Revealing the Correlations between Growth Recipe and Microscopic Structure of Multi-alkali Photocathodes

Seon Woo Lee[1], Klaus Attenkofer[1], Marcel Demarteau[1]
Henry Frisch[1,2], Junqi Xie[1], John Smedley[3]

1. Argonne National Laboratory

2. University of Chicago

3. Brookhaven National Laboratory

Saturday, June 11, 2011

Content

- Roadmap to optimize cathode growth recipe
- Physics of cathode emission
- In-situ X-ray Scattering
  - X-ray diffractometry (XRD)
  - X-ray Reflectometry (XRR)
- Conclusion

Roadmap : to optimize cathode

Optimizing Cathode Growth Recipe

1. Correlation between Functionality and Structure

- Fundamental physics of cathode emission
  - Three step Spicer model
    - The absorption of photons and generation of photoelectrons
    - The transport of the electrons from the point of generation to the surface
    - The escape from the surface

2. Correlation between Recipe and Structure

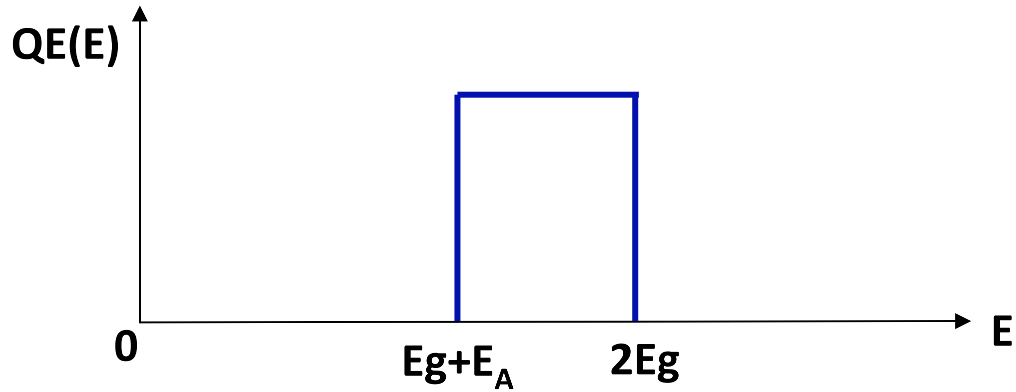
- Tuning various growth parameters
  - Temperature / growth rate
  - Composition of materials
  - Grain size and thickness of the film

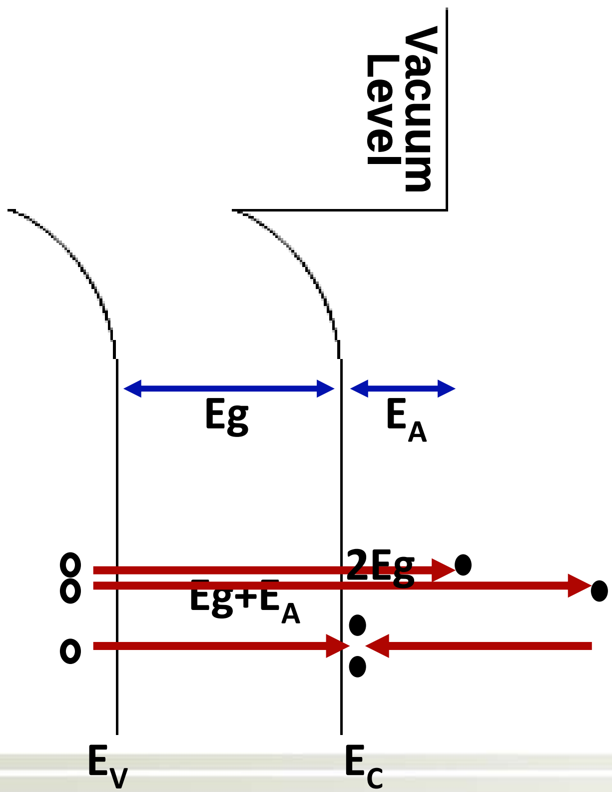
3. In-situ Visualization Tool of Microscopic Structure

- X-ray Diffraction
  - Crystallographic structure, chemical composition, grain size, crystalline orientation
- X-ray Reflectivity
  - Control of thickness, various defects, surface roughness

To Achieve Maximal Quantum Efficiency

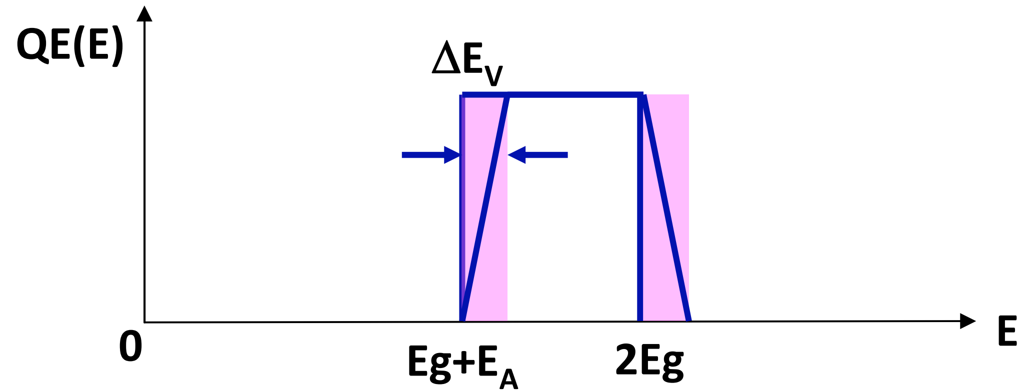
1. Correlation between Functionality and Structure
- Fundamental physics of cathode emission

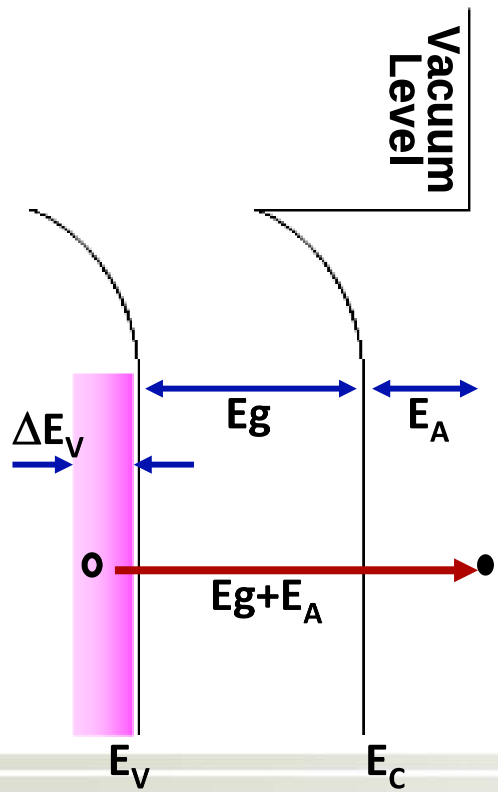




QE(E): Quantum Efficiency
Eg : Energy Band Gap
Ec : Bottom of Conduction Band
Ev : Top of Valence Band
E_A : Electron Affinity
● : Electron
o : Hole

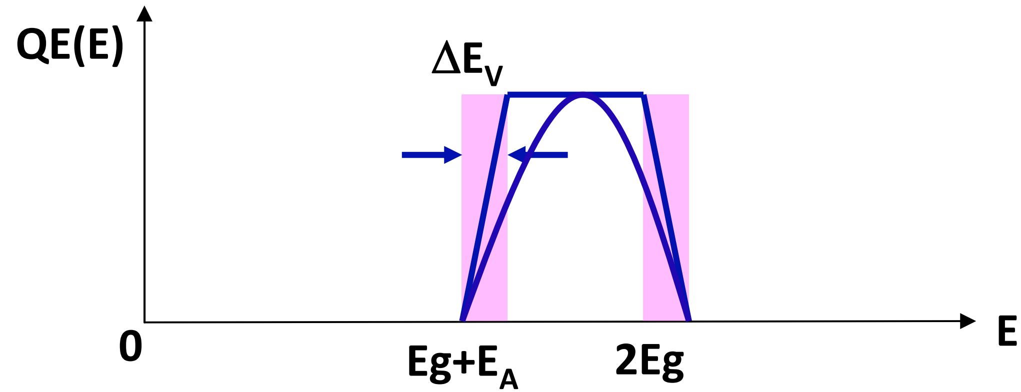
1. Correlation between Functionality and Structure
- Fundamental physics of cathode emission

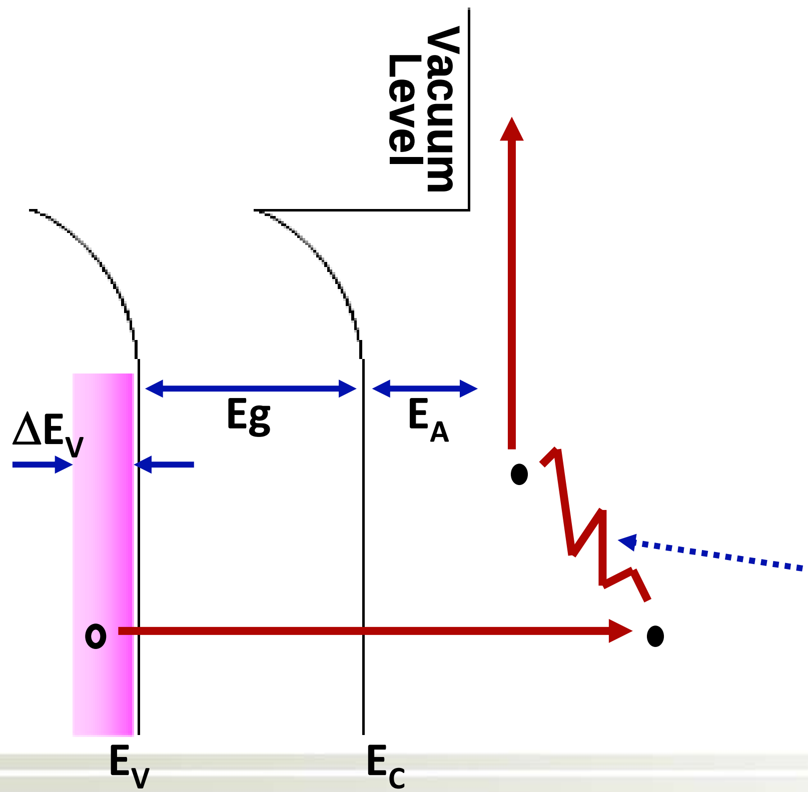




QE(E): Quantum Efficiency
Eg : Energy Band Gap
Ec : Bottom of Conduction Band
Ev : Top of Valence Band
E_A : Electron Affinity
● : Electron
o : Hole

