Photocathodes – A Materials Science Perspective

Applying the tools of modern material science to cathode design

The BNL-LANL cathode collaboration

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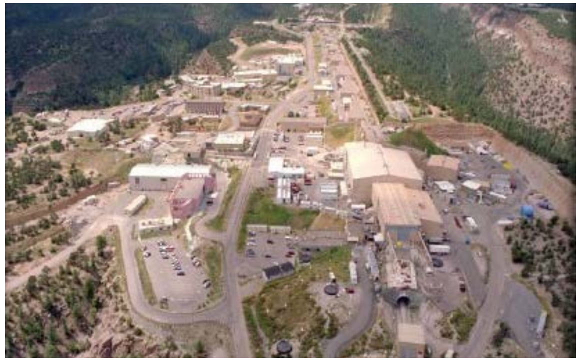
IVESC 2020

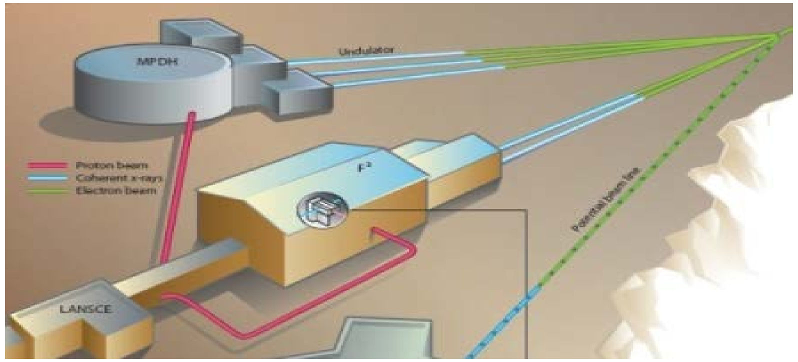
Talk Outline

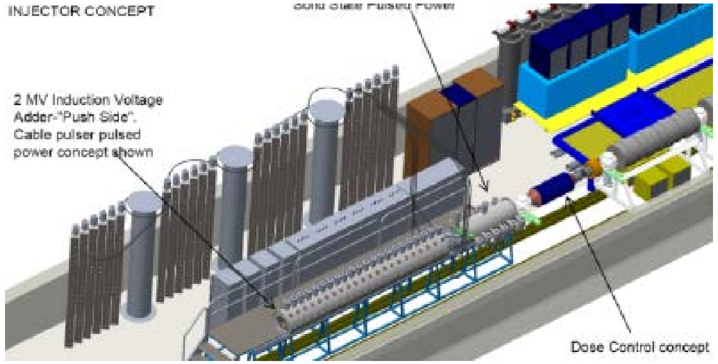
- **Introduction**
- **Motivation for continued progress**
- **Overview of the approach**
  - Improved synthesis techniques
  - *In operando* x-ray analysis
  - Reduction to practice
  - Target compatibility with working injectors
  - Extend photo-physics capability to other applications
- **Examples of recent results**
- **Summary**

Why does Los Alamos care about electron source design?

- **Accelerator R&D is crucial for delivering LANL mission AND preparing for tomorrow:**
  - LANL anticipates an advanced dynamic mesoscale material science capability and advanced cathodes are an enabling technology
  - Closes technology gaps to enable accelerator upgrades to other LANL accelerators
  - Important for recruitment/retention of leaders in the accelerator field
  - National / international stature translates to sponsor confidence
- **Investments in electron source design are consistent with being both a <u>material science laboratory as well as NNSA's primary accelerator capability</u>**







Alignment between BNL and LANL affords new opportunities, leveraging of programs, long-term sustainability, and equipping of future leaders

N. Moody; J. Smedley; K. Jensen; H. Yamaguchi; F. Liu; J. DeFazio; M. Gaowei; C.W. Narvaez Villarrubia; J. Xie; J. Sinsheimer; D. Strom; V. Pavlenko; A. Mohite; E. Batista; S. Lambrakos; A. Shabaev; M. Hoffbauer; J. Pietryga; I. Robel; S. Schubert; J. Wong; J. Feng; S. Karkare; H. Padmore; J. Power; M. Conde; E. Muller; Z. Ding; K. Attenkofer; X. Liang; J. Xie; and J. Kühn

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APPLIED CATHODE ENHANCEMENT AND ROBUSTNESS TECHNOLOGIES

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Ongoing Goal: understand and exploit correlations between material science and cathode performance to gain control parameters for designer cathodes

Material Science Design Choices	Material Science Observables	Electron Source Design Choices	Electron Source Observables
• Substrate choice • Substrate orientation • Synthesis methods • Growth rate • Duration of growth • Substrate temperature • Coating composition • Coating thickness • Surface termination	• Real-time stoichiometry • Real-time thickness • Roughness • Texturing • Grain boundaries • Phase purity • Heterostructure • Reactivity • Photoconductivity • Optical transmission	• Applied field gradient • Drive laser wavelength • Laser time / spatial structure • Ambient environment (gases, etc.) • Operating temperature	• Quantum efficiency • MTE • Response time • Dark current • Lifetime • “Quality” parameter or cost function

Linked by physics models and x-ray tools such as XRR, XRF, XRD, XPS

Where are the frontier applications in photoemission sources?

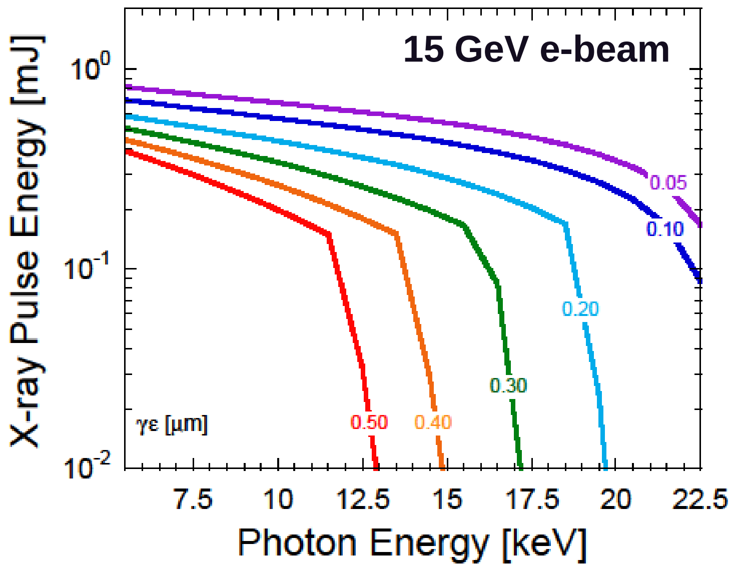
- **XFELs (LCLS-II, MaRIE-class)**
  - moderate currents (still under 1 mA);
  - emittance improvement is a limiting/enabling technology (ideally ~0.1 µm)
  - the electron source will determine the beam properties

- **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)

- **Electron cooling of ion machines**
  - Requires high current with long operational life, other requirements are modest (~50 mA with 5µm emittance)

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

Emittance leverage for XFELs: Electron source sets ultimate limits on achievable electron beam quality, which sets ultimate limits on photon beam



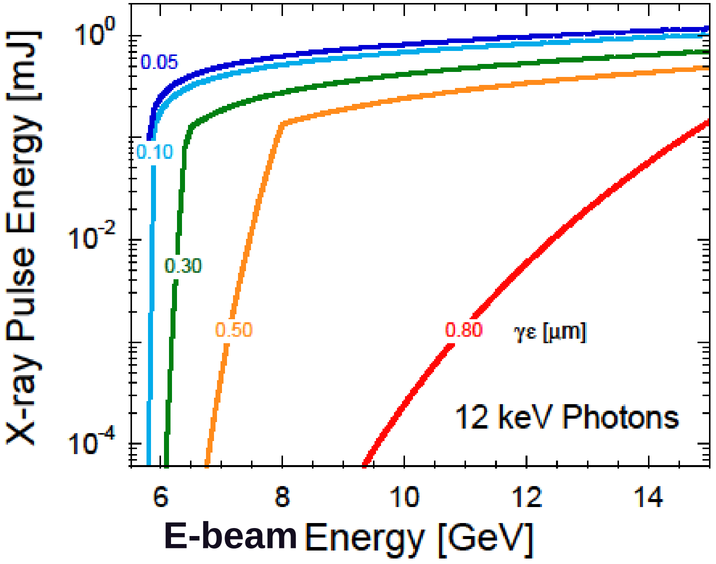


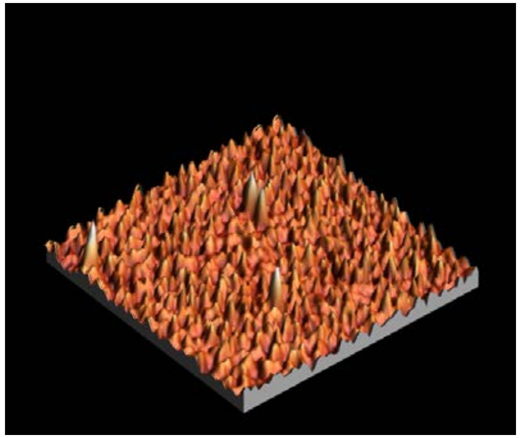
TABLE II. LCLS-II/HXR Case Study Parameters

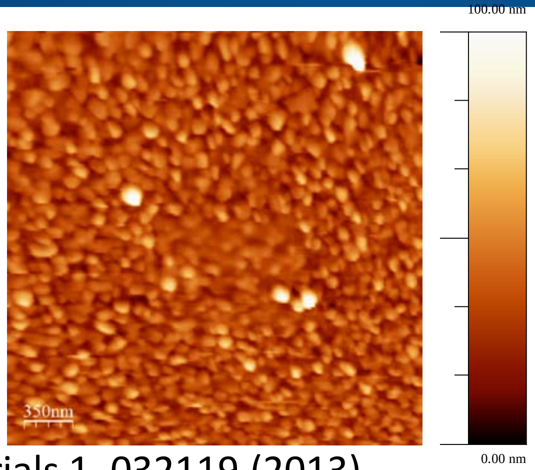
Parameter	Definition	Value
E_b	Beam Energy	15 GeV
σ_η	Energy Spread	1.5 MeV
L_u	Undulator Length	140m
λ_u	Undulator Period	26mm
I_{peak}	Peak Current	3.5 kA
β	Mean Beta	30 m
Q_b	Bunch Charge	100 pC

- ***Photocathode upgrade presents a low-cost investment for improved performance of existing machines***
- ***Emittance suppression at the cathode enables machine designs with lower emittance budget***

Moody, N.A., et al., *Perspectives on Designer Photocathodes for X-ray Free-Electron Lasers: Influencing Emission Properties with Heterostructures and Nanoengineered Electronic States.* Physical Review Applied, 2018. **10**(4): p. 047002.

Traditional Sequentially Grown K_2CsSb – High QE but Very Rough

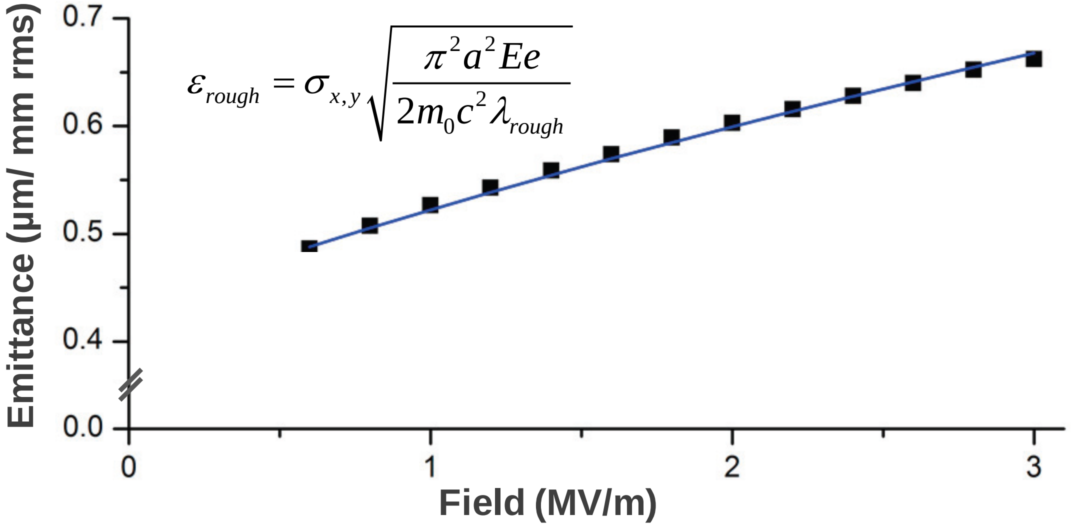




S. Schubert et al., APL Materials 1, 032119 (2013)

25 nm roughness,
100 nm spatial period

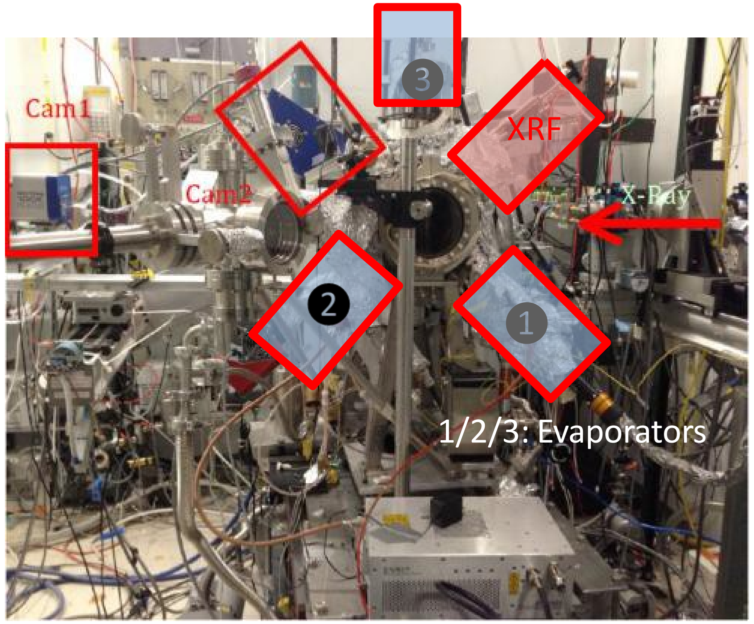
Emittance vs field measured with Momentatron, 532 nm light



