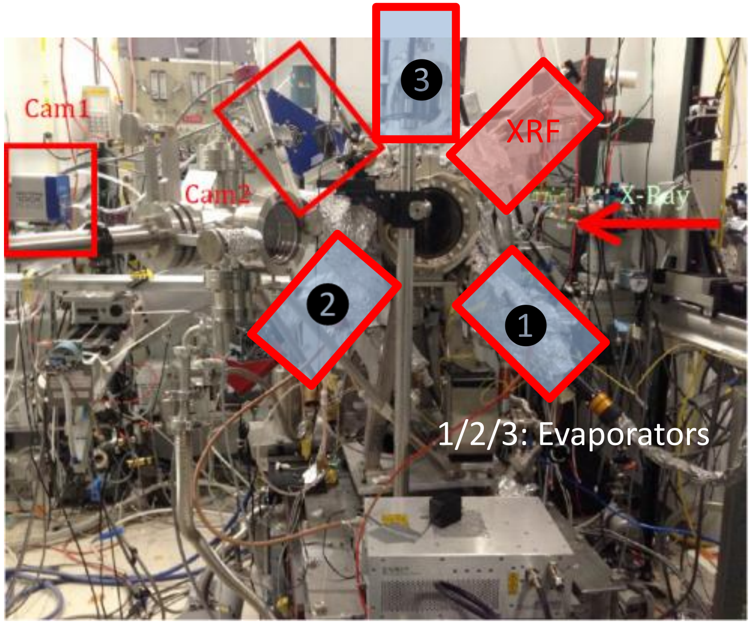
T. Vecchione, et al, Proc. of IPAC12, 655 (2012)

We now understand why sequential growth causes roughness, and can achieve near-atomic roughness with Alkali antimonides!

(Next Section)

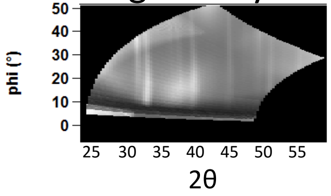
In operando analysis during growth
(setup at NSLS/X21 & CHESS G3 – ISR soon)

- Growth and characterization system

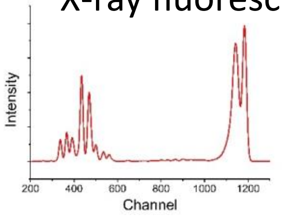


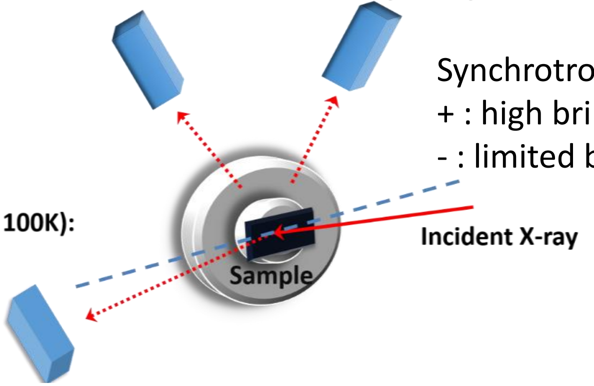
In-situ UHV growth system (10^{-10} ~ 10^{-11}Torr) installed at G3, CHESS

Wide angle X-ray diffraction



X-ray fluorescence



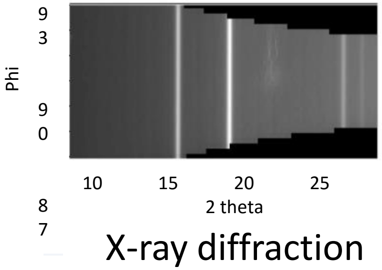


Camera 2 (PILATUS 100K):
WAXD

Fluoresence detector
(Vortex)

Synchrotron Radiation
\+ : high brilliance, …
\- : limited beamtime

Camera 1 (PILATUS 100K):
XRD, XRR

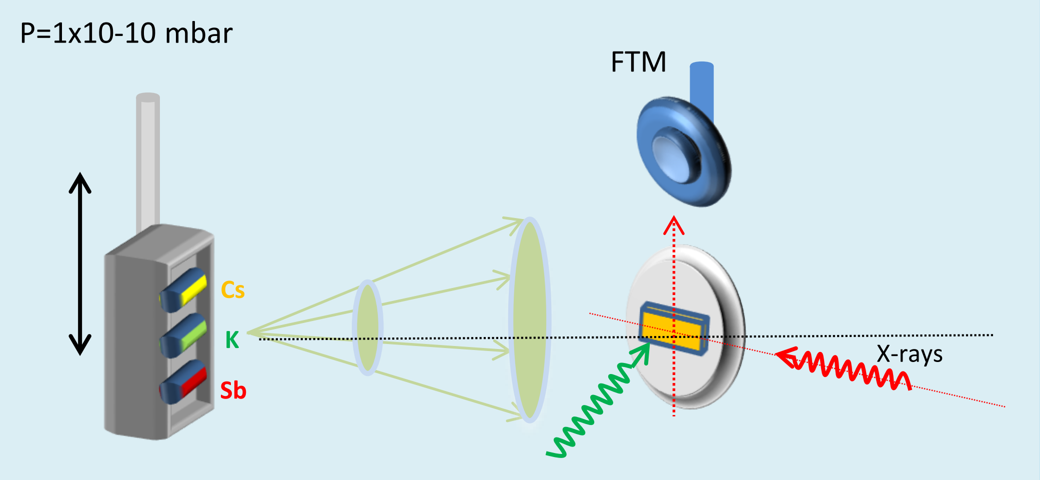


X-ray diffraction

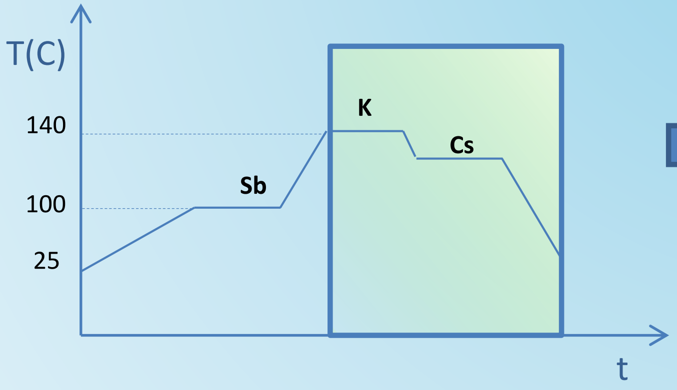
X-ray reflectivity

Experimental set up: K_2CsSb cathode growth

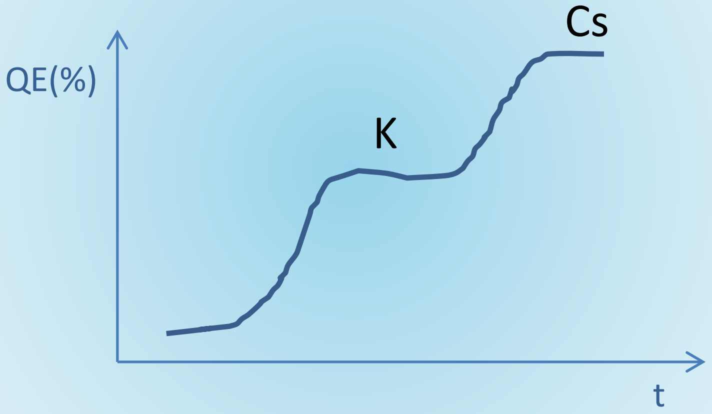
Horizontal evaporation of three sources:



Recipe:

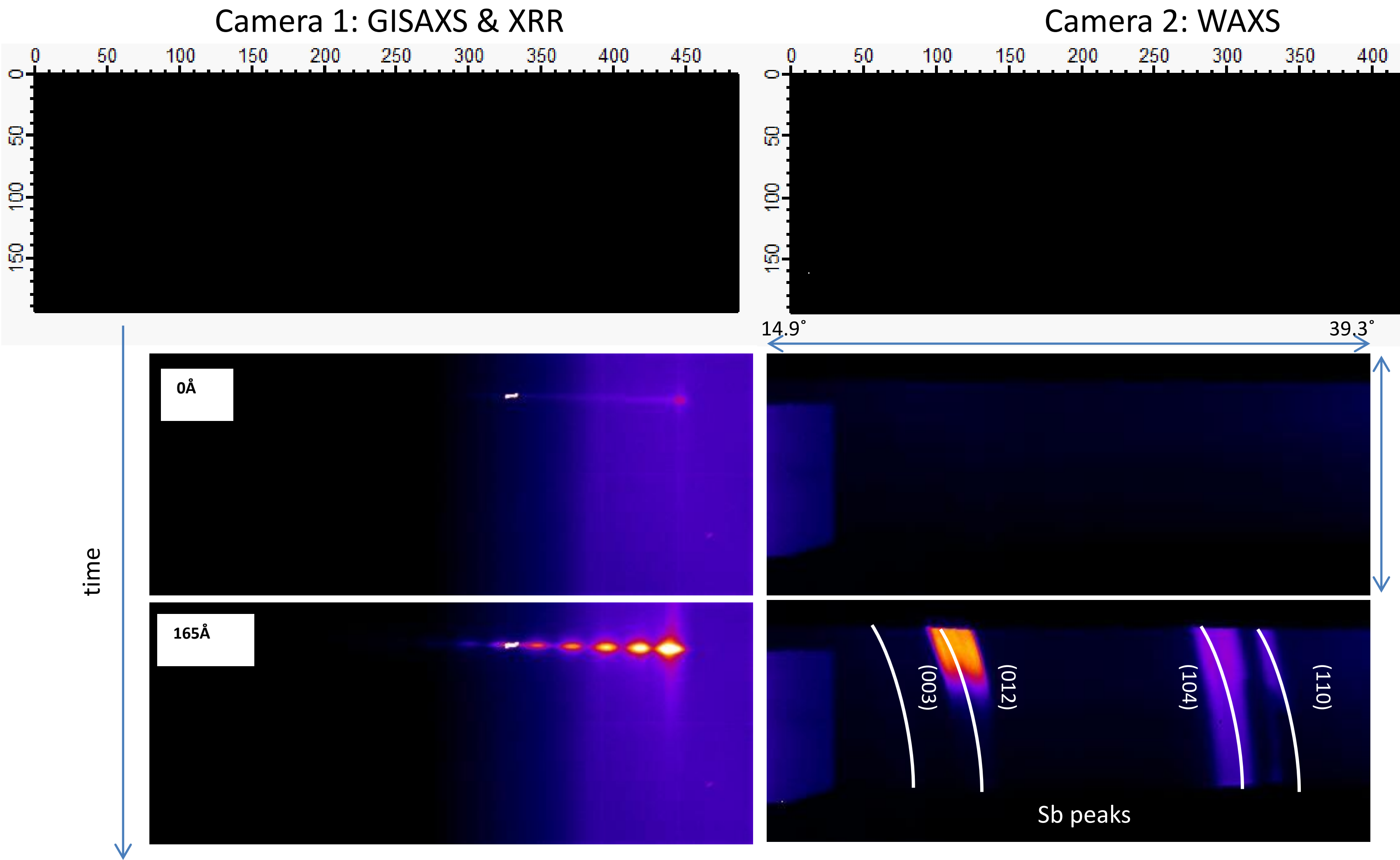


QE during growth (532 nm laser)

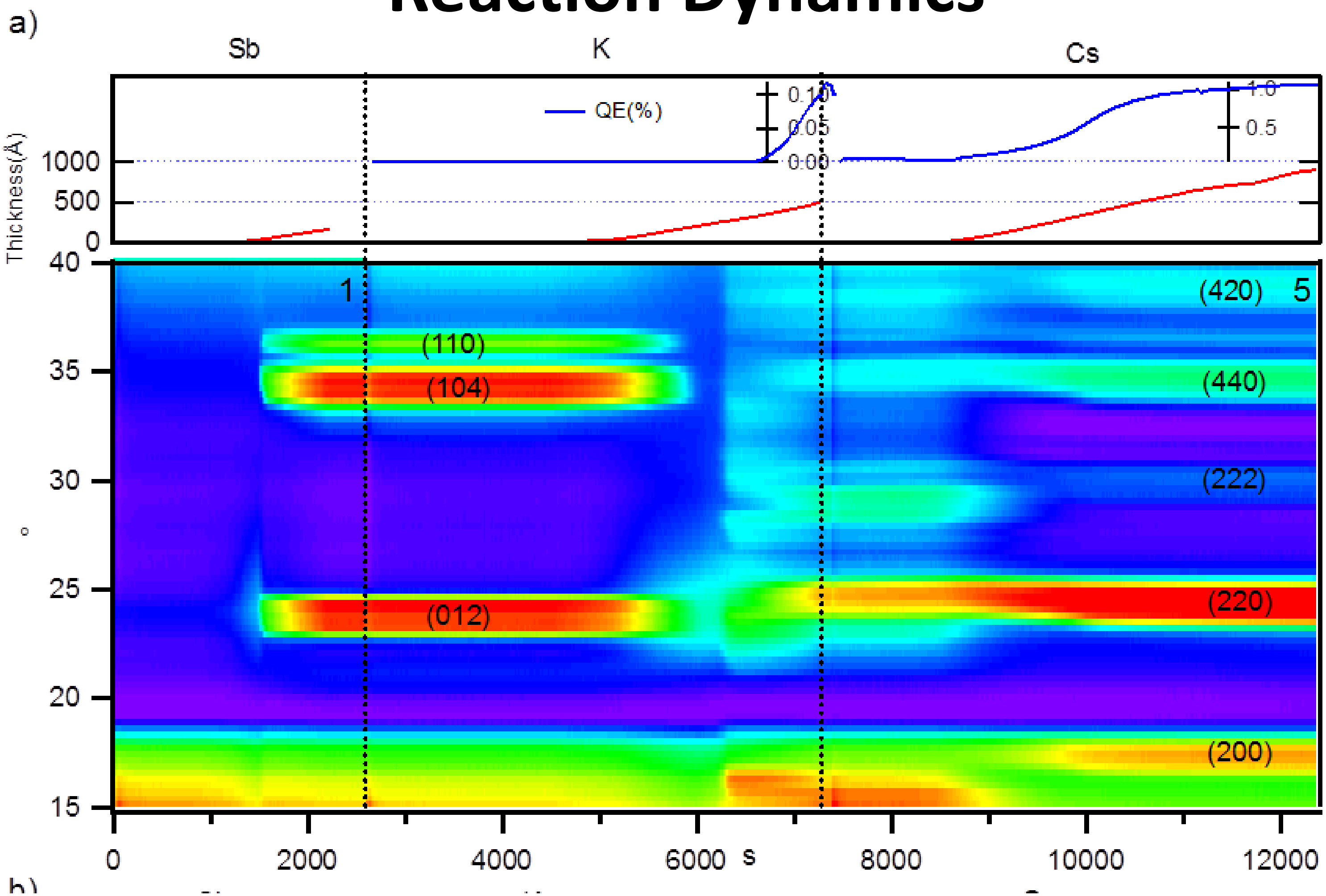


Simultaneously Acquire XRD and GISAXS

- Understanding reaction dynamics through crystalline phase evolution
- Map the thickness and roughness evolution of the cathode
- Is there a correlation between reactivity, QE and roughness?



