Visualization of Structure and Composition During Photocathode Growth

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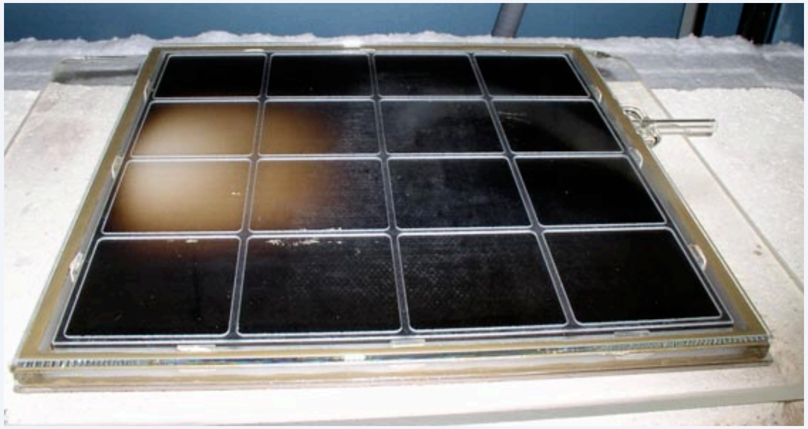
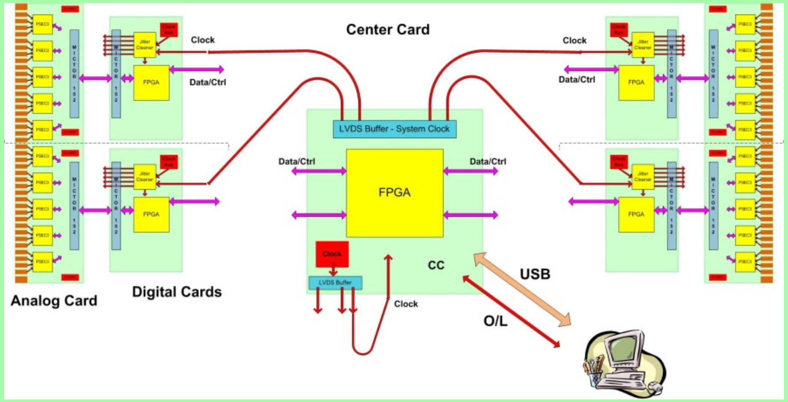
The 4 `Divisions' of LAPPD

Hermetic Packaging



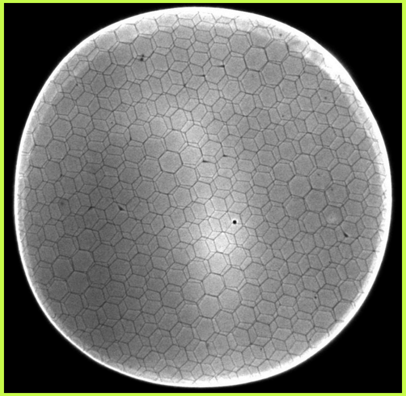
See Bob Wagner's talk

Electronics/Integration



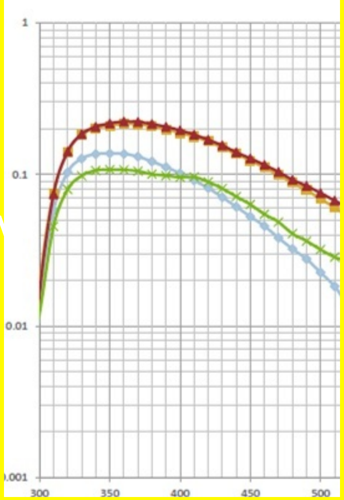
See Henry Frisch's Talk

MicroChannel Plates



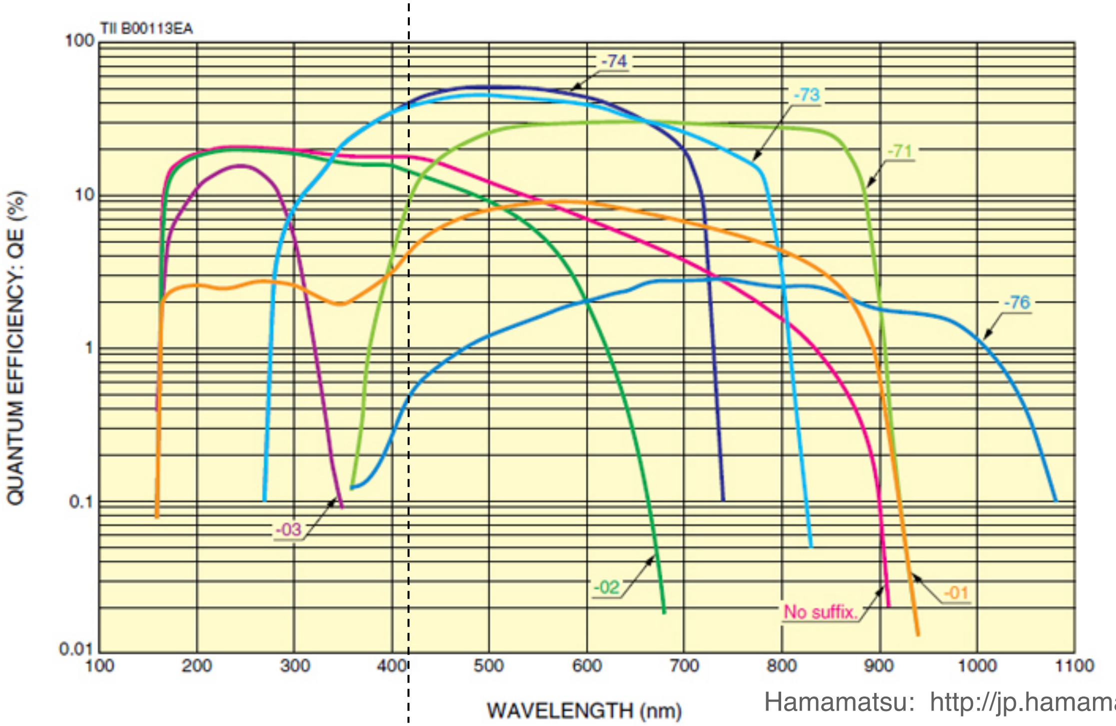
See (hear) Bob Wagner's
& Ossy Siegmundtalk

Photocathodes



This Talk

What is a Photocathode?