1. Correlation between Functionality and Structure
- Fundamental physics of cathode emission

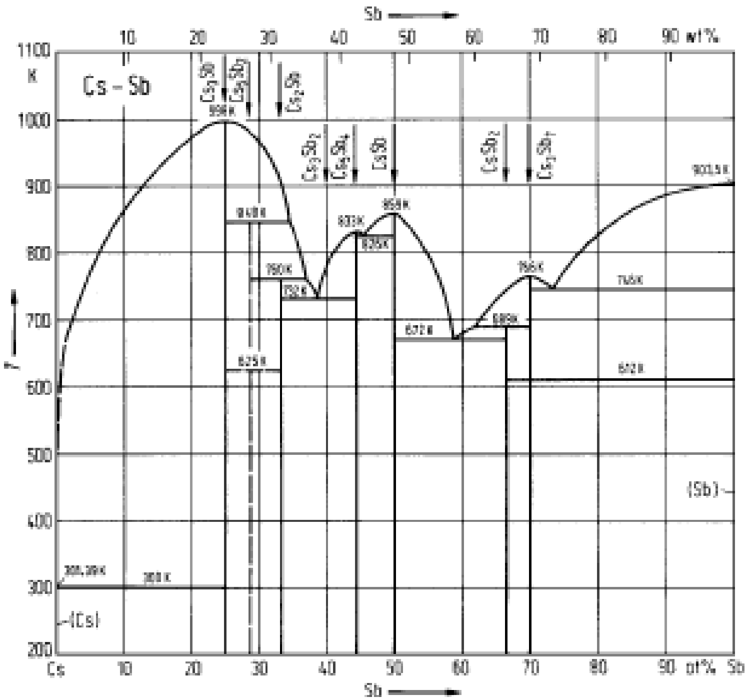


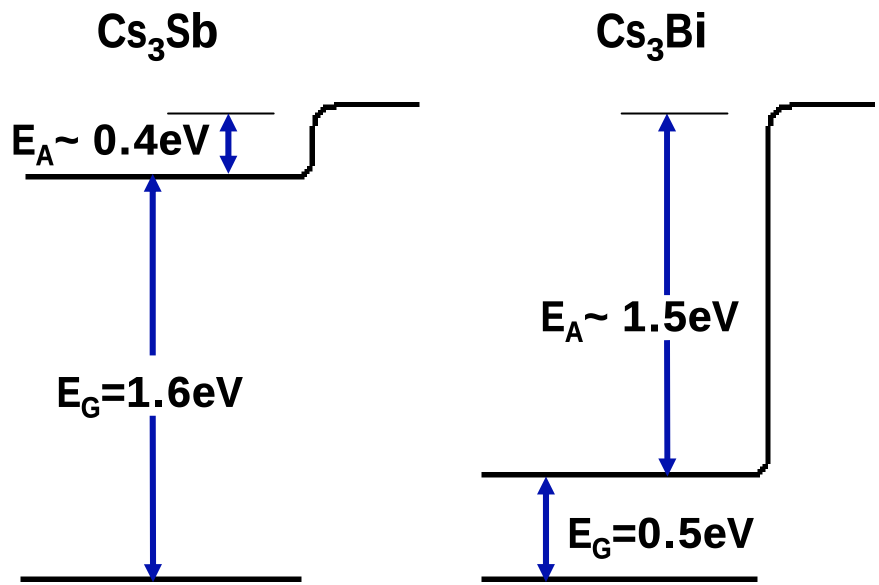


QE(E): Quantum Efficiency
Eg : Energy Band Gap
Ec : Bottom of Conduction Band
Ev : Top of Valence Band
E_A : Electron Affinity
● : Electron
o : Hole

- e-phonon scattering
- e-grain boundary scattering
- e-impurity scattering

What do we know about the chemistry of multialkalis?

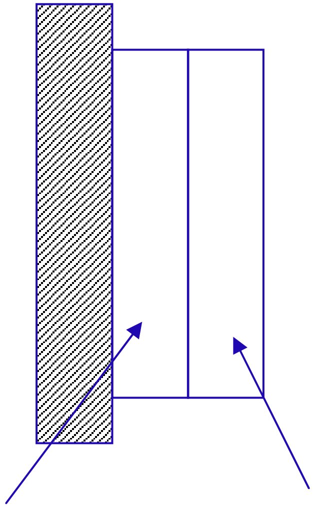


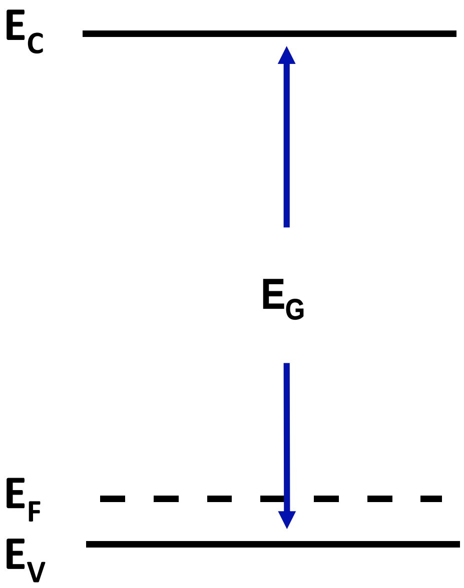


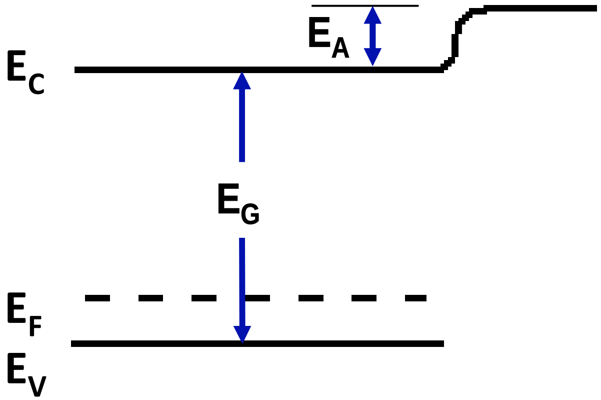
Effect of E_G to E_A ratio on quantum yield

- Very rich phase diagram
  - Each phase corresponds to individual chemical compound with individual
    - Band structure / Band gap / Optical absorption properties
  - Resulting phase depends on
    - Local atomic concentration ratio
    - Kinetic energy during interdiffusion
    - Activation energy of defects
- Consequences of rich phase diagram
  - Strong recipe dependency
  - However
    - Good opportunity to engineer heterogeneous cathode
    - Lateral and transversal engineering possible

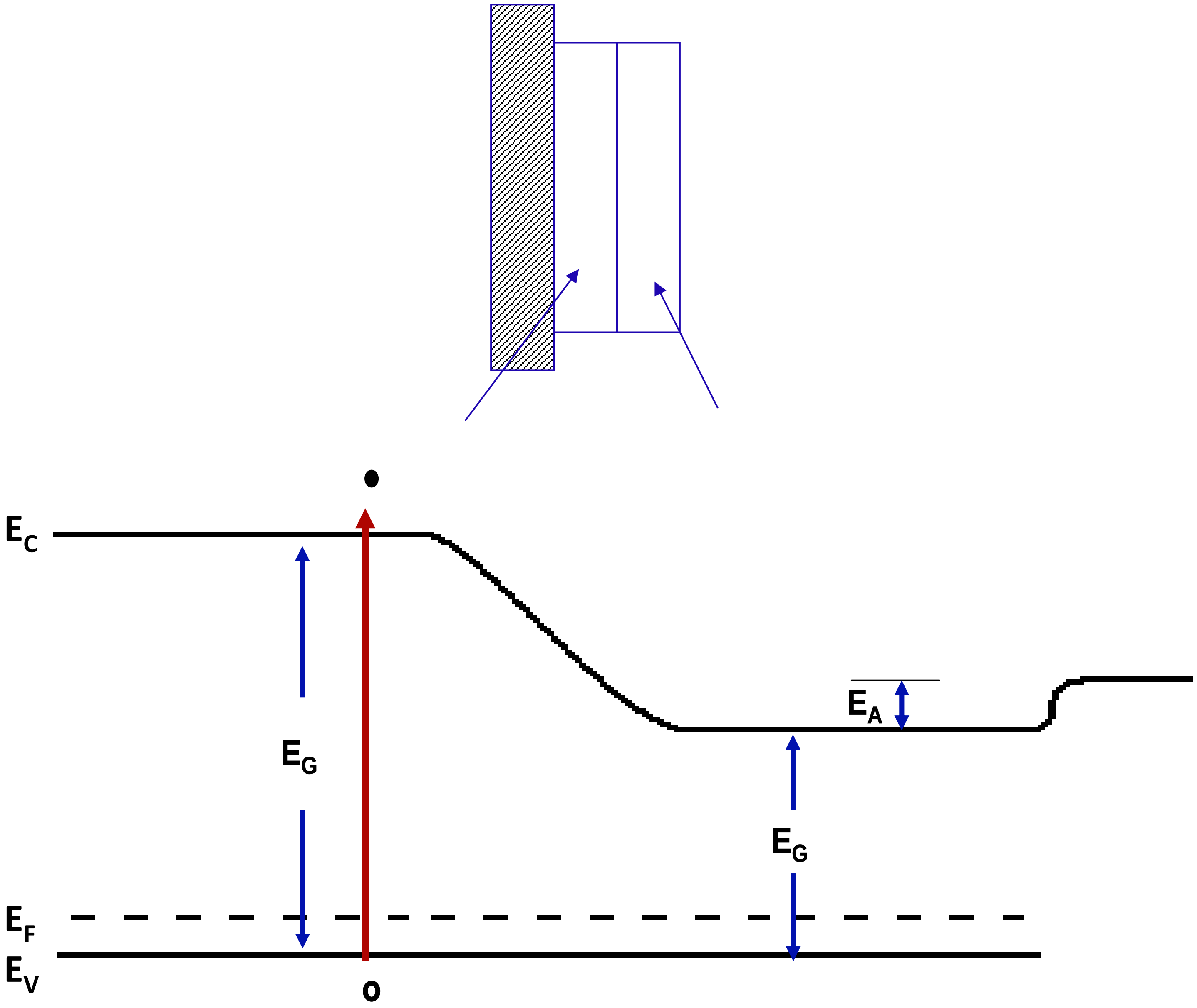
Example for ‘good’ non-heterogeous multialkali cathode