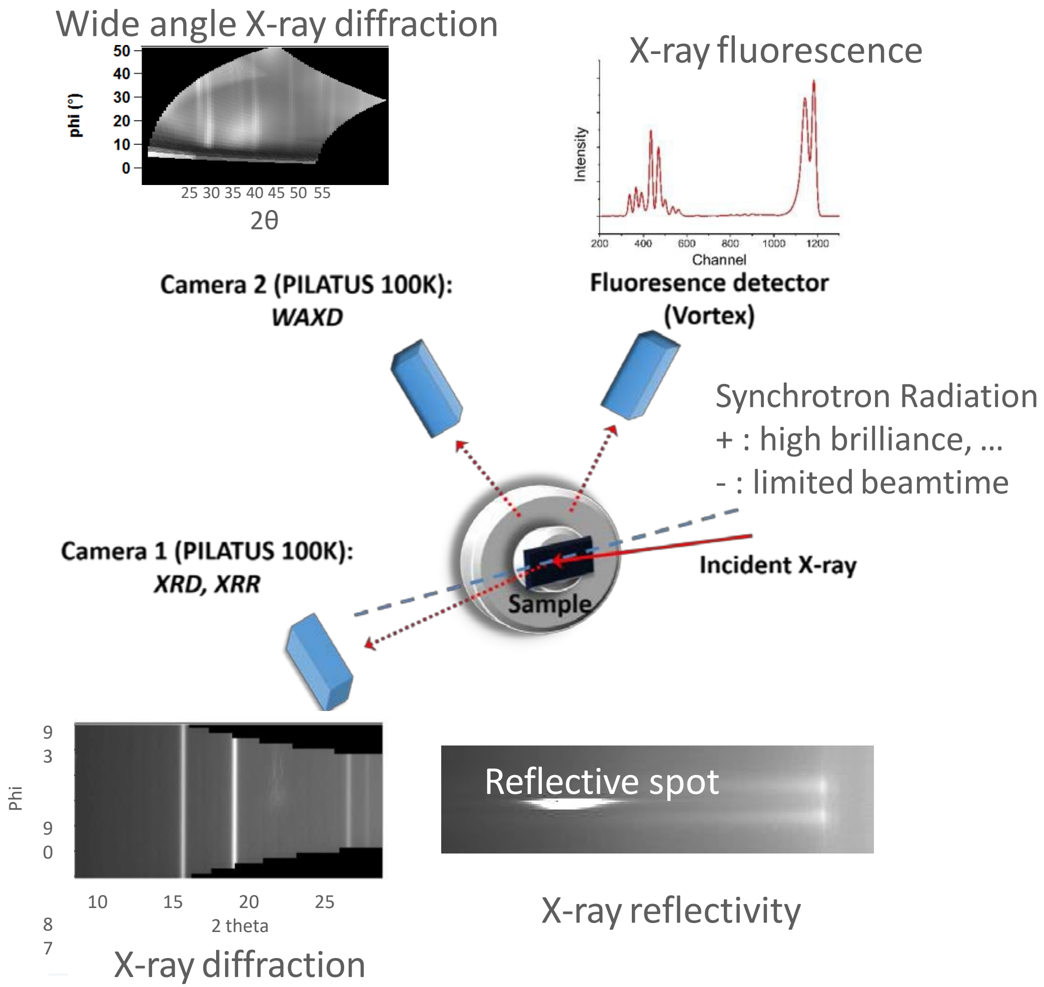
T. Vecchione, et al, Proc. of IPAC12, 655 (2012)

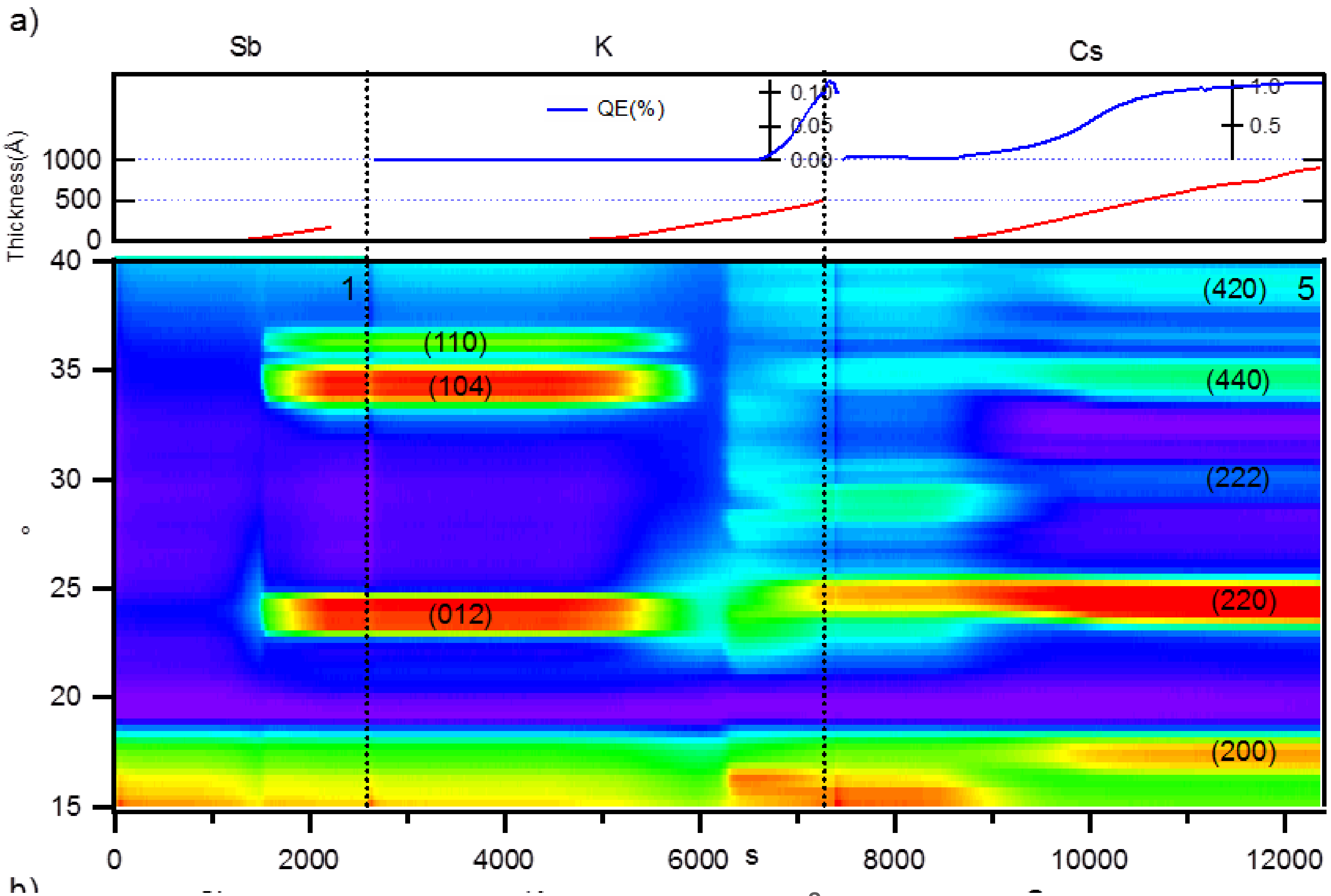
In operando analysis during growth
(setup at NSLS/X21 & CHESS G3 & NSLS-II/ISR)

- Growth and characterization system



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





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

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

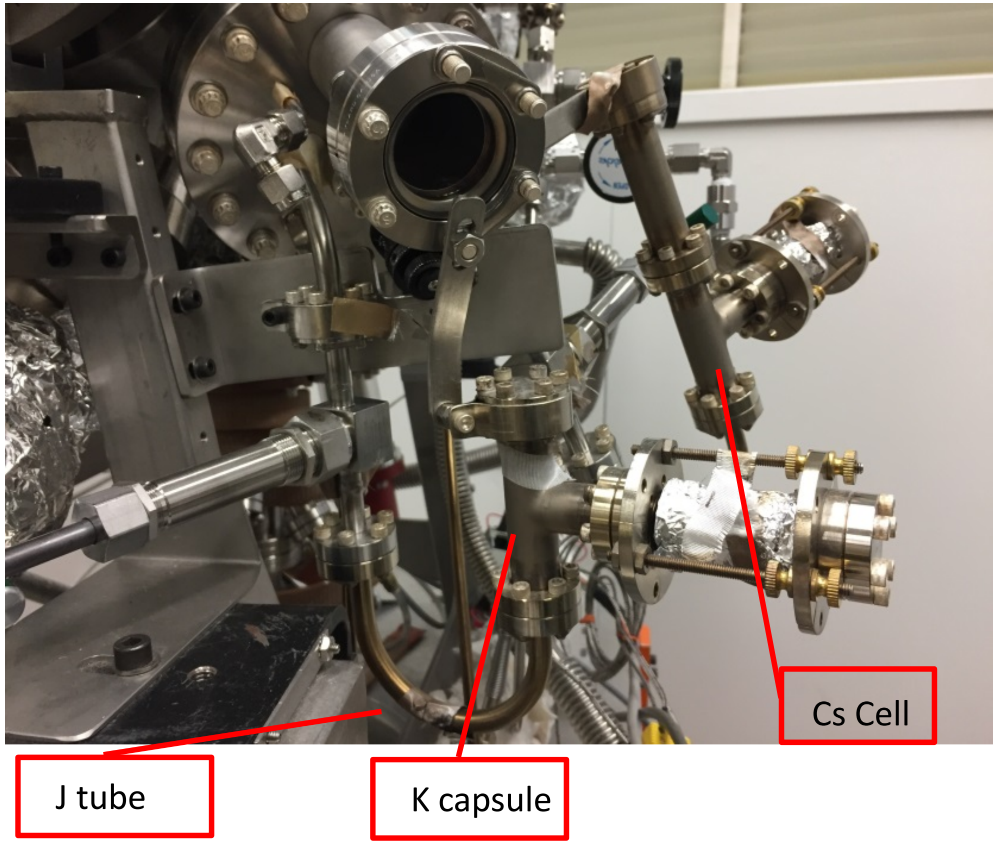
QE increase corresponds with K_xSb crystallization

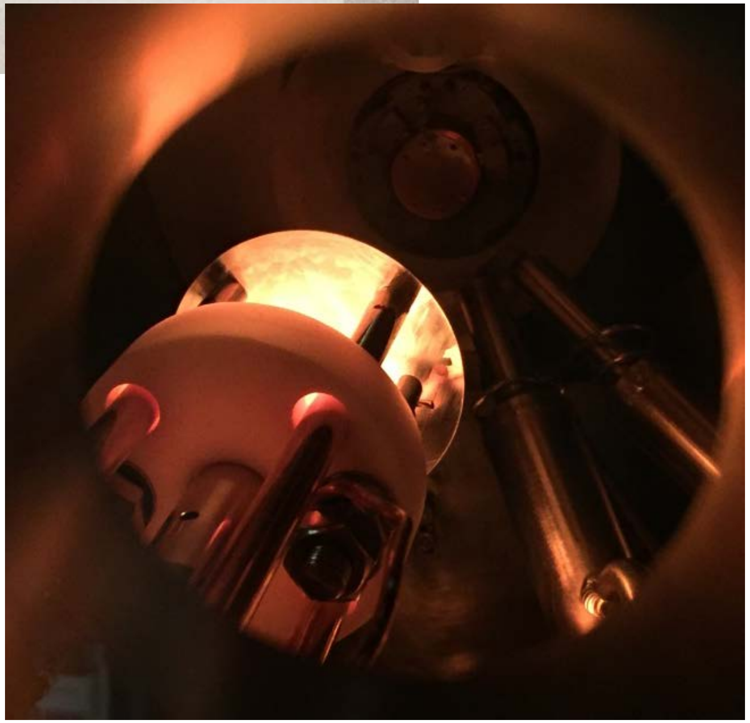
Cs increases lattice constant and reduces defects