Suffix	Photocathode	Input Window
−71	GaAs	Borosilicate Glass
−73	Enhanced Red GaAsP	Borosilicate Glass
−74	GaAsP	Borosilicate Glass
−76	InGaAs	Borosilicate Glass
Non	Multialkali	Synthetic Silica
−01	Enhanced Red Multialkali	Synthetic Silica
−02	Bialkali	Synthetic Silica
−03	Cs−Te	Synthetic Silica

Hamamatsu: http://jp.hamamatsu.com/products/sensor-etd/pd014/index_en.html

- Various cathodes are feasible
  - Only semiconductor cathodes are useful for detection applications
  - Multi-alkali are the the only cathodes available at 400nm and polycrystalline
- Focus on Multi-alkali cathodes:
  - Cost efficient thin film technology
  - Low dark current
  - High conductivity
  - Relative robust (unclear what destroys the cathode)

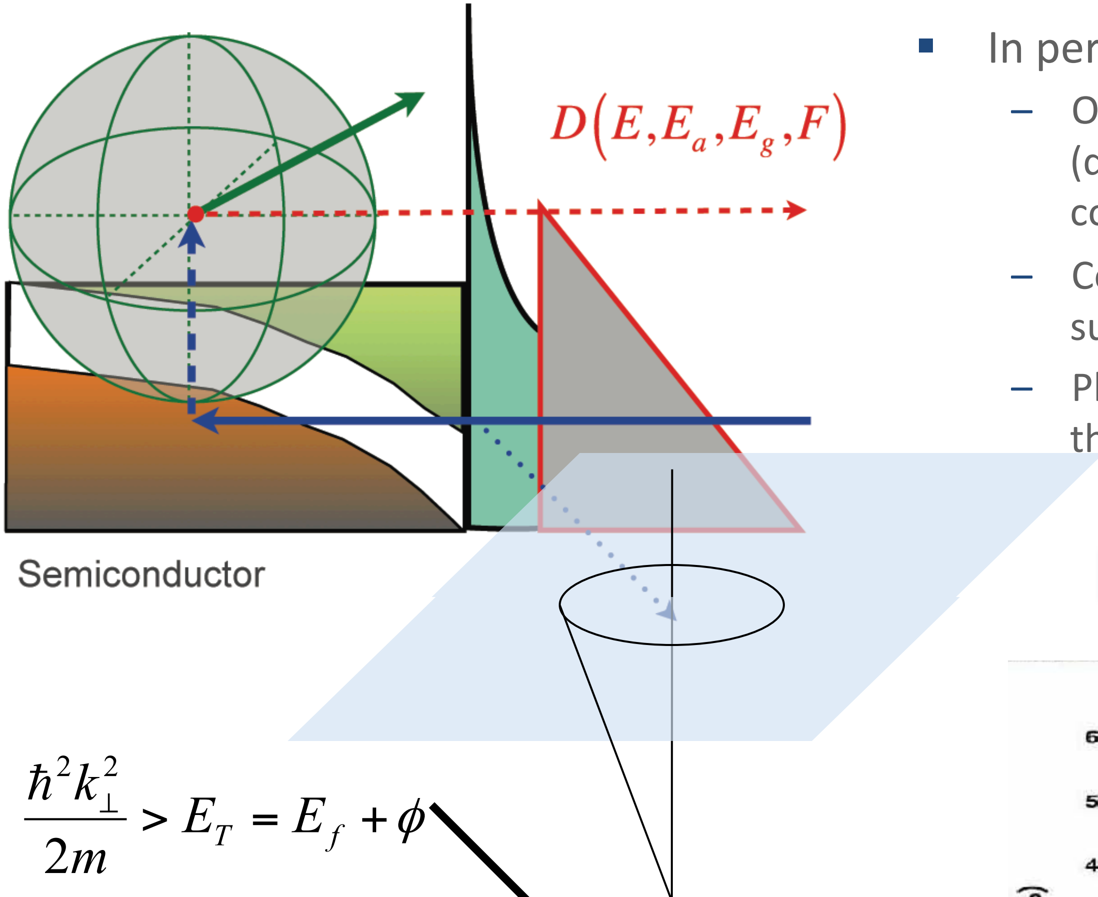
Goals and Activities

- Goals of the project
  - High Quantum Efficiency
    - Unclear what number but larger 50%
    - Response optimized at 400nm
    - First approach: low count rate application
  - High production yield
    - Low variation from batch to batch
    - Independent from "personal experiences" ; can be performed by control system
  - Low production cost
    - Short production cycle
    - Large parameter-acceptance
- Activities:
  - Basic sciences:
    - General understanding and modeling of growth process
    - Pre-selection of optimization parameter space
    - Recipe suggestions
  - Engineering
    - Reproducibility of evaporators
    - Development of process-control parameters
    - Designing process environment for optimized recipe

Basic Sciences

- Visualizing what happens during the growth:
  - Scattering experiments have proven very power full
  - To do:
    - Learning how to analyze data (especially diffuse scattering)
    - Automatic data analysis with automatic creation of rate constants
    - Improving evaporator system to allow "arbitrary" recipe
    - Reconstruction of spatial model
    - Simulation of thin film growth
- What we need from the material:
  - Single crystal in surface normal direction
    - Unclear what is the best lateral size
    - Minimizing impurity scattering (avoiding solid state alloying?)
  - Creating electric fields
    - Substrate effects
    - Doping
    - Layered structures
  - Influence of surface states on dark current

What Determines the Quantum Efficiency?