Reaction Dynamics



Antimony evaporated on Si, 0.2 Å/s; crystallize at 4nm

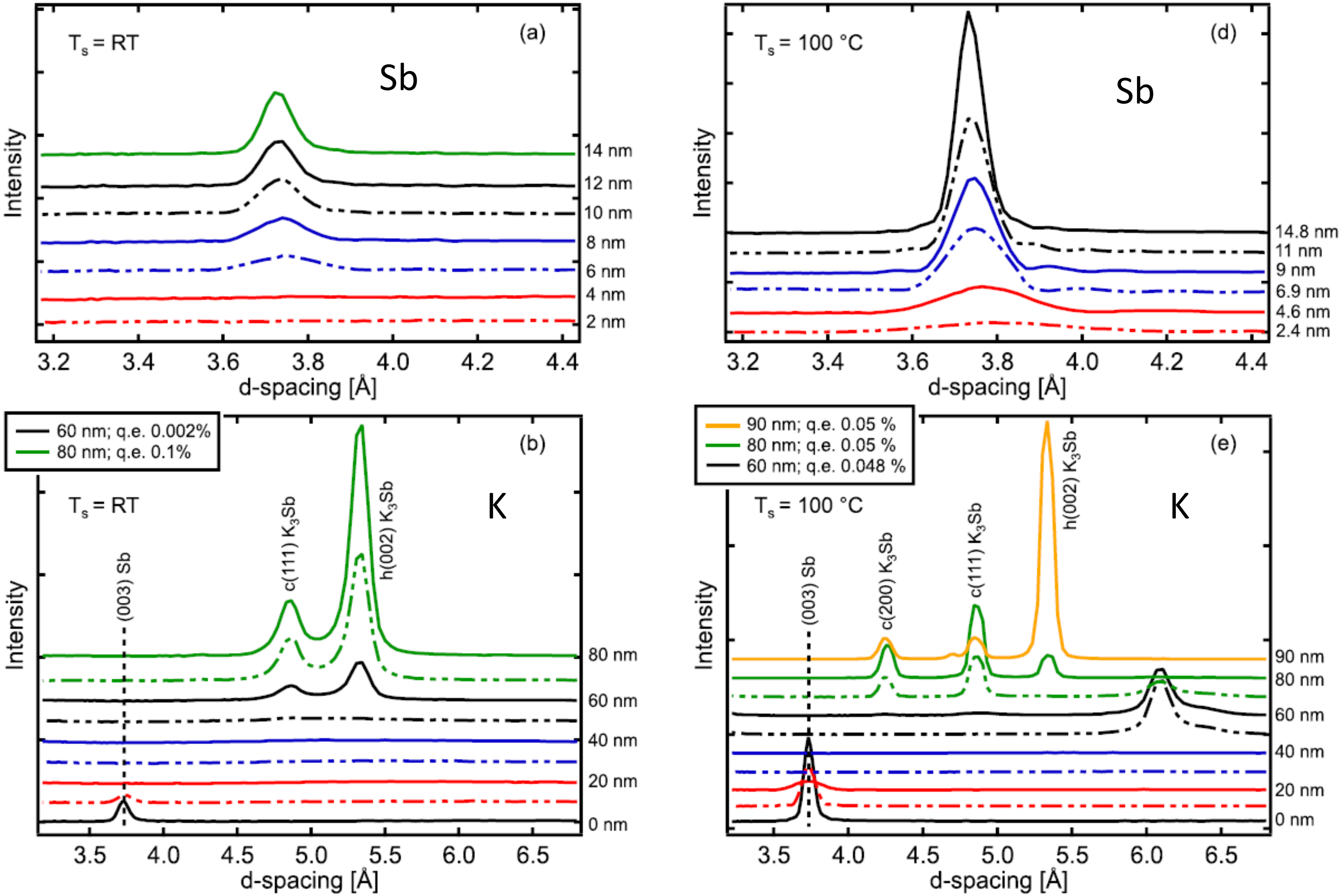
K deposition dissolves Sb layer - This is where roughening occurs!

QE increase corresponds with K_xSb crystallization

Cs increases lattice constant and reduces defects

M. Ruiz-Osés et al., APL Mat. 2, 121101 (2014)

Stepwise High Resolution XRD
A little bit of Potassium goes a long way…



S. Schubert et al., J. Appl. Phys. 120, 035303 (2016)

Stepwise High Resolution XRD
A little bit of Potassium goes a long way…

Room Temperature

Recrystallization to K_3Sb

Better QE of K_3Sb

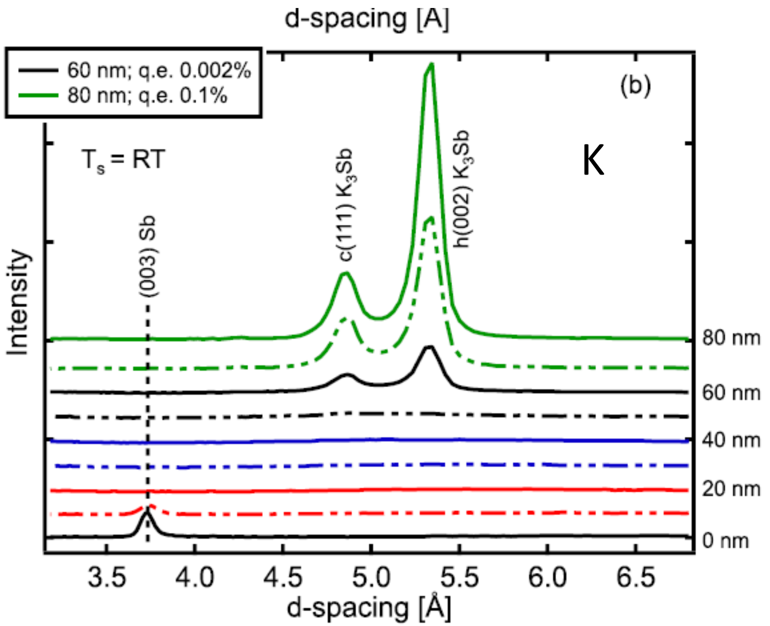
Principally Hexagonal

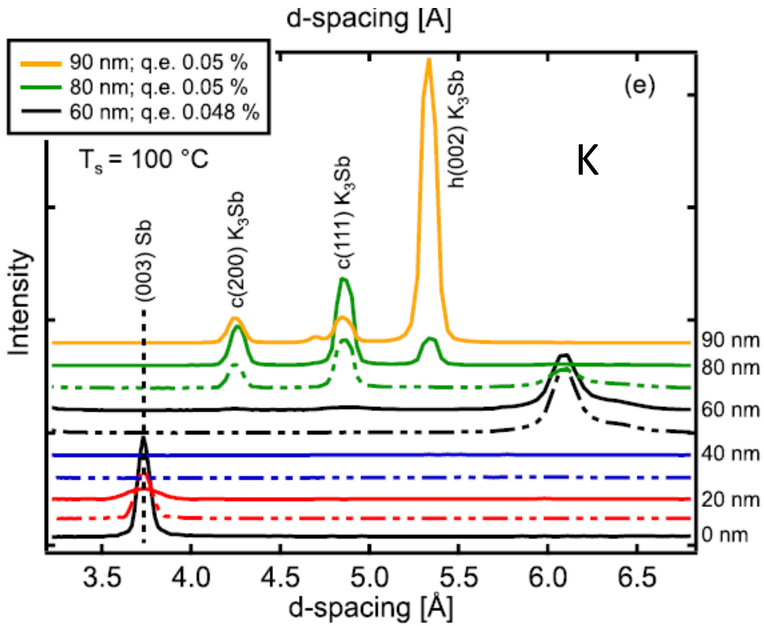
100C Substrate

Recrystallization to K_xSb

Cubic K_3Sb first

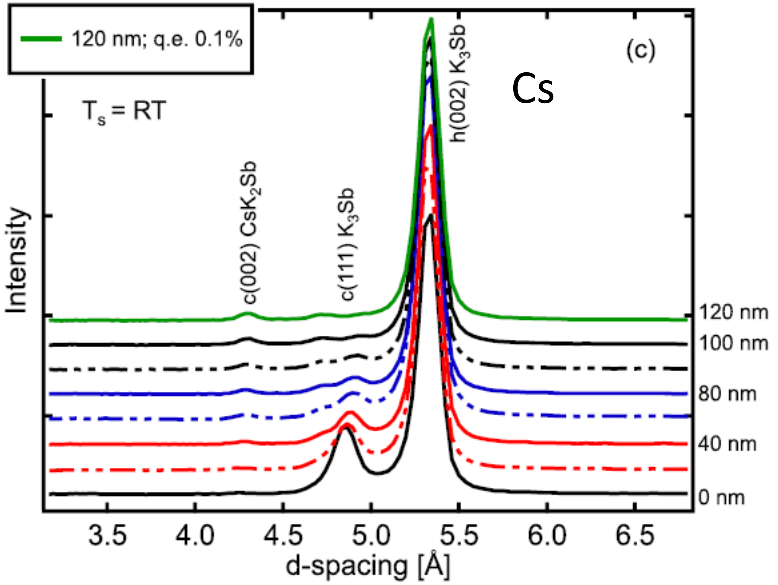
Eventually Hex appears (oops!)