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

Ternary Co-evaporation

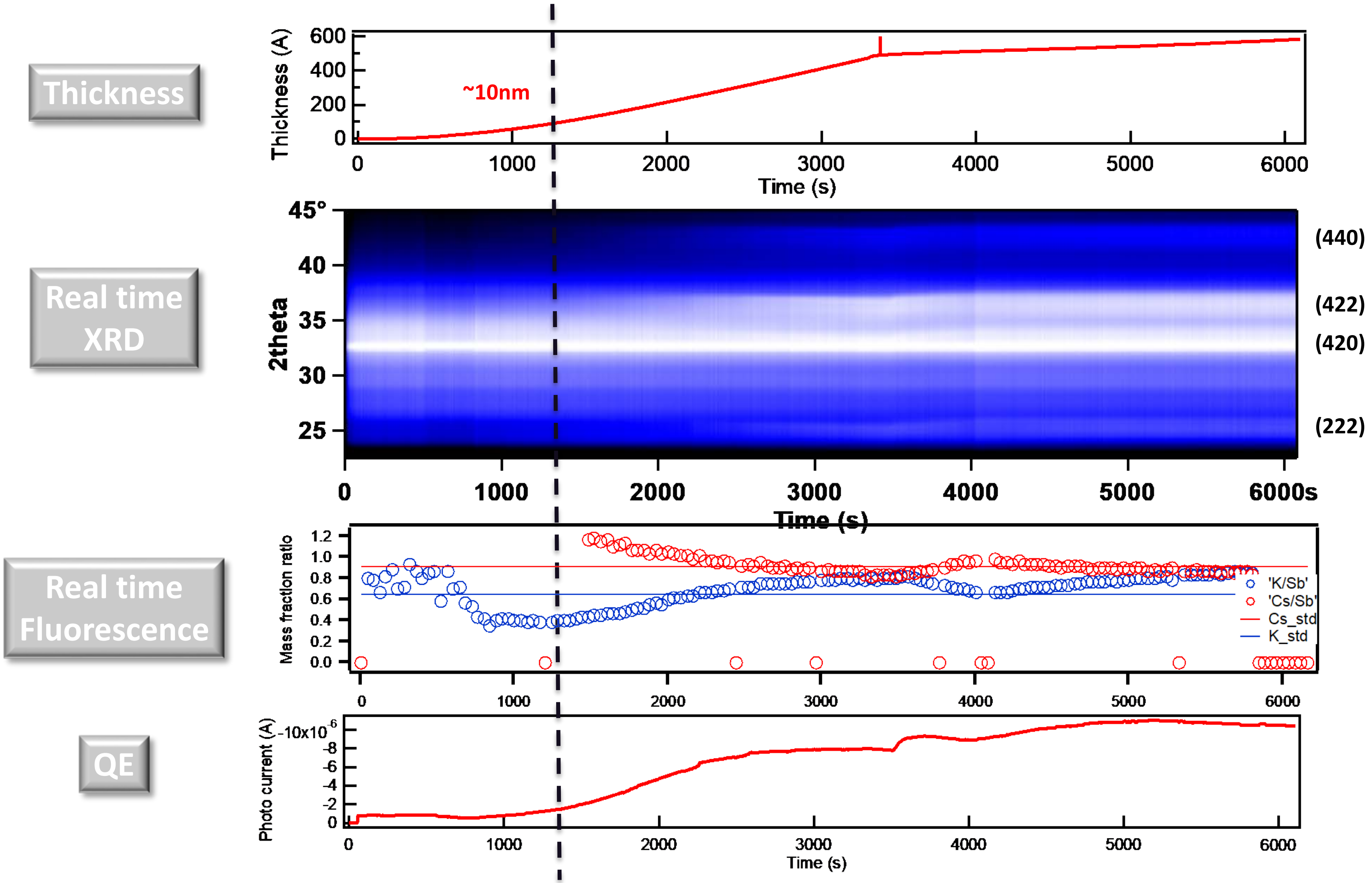
Simultaneously evaporate from Sb evaporator and K,Cs effusion cells





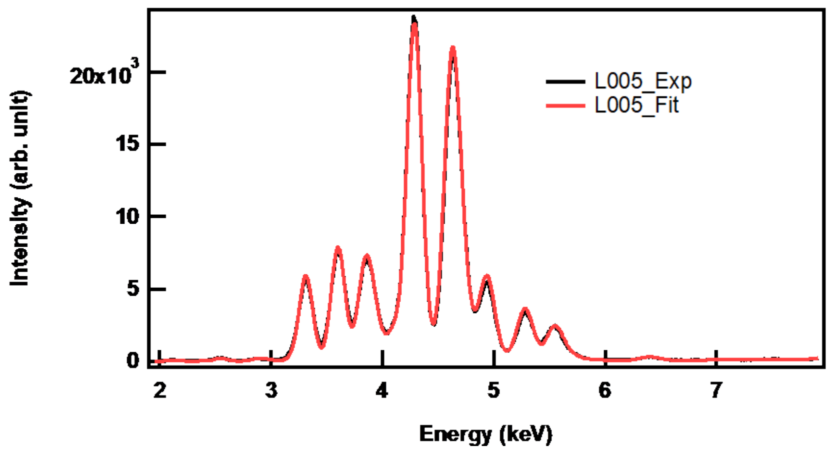
Growth rate are controlled by J tube temperature, valve and shutter

Stoichiometry controlled by real time XRF



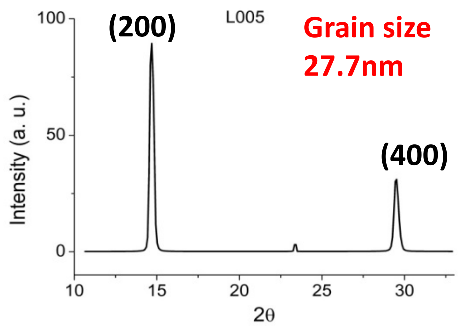
Thickness
Real time XRD
Real time Fluorescence
QE
Thickness (A)
~10nm
Time (s)
2theta
(440)
(422)
(420)
(222)
6000s
Time (s)
Mass fraction ratio
'K/Sb'
'Cs/Sb'
Cs_std
K_std
Photo current (A)
-10x10-6
Time (s)

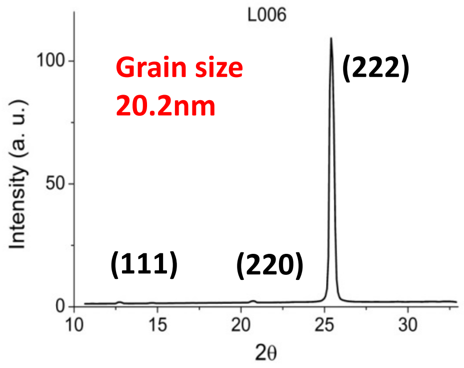
Stoichiometry & Structural Analysis



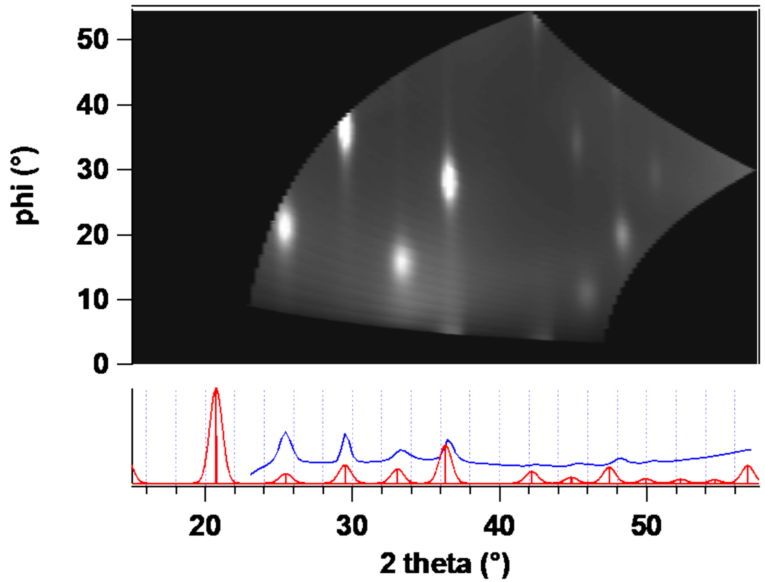
	K	Sb	Cs
L004 Si	2.50	1.00	1.16
L005 Si	2.37	1.00	0.91
L006 Si	2.21	1.00	0.95
L011 Si	2.07	1.00	0.94
L012 MgO	1.98	1.00	0.88

Good K/Cs/Sb ratio!





Camera 1



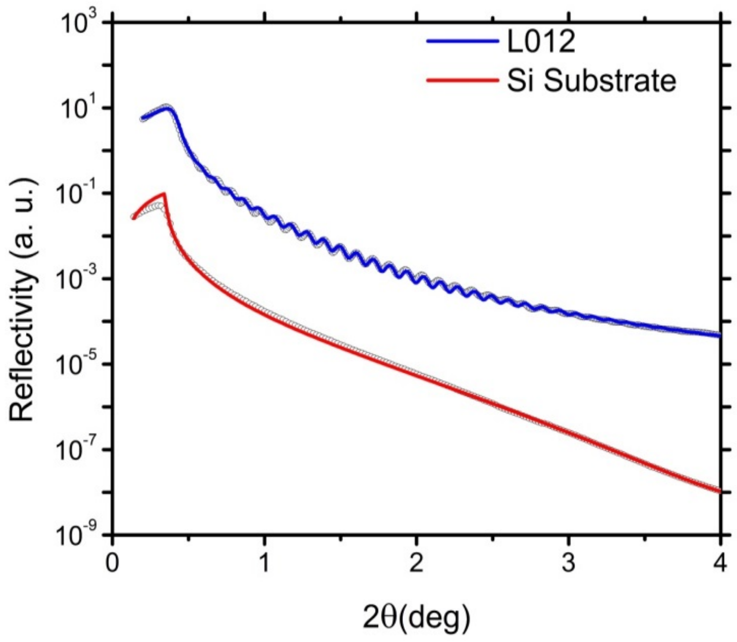
Highly textured K_2CsSb phase!

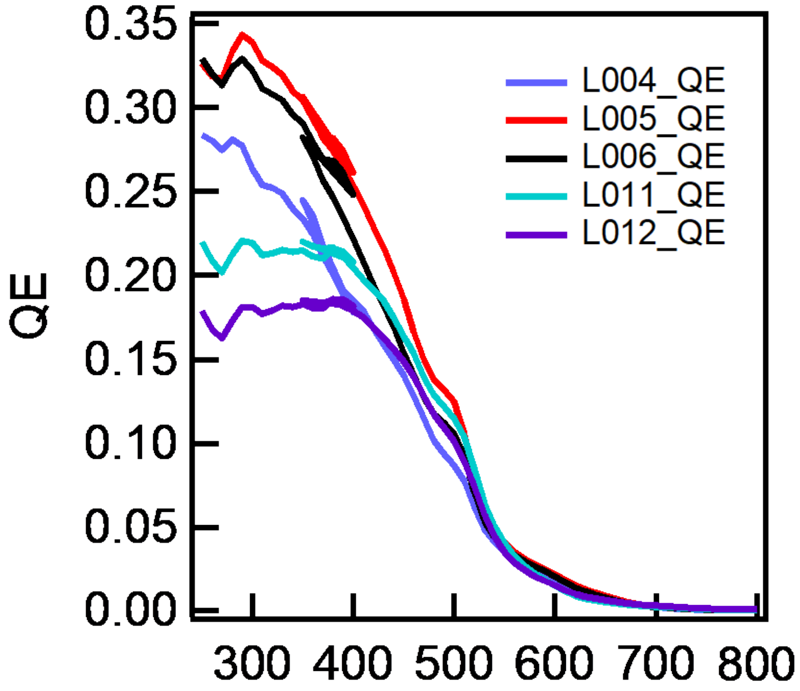
Camera 2

mm size lateral grains

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

Stoichiometry & Structural Analysis





	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

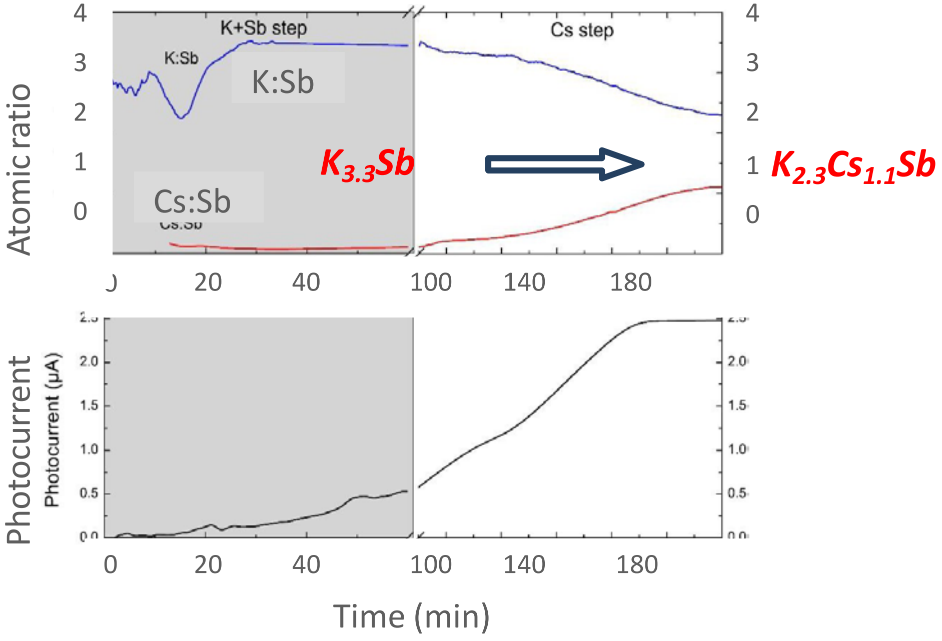
Simultaneous evaporation of all constituents results in no crystal phase transformation

Smooth, reproducible and **ultra-high QE**. Highly Crystalline!