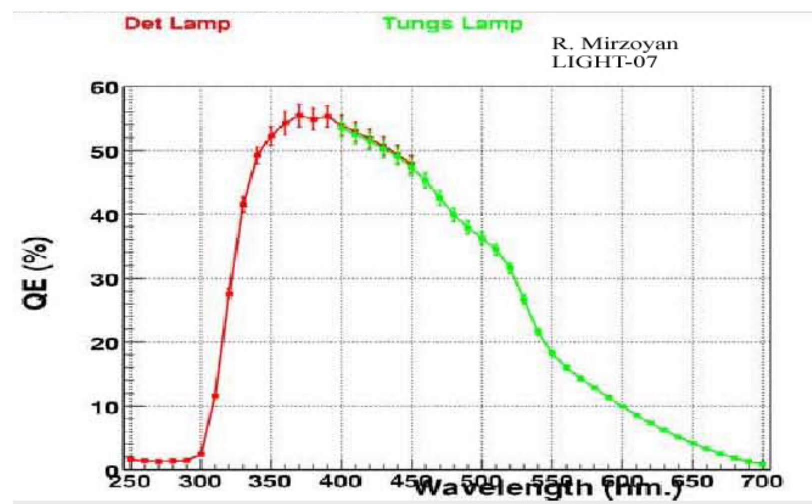


- In perfect Material (multi-alkali)
  - Original photoelectron direction is random (due to s-p character of valence & conduction band).
  - Cone determined by kinetic energy and surface barrier.
  - Phonon scattering helps to increase slightly the escape probability.

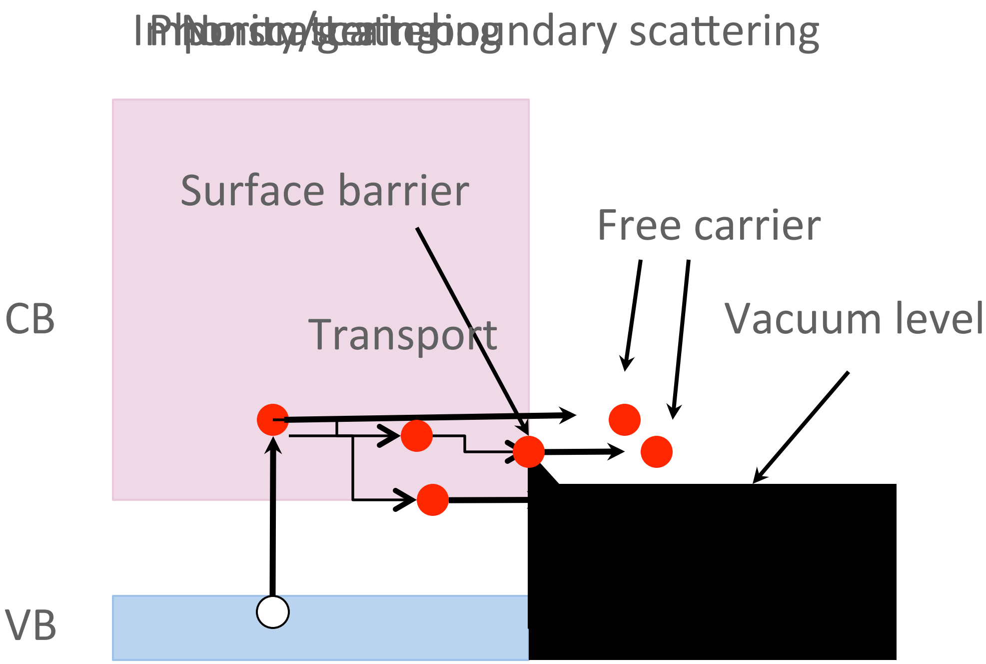
$$\frac{\hbar^2 k_\perp^2}{2m} > E_T = E_f + \phi$$

$$QE(\nu) \propto (h\nu - \phi)^2$$

Maximal QE ~ 60%?



Why does Materials Quality Play a Role?

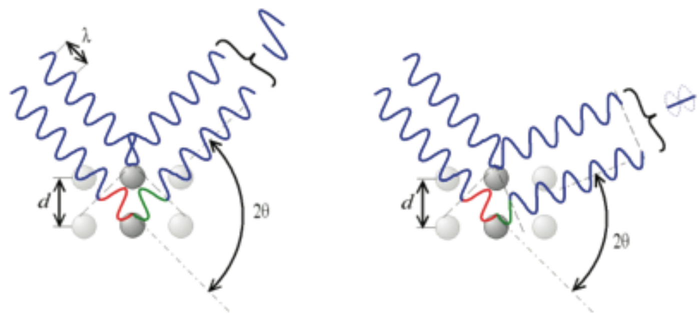


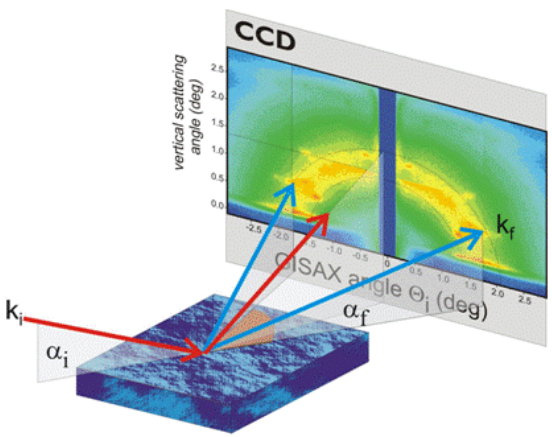
Material composition determines:

- Band gap
- Work function
- Surface barrier

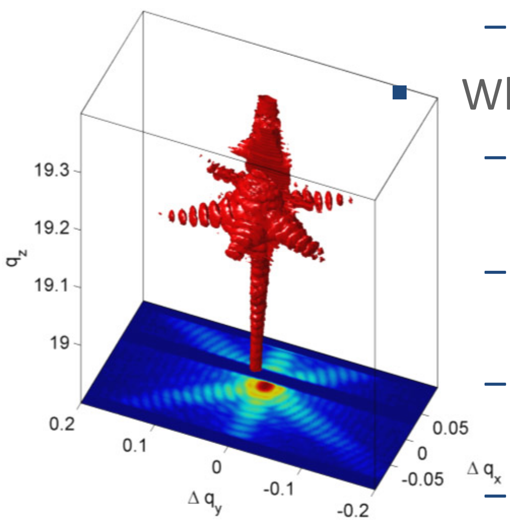
- Description of cathode functionality in Spicer-Three-Step-Model
  - Absorption, Transport, emission
- No scattering:
  - Photon energy is converted in kinetic energy of photoelectron
  - Electron will be emitted (as long as momentum perpendicular to surface is large enough)
- Phonon scattering
  - Small energy loss per scattering event
  - Randomizing direction
- Impurity/grain boundary scattering
  - Large energy loss per scattering event
  - Small probability to escape!

X-ray Scattering: A Perfect In-Situ Tool to Analyze Composition, Structure, and Chemistry!





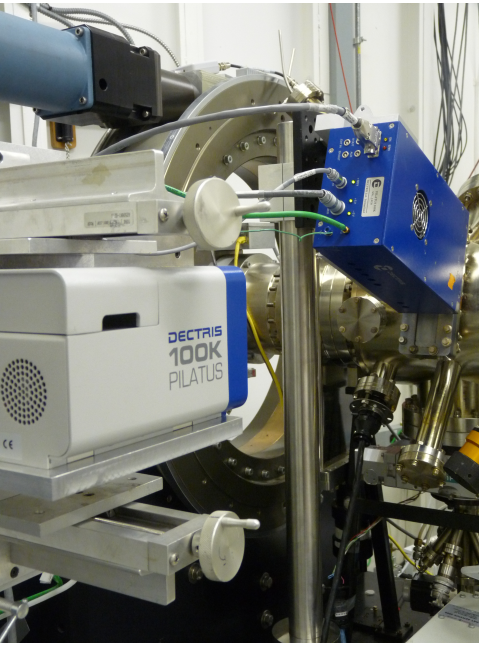
general GISAX-setup

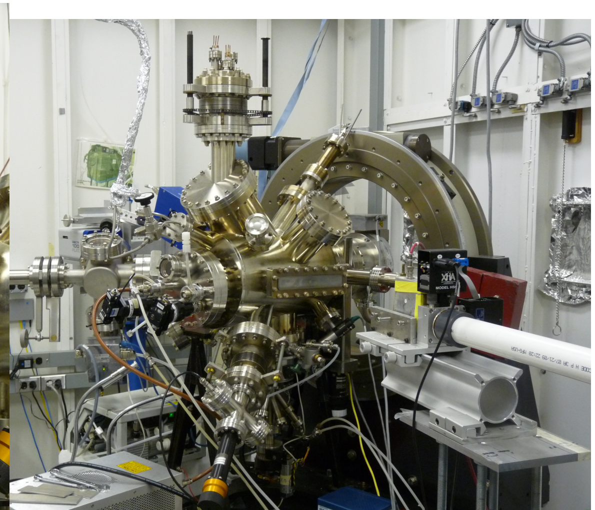


- The elementary process
  - Each atom scatters X-rays in 4π
  - An ensemble of atoms:
    - Crystalline form produces "bragg"-peaks
    - Amorphous materials produce a "Pair-Distribution-Pattern"
- Single wavelength diffraction:
  - Single crystal produces typically only one reflection (or none)
  - A powder of single crystals produce Rings
- What information is in the diffraction pattern
  - 2-Theta position is a measure for the lattice-plane distance
  - Phi-position reflects orientation of the crystallites
  - Width and shape of the reflection reflects crystallite size and/or strain of the crystal
  - Detailed analysis of peak-shapes will produce electron-density map of sample