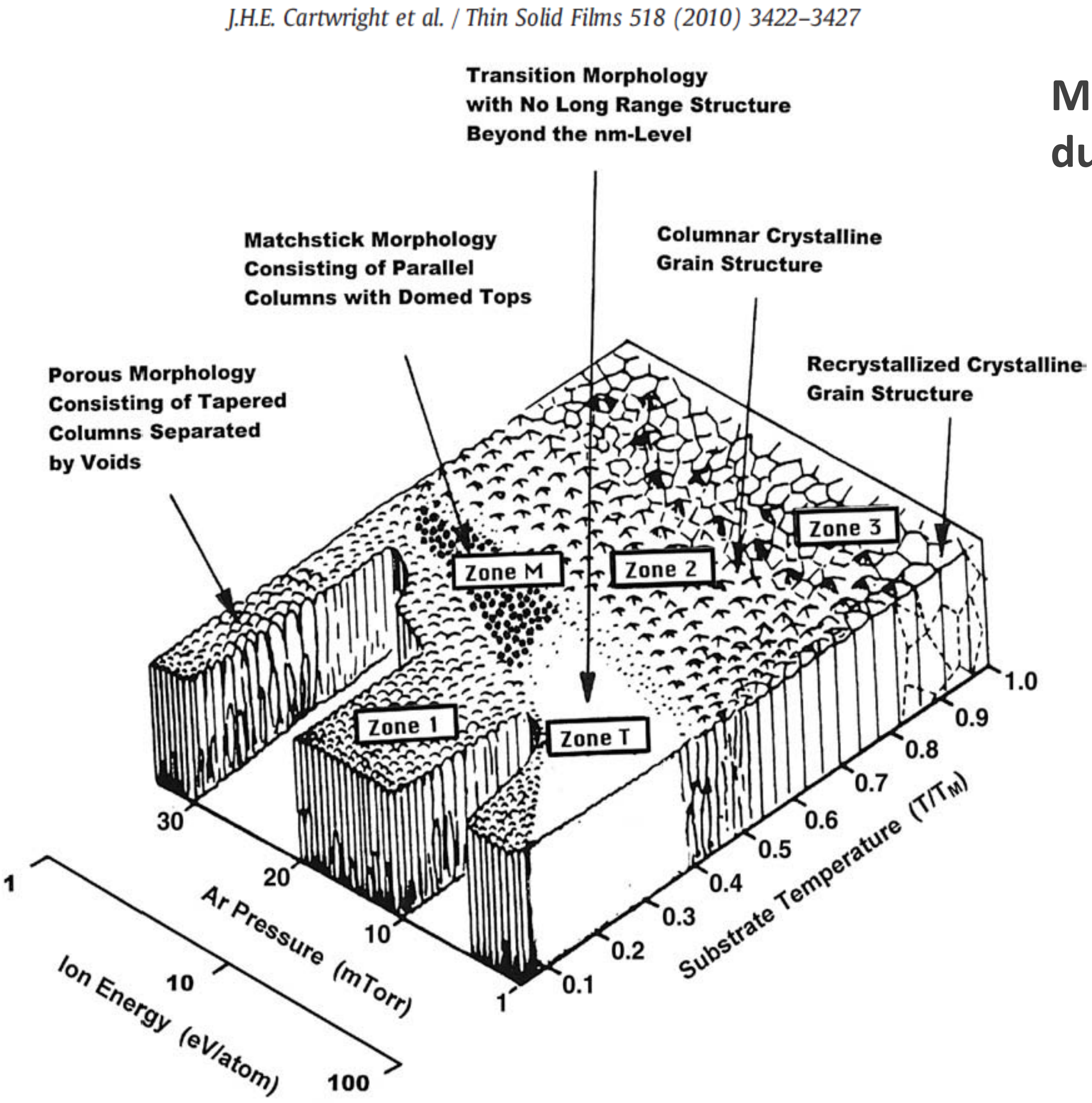




Example for 'good' non-heterogeous multialkali cathode



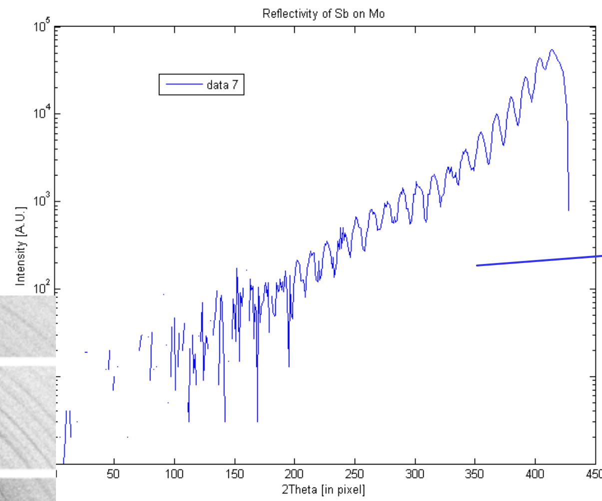
What do we have to know about the growth?

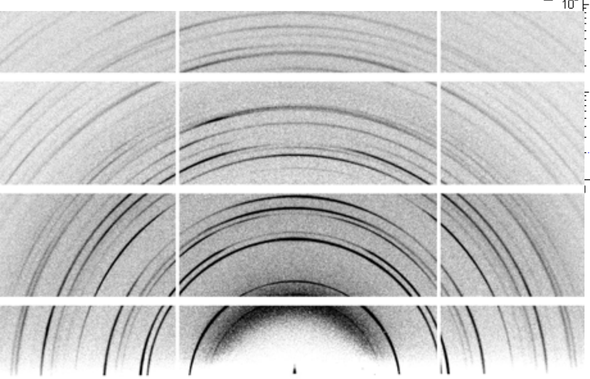


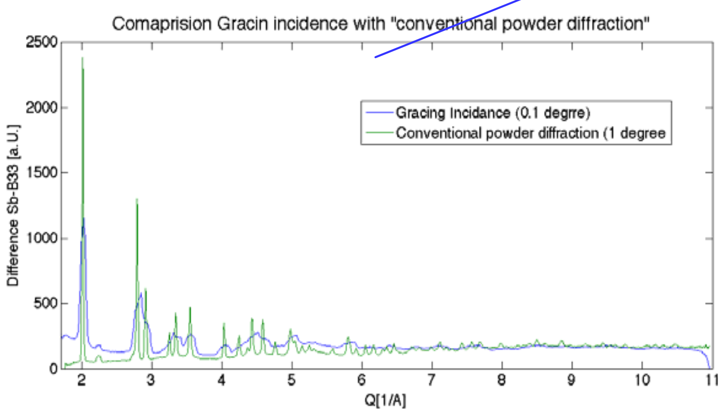
Movie like characterization during the growth:

- Macroscopic film properties
  - Film thickness
  - Roughness
- Microscopic composition
  - Which phases are present
  - Lateral and transversal homogenuity
  - Crystalline size
  - Preferential crystal growth
- Surface composition
  - Local workfunction
  - Chemical composition

How can we microscopically visualize growth?
- X-ray diffractometry (XRD), X-ray reflectometry (XRR)







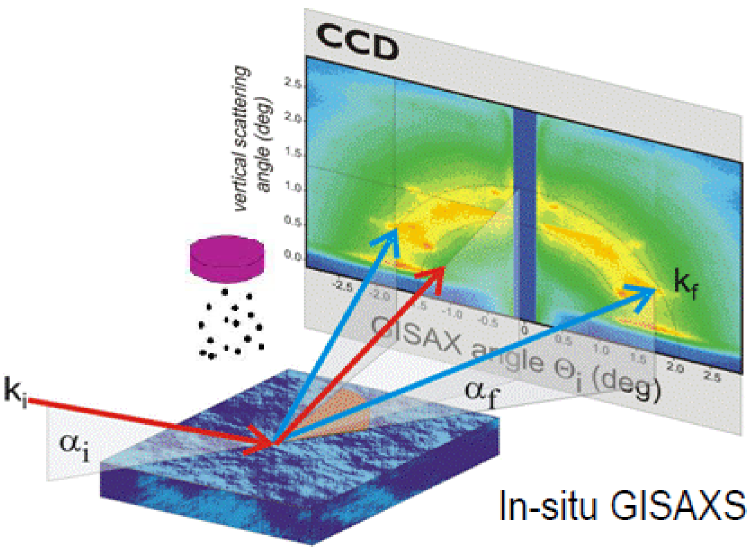
Movie like characterization during the growth:

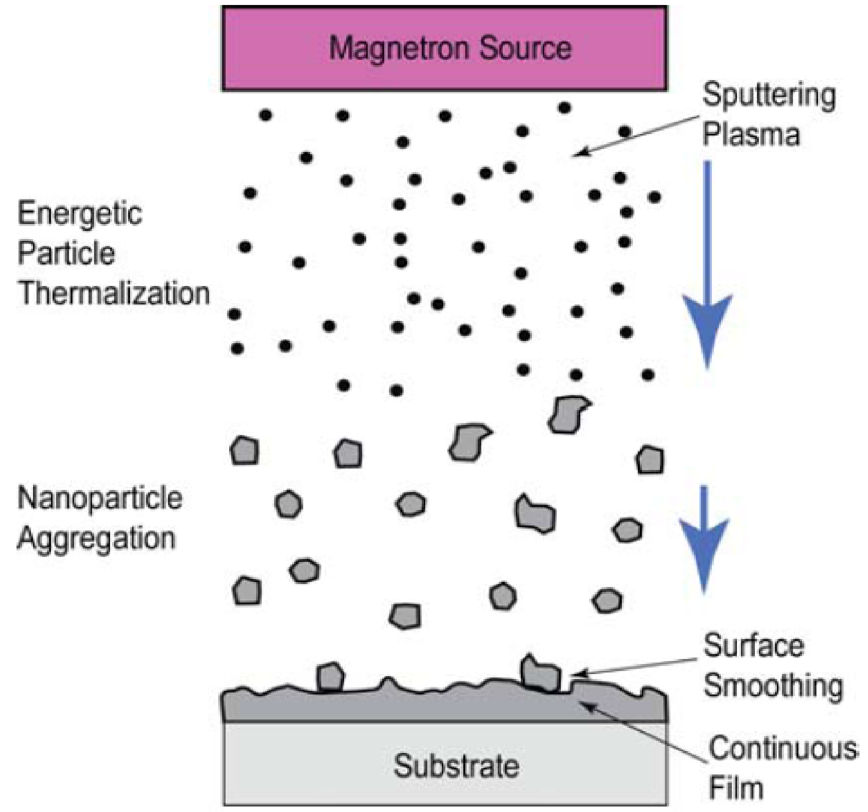
- Macroscopic film properties
  - Film thickness
  - Roughness
- Microscopic composition
  - Which phases are present
  - Lateral and transversal and homogenuity
  - Crystalline size
  - Preferential crystal growth