2-step Co-evaporation

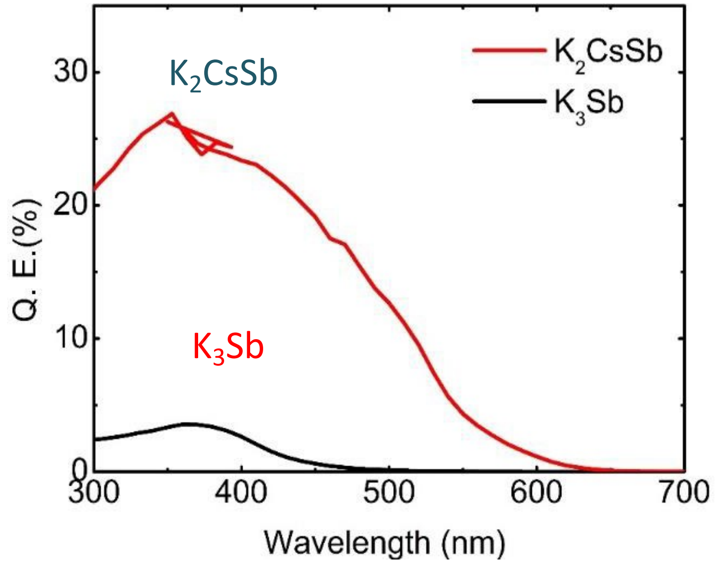
Two-step recipe:

1. K+Sb co-deposition, maximize QE at 380 nm, @ ~120℃
2. Cs deposition on top @ ~100℃ 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

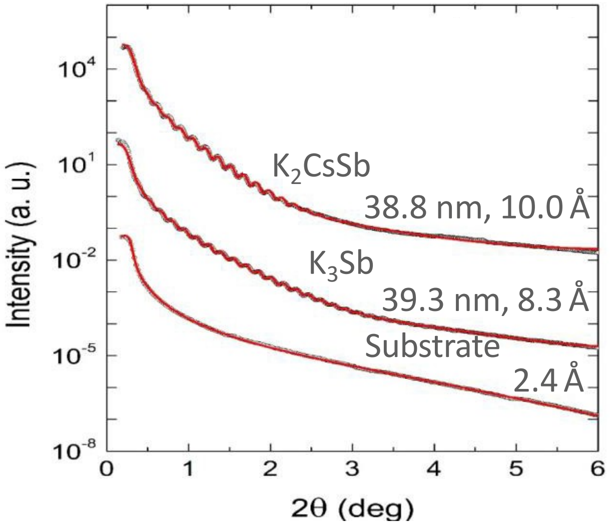
Most of the performance advantages of Ternary co-evaporation, but MUCH easier

2-step Co-evaporation

XRR

Sub-nm roughness

Similar thickness, roughness from K_3Sb to K_2CsSb

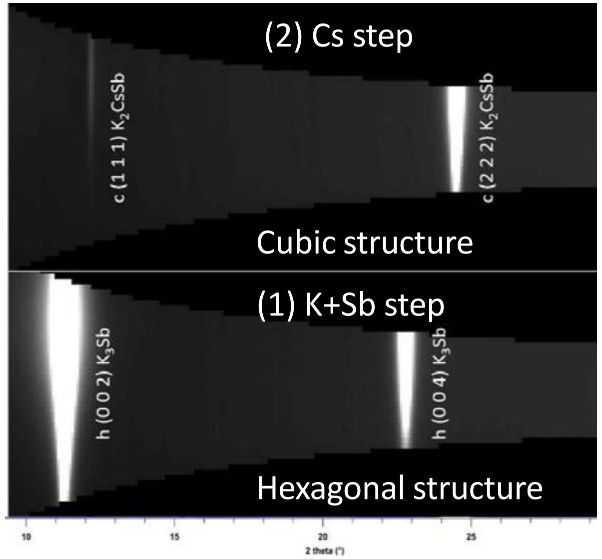


XRD

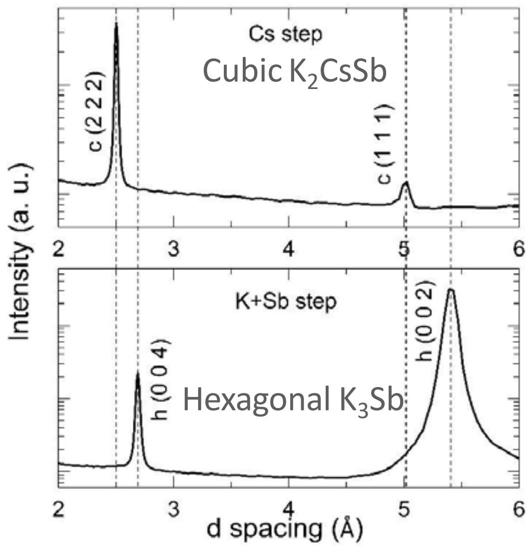
Full conversion from hexagonal K_3Sb to perfect cubic K_2CsSb

Textured XRD pattern

θ-2θ scan

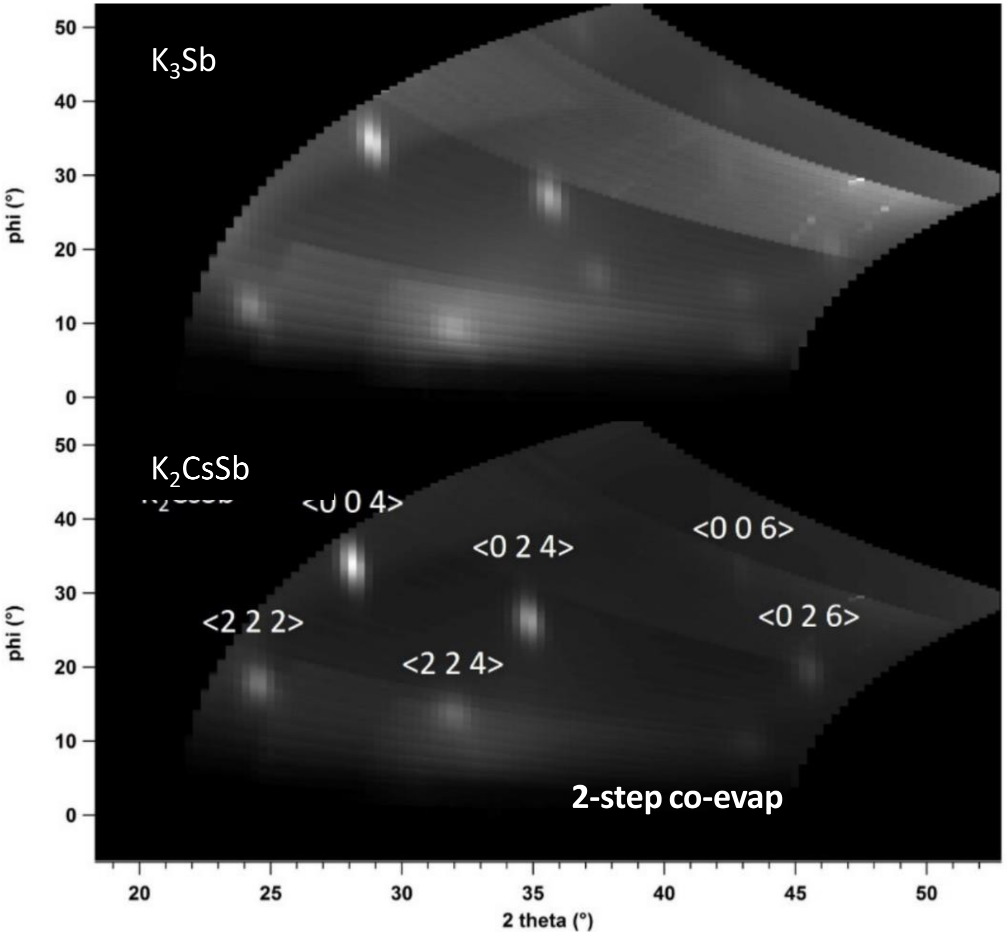


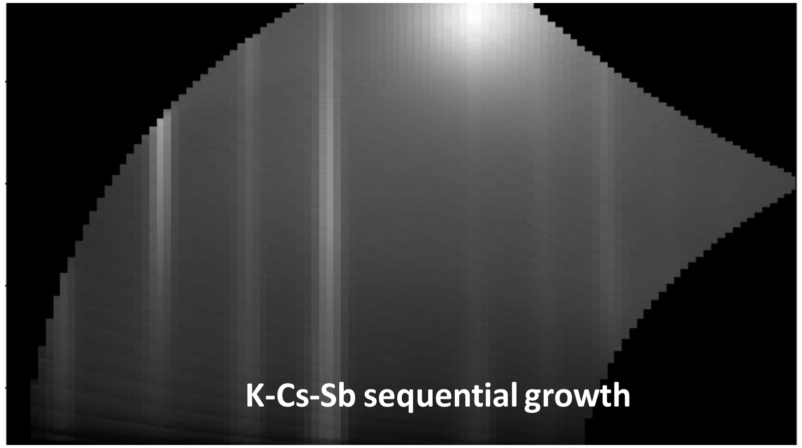
θ-2θ scan

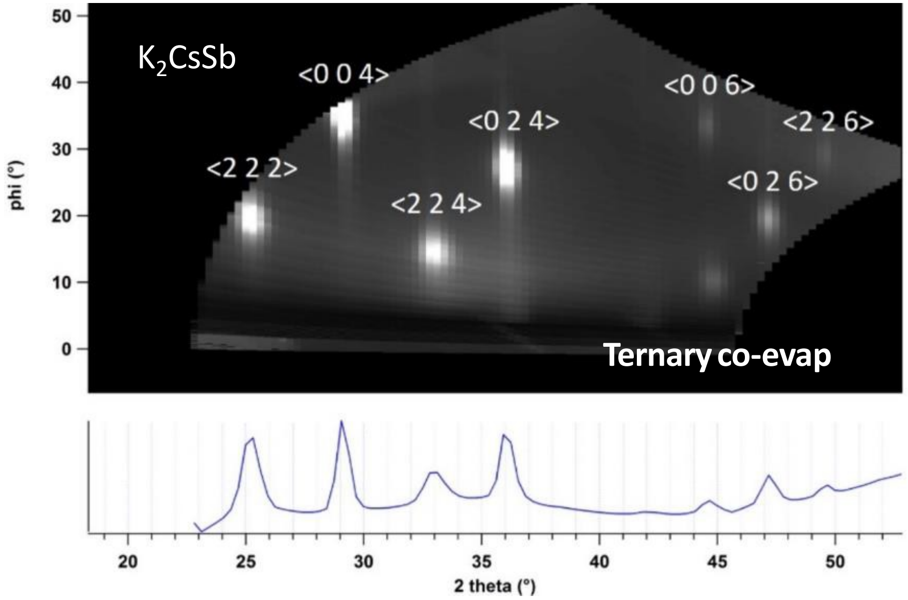


Diffraction arcs – textured film (both on Si (1 0 0) & Si (1 1 1))