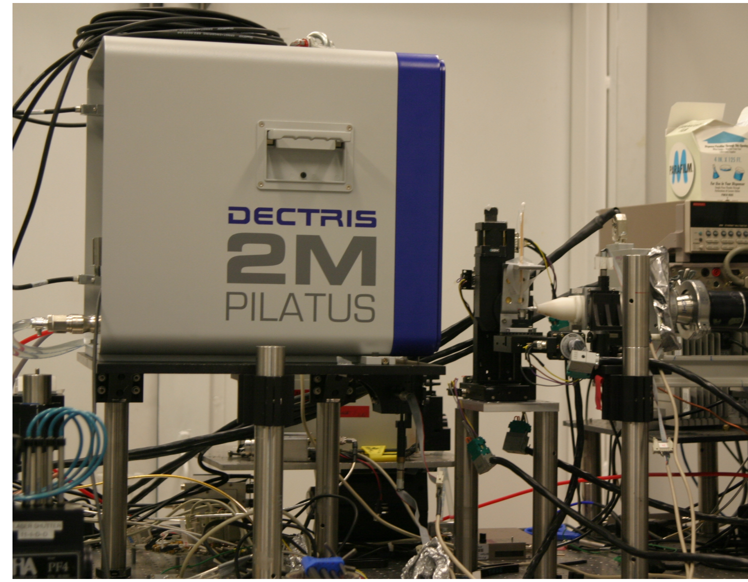
The Experimental Setup

BNL





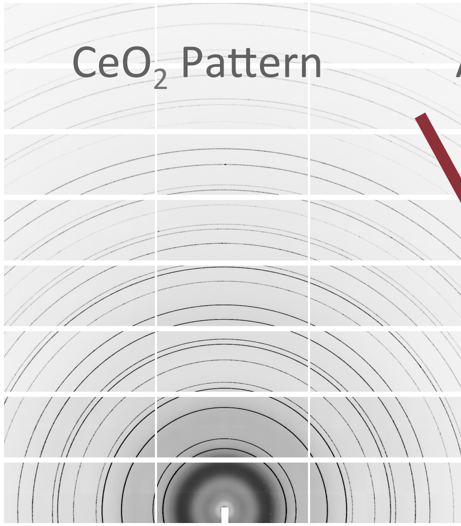
ANL



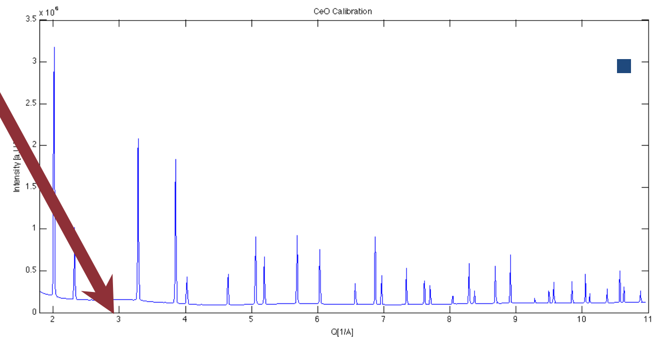
- Experiments take place at BNL/NSLS I and ANL/APS
- Currently no dedicated insitu chamber available
- However: New chamber for BNL in commissioning and transportable evaporator under design

Data-Processing

CeO$_2$ Pattern

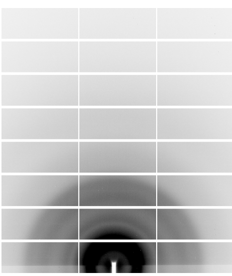


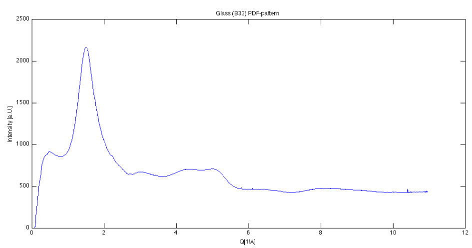
Azimuthal Integration and fit of peak positions

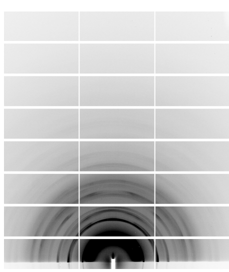


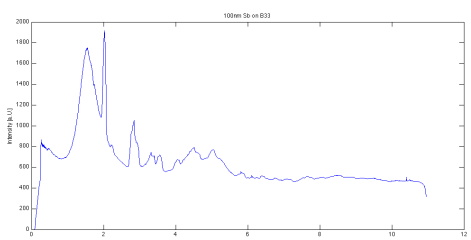
Data-Analysis:

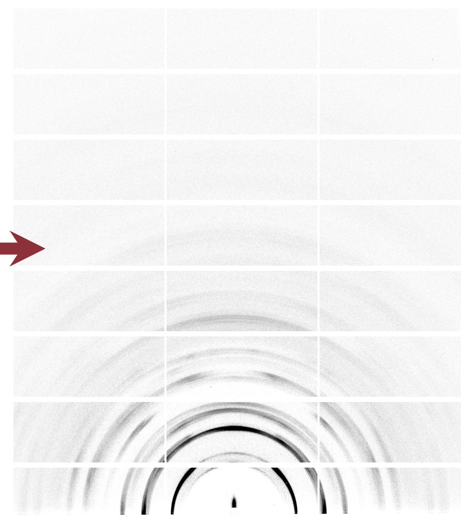
- Calibration with known standard (CeO2)
- "Empty"-pattern (B33)
- Sb-on B33 pattern
- Result: Difference showing only Sb-film and changes on glass-subtrate