Surface composition
  - Local workfunction
  - Chemical composition

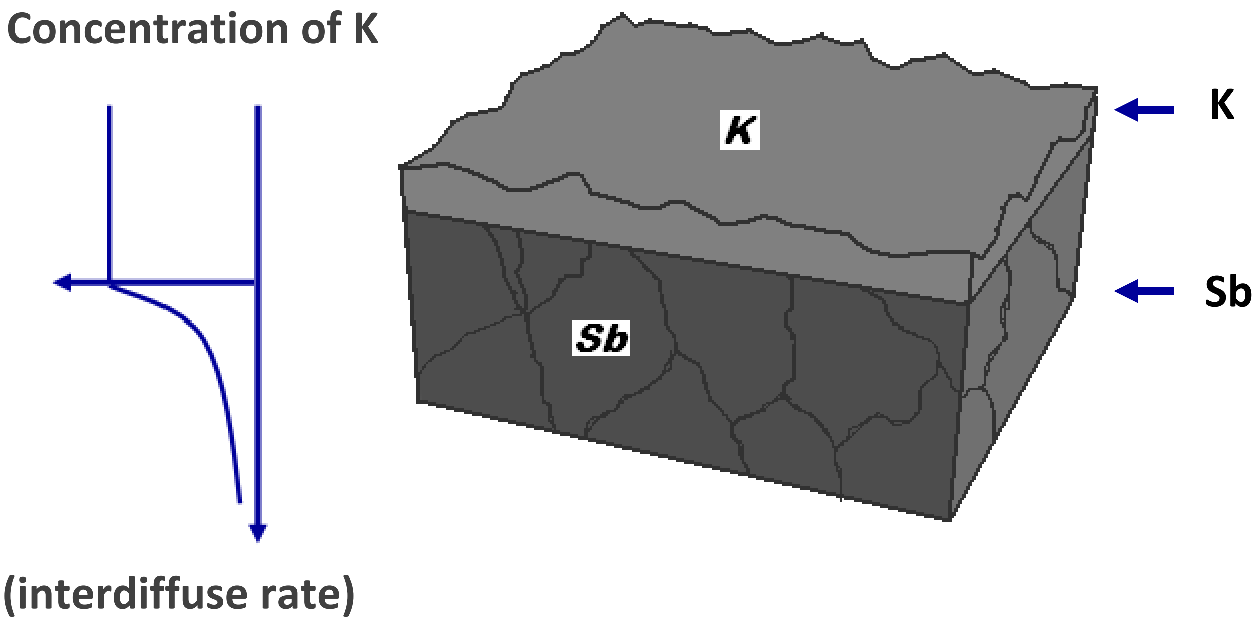
PEEM: collaboration with Howard Padmore (ALS)

How can we microscopically visualize growth?
- X-ray diffractometry (XRD)
- XRD provides in-situ texture monitoring





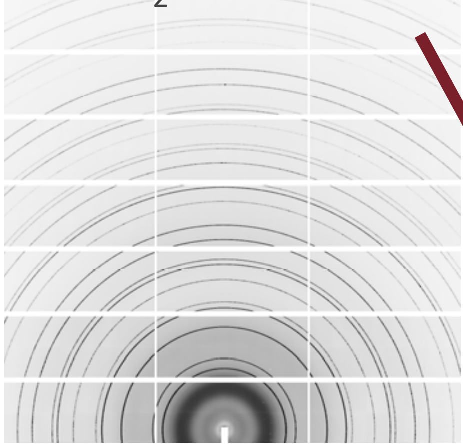
The Recipe and the Microscopic Picture (Example of Burle Recipe)



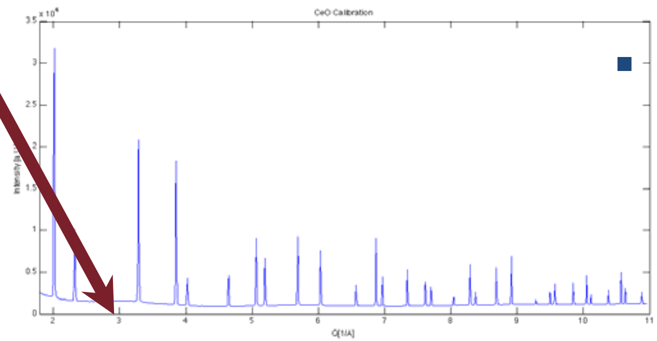
- First X-ray scattering results for Sb-film
  - Film is amorphous for thicknesses <8nm
  - Above "full" film crystallizes with high texturing)
  - Crystal structure strongly depends on substrate and evaporation method
- Interdiffusion rate will depend on
  - Temperature
  - Defect structure of film
  - Speciation of Alkali in grain boundary and inner grain will be different.

Data-Processing

CeO$_2$ Pattern

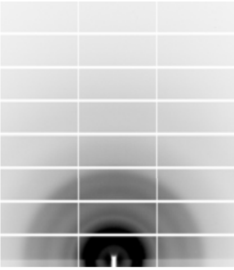


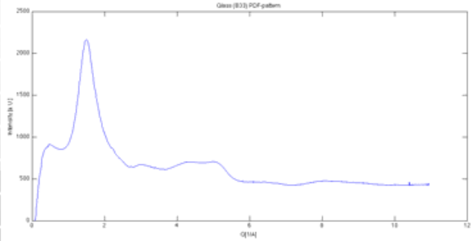
Azimuthal Integration and fit of peak positions

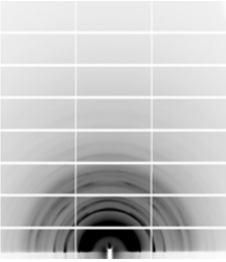


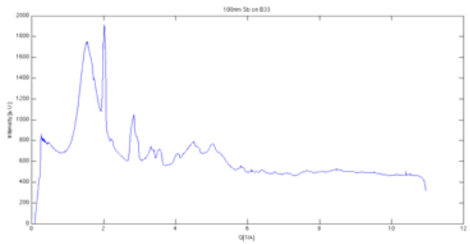
Data-Analysis:

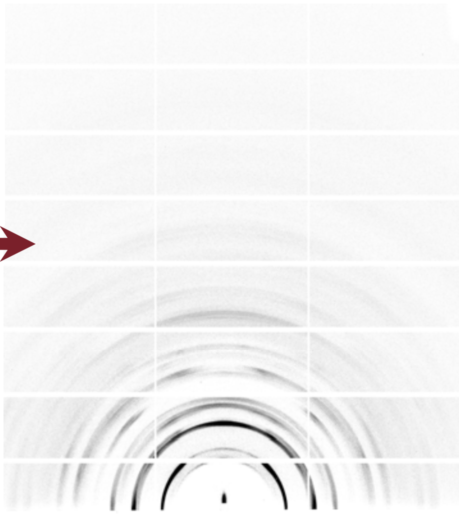
- Calibration with known standard (CeO2)
- “Empty”-pattern (B33)
- Sb-on B33 pattern
- Result: Difference showing only Sb-film and changes on glass-subtrate

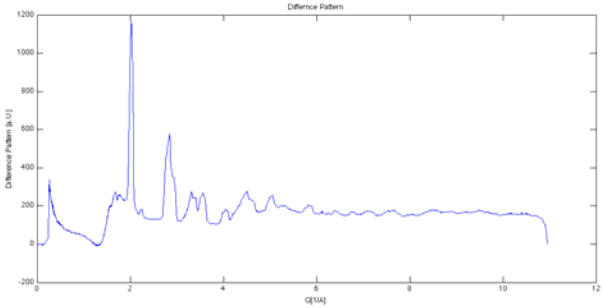






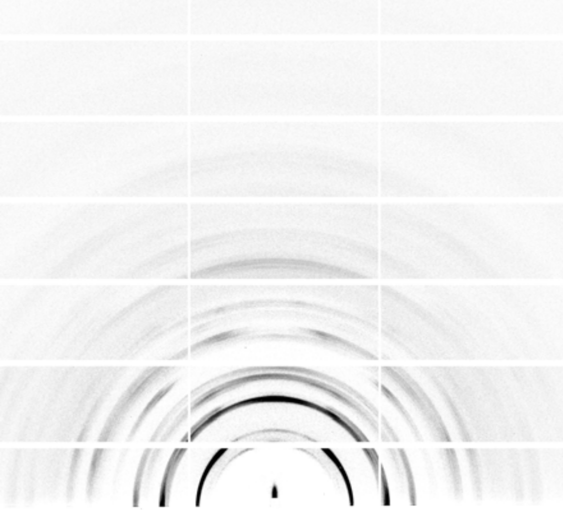


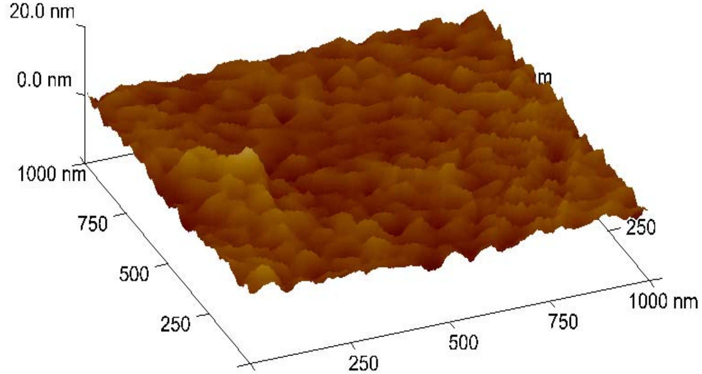


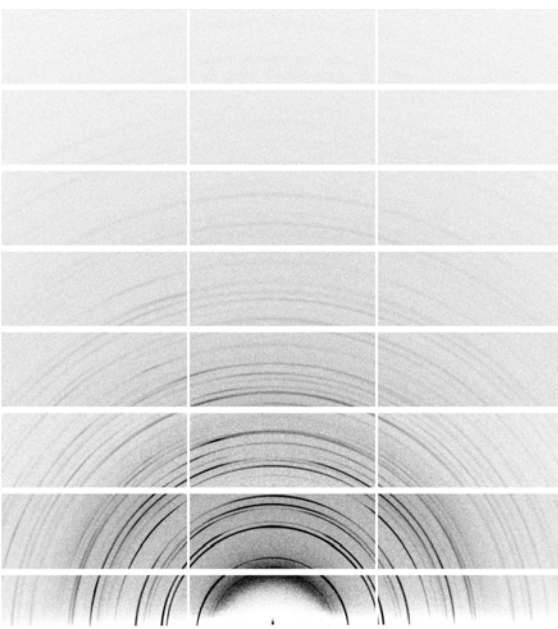


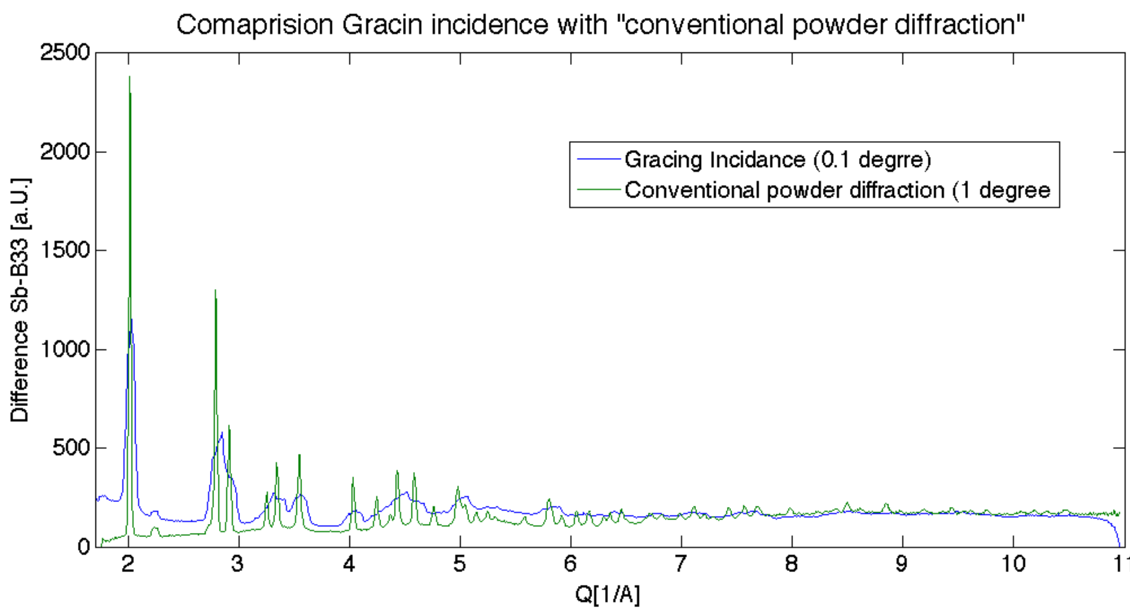
Gracing Incidence Techniques:

- Theta-angle determines Probe-depth
- Angle of total reflection is ~0.2degrees
- Note:
  - Peak broadening
  - Distinct azimuthal pattern
  - Peak broadening is different for different orientations!