S. Schubert et al., J. Appl. Phys. 120, 035303 (2016)

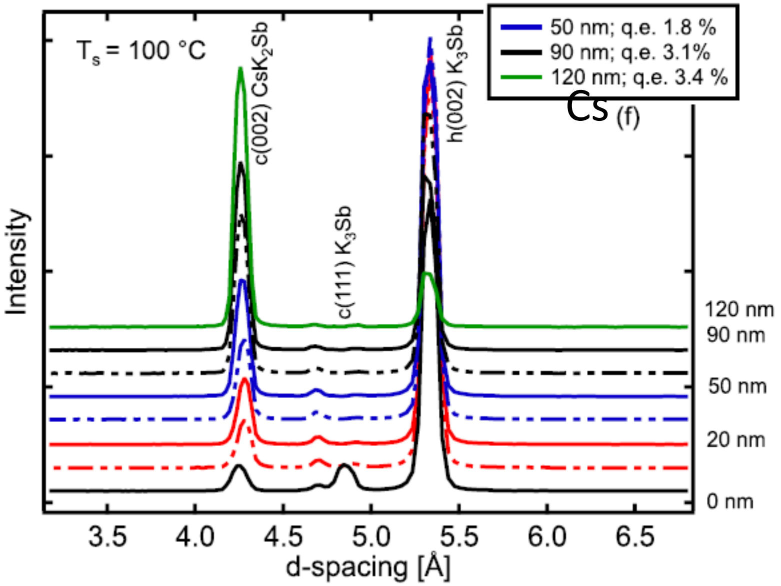
Stepwise High Resolution XRD



Room Temperature

K_3Sb resists Cs incorporation

QE never improves



100C Substrate

Cubic K_3Sb converts quickly

Hex K_3Sb mostly converts

S. Schubert et al., J. Appl. Phys. 120, 035303 (2016)

Stepwise High Resolution XRD

100C without “too much” K

15 nm Sb, 70 nm K

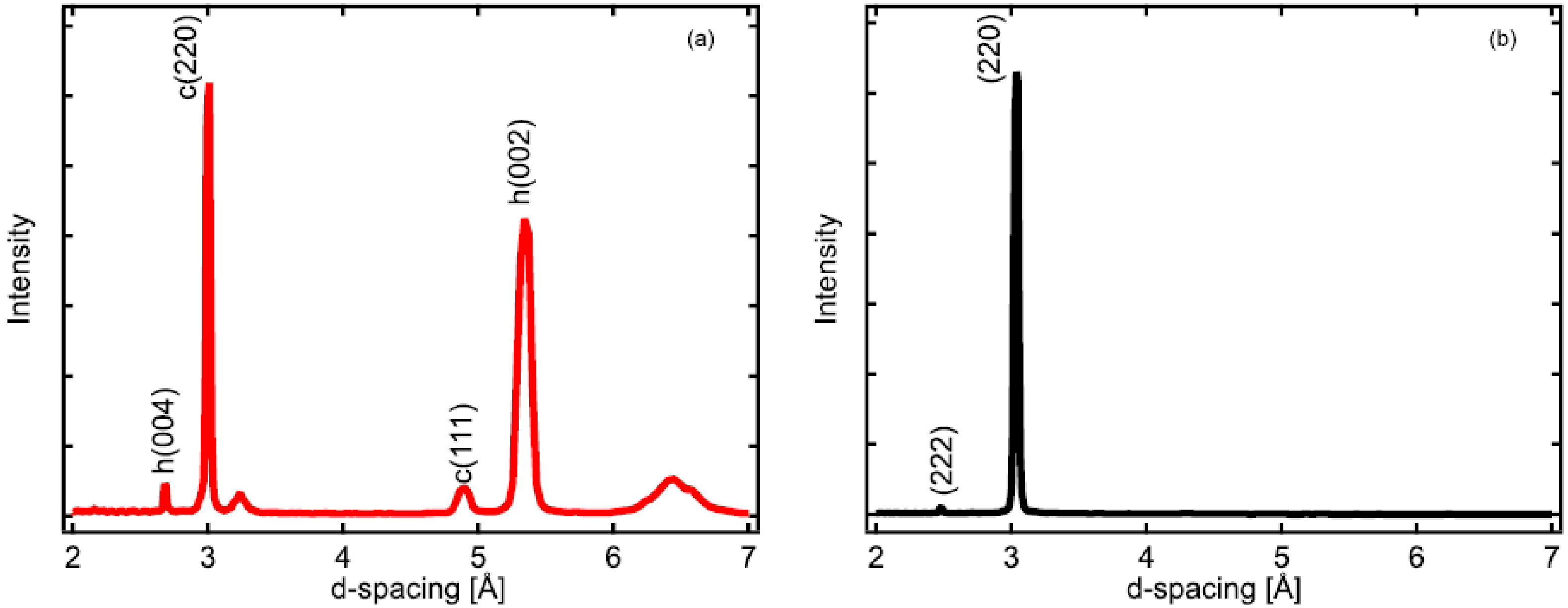
Stop at “mixed phase” K_xSb

lower QE of K_3Sb

90 nm Cs sufficient

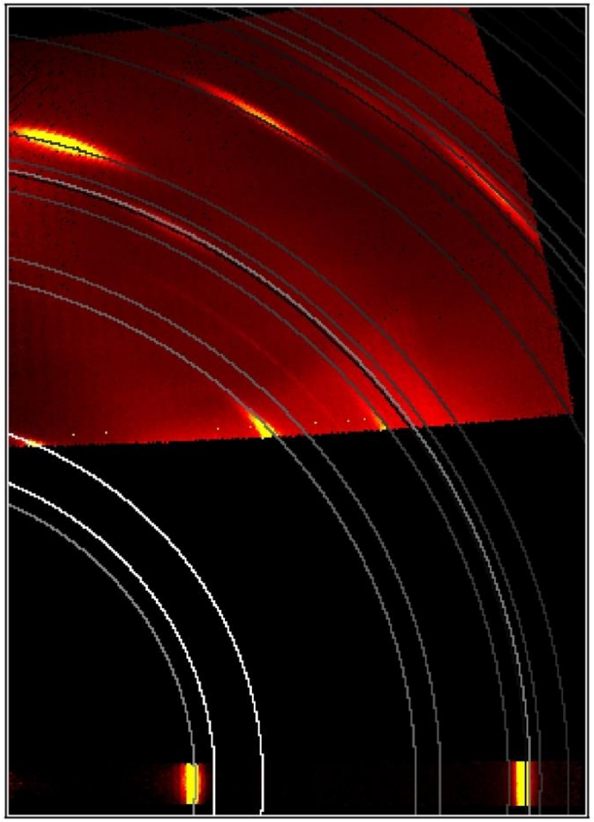
Full conversion to CsK_2Sb

QE = 6.7% at 532 nm

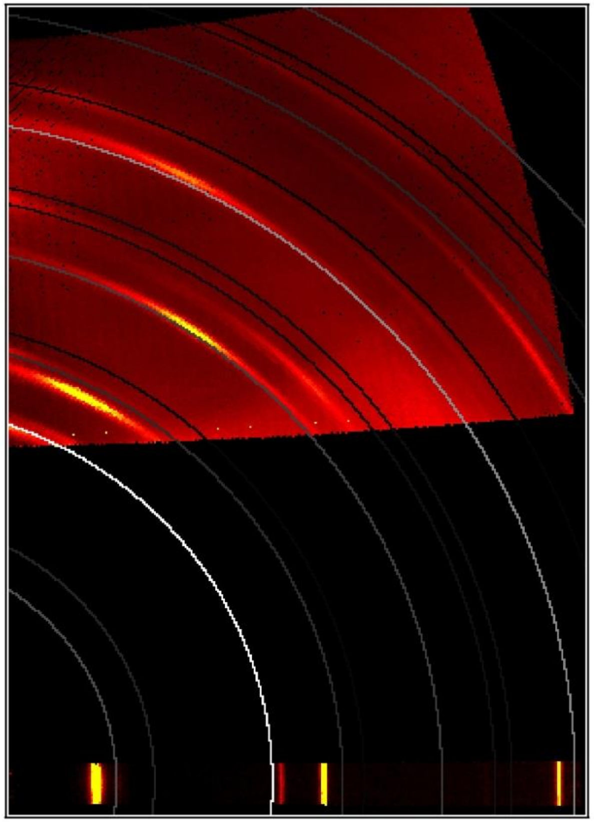


S. Schubert et al., J. Appl. Phys. 120, 035303 (2016)

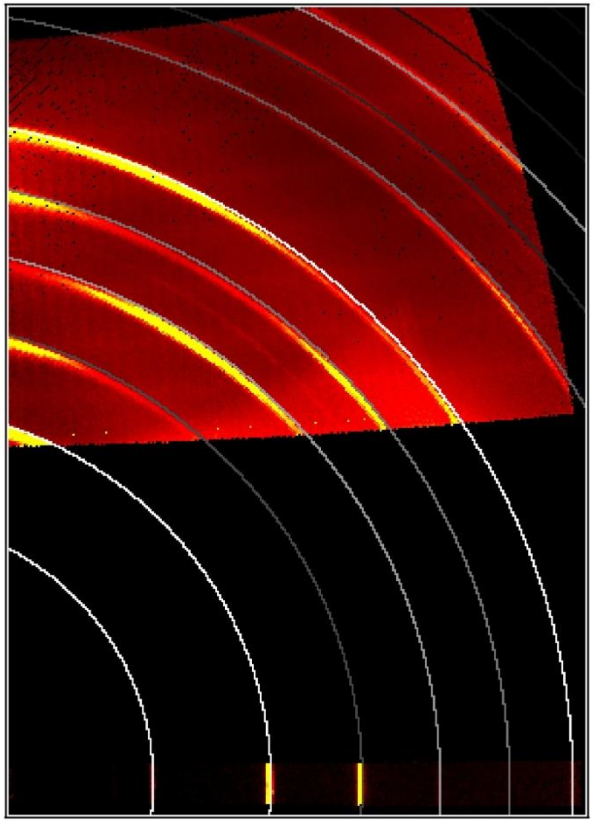
Cathode Texture



Sb evaporated at RT
Clear [003] texture



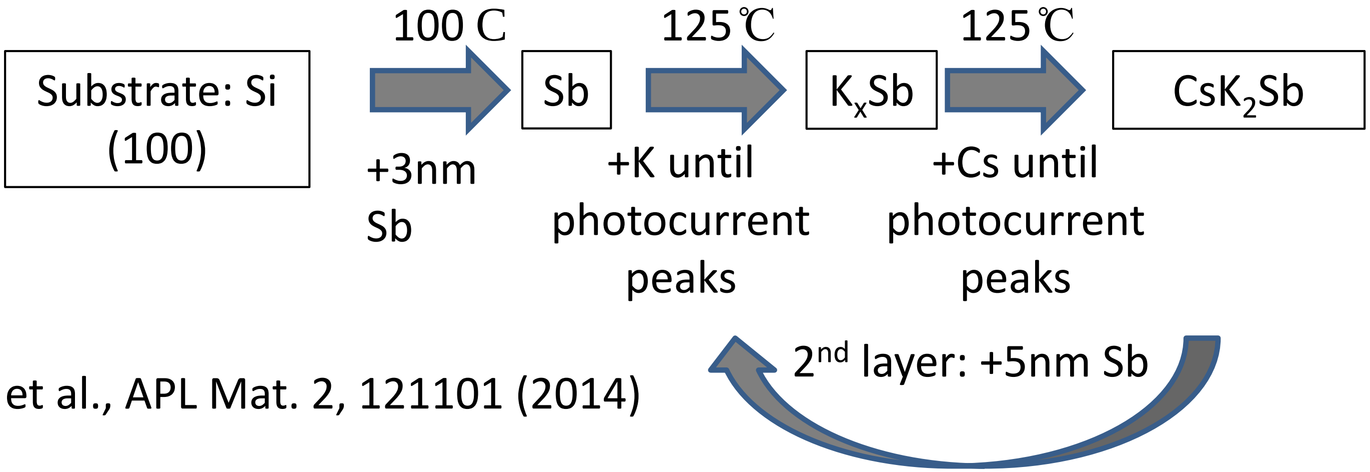
Add Potassium at 140C
Textured final film
But not K_3Sb



Add Cesium at 140C
Textured final film
Both [220] & [222]
(domains?)
Final QE 7.5% @ 532nm

Engineering a Smoother Cathode

Idea: Never let Sb crystalize



Substrate: Si (100)

100 C

+3nm Sb

Sb

125℃

+K until photocurrent peaks

K_xSb

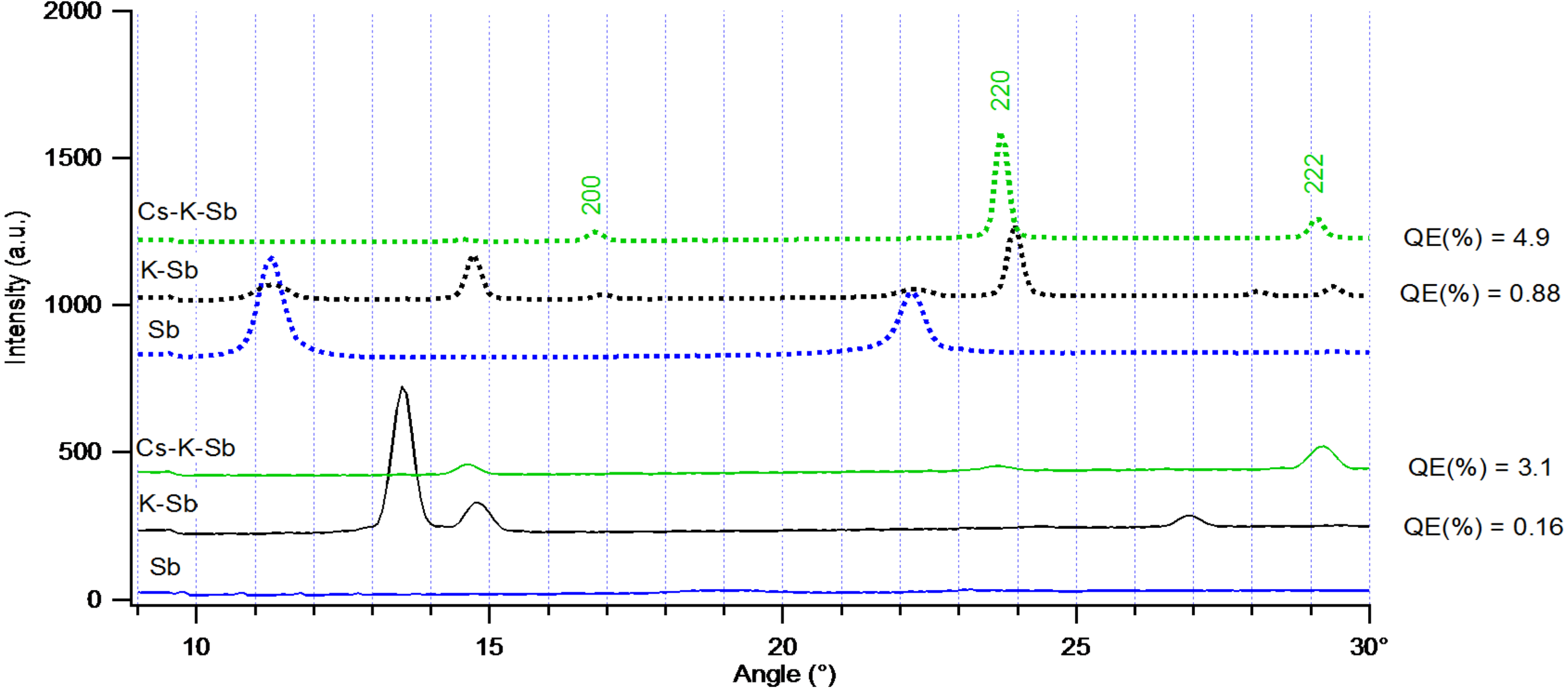
125℃

+Cs until photocurrent peaks

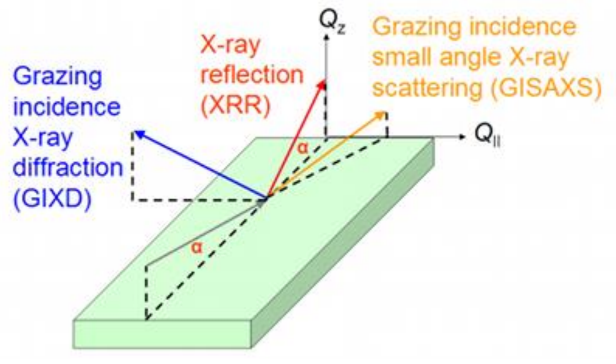
CsK_2Sb

2nd layer: +5nm Sb

M. Ruiz-Osés et al., APL Mat. 2, 121101 (2014)



X-ray reflectometry (XRR) provides in-situ thickness monitoring

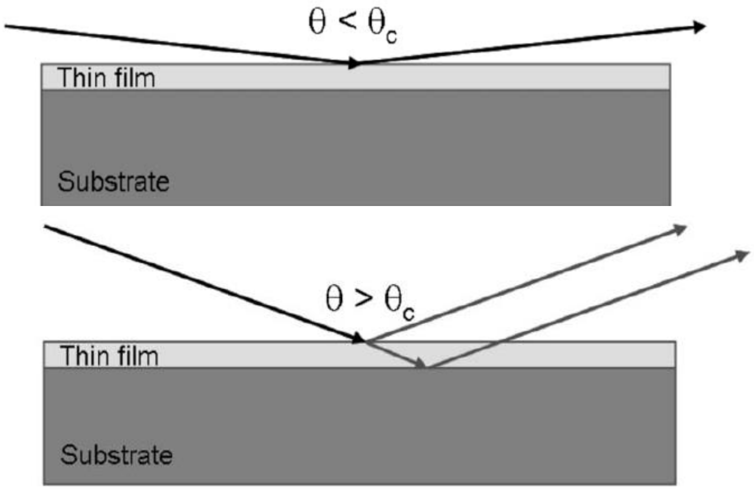


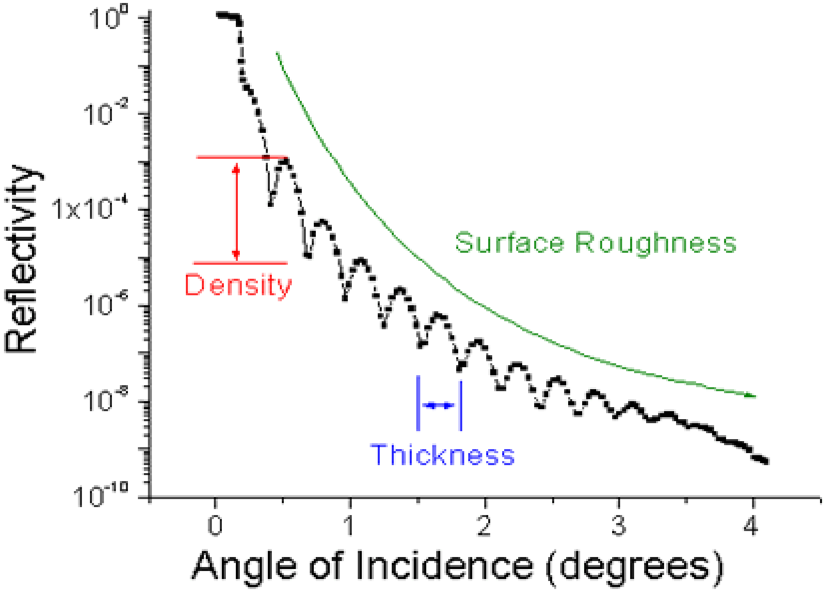
Understand ‘sticking’ coefficient of materials to substrates at various temperatures