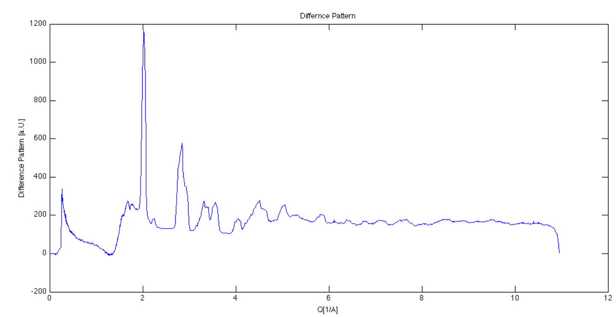




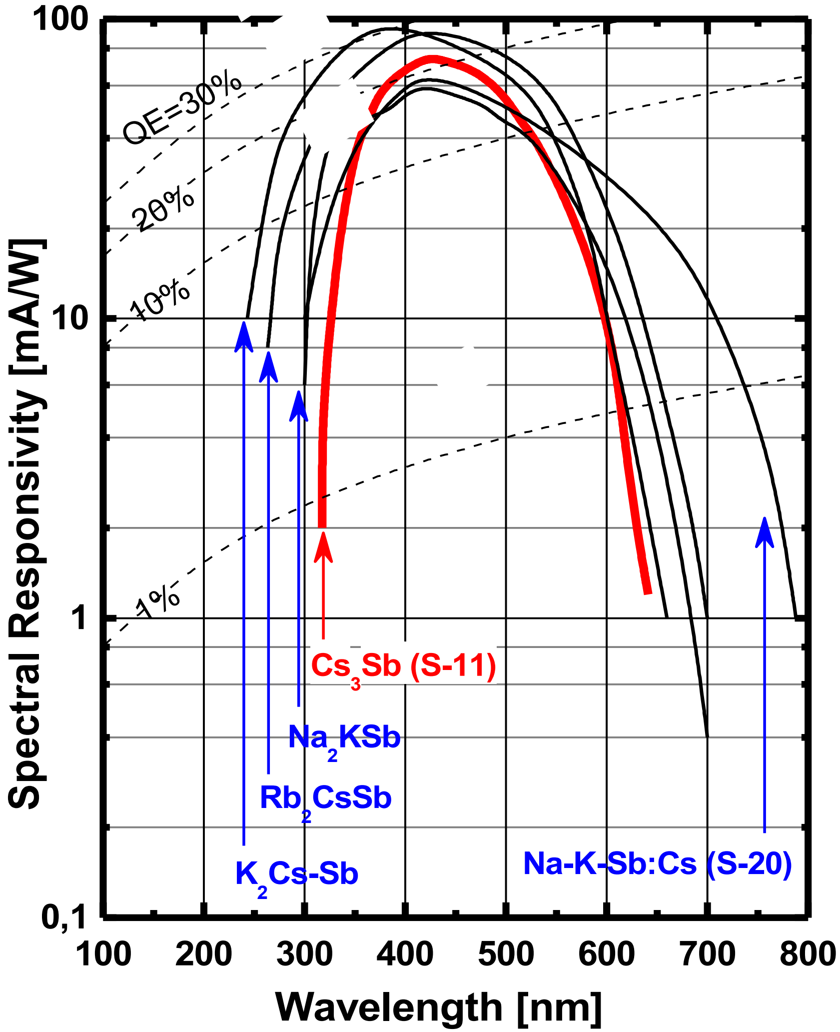




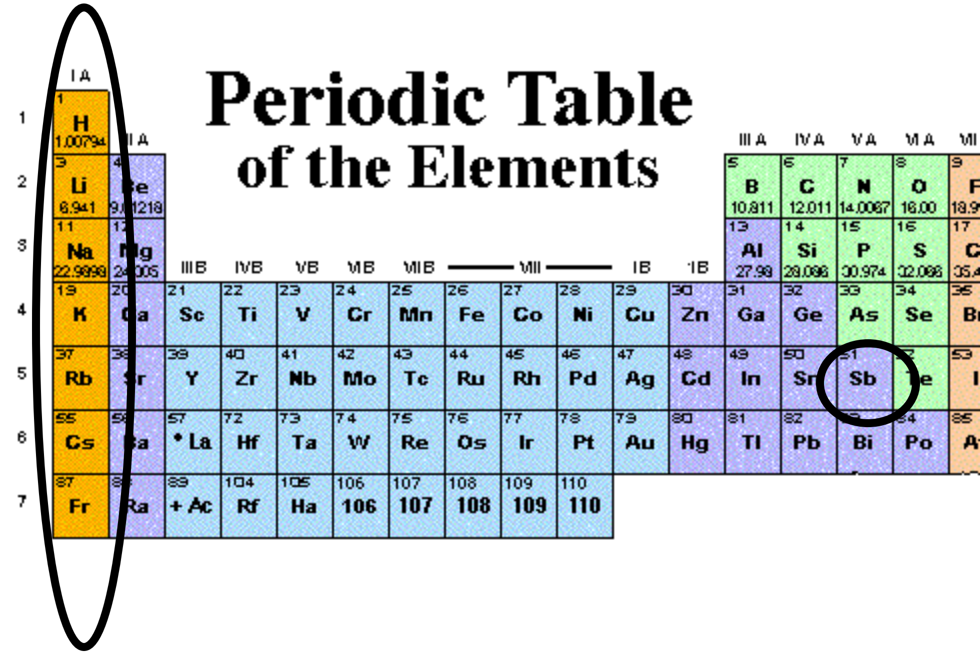




A Closer Look to Multi-Alkali Cathodes