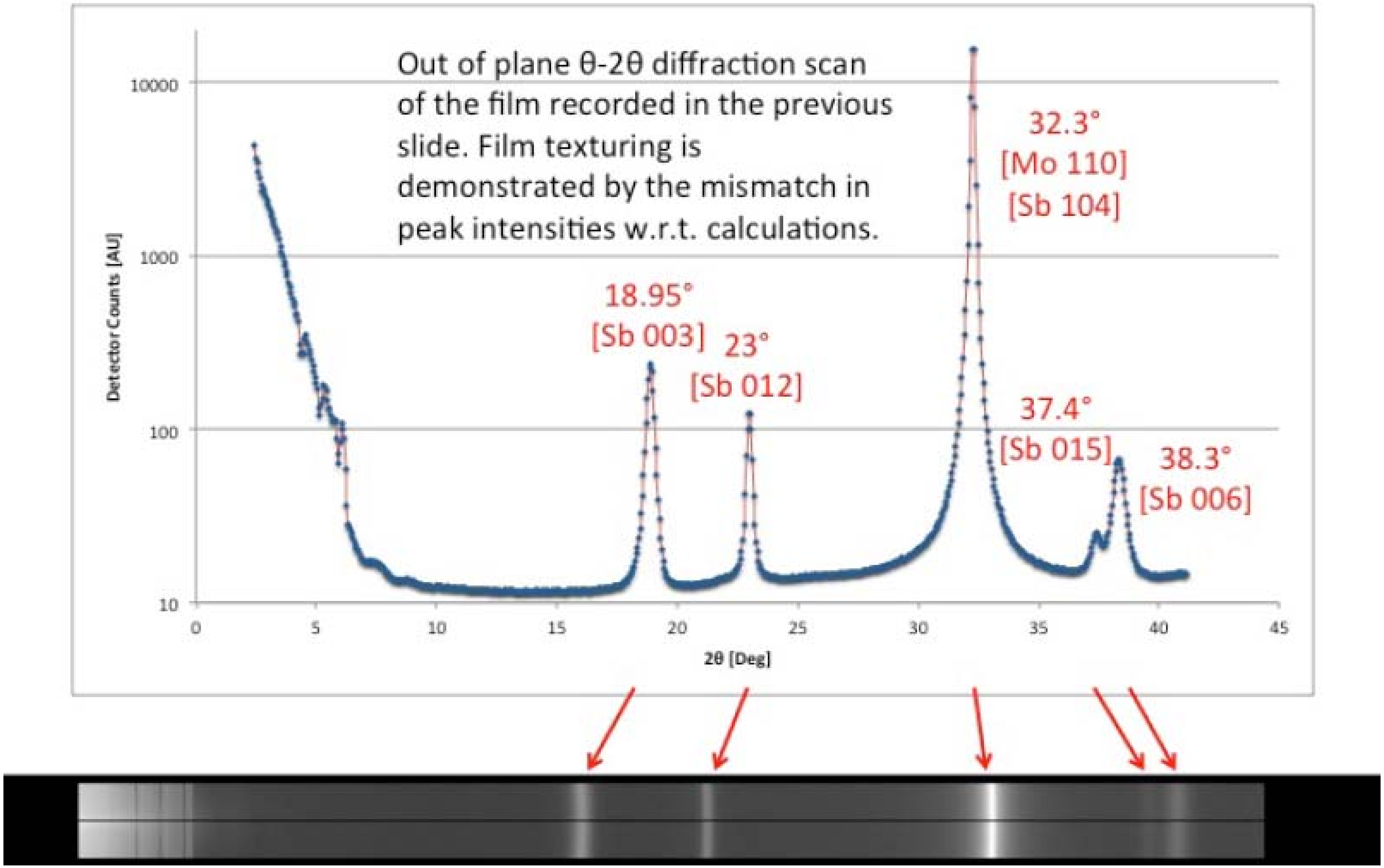






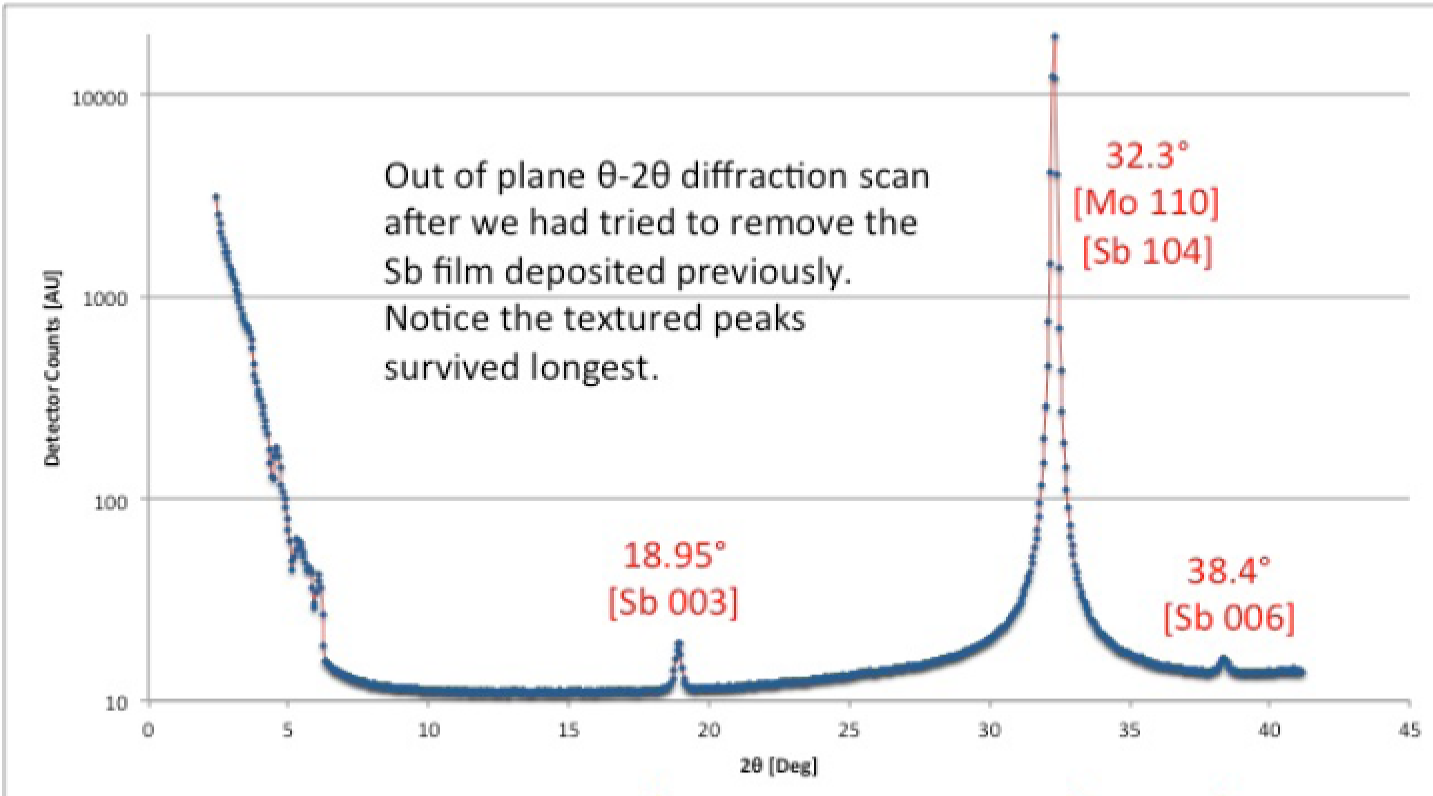
4-27-2011
Scan 186: a2scan nu 4 40 zeta 2 20 36 10
Image Center: 271 x 97

Sb Film on Mo Substrate
Thickness: 80 Å (guess)
Deposited at >> 200 °C (guess)



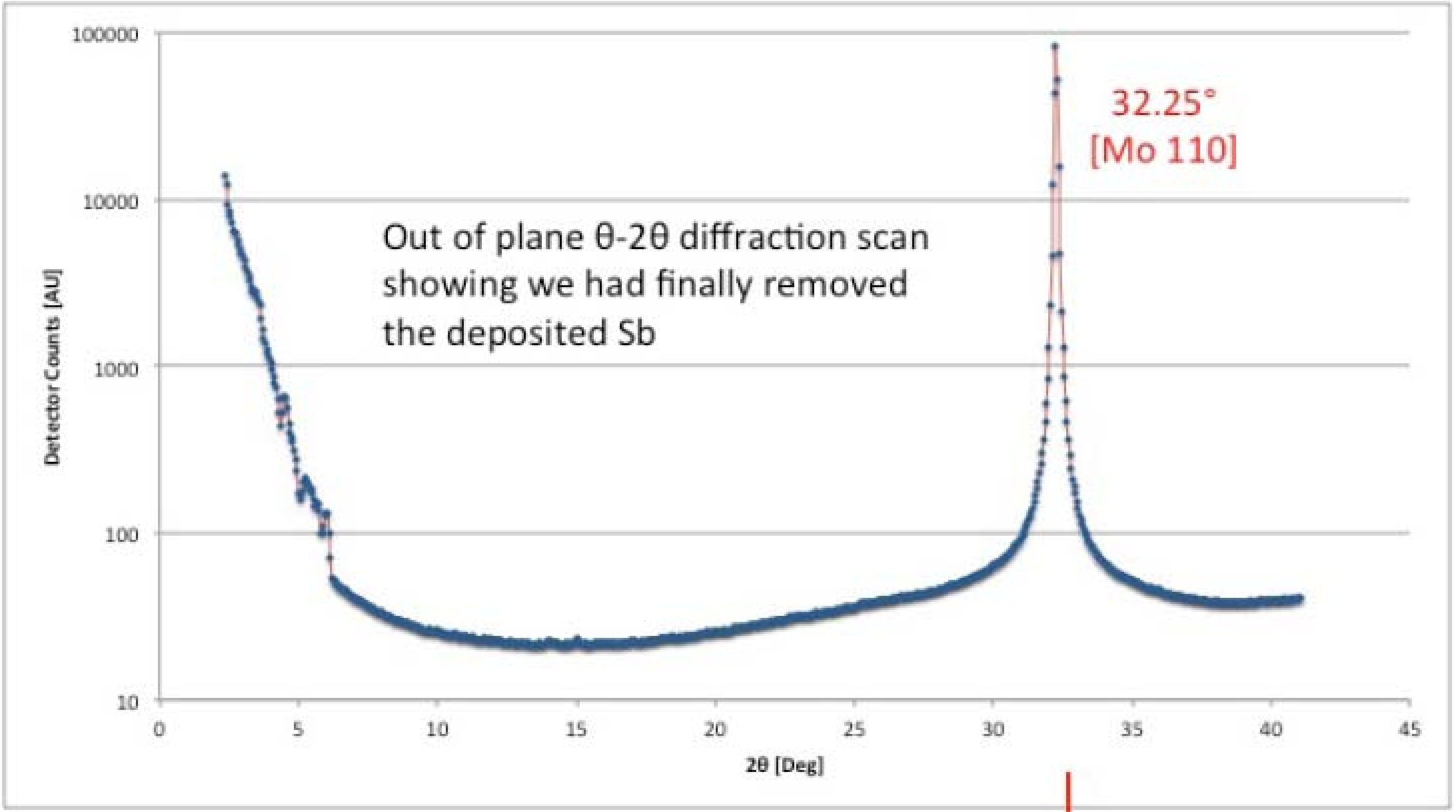
4-27-2011
Scan 189: a2scan nu 4 40 zeta 2 20 36 10
Image Center: 271 x 97