Crystal Quality – XRD comparison

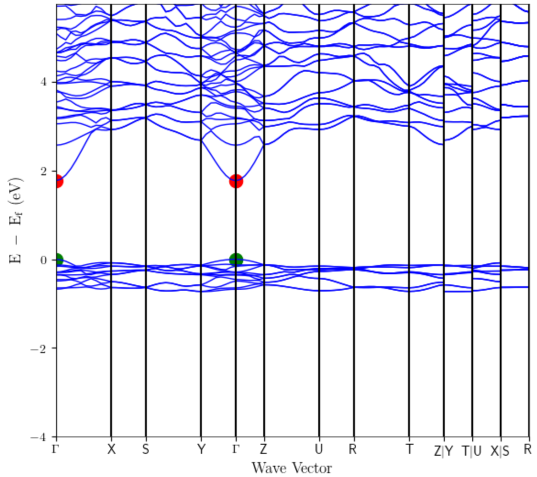




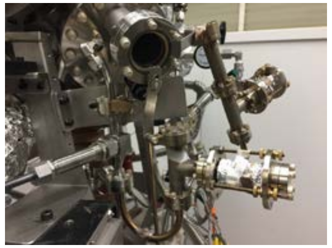


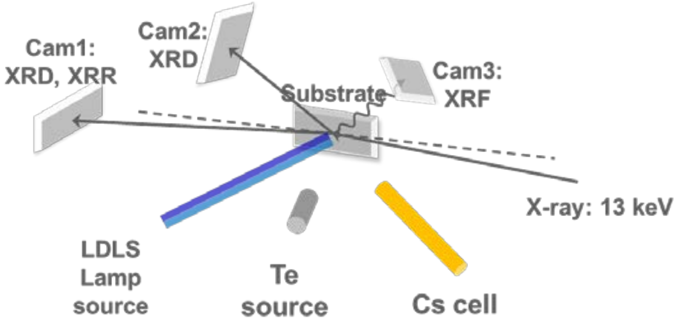
Large Grain, highly textured

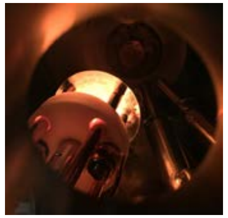
Example of success in one study being applied to adjacent problem: studies of K_2CsSb enabled growth of Cs2Te

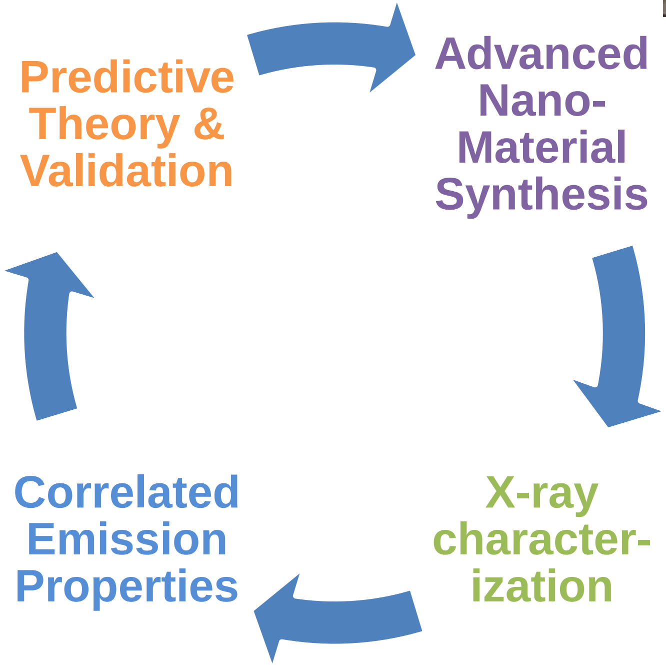


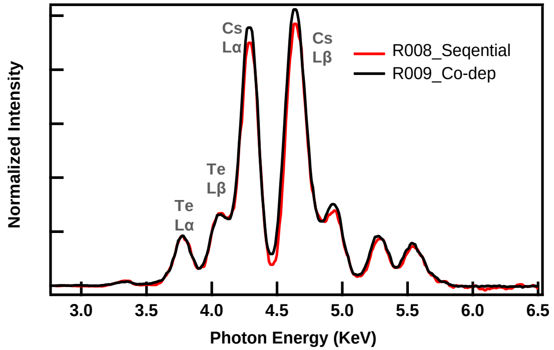
HKL	Theory_d spacing	Exp_d spacing
222 Cs_2Te	2.307	2.315
111 Cs_2Te	4.613	4.615

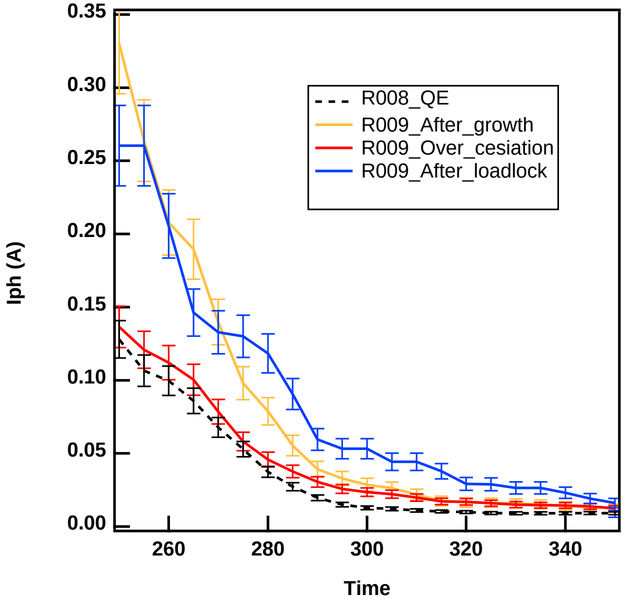




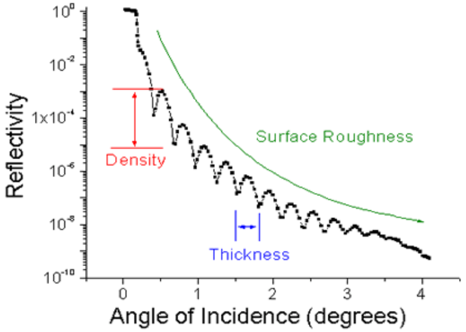


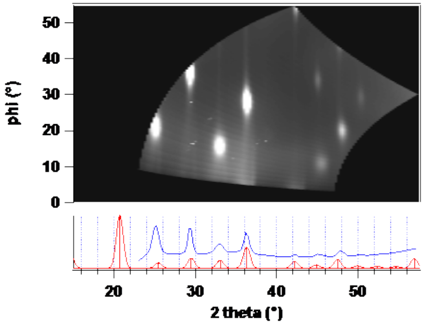






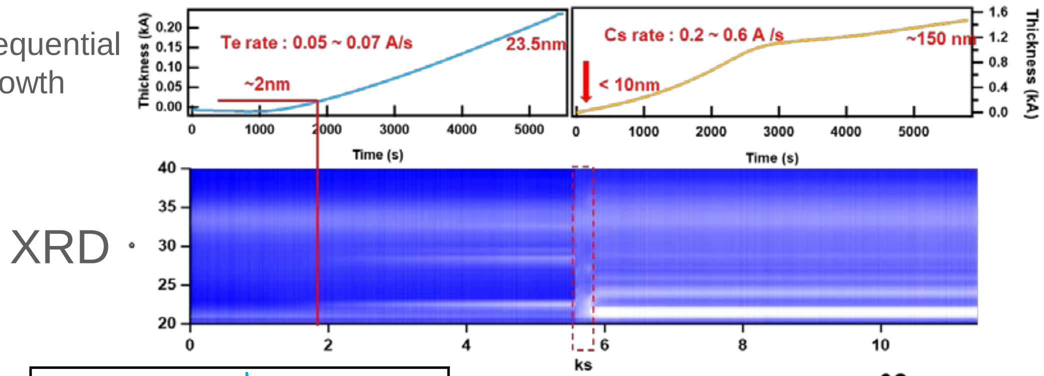
Next step: transfer to procedure not requiring synchrotron light source

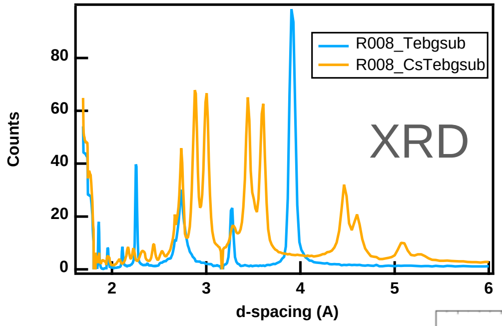


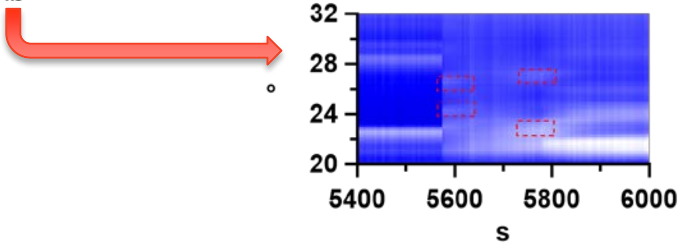


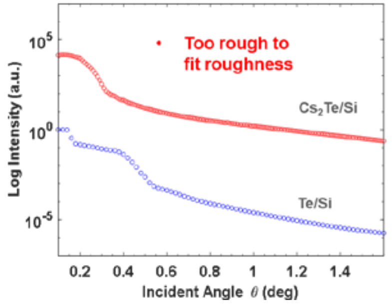
Cs-Te Results (presented by Mengjia Gaowei at P3-2018) show the efficacy of real-time characterization: co-deposition gives smooth single phase