Observe the intermixing vs layering of materials

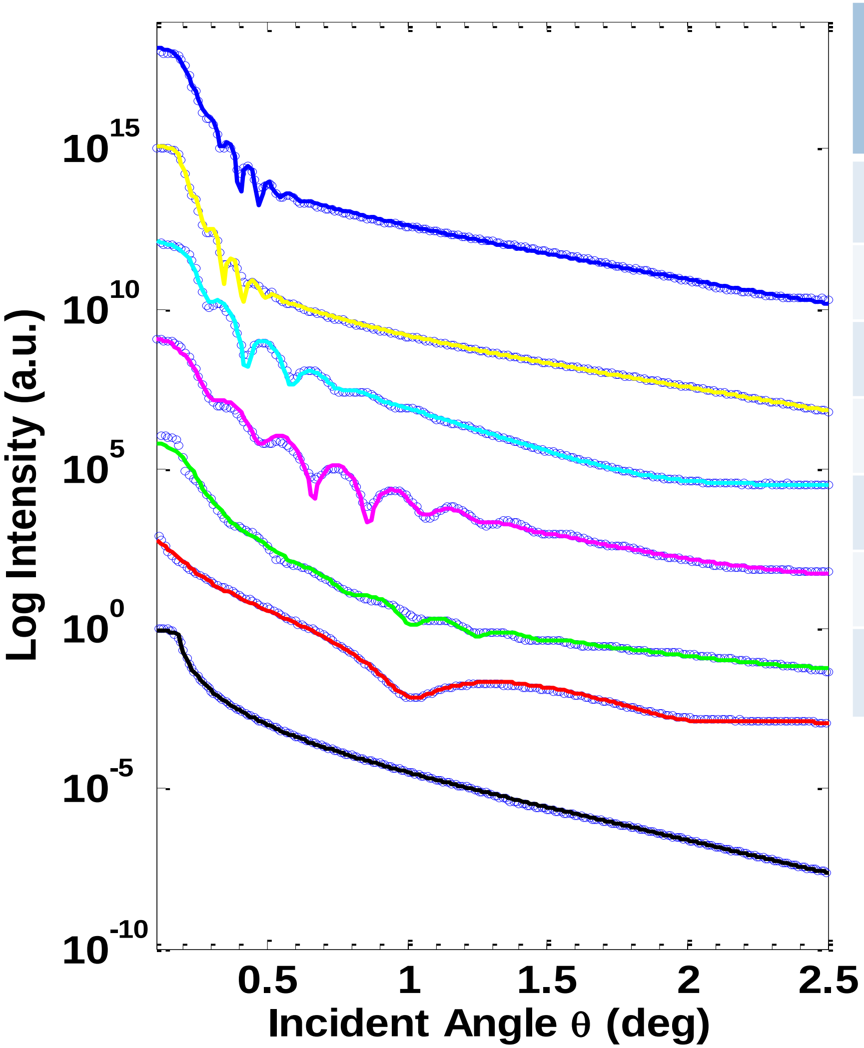
Observe the onset of roughness

$$\theta_c = \arccos(n_{medium} / n_{air})$$





XRR shows roughness evolution

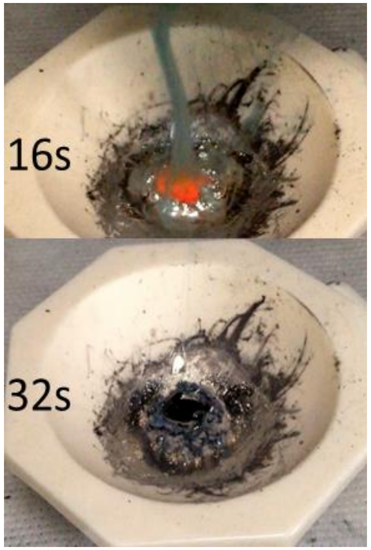


Deposited Layers	Total Thickness (Å)	Roughness (Å)
Cs-K-Sb-Cs-K-Sb/Si	469	32
K-Sb-Cs-K-Sb/Si	449	36
Sb-Cs-K-Sb/Si	200	21.3
Cs-K-Sb/Si	174	13.2
K-Sb/Si	141	10.5
Sb/Si	35	2.9
Si Substrate	-	3.1

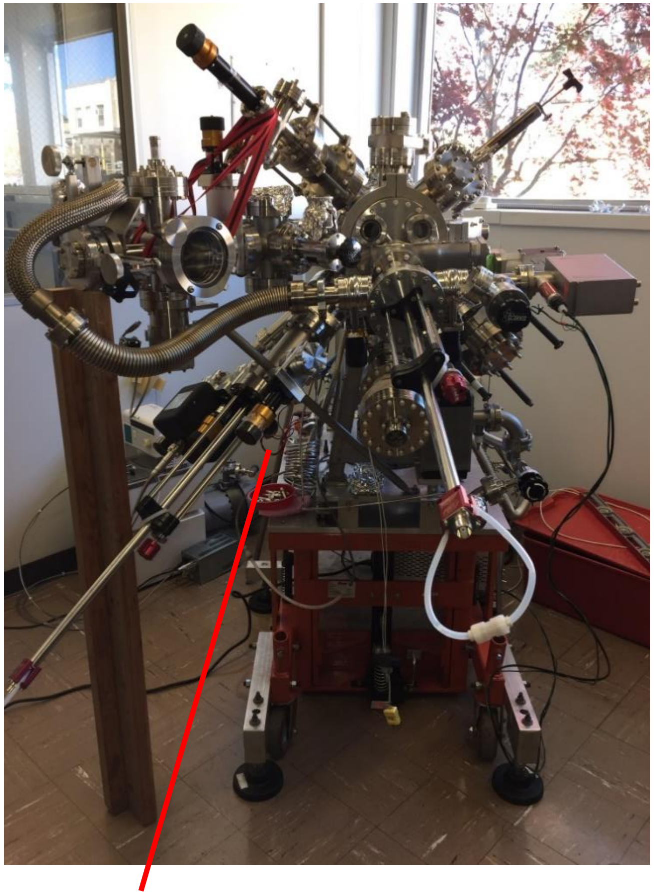
The substrate fit includes 1.5 nm of SiO_2

Multi-layer subcrystalline film is smoother,
At slight loss of QE

Sputter growth of Bi-alkali photocathode



Sputter target and sputter gun was product of RMD. Inc. Photos of sputter target prep are contributed by H. Bhandari



K_2CsSb
sputter gun

Before

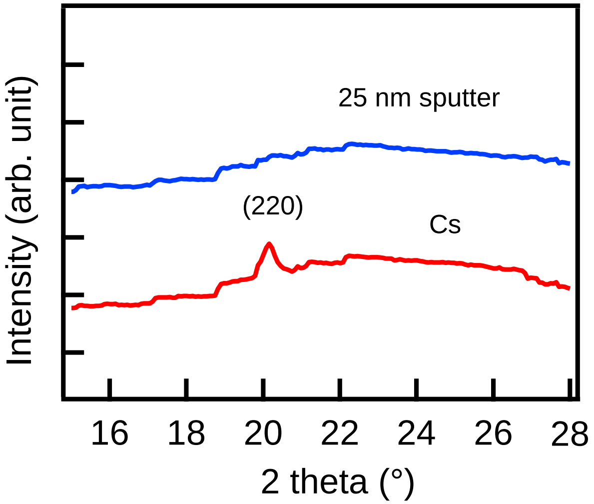
Sputtering

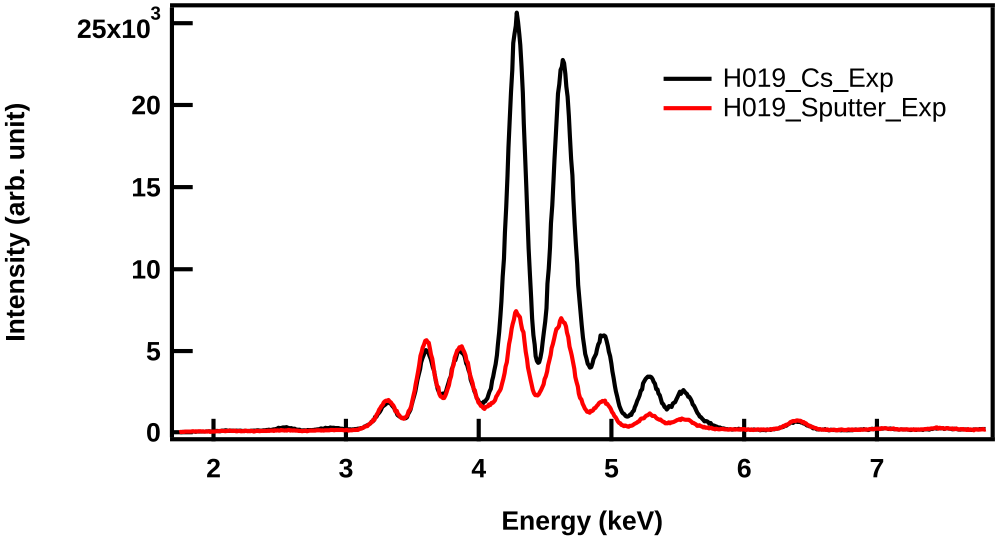
Sputter Growth

25 nm K_2CsSb + layers of (total 30 nm) Cs evap.

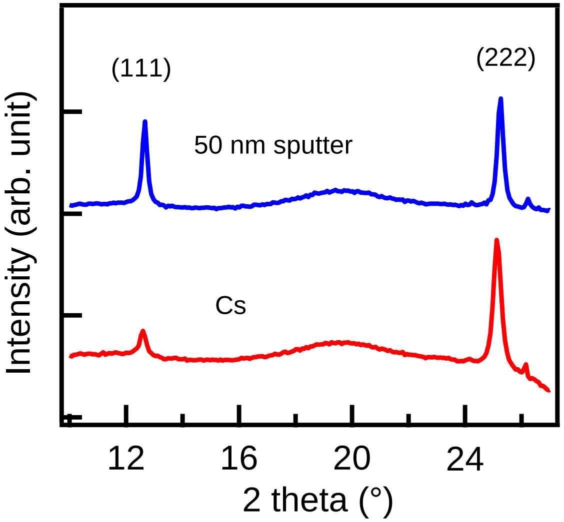
Silicon substrate at 90 C, layer barely crystalline

25 nm sputtered layer + Cs



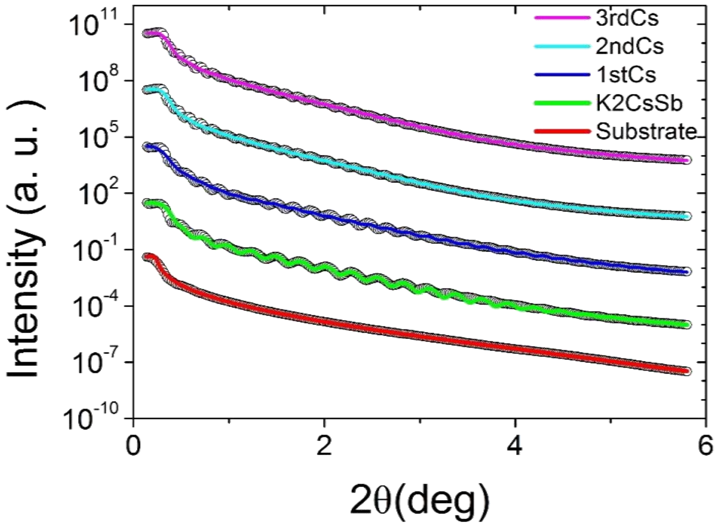


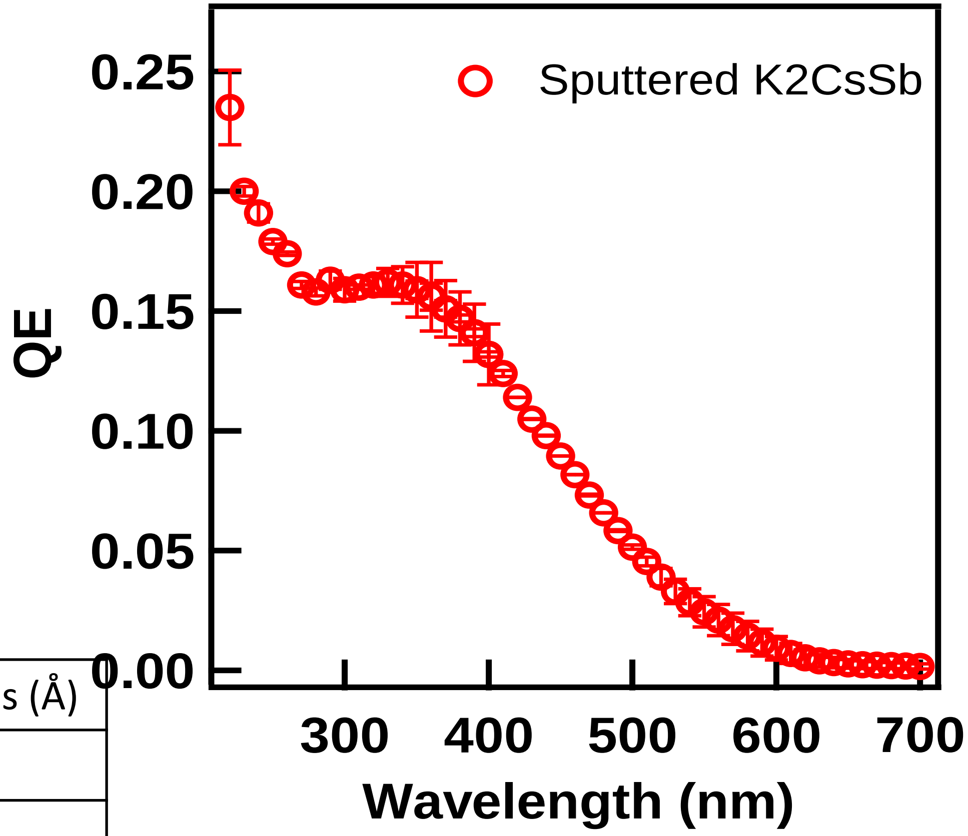
50 nm sputtered layer + Cs



layer	K (±0.1)	Sb (±0.05)	Cs (±0.05)	K/Cs
K_2CsSb sputter	0.85	1.00	0.41	2.08
Cs	0.84	1.00	1.75	0.48