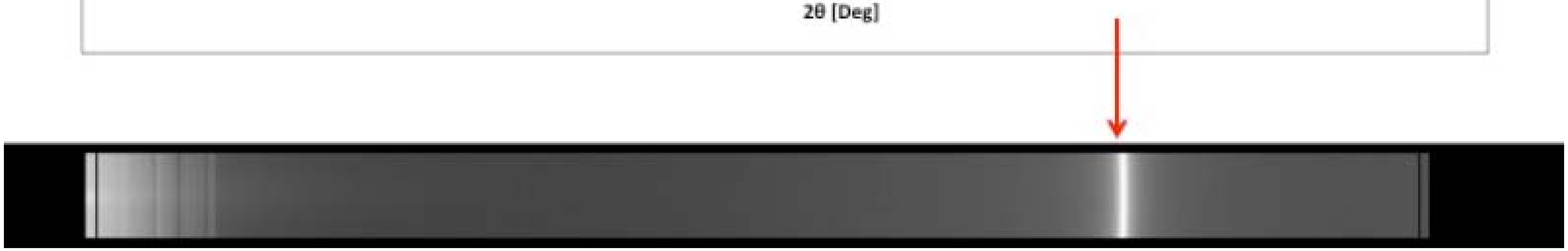
Mo Substrate
w/ residual Sb film



4-28-2011
Scan 199: a2scan nu 4 40 zeta 2 20 36 30
Image Center: 265 x 96

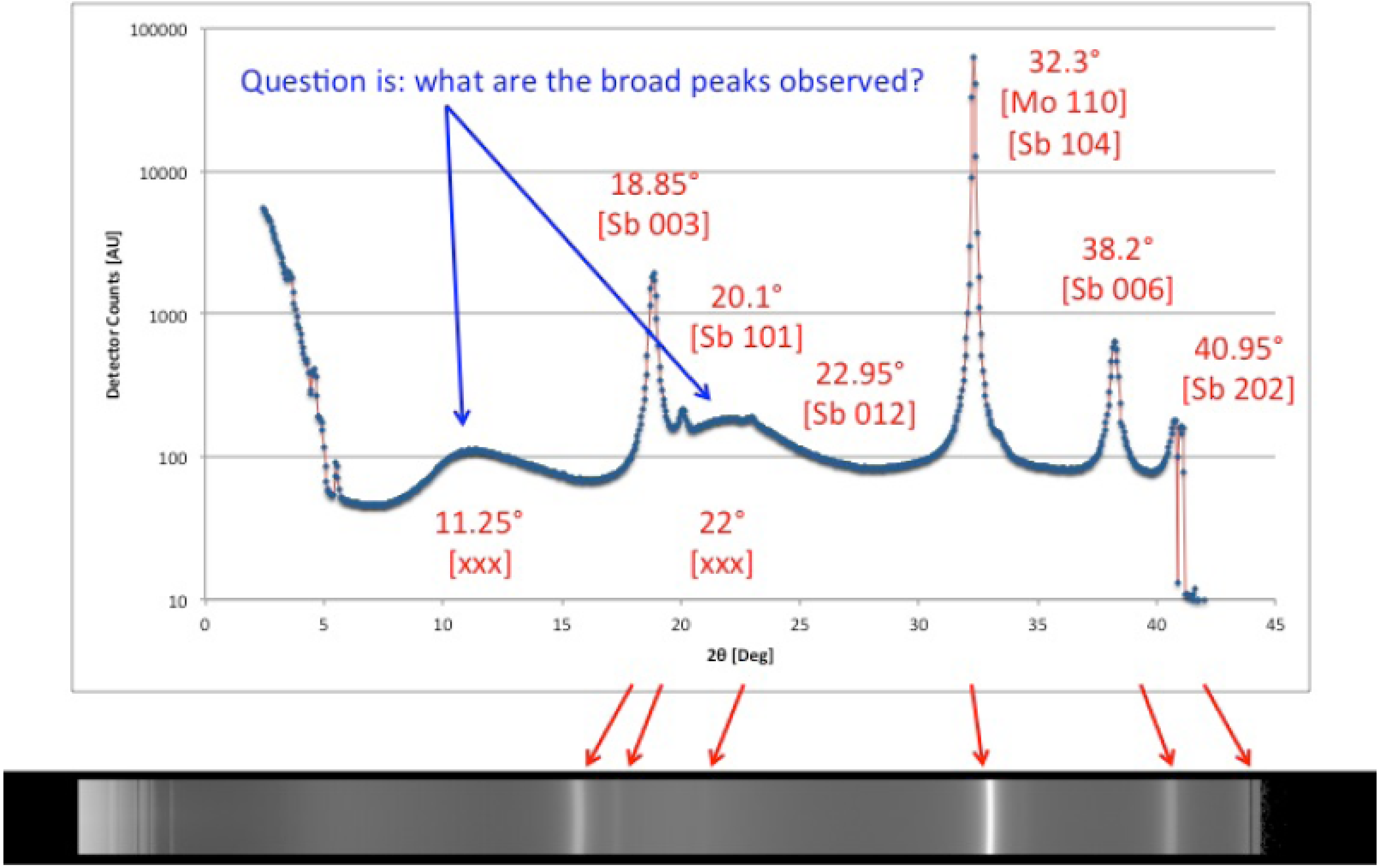
Clean Mo Substrate





4-30-2011 Scan 278
a2scan nu 4 40 zeta 2 20 36 30
Image Center: 270 x 96

K_2CsSb Film?
Thickness: 200 Å Sb + 400 Å of K + 200 Å of Cs (guess)
Deposited at between 120 - 140 °C, estimated to be ~ 130 °C



Reference Data for Powder-Pattern Peaks: λ = 1.2398 Å

2θ intensity h k l

Mo

2θ	intensity	h k l
32.36	100	1 1 0
46.39	16	2 0 0

Sb

2θ	intensity	h k l
19.02	25	0 0 3
20.18	4	1 0 1
23.00	100	0 1 2
32.01	70	1 0 4
33.48	56	1 1 0
37.49	12	0 1 5
38.55	35	0 0 6
41.00	26	2 0 2
46.99	15	0 2 4

K

2θ	intensity	h k l
24.30	100	1 1 1
28.12	75	2 0 0
40.05	60	2 2 0

K_3Sb

2θ	intensity	h k l
13.31	393	0 0 2
13.64	279	1 0 0
15.18	511	1 0 1
23.73	999	1 1 0
24.30	954	1 0 3
26.80	56	0 0 4
27.31	307	1 1 2
27.47	55	2 0 0
28.30	90	2 0 1
34.23	309	2 0 3
36.10	126	1 1 4
36.49	44	1 0 5
36.62	70	2 1 0
37.26	75	2 1 1
40.68	52	0 0 6
41.73	144	3 0 0
42.08	287	2 1 3
43.10	17	1 0 6
43.99	80	3 0 2
43.99	80	2 0 5

KSb

2θ	intensity	h k l
10.98	80	1 0 0
11.77	61	0 0 2
12.21	54	1 0 2
14.36	68	1 1 1
15.65	79	0 1 2
15.99	43	1 1 2
17.81	53	1 1 1
21.41	68u	1 0 4
21.48	u	0 2 1
22.06	87	2 0 0
22.75	49	2 1 1
22.98	52	1 2 1
23.80	100	1 1 4
25.32	55	1 2 1
27.27	83u	2 1 1
27.31	u	0 2 3
28.38	16	1 2 2
29.06	19	2 2 1
30.07	70	2 2 3
31.09	17	2 1 2
31.50	19	0 1 5
31.98	39	3 1 2
31.98	39	1 1 4
32.30	48	1 2 3
33.35	37	3 0 0
33.35	37	3 1 4
35.61	17	3 1 5
42.53	16	3 1 7
44.94	16	2 1 8

Cs

2θ	intensity	h k l
21.98	100	1 0 1
22.77	46	0 0 4
27.33	58	1 0 3
32.33	74	1 1 2
35.87	28	1 0 5
43.22	17	2 0 0
46.08	14	1 0 7
46.45	27	1 1 6
46.51	67	0 0 8

Cs_3Sb

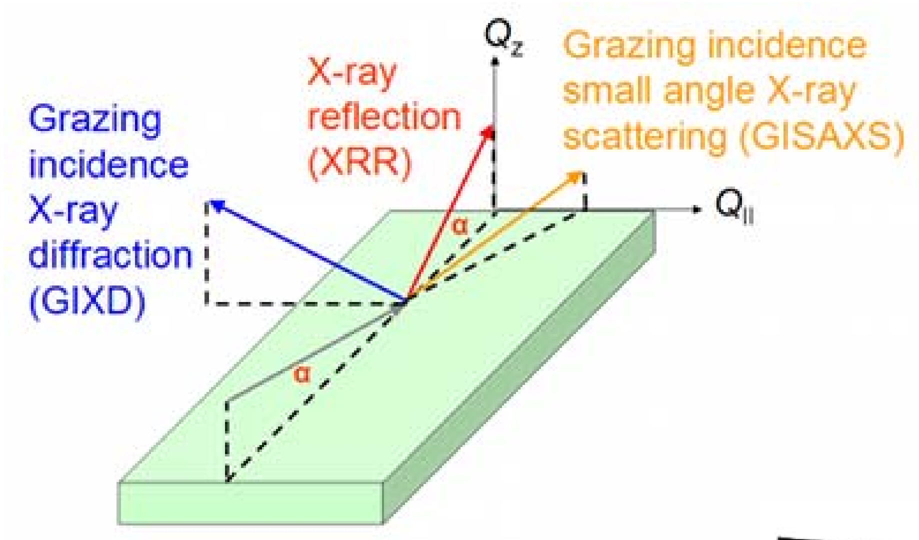
2θ	intensity	h k l
22.19	100	2 2 0
31.56	25	4 0 0
38.87	60	4 2 2
45.17	20	4 4 0