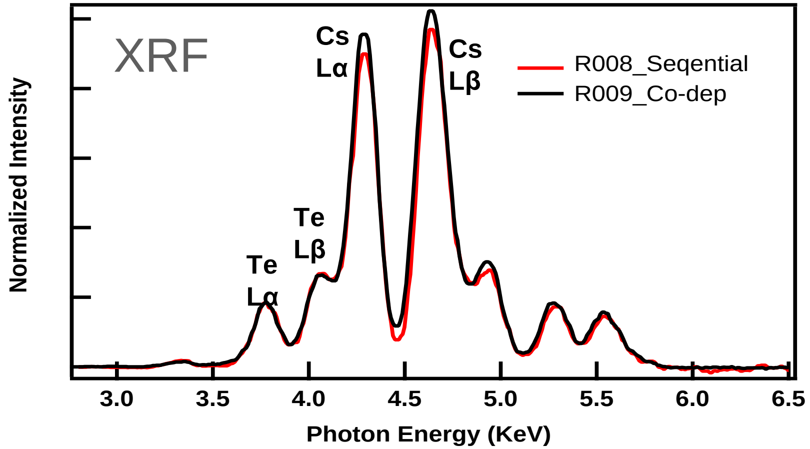
Sequential growth



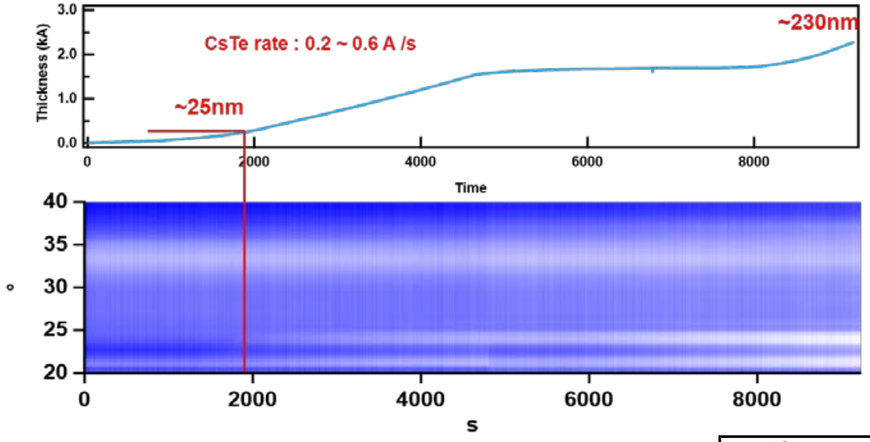


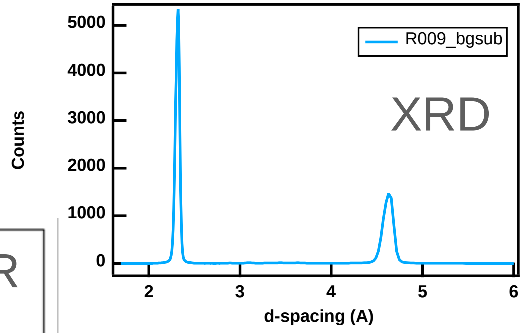


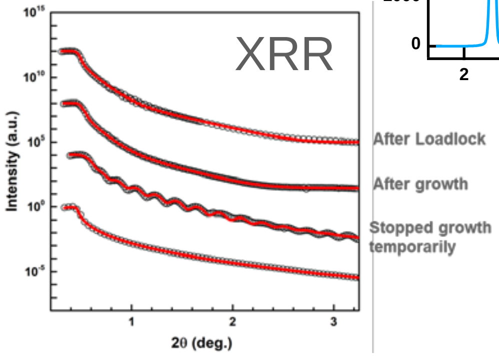




Co-deposition growth





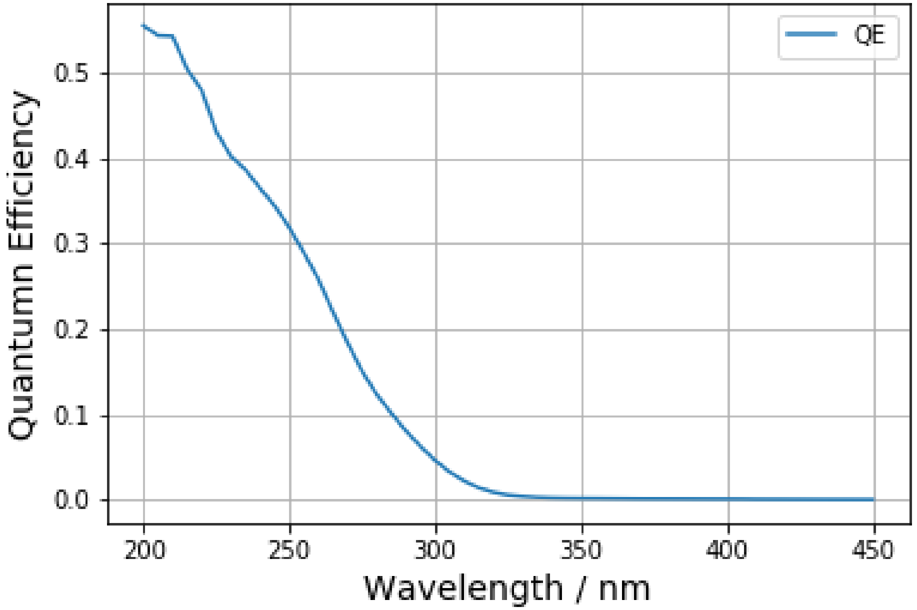


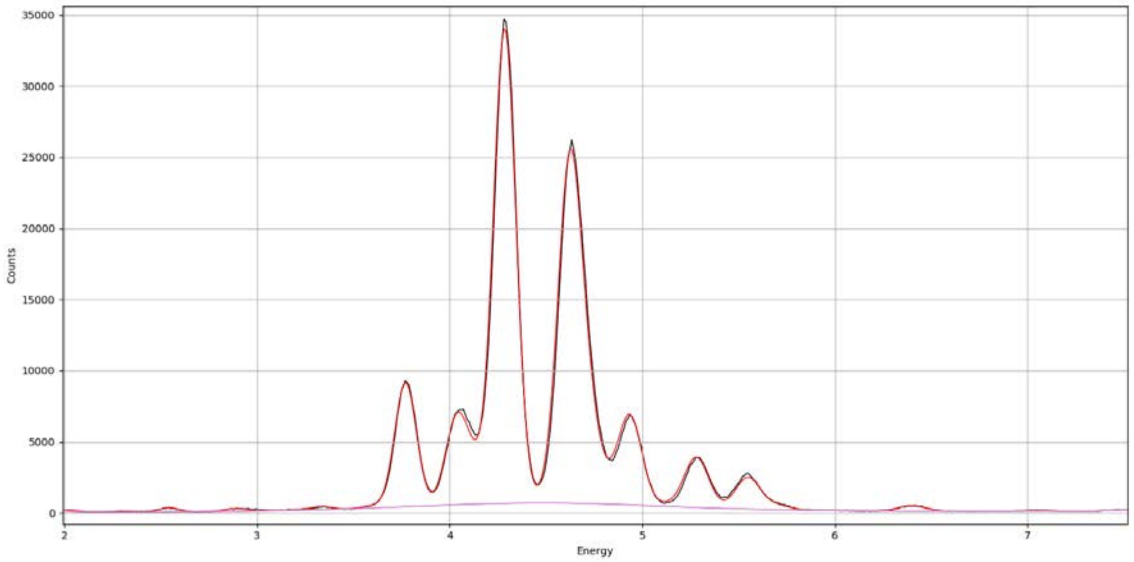
- Nearly all of the crystalized Te has dissolved
- Low counts in diffraction peaks
- Multiple phase of Cs-Te compound co-exist

- Well crystalized
- Single phase, smooth

Real-time supervision of Cs-Te growth: record QE and perfect stoichiometry

CsTe	Te	Cs
Q007	1	1.98





M. Gaowei, J. Sinsheimer, D. Strom, J. Xie, J. Cen, J. Walsh, E. Muller, and J. Smedley
Phys. Rev. Accel. Beams 22, 073401 (2019)

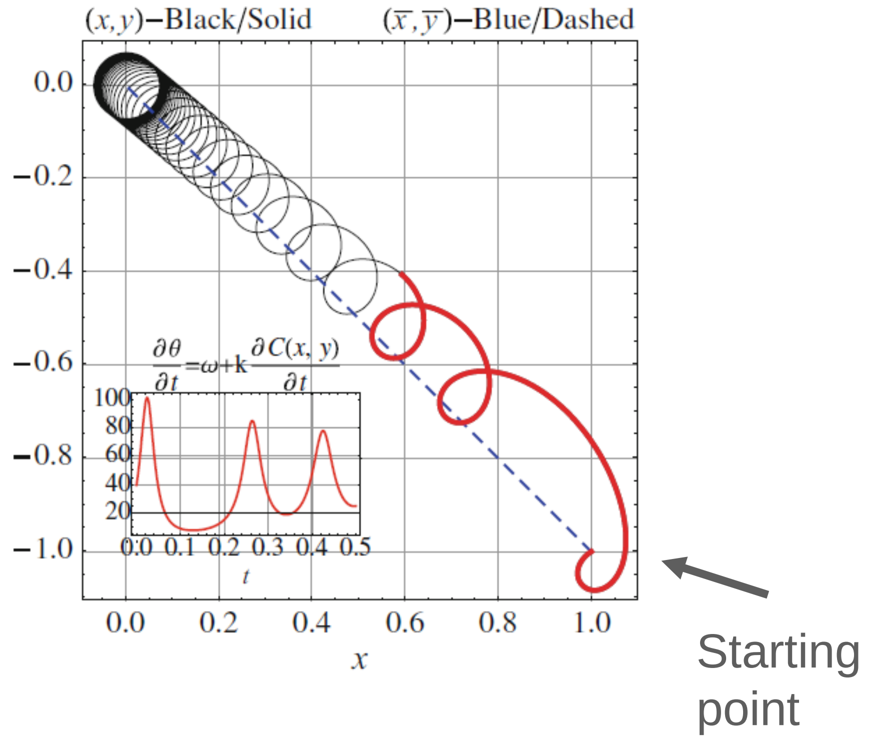
Towards automated growth: control and supervision of material growth without a synchrotron (at least not every time)

- **Goal:**
  - Automatically identify ideal growth conditions
  - Maintain ideal growth in dynamic conditions where “correct” parameters may shift with time

- **Algorithm: extremum seeking (ES)**
  - Applies sinusoidal variation to inputs
  - Minimizes cost parameter with (multiple) inputs
  - Works by spending more time near minimum than at higher values

- **ES algorithm:**
  - $\frac{dx}{dt} = \alpha\omega \cdot \sin(\omega t + kC)$
  - X: input value
  - α, k, ω are tuning parameters
  - C is the function to be minimized

- **Next step: characterize the material using x-ray toolset**



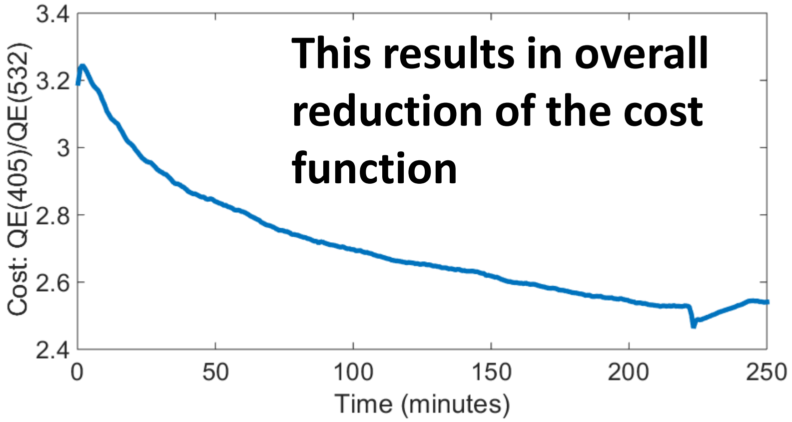
Example of ES for motion where

$$\frac{d\theta}{dt} = \omega + \frac{dC}{dt}$$

$$C = x^2 + y^2$$

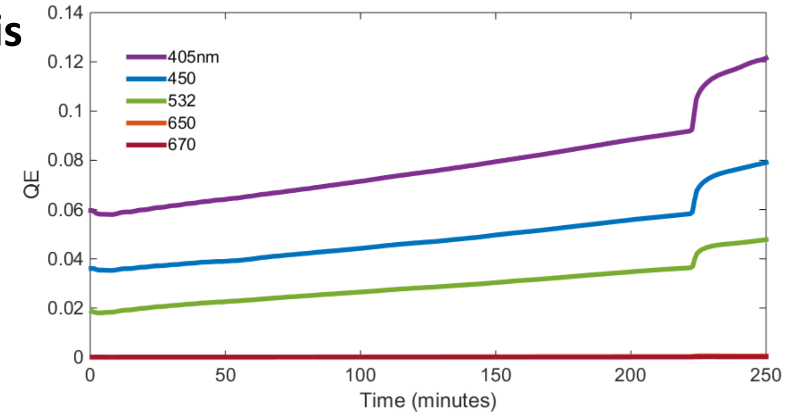
First results using ES growth algorithm are encouraging: Cs_3Sb with max QE before/after cooling 9% / 15%

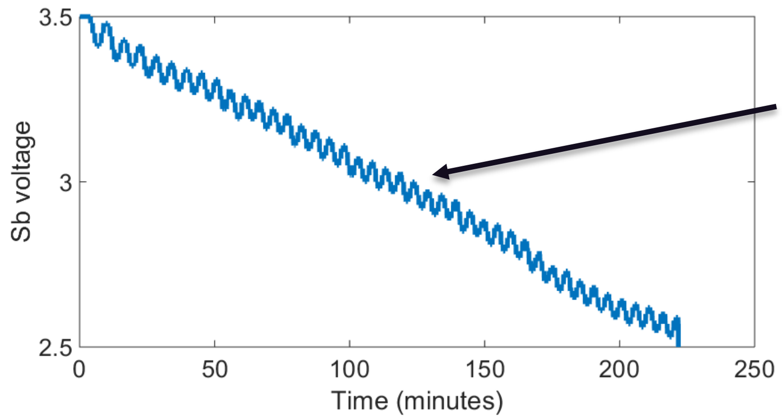
- **Growth conditions:**
  - Sample temperature: 125° C
  - Cs temperature: 180 ° C
  - Initial Sb flux ~ .01 A/s
- **Parameter optimized: Sb flux/voltage**
- **Cost function minimized: QE(405)/QE(532)**
- **Next steps:**
  - More materials: K_2CsSb, CsTe
  - More parameters optimized
  - Better performance/stability for thin cathodes



This results in overall reduction of the cost function

If the cost function is chosen correctly, this increases the QE





Algorithm applies sinusoidal variation to input, spending more time where cost function is lower

The ACERT collaboration published recent advances in many aspects of electron source design

- **Time-dependent x-ray analysis of photocathode growth**
  - Schubert, S., et al., *Bi-alkali antimonide photocathode growth: An X-ray diffraction study*. Journal of Applied Physics, 2016. **120**(3): p. 035303
  - Ding, Z., et al., *In-situ synchrotron x-ray characterization of K2CsSb photocathode grown by ternary co-evaporation*. Journal of Applied Physics, 2017. **121**(5): p. 055305.
  - Gaowei, M., et al., *Synthesis and x-ray characterization of sputtered bi-alkali antimonide photocathodes*. APL Materials, 2017. **5**(11): p. 116104.
- **Etalon wave interference effects: ultra-fast photocathode and recovered QE for near-threshold emission**
  - Alexander, A., N.A. Moody, and P.R. Bandaru, *Enhanced photocathode performance through optimization of film thickness and substrate*. JVST-B, 2017. **35**(2): p. 022202
- **Tunneling effects of single-layer and multi-layer 2D barriers on a photoemitter**
  - Wang, G., N. Moody, et al., *Overcoming the quantum efficiency-lifetime tradeoff of photocathodes by coating with atomically thin two-dimensional nanomaterials*, Nature npj 2D Materials **2**(17), 2018.
- **Enhanced quantum efficiency using plasmons**
  - Alexander, A., N.A. Moody, and P.R. Bandaru, *Enhanced quantum efficiency of photoelectron emission, through surface textured metal electrodes*. Journal of Vacuum Science & Technology A, 2016. **34**(2): p. 021401.
- **Effect of quantum confinement on electron emission**
  - Makarov, N.S., et al., *Quantum Dot Thin-Films as Rugged, High-Performance Photocathodes*. Nano Letters, 2017. **17**(4): p. 2319-2327.
- **Lifetime enhancement using 2D films (hBN and graphene)**
  - Yamaguchi, H., et al., Active bialkali photocathodes on free-standing graphene substrates. npj 2D Materials and Applications, 2017. 1(1): p. 12.
  - Liu, F., et al., Single layer graphene protective gas barrier for copper photocathodes. Applied Physics Letters, 2017. 110(4): p. 041607.
- **First principles model of cathode degradation and new lifetime metric**
  - Wang, G., et al., Degradation of Alkali-Based Photocathodes from Exposure to Residual Gases: A First-Principles Study. The Journal of Physical Chemistry C, 2017. **121**(15): p. 8399-8408.
  - Pavlenko, V., et al., Kinetics of alkali-based photocathode degradation. AIP Advances, 2016. **6**(11): p. 115008

Summary of what we have learned across multiple collaboration efforts

- Real-time x-ray characterization 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 constituent metals
- Conformal coating of structured surfaces possible
- Real time XRF feedback provides option of ternary co-evaporation, producing best cathode
- Can consider ultra thin (under 10 nm) cathodes to improve response time but not suffer catastrophic loss in QE, thanks to Etalon optimization of substrate, cathode, thickness, wavelength
- Progress in surface coatings, some of which may enhance emission while protecting surface
- Hypothesized ‘cost function’ or quality parameter that may guide growth without synchrotron
- Progress toward automated growth with anticipated validation studies (XRF, XRD, XRR, etc.)
- Applications of photophysics extend well beyond photoemission (detectors, sensors, power sources, etc.)