Surface roughness & QE of Sputtered Photocathodes



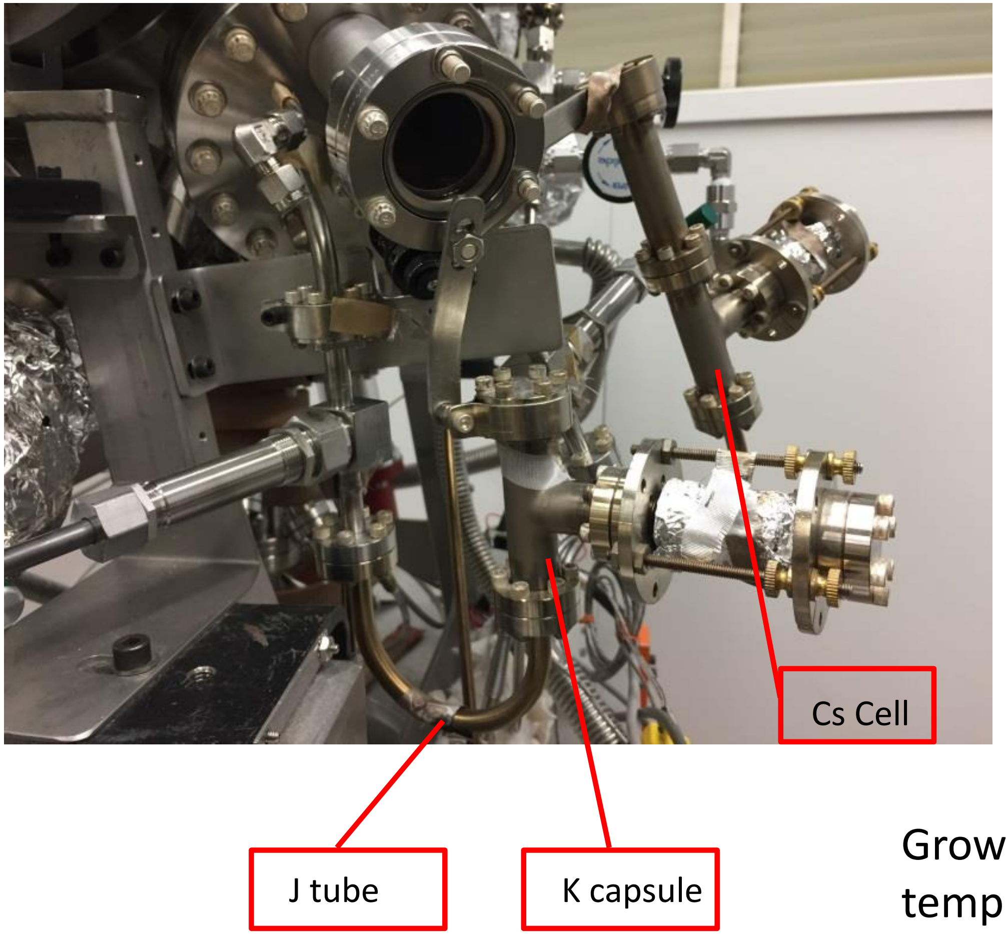


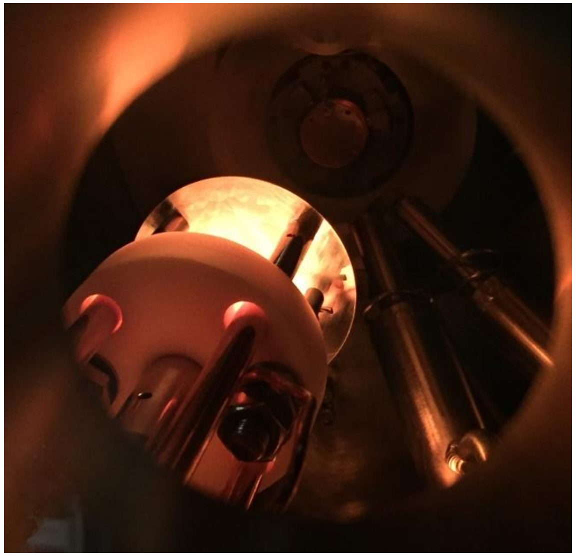
	Thickness (Å)	Roughness (Å)
3rd Cs	416.0	5.67
2nd Cs	341.3	4.94
1st Cs	249.5	4.91
sputter K_2CsSb	234.2	5.17
SiO_2	10.24	3.27
Substrate (Si)	---	3.75

- Peak QE > 20%
- Green QE: 4.3%

Ternary Co-evaporation

Simultaneously evaporate from Sb evaporator and K,Cs effusion cells





In situ, In operado XRR, XRF, XRD & Quantum efficiency (QE) measurement

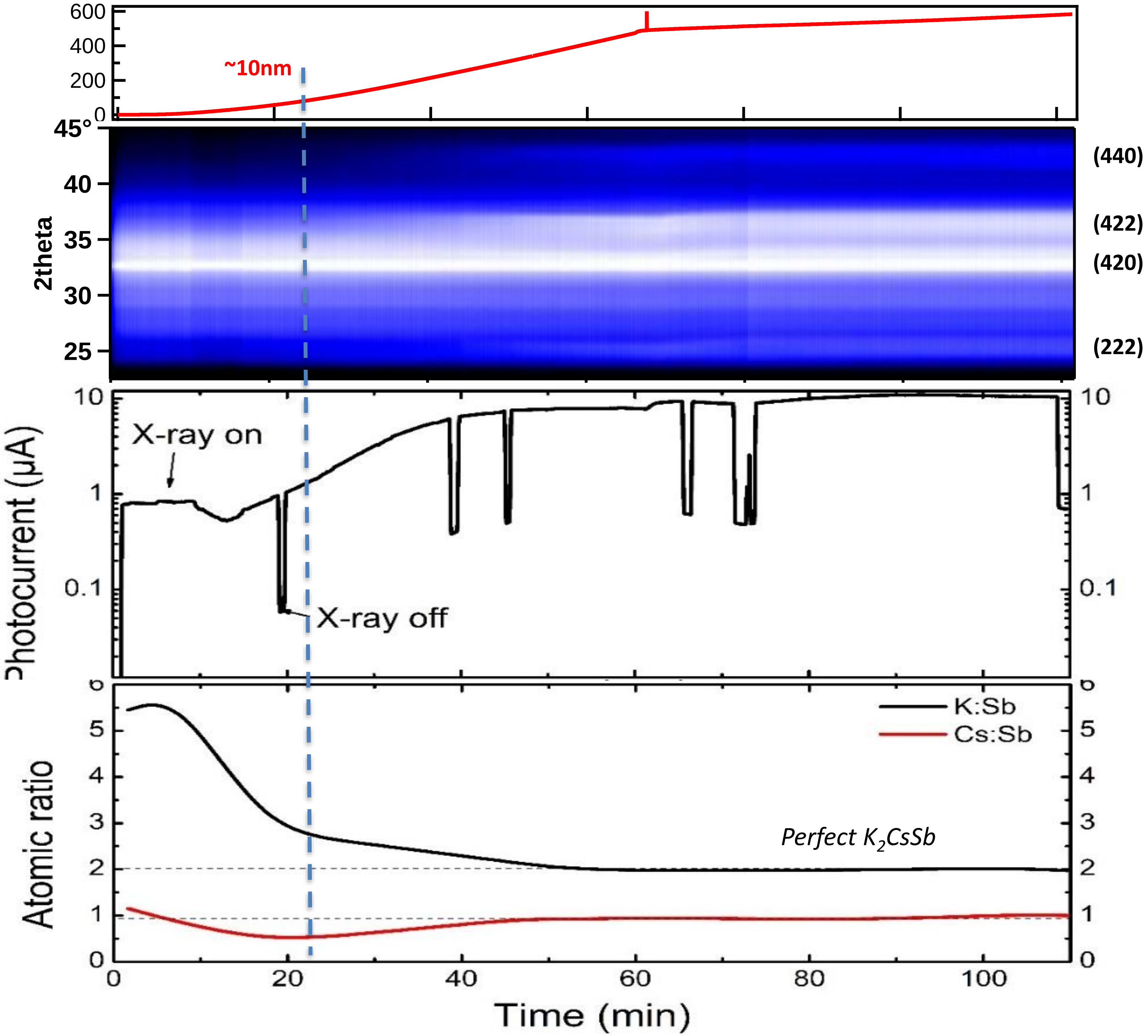
Growth rate are controlled by J tube temperature, valve and shutter

Thickness

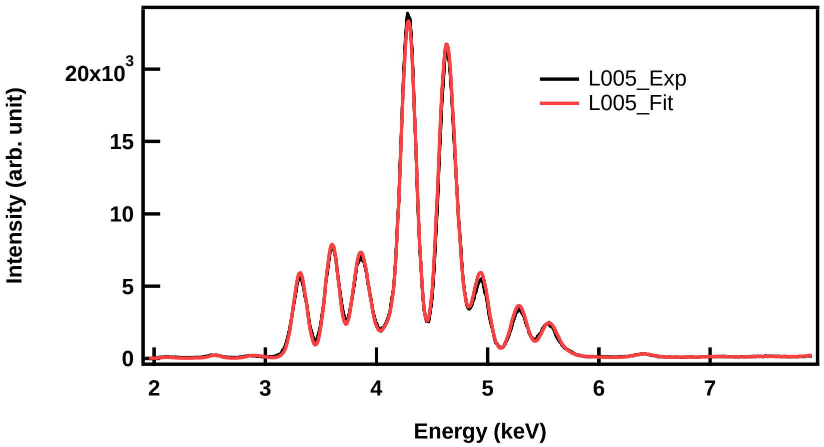
Real time XRD

QE

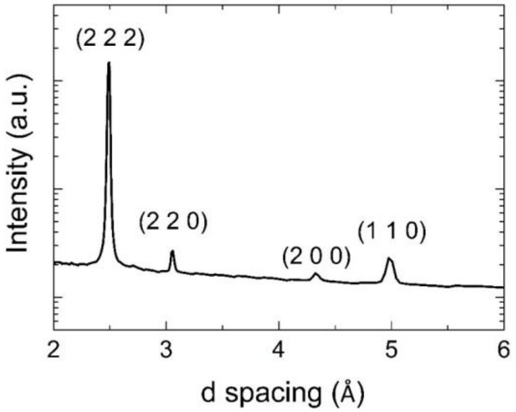
Real time Fluorescence



Stoichiometry & Structural Analysis



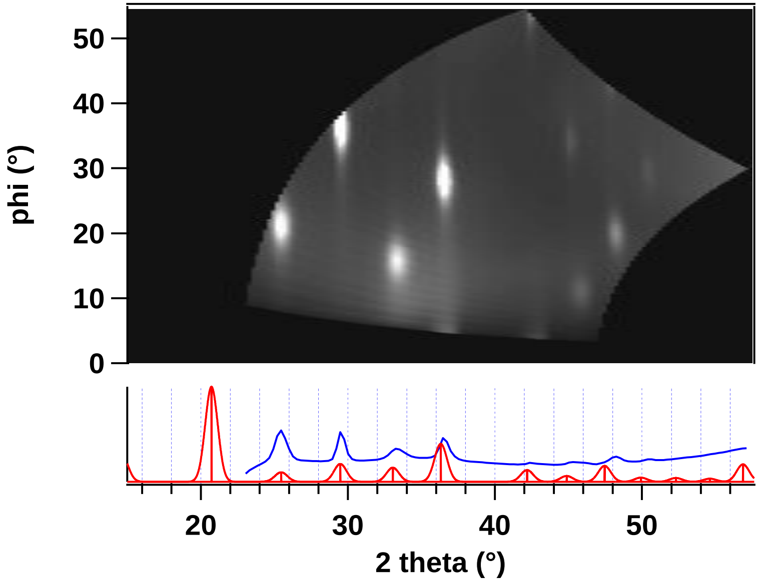
Camera 1



	K	Sb	Cs
L004 Si	2.50	1.00	1.16
L005 Si	2.37	1.00	0.91
L006 Si	2.21	1.00	0.95
L011 Si	2.07	1.00	0.94
L012 MgO	1.98	1.00	0.88

Good K/Cs/Sb ratio!

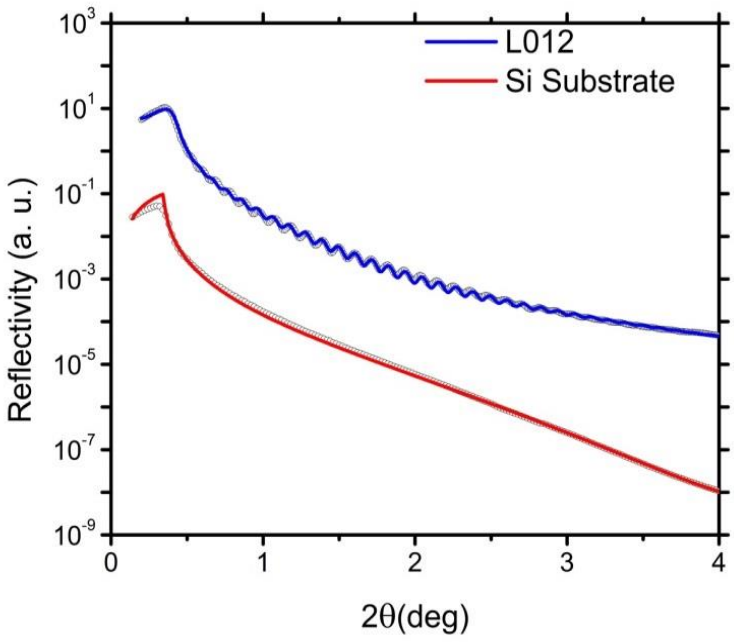
Camera 2

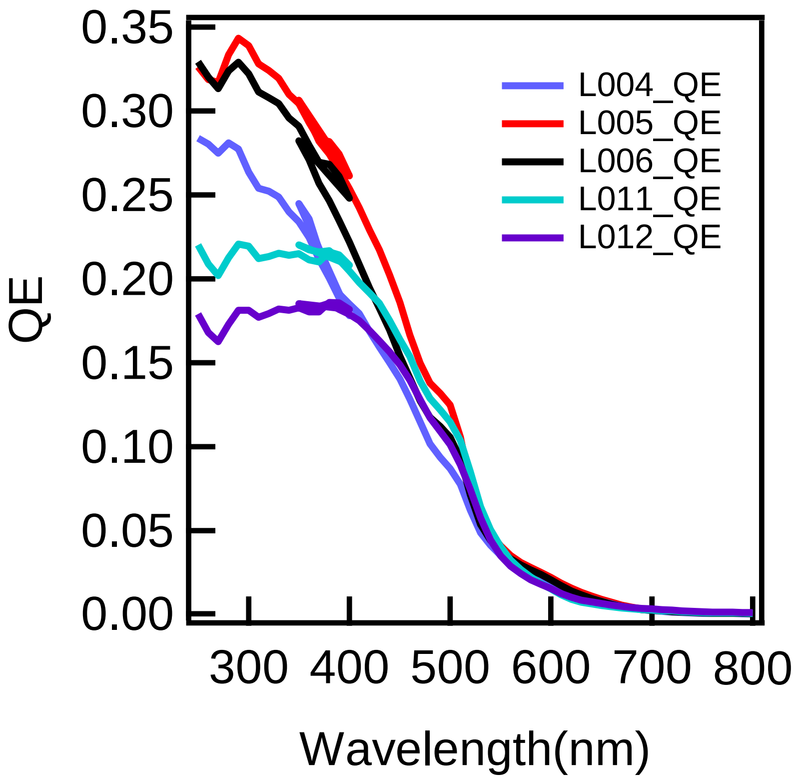


Highly textured K_2CsSb phase!