CsSb

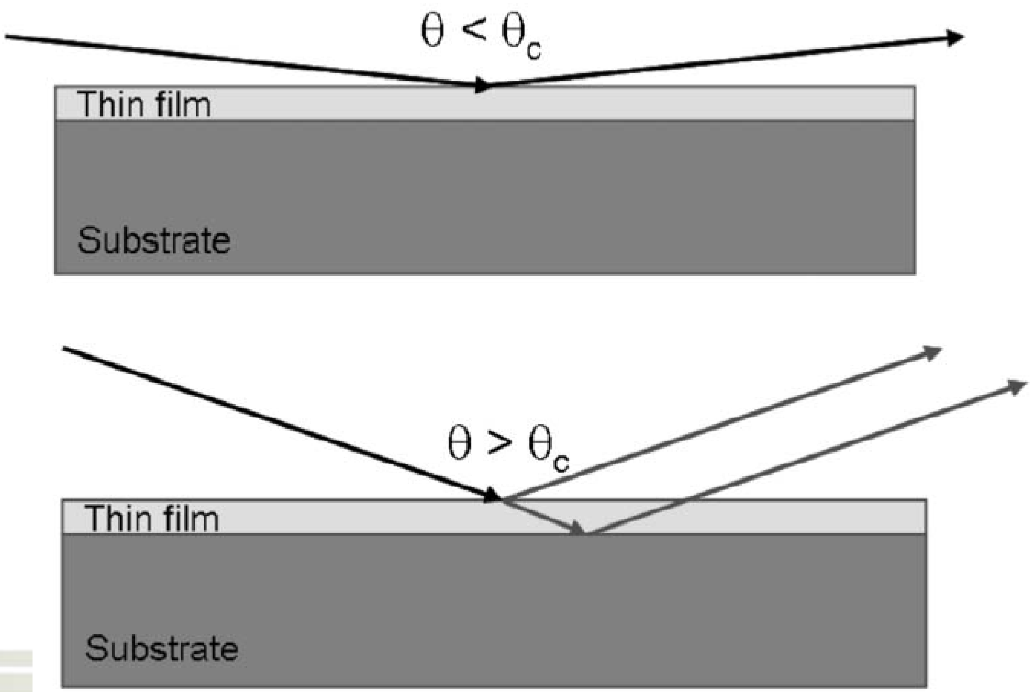
2θ	intensity	h k l
10.71	10	0 0 2
10.81	29	1 0 1
17.26	10	1 1 2
18.84	25	0 1 3
19.61	55	2 0 1
20.16	13	0 2 1
21.07	100	1 1 3
21.21	26	2 1 0
21.63	35	1 2 0
21.71	15	2 0 2
22.23	13	0 2 2
22.28	42	1 2 1
23.52	24	1 0 4
23.82	39	2 1 2
24.20	21	1 2 2
25.33	20	0 2 3
25.48	31	1 1 4
27.06	26	1 2 3
27.72	25	2 2 1
32.01	24	3 1 2
33.62	12	0 3 3
35.07	16	3 2 1
35.50	18	2 3 1
37.29	22	3 1 4

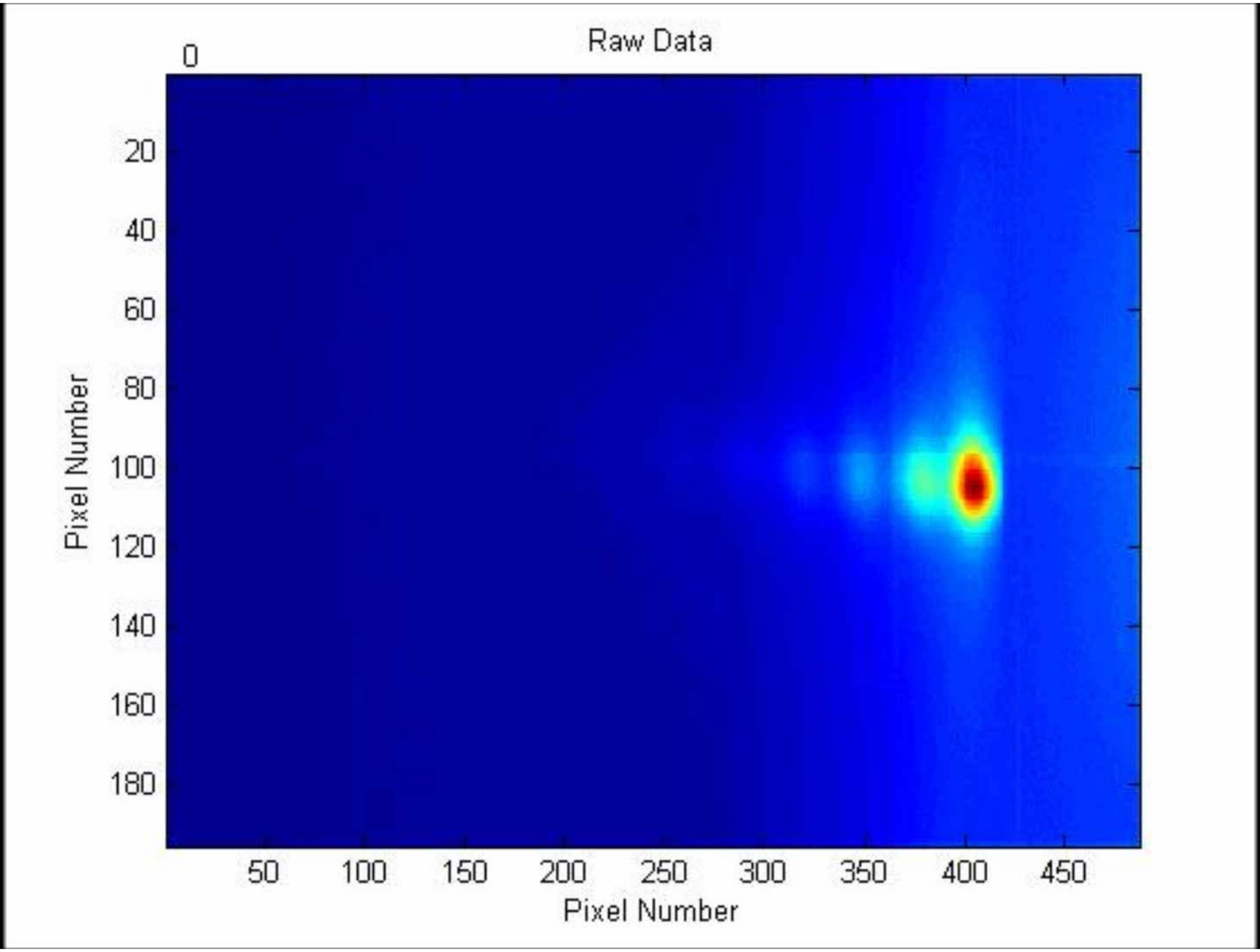
Many peaks between 10-15° and 20-25°!

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

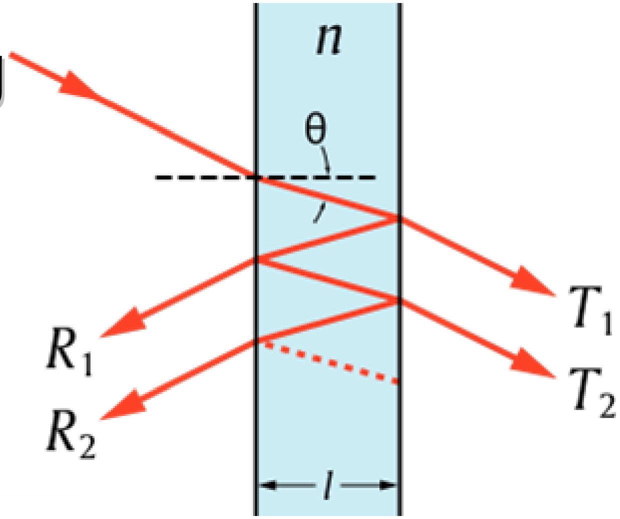


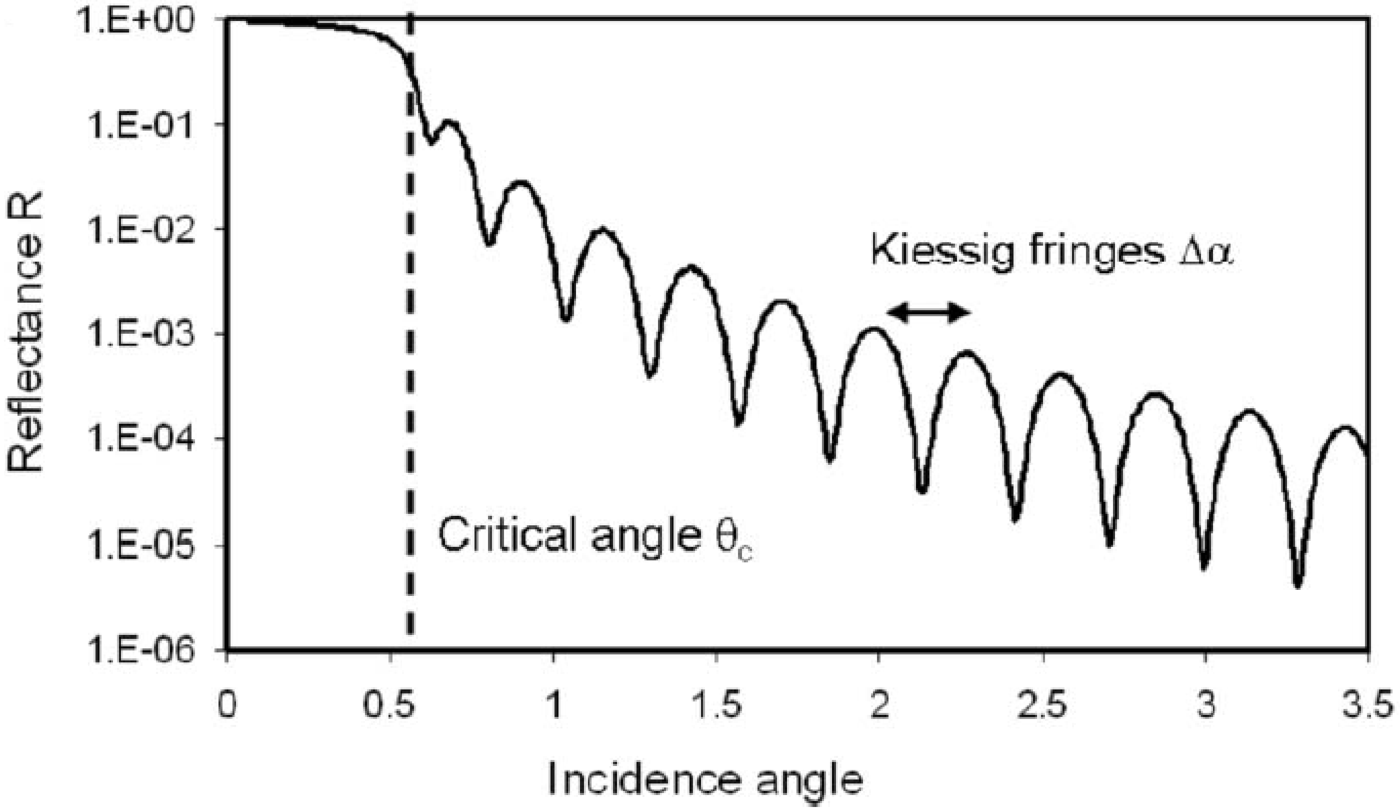
$$\theta_c = \arccos(n_{medium} / n_{air})$$