Summary: Changes to the LANL / BNL photocathode programs are a strategic response to evolving needs and opportunities within NNSA

- **The Materials by Design strategy engages the broader material science communities at both LANL and BNL**
- **Progress has been non-linear with time and investment**
  - Techniques honed for one application can be rapidly applied to many others
  - Example: Cs_2Te following successes of smooth K_2CsSb
- **We enter a cycle of using accelerator-based tools to improve accelerators**
  - providers of advanced tools of material science (accelerator based x-ray light sources) are now availing themselves of the same capabilities to improve the next-generation machines
- **We are looking to define future collaborations**
  - Make our solutions available and partner to tackle new problems

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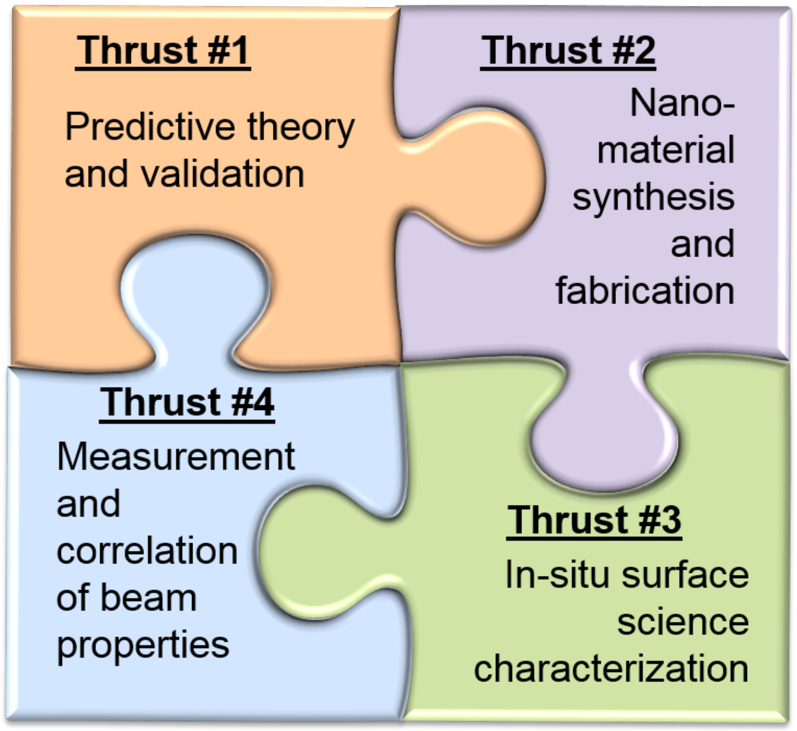
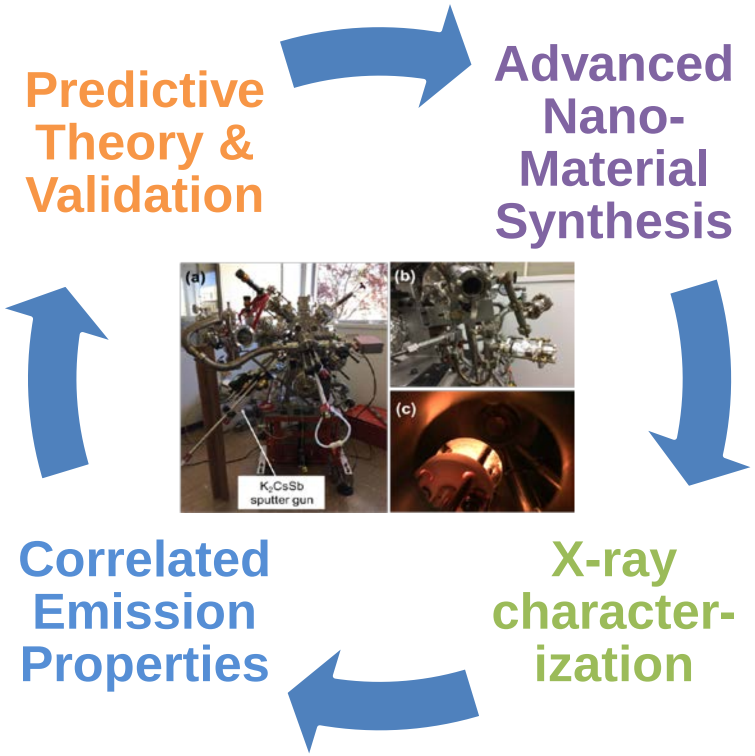
LANL's approach consists of four pillars and advances the TRL of new techniques for specific needs and applications





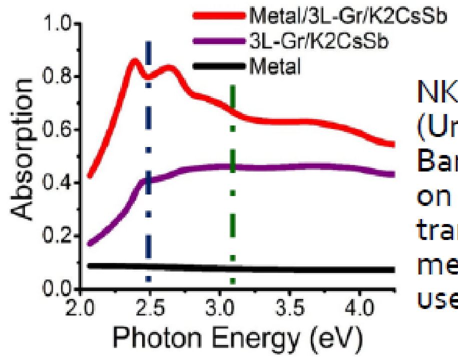
Research		Development		Demonstration	Production
Basic	Applied	Exploratory	Advanced		

Technology Readiness Levels (1-9)

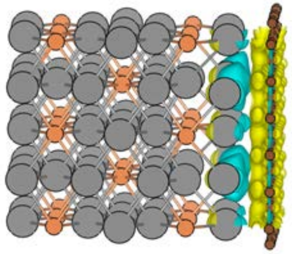
1	2	3	4	5	6	7	8	9
Basic Principles	Technology Concept	Proof of Concept	Component Validation	Field Validation	Prototype Demo.	System Demo.	System Complete	Product in use

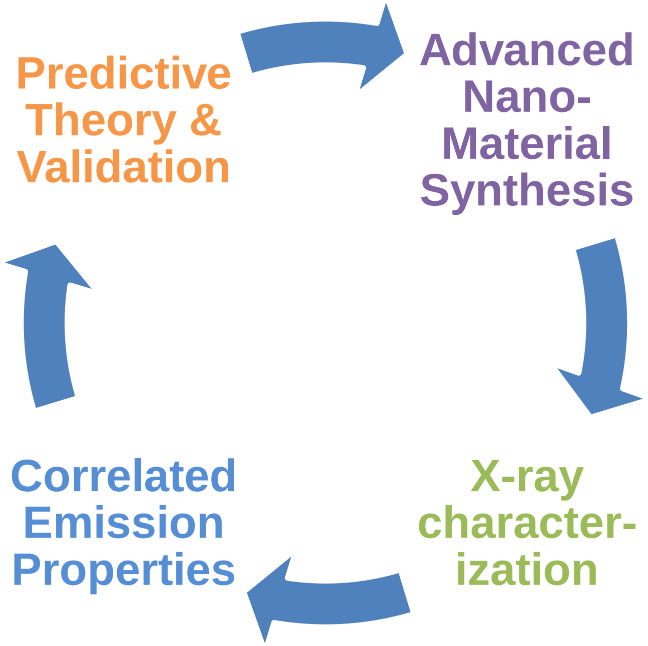
Goal is to develop and perfect the technologies using x-ray characterization and transition it to groups without such tools.

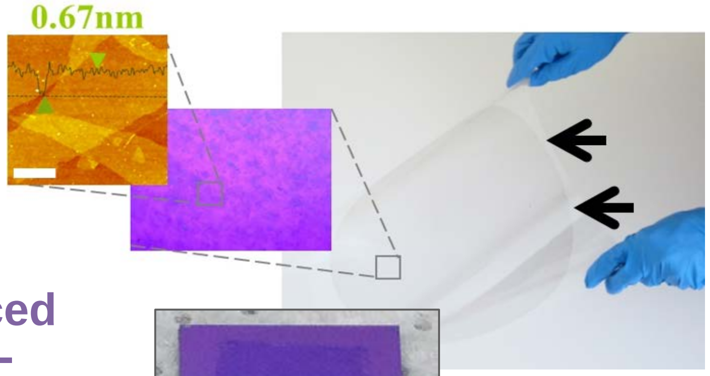
Progress toward cathode integration with 2D coatings for protection and enhancement

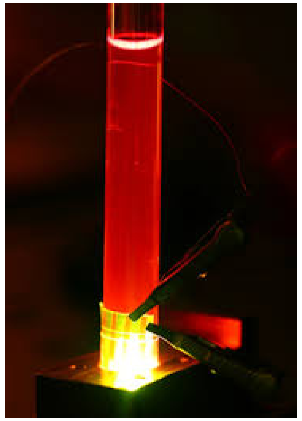


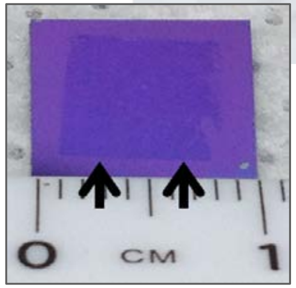
NKD Gen software (University of Barcelona) based on conventional transfer matrix methodology was used.