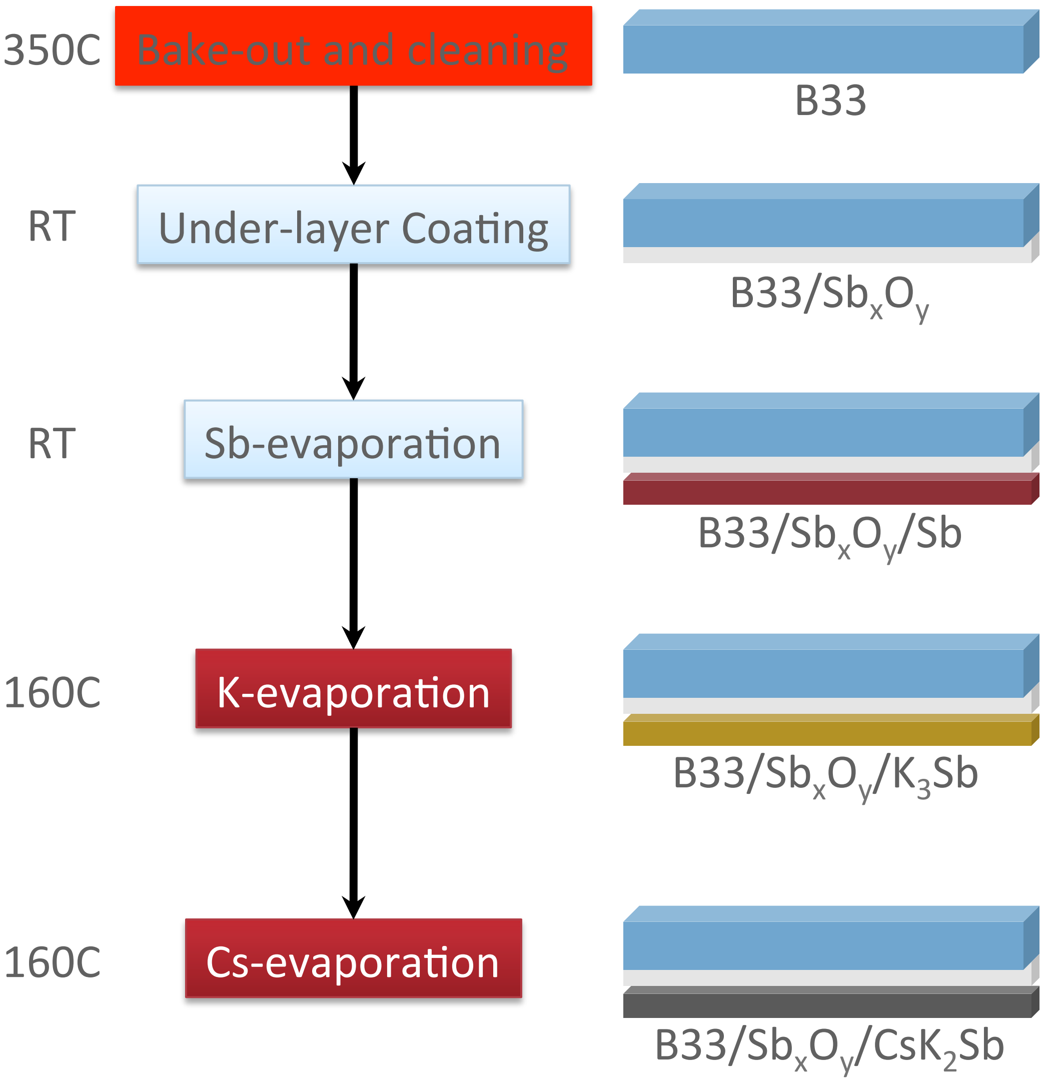


A. Lvashenko



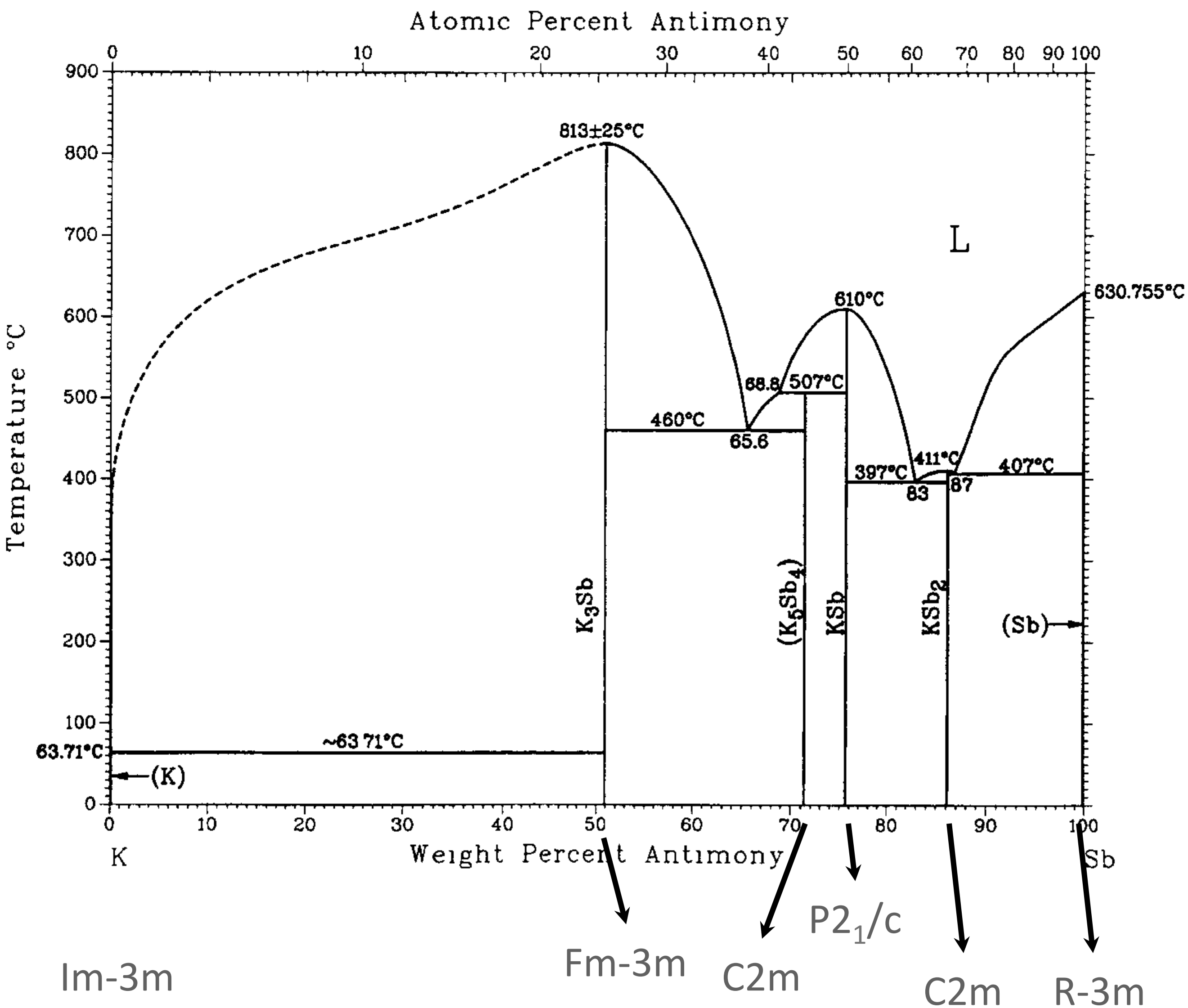
- Typical compound: SbA_3
- A: (Li), Na, K, Cs
- Various combinations are possible