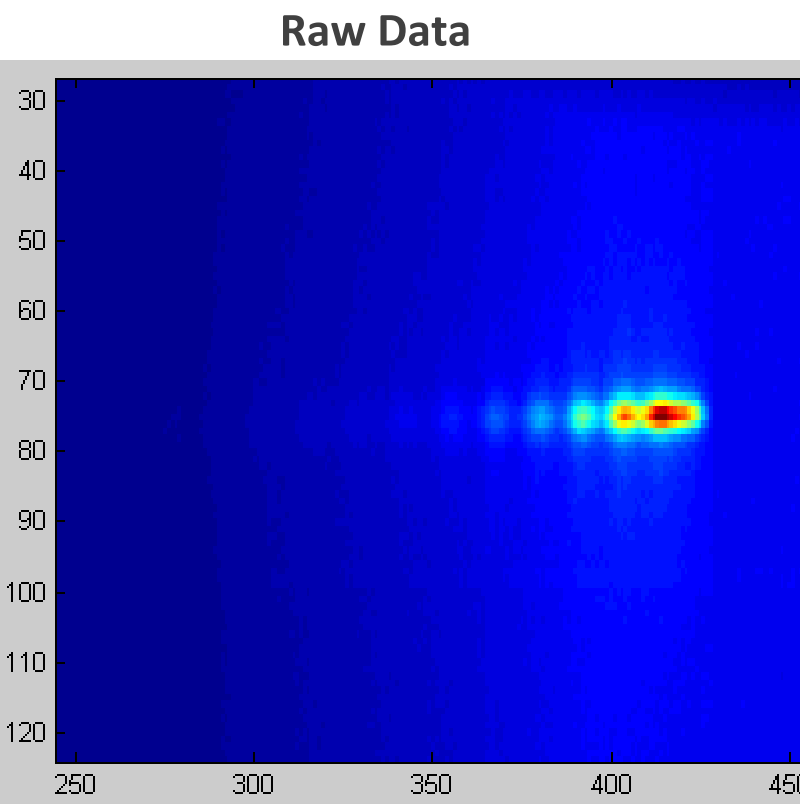

Raw Data
0
20
40
60
80
100
120
140
160
180
Pixel Number
50
100
150
200
250
300
350
400
450
Pixel Number

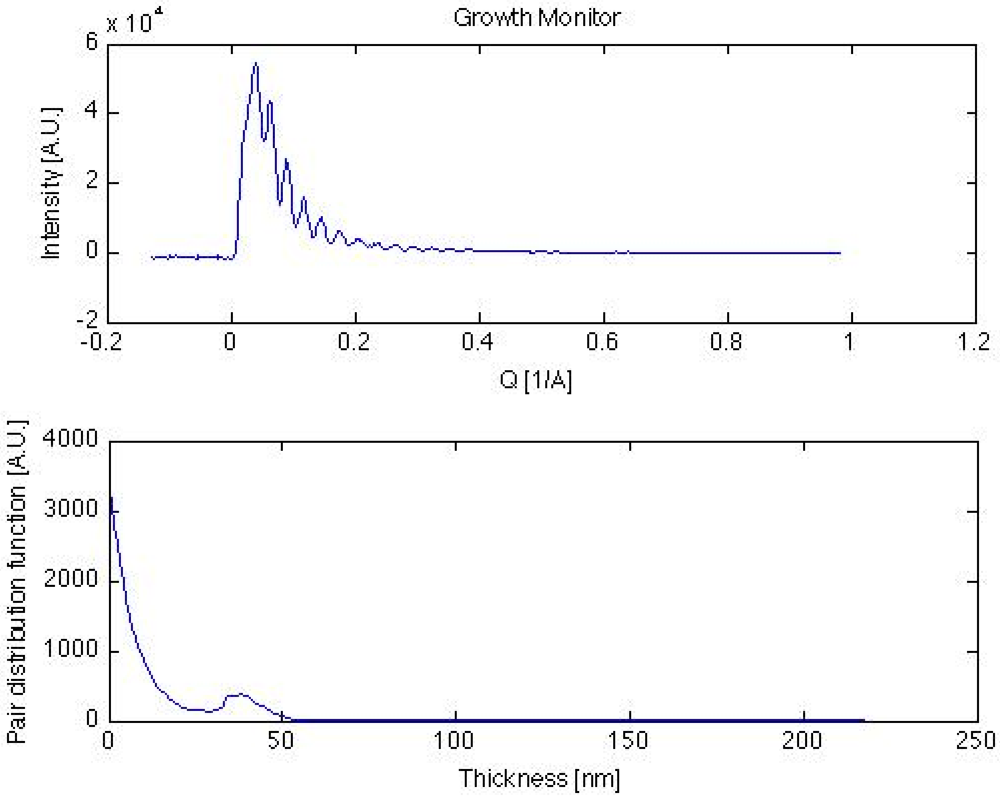
X-ray reflectometry (XRR)
- provides in-situ thickness monitoring





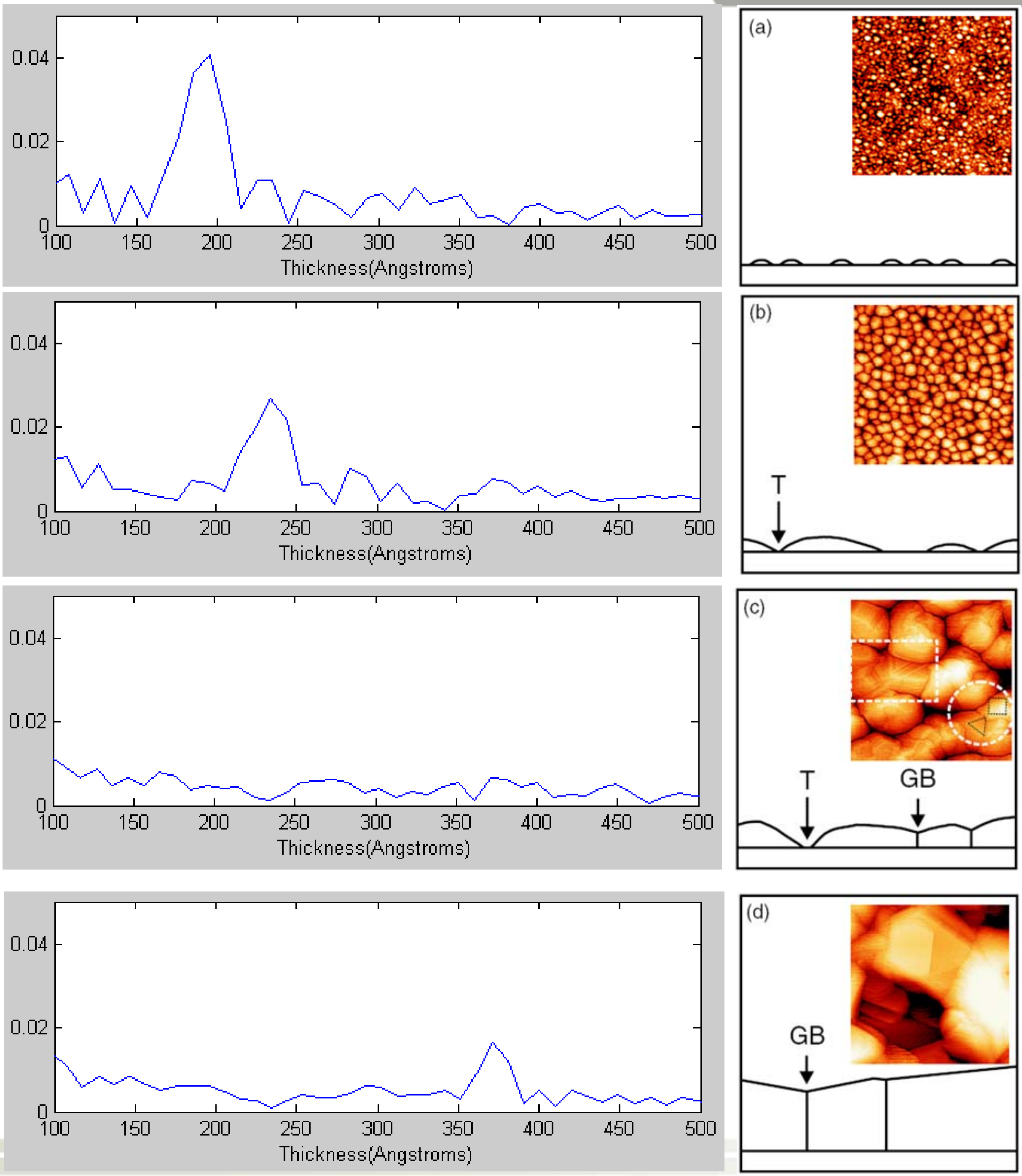
Example for 1 sec exposure at BNL/X21





- Film thickness measured between 37-39 nm
- Nominal thickness (SEM calibration) 37 nm
- Data accumulation time : 1 second at X21,NSLS-BNL (takes 30 ms at 11-IDD, APS-ANL)

Sb -> K


0.04
0.02
0
100
150
200
250
300
350
400
450
500
Thickness(Angstroms)
(a)
(b)
T
(c)
T
GB
(d)
GB

Conclusion

- The potential of theory inspired multi-alkali photocathode development
  - Band structure engineering by tuned phase segregation
  - Deep understanding of growth will help to develop
    - Large area photocathode
    - High quantum efficiency and high production yield
    - Wavelength tunability

- Collaborators
  - Klaus Attenkofer , Seon Woo Lee (ANL)
  - John Smedley, Triveni Rao (BNL)