This works for the entire Alkali antimonide family – we've created pseudo single crystals with a wide range of stoichiometries

Surface Roughness & QE





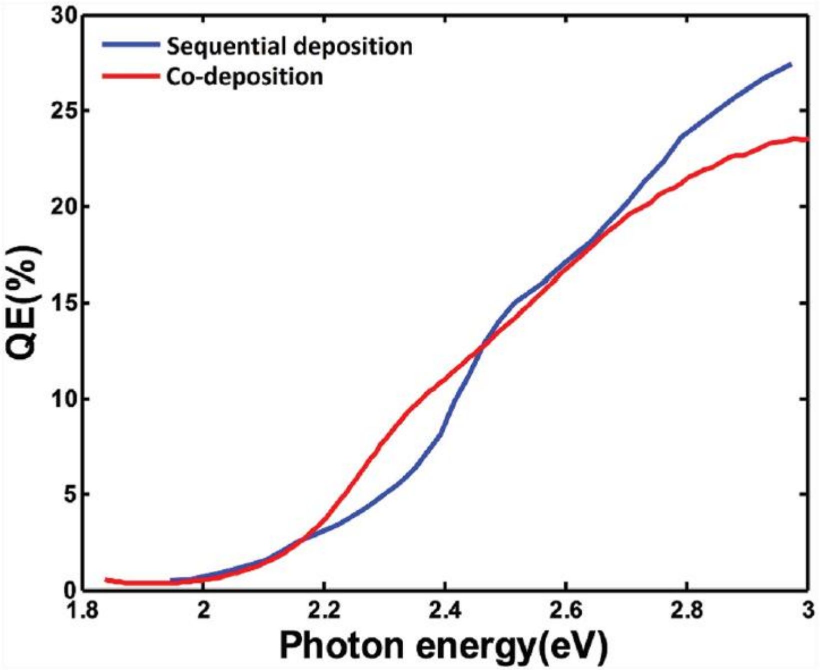
	QE@532nm(%)	Roughness(A)	Thickness (A)	Grain size (A)
L004 Si	4.9	3.5	234	155
L005 Si	5.8	11.5	815.3	277
L006 Si	5.4	13.8	757.5	202

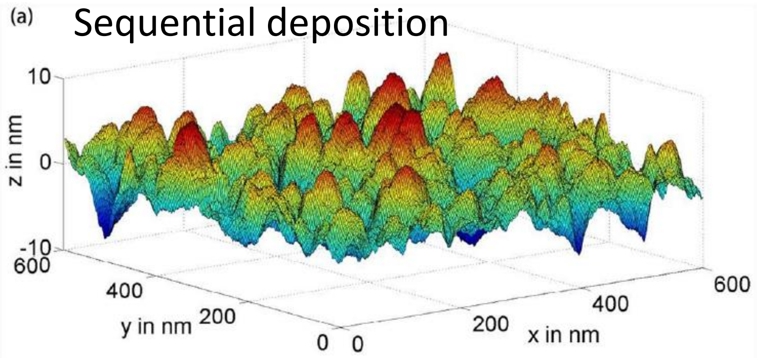
Simultaneous evaporation of all constituents results in no crystal phase transformation

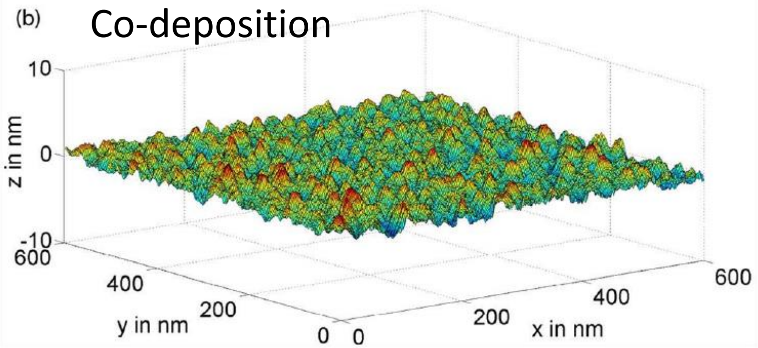
Smooth, and High crystal quality => High QE

Co-deposition leads to efficient and ultra-smooth cathodes
Ternary Co-evaporation at LBNL

Co-deposited K2CsSb yield spectrum







Quantity	Sequential deposition	Co-deposition
RMS roughness (nm)	2.5	0.6
ϵ_5 (μm/mm rms)	0.18	0.07
ϵ_{20} (μm/mm rms)	0.36	0.14
ϵ_{100} (μm/mm rms)	0.80	0.31

5 MV/m

20 MV/m

100 MV/m

J. Feng et al., J. Appl. Phys., 121(4) 044904, 2017

20 MV/m

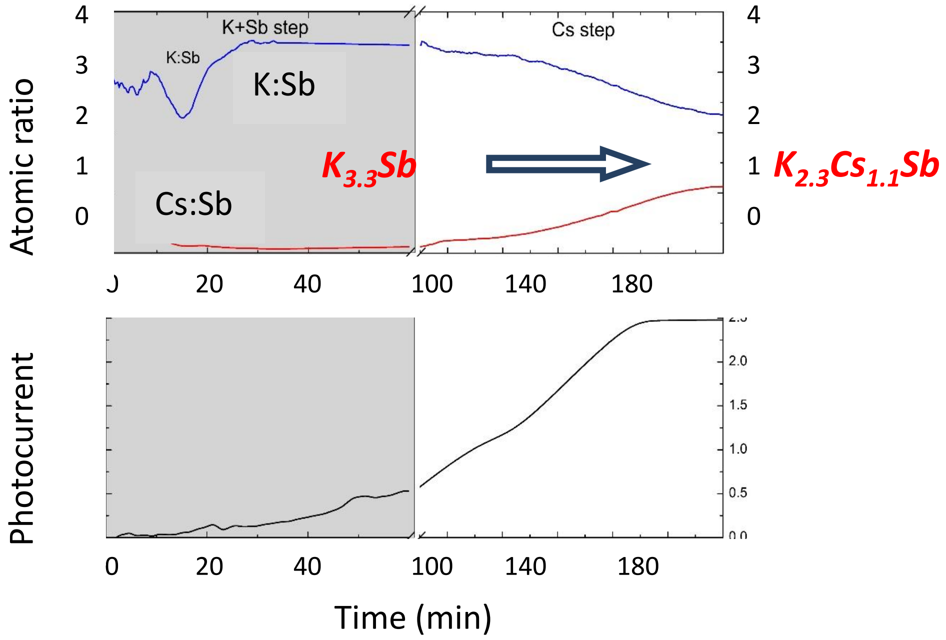
- significant emittance degradation for sequential method
  - no practical degradation with co-deposition

- LN2 threshold emission
  - significant degradation, even with co-deposition
  - we need films smoother than 0.6 nm!!

2-step Co-evaporation

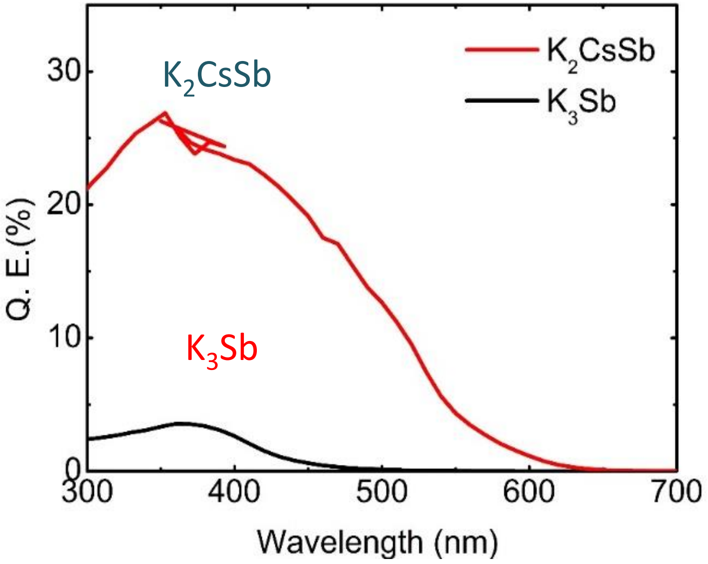
Two-step recipe:

1. K+Sb co-deposition, maximize QE at 380 nm, @ ~120°C
2. Cs deposition on top @ ~100°C until QE (530 nm) maximizes



K:Sb becomes close to 3:1 shortly after K-Sb co-deposition starts

Spectral response:



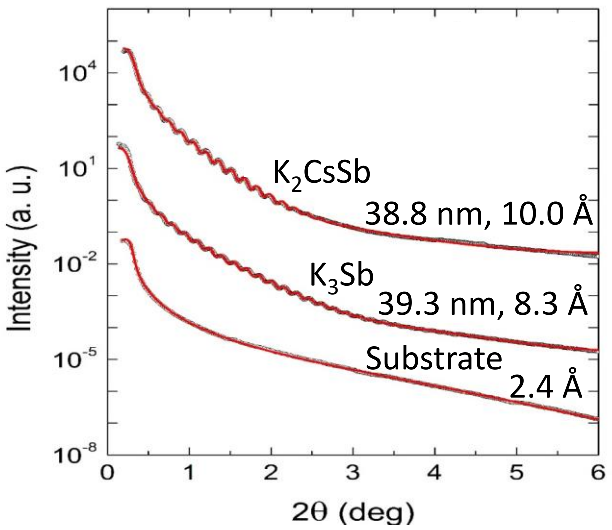
- K_3Sb layer: peak 3.5% at 360 nm;
  0.047% at 530 nm
- After Cs: peak 26% at 360 nm;
  7% at 530 nm

Most of the performance advantages of Ternary co-evaporation, but MUCH easier

2-step Co-evaporation

XRR

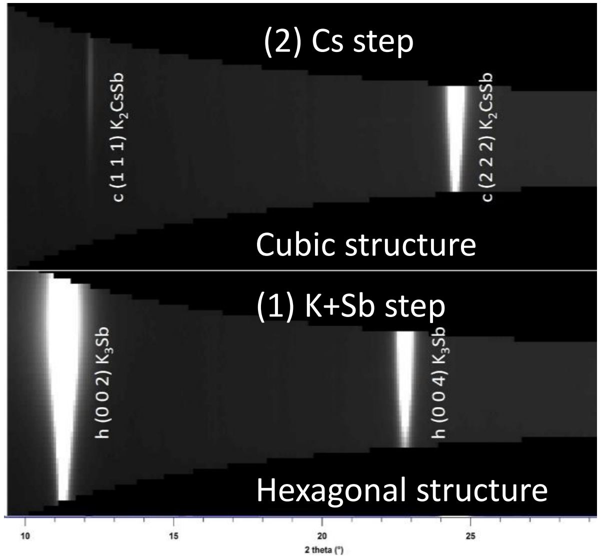
Sub-nm roughness
Similar thickness, roughness from K_3Sb to K_2CsSb



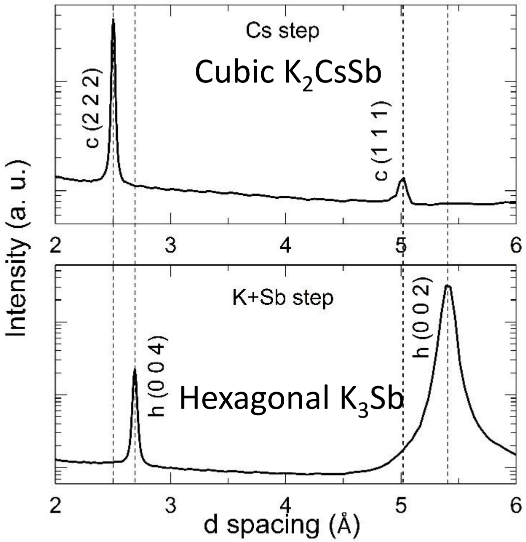
XRD

Full conversion from hexagonal K_3Sb to perfect cubic K_2CsSb
Textured XRD pattern

θ-2θ scan



θ-2θ scan

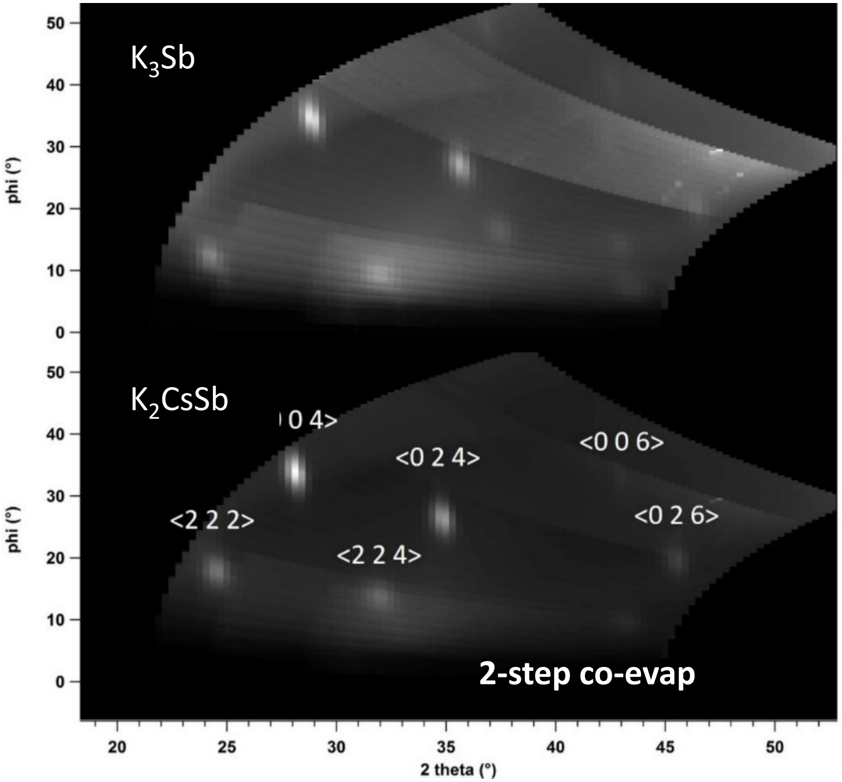


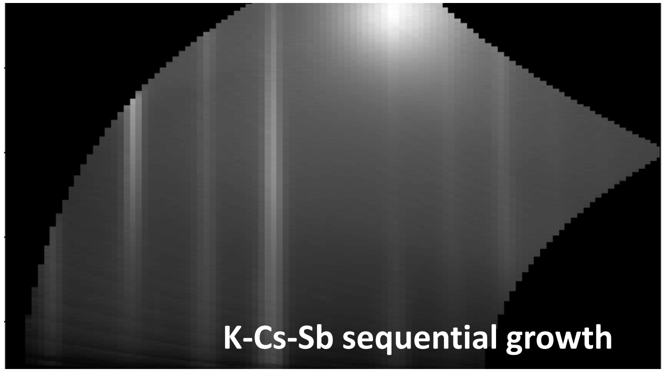
Diffraction arcs – textured film (both on Si (1 0 0) & Si (1 1 1))