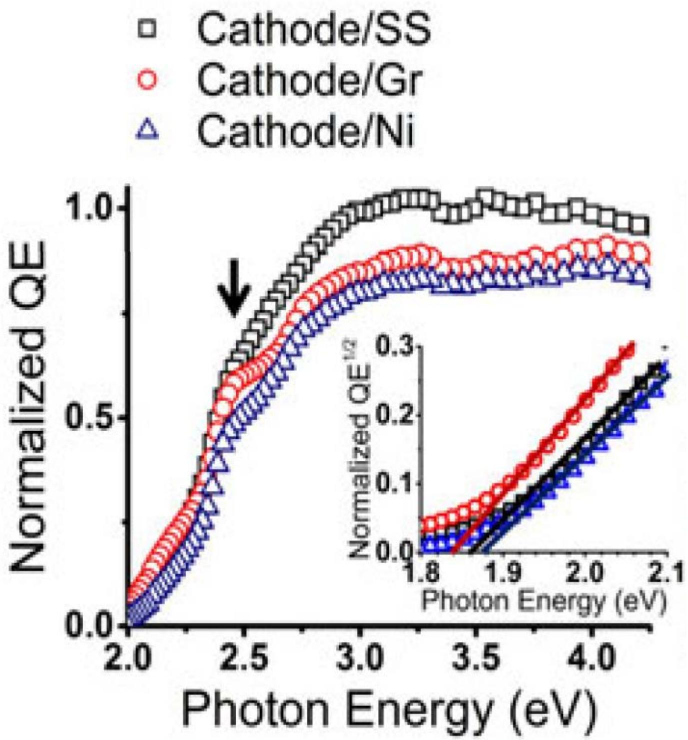


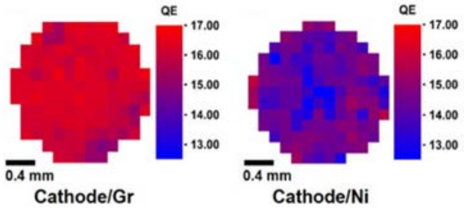


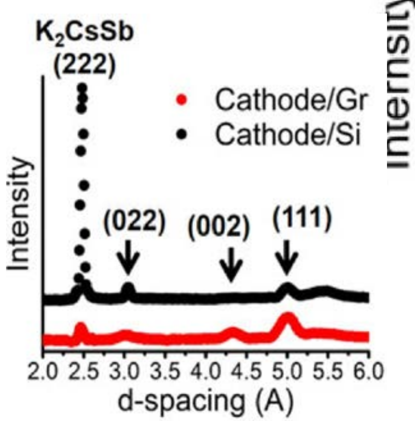


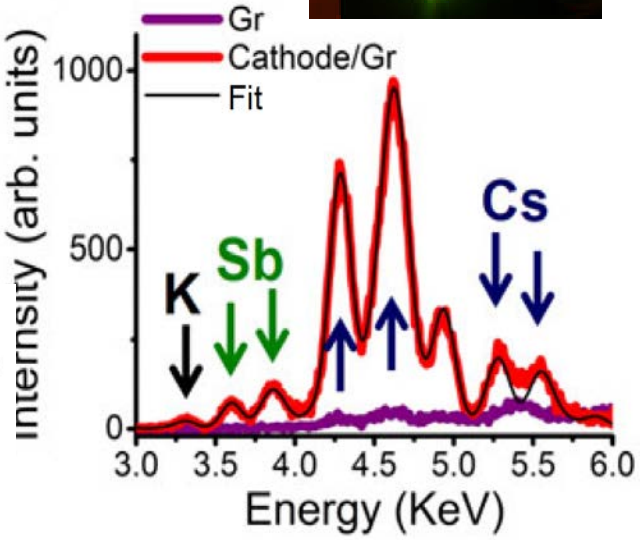




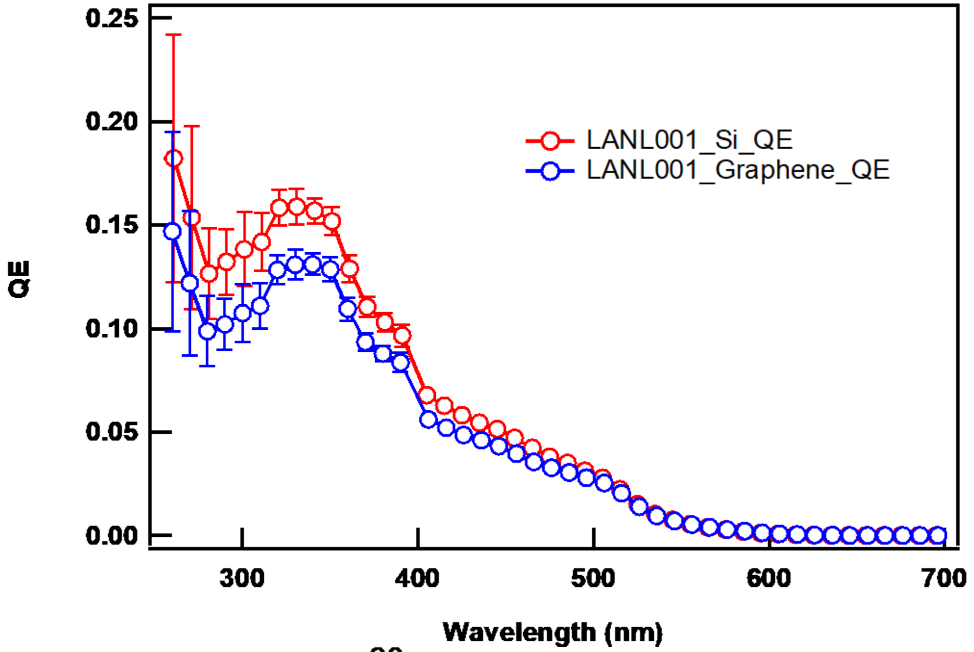


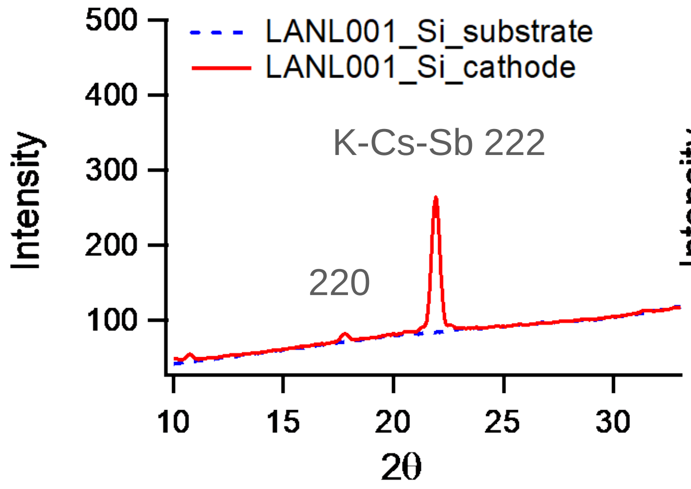




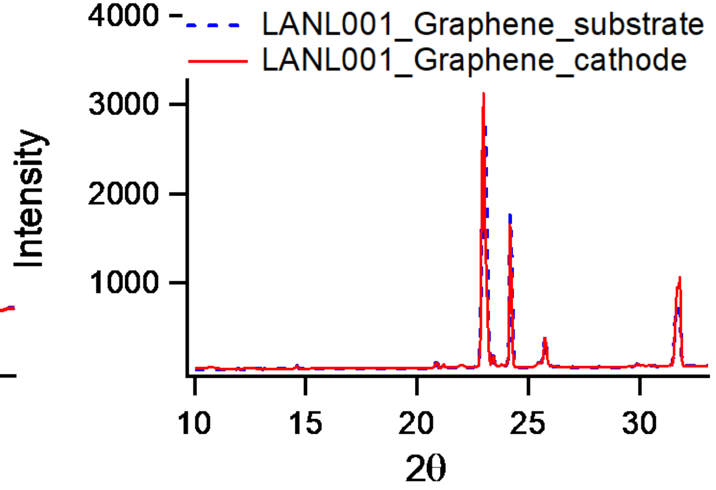


Growth on Graphene and Silicon

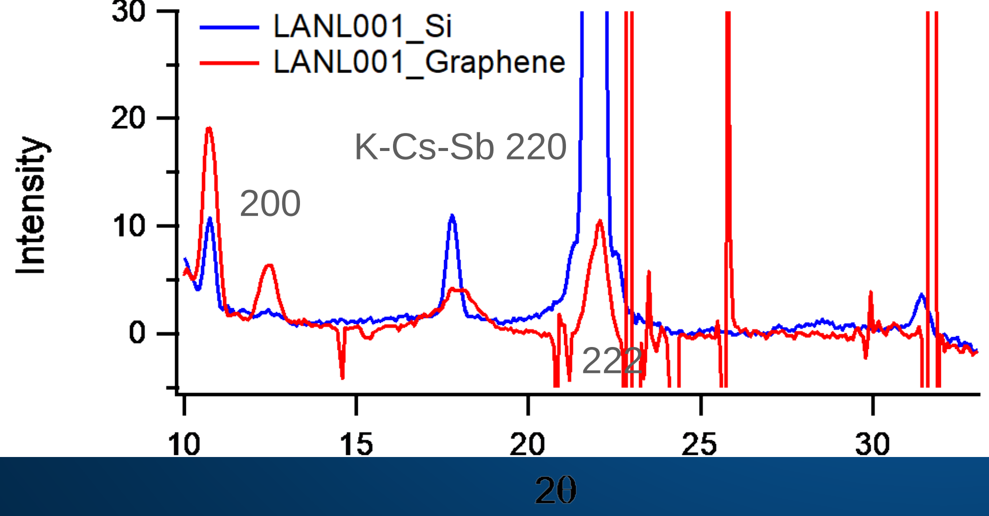




Clear cathode peak after growth



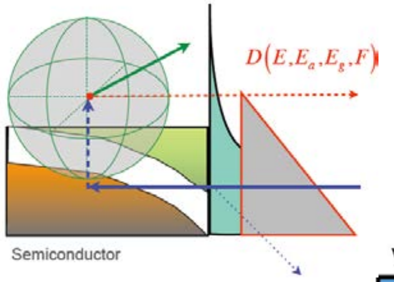
No obvious XRD peak observed after growth

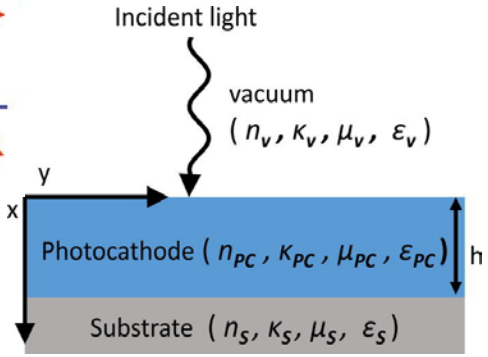


Zoom in: weak cathode peak on graphene observed, similar in position as Si, broader in width.

XRR shows cathode 20 nm thick on Si, 10 nm on graphene

Development of ‘Etalon’ (wave interference) thin film cathodes allows for design of fast response cathode with reasonable QE





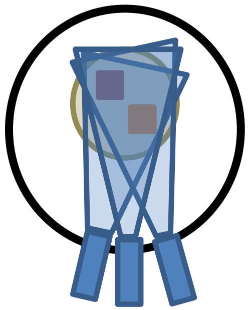
$$a(x) = \frac{P_a(x)}{P_{in}} = -\left(\frac{\kappa_{PC}\, k\tilde{n}_{PC}}{\mu_o \mu_{PC}}\right) |E_o(1 + r_{V-PC})|^2 e^{-x/\lambda_{opt}}$$

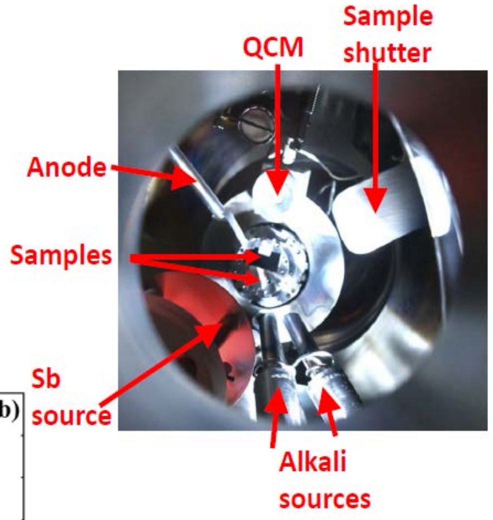
Predictive Theory & Validation

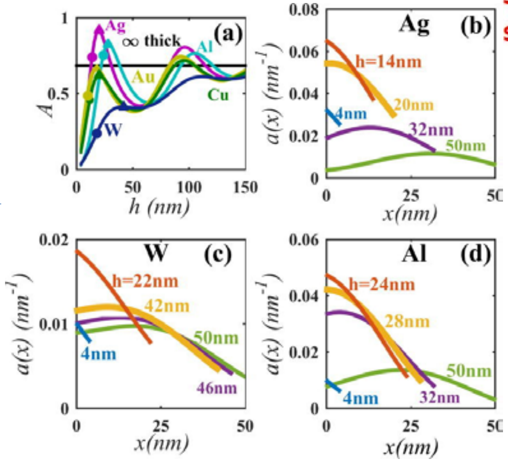
Advanced Nano-Material Synthesis

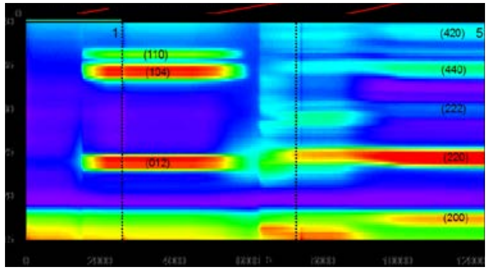
X-ray character-ization

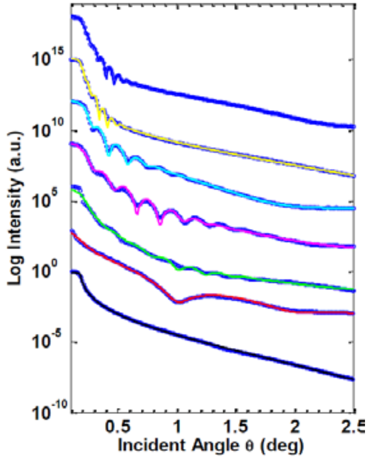
Correlated Emission Properties

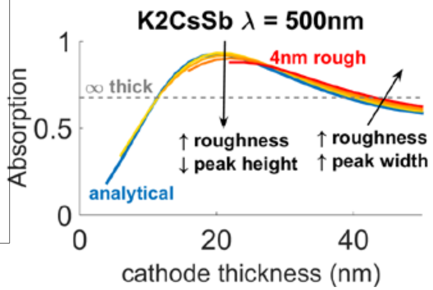












Etalon effect predicts QE enhancement in Cs3Sb at predicted combinations of substrate, thickness, wavelength