Crystal Quality

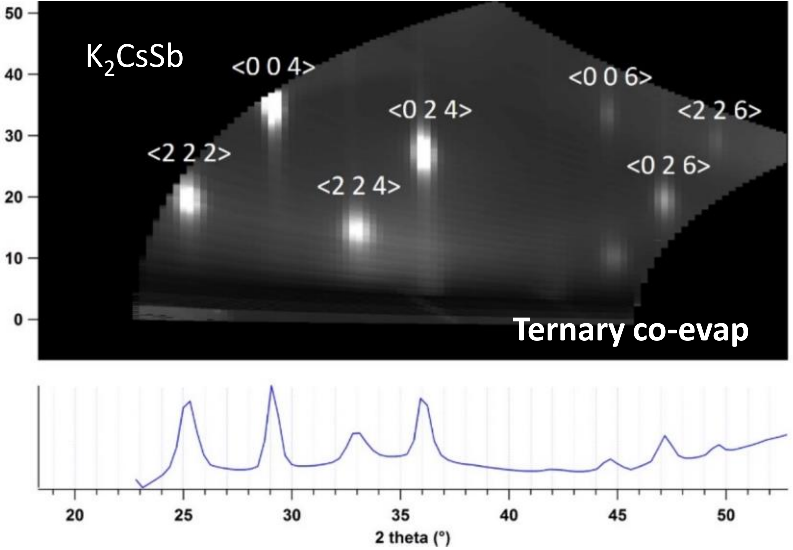
Wide angle X-ray diffraction patterns

Two-step recipe





Ternary co-deposition

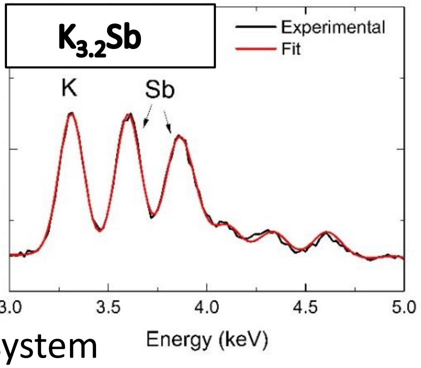


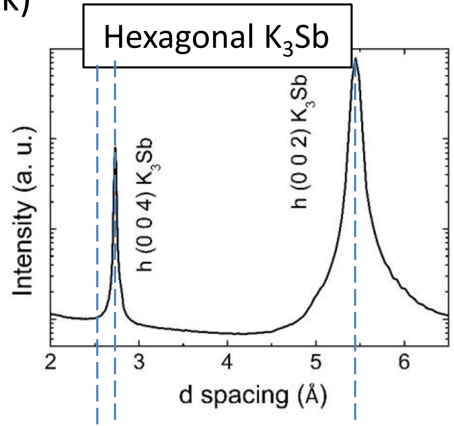
Large Grain, highly textured

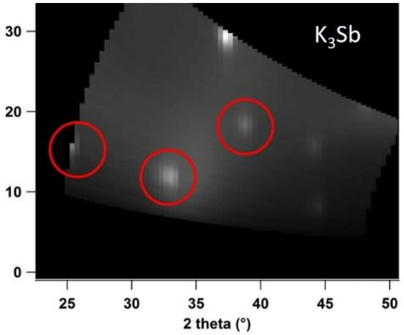
Effusion cells – bilayer photocathode

Controllable stoichiometry, crystal structure from effusion cells – ***Heterojunction fabrication***

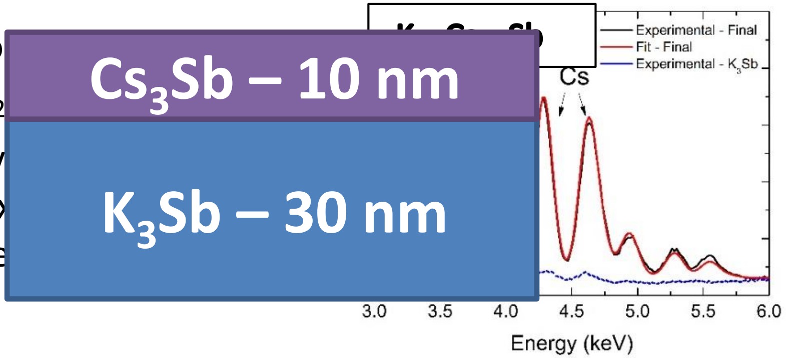
- K_3Sb layer (K-Sb co-dep at 120 °C, ~30 nm thick)
  - Stoichiometry: $K_{3.2}Sb$
  - Crystal structure: Hexagonal; highly textured

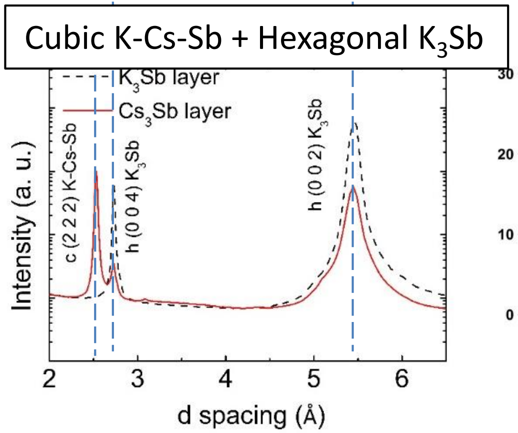


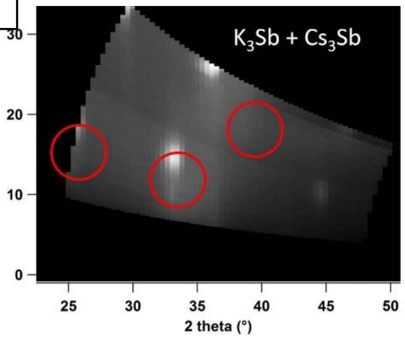




- 5 min exposure to unbaked system
- Cs_3Sb layer (Cs-Sb co-dep at RT, 10 nm thick)
  - Sto
    $K_{2.2}$
  - Cry
    Hex
    coe

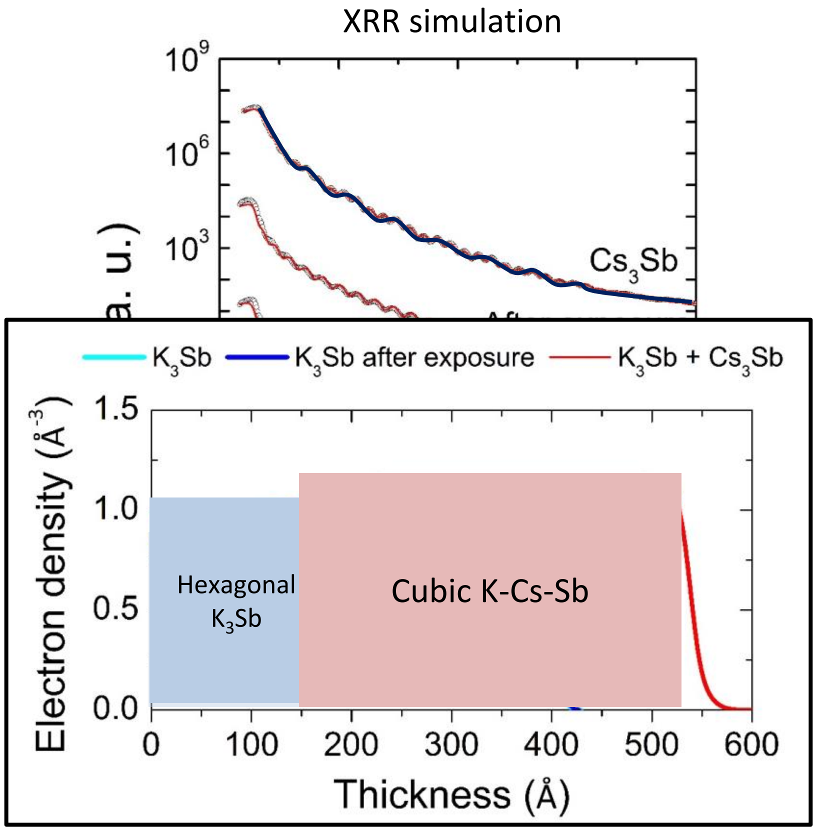






Effusion cells – bilayer photocathode

- Bilayer structure



Different stages during bilayer photocathode fabrication

Stage	Thickness (Å)	Roughness (Å)
After Cs_3Sb	**543** (-7.10, 6.46)	**7.89** (-0.15, 0.21)

- From K_3Sb to K_3Sb/Cs_3Sb:

XRD result: thin K_3Sb at bottom,
thick K-Cs-Sb at top

Final bilayer photocathode

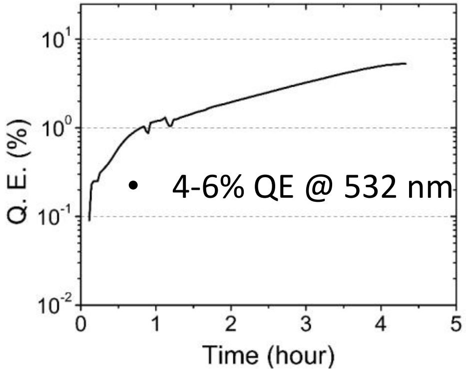
Layer	Thickness (Å)	Roughness (Å)	Electron density (Å^{-3})
K-Cs-Sb	**373** (-2.0, 1.2)	**7.89** (-0.06, 0.08)	**1.16**
Interface	**7.86** (-3.55, 4.20)	**7.10** (-0.52, 1.14)	**1.03**
K_3Sb	**154** (-3.5, 3.9)	**30.3** (-2.3, 1.3)	**0.99**
Substrate	-	2.32	0.72

Not the heterojunction we were trying for… but still a sharp heterojunction

K_2CsSb thermal decomposition

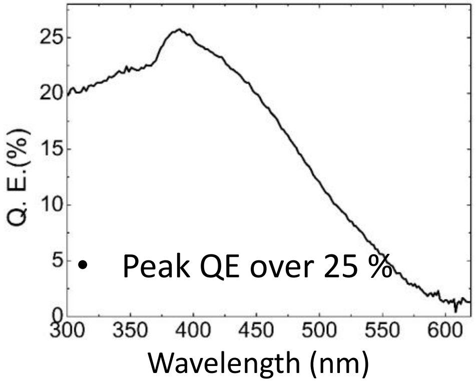
Photocathode growth and lifetime study at Berkeley Lab

Typical QE increase curve during K-Cs-Sb co-dep growth



- 4-6% QE @ 532 nm

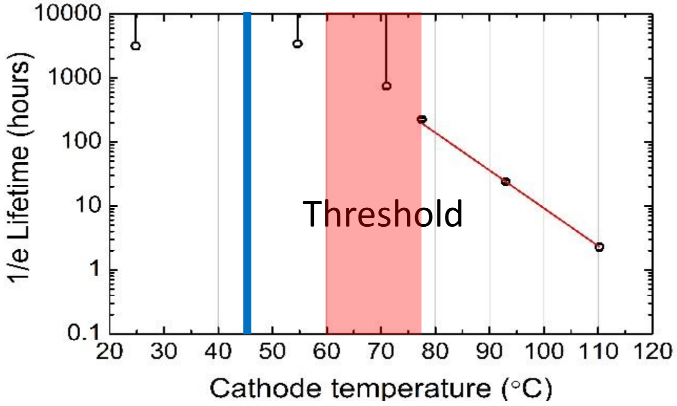
Typical spectral response of K-Cs-Sb photocathode



- Peak QE over 25 %

Lifetime at elevated cathode temperature

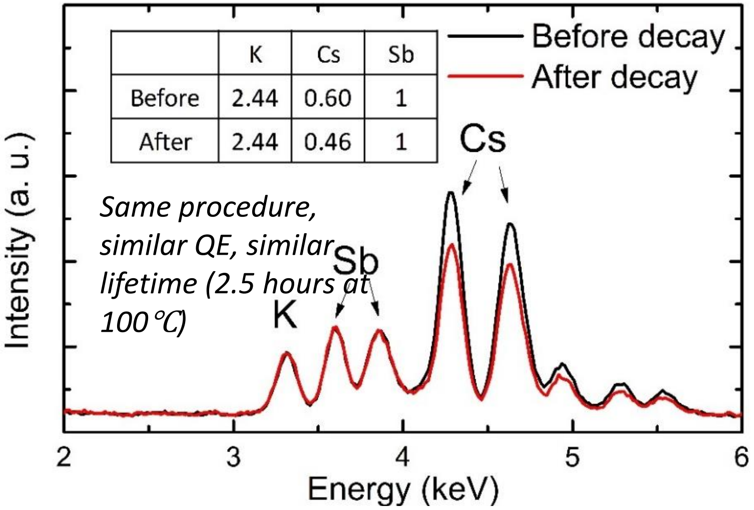
Temperature (°C)	Exponential fit – first term		Exponential fit – second term	
	Decay constant (τ_1)	Amplitude (A_1)	Decay constant (τ_2)	Amplitude (A_2)
RT	3167	1.06	-	-
55	3443	1.08	-	-
71	741	1.05	-	-
77	761.9	0.51	15.7	0.52
93	114.3	0.39	7.63	0.61
110	28.8	0.18	1.65	0.85



K$_2$CsSb thermal decomposition

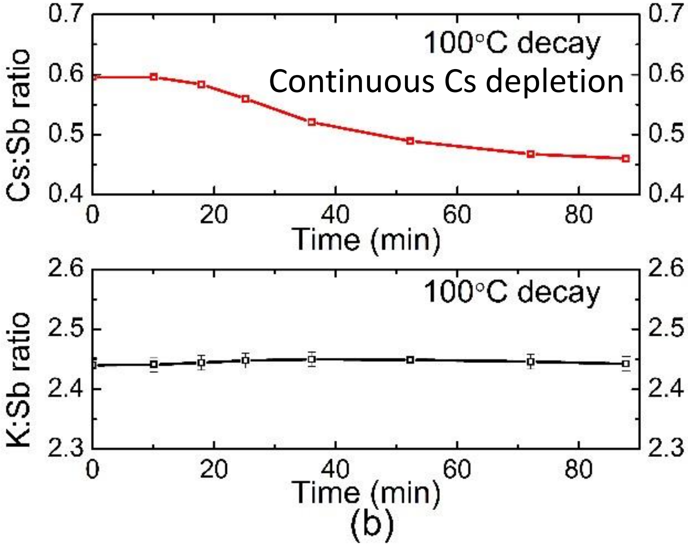
X-ray characterization on co-deposited K-Cs-Sb at CHESS, decayed at 100℃

X-ray fluorescence

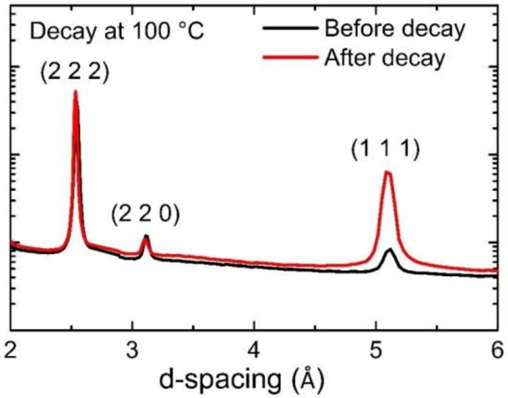


	K	Cs	Sb
Before	2.44	0.60	1
After	2.44	0.46	1

Same procedure, similar QE, similar lifetime (2.5 hours at 100℃)



X-ray diffraction



Peak shift 0.34% lattice constant decrease

A small amount of Cs leaves the lattice

X-ray reflectivity

Layer	Thickness (Å)	Roughness (Å)
After decay	516 (-4.49, 3.81)	13.9 (-0.10, 0.25)
Before decay	541 (-2.76, 4.02)	11.5 (-0.24, 0.63)
Substrate	-	2.35 (-0.01, 0.02)

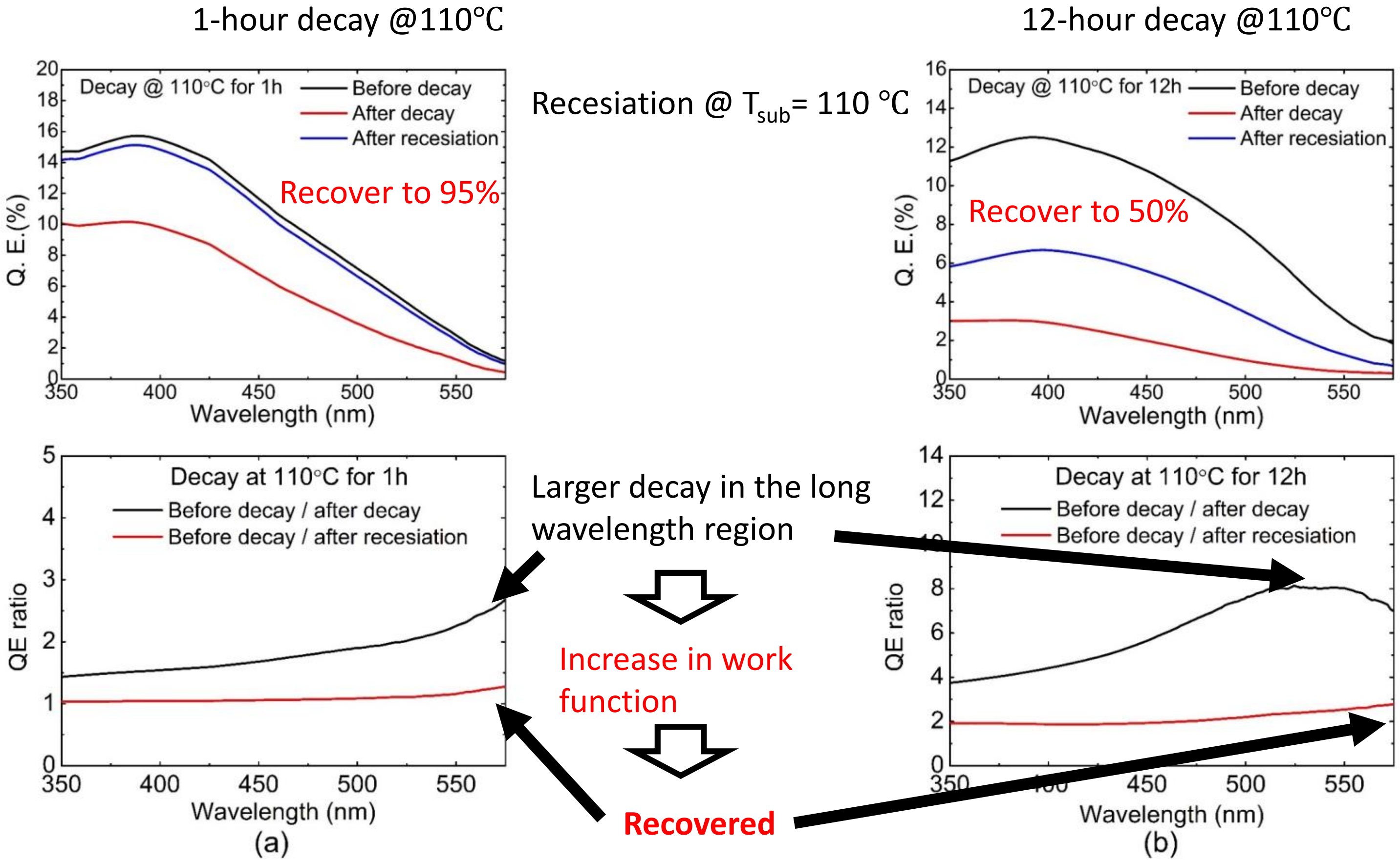
5% thickness decrease

Cs leaves the surface/grain boundaries

Major cause

K_2CsSb thermal decomposition

Spectral response measurement and recesiation at Berkeley Lab



1-hour decay @110℃

12-hour decay @110℃

Recesiation @ T_{sub}= 110 ℃

Recover to 95%

Recover to 50%

Larger decay in the long wavelength region

Increase in work function

Recovered

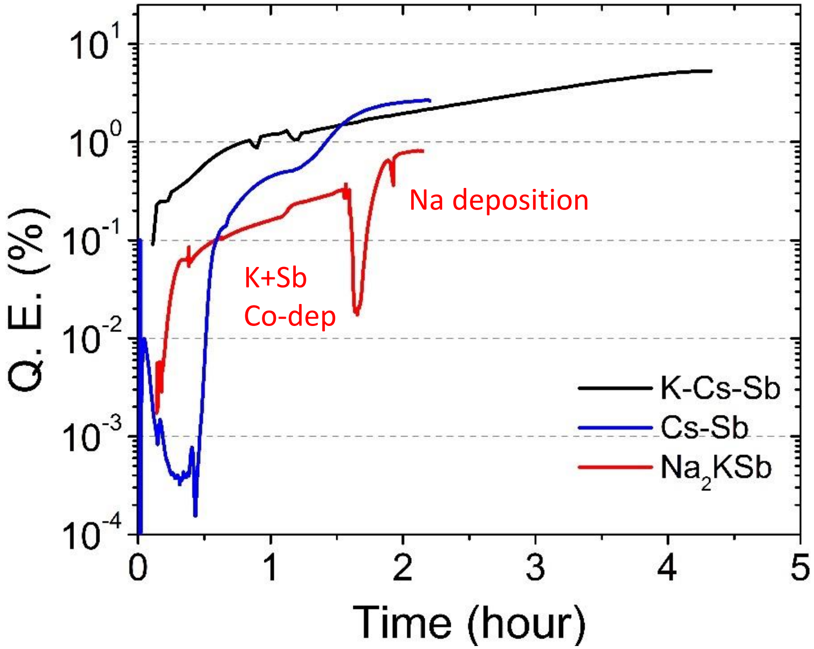
(a)

(b)

Alkali Antimonide thermal decomposition

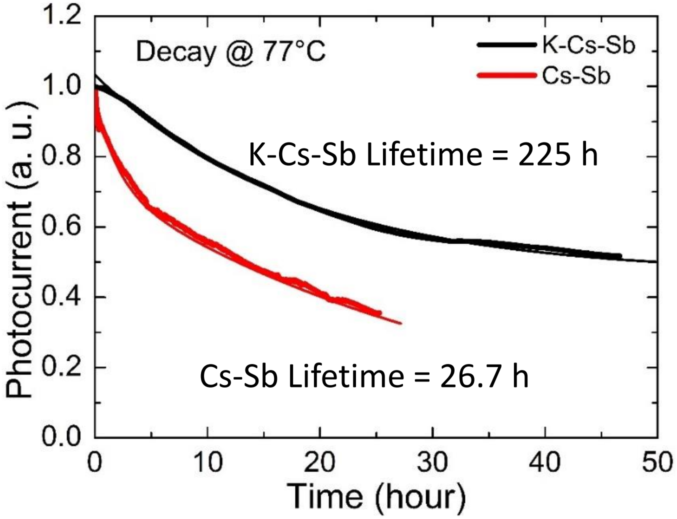
Comparison with other alkali antimonide

Co-deposited Cs-Sb and sequential Na-K-Sb



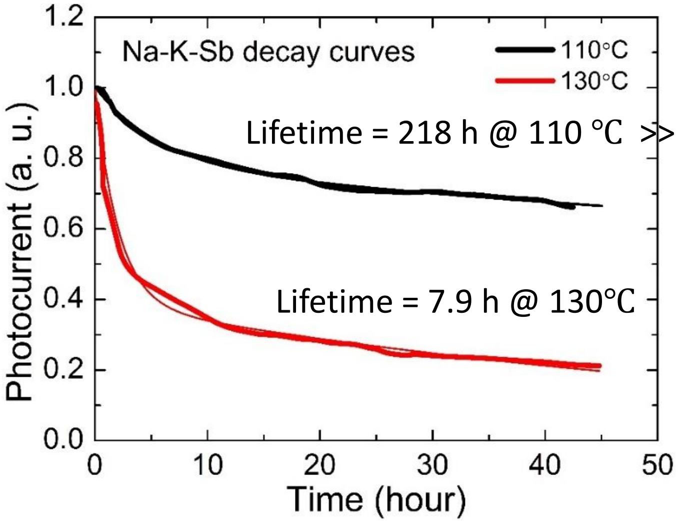
Na deposition

K+Sb Co-dep



K-Cs-Sb Lifetime = 225 h

Cs-Sb Lifetime = 26.7 h



Lifetime = 218 h @ 110 °C >> K-Cs-Sb

Lifetime = 7.9 h @ 130°C

Robustness (lifetime at higher T_{sample}):

Na-K-Sb > K-Cs-Sb > Cs-Sb

Alkali Antimonide Cathodes

What we've learned

- We now have a tool which is capable of optimizing growth parameters for figures of merit other than Quantum Efficiency, and to specifically target material properties.
- We understand the formation chemistry of these materials, and why traditional deposition results in rough cathodes
- RMS roughness down almost 2 orders of magnitude, to ~atomic scale
- Avoiding crystalline Sb helps, as does co-evaporating alkali
- Sputter deposition is good – easy to do, covers large area, almost atomically smooth even for thick films – but alkali poor
- Real time XRF feedback provides option of ternary coevaporation, producing best cathode
- Can now consider heterojunctions and doping of alkali antimonides (following a similar development path to the III-V materials)
- Can consider ultra thin (under 10 nm) cathodes to improve response time
- Conformal coating of structured surfaces possible

Thanks for your attention!

- Thanks to K. Attenkofer, S. Schubert, M. Ruiz Oses, J. Xie, J. Kuhn, M. Schmeißer, J. Wang, H. Padmore, E. M. Muller, M. Gaowei, J. Walsh, T. Vecchione, J. Sinsheimer, Z. Ding
- DOE Office of Science – Basic Energy Science and Nuclear Physics

Stony Brook University

Berkeley Lab

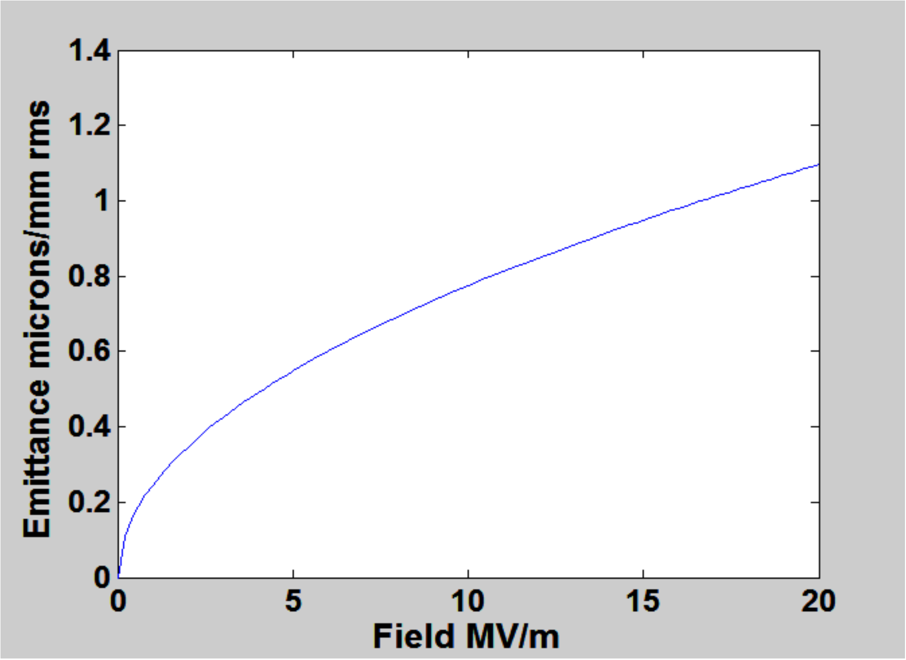
Brookhaven National Laboratory

Office of Science
U.S. Department of Energy

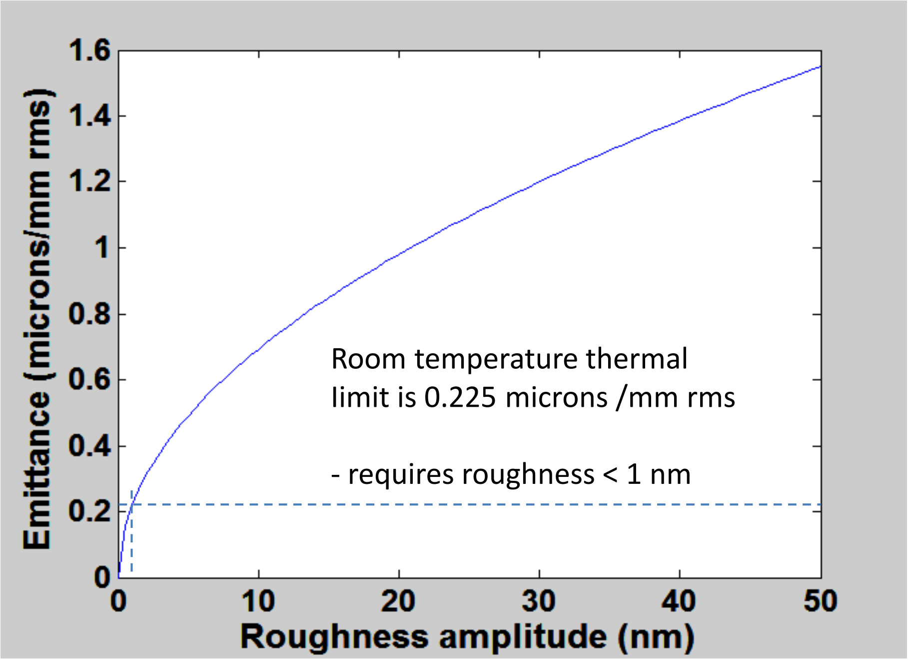
Roughness and Emittance

$$\varepsilon_{rough} = \sigma_{x,y}\sqrt{\frac{\pi^2 a^2}{2m_0 c^2 \lambda} Ee}$$

D. Xiang et al. Proceedings of PAC07, Albuquerque, New Mexico, USA



Field dependent emittance growth: 20 nm amplitude, 80 nm period



Room temperature thermal limit is 0.225 microns /mm rms

- requires roughness < 1 nm

Emittance growth at 20 MV/m, period 4 x amplitude.

Calculations by H. Padmore