What Can We Learn from the Past?



- The cathode of interest: CsK_2Sb
- Recipe from different communities
  - Various recipes are available
  - Recipe includes:
    - Process timing
    - Process temperatures (and ramps)
    - Evaporator design, pump rates, details of materials.....
    - Recipe depends on evaporator system
- Groups of recipes
  - Either Co-evaporation or sequential evaporation
  - Interlayer between glass and cathode or none

What Happens on an Atomistic Level?



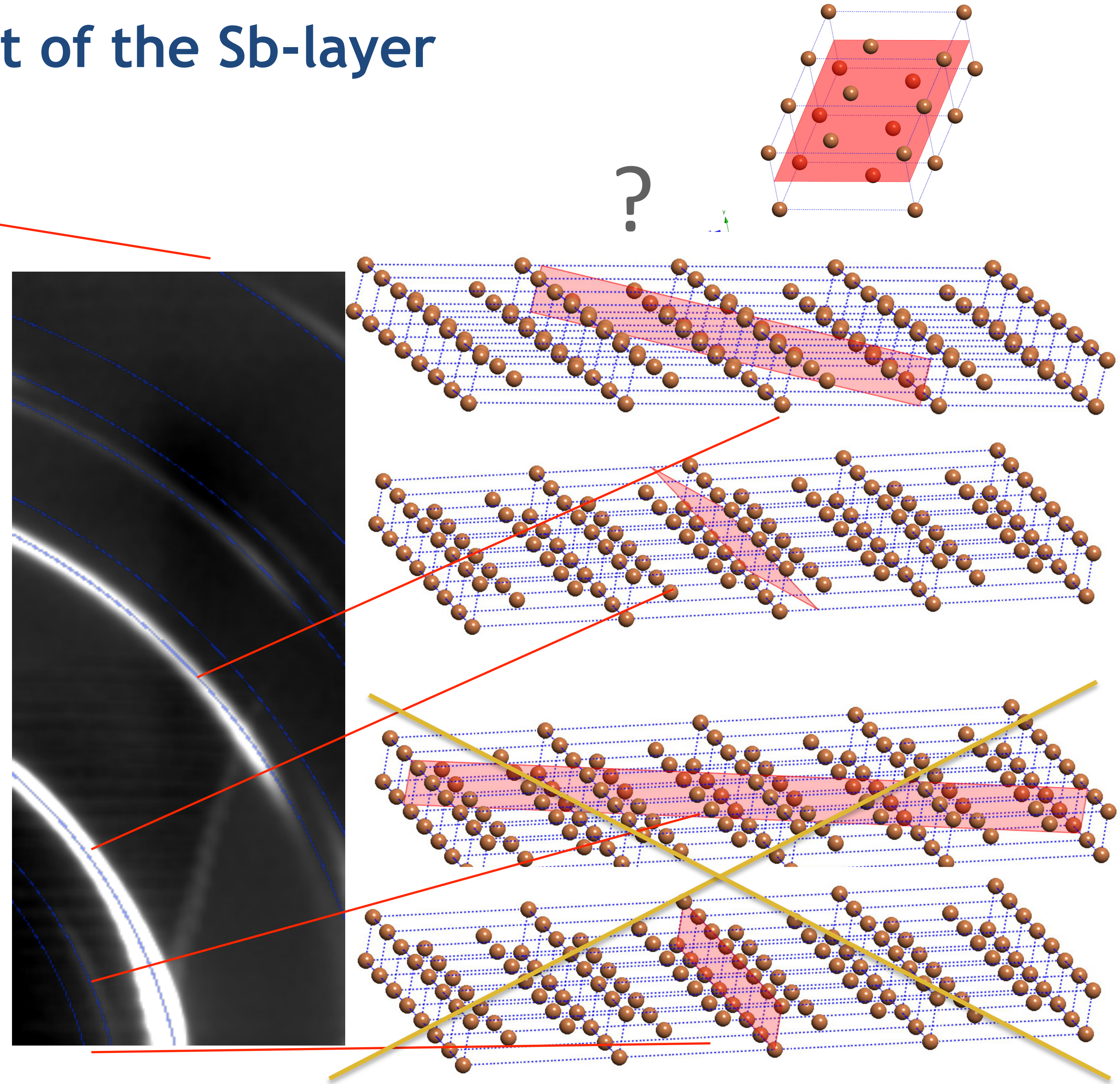
- B33 (substrate)
  - How clean is clean
  - Is there any influence of surface states
- Interlayer
  - Chemical composition
  - Roughness
  - structure
- Conversion of Sb-Metal -> K_3Sb
  - Influence of Sb-Metal structure on final K_3Sb structure?
  - Final structure
  - Final composition
- Conversion of K_3Sb -> CsK_2Sb
  - Same questions as above

Pre-alignment of the Sb-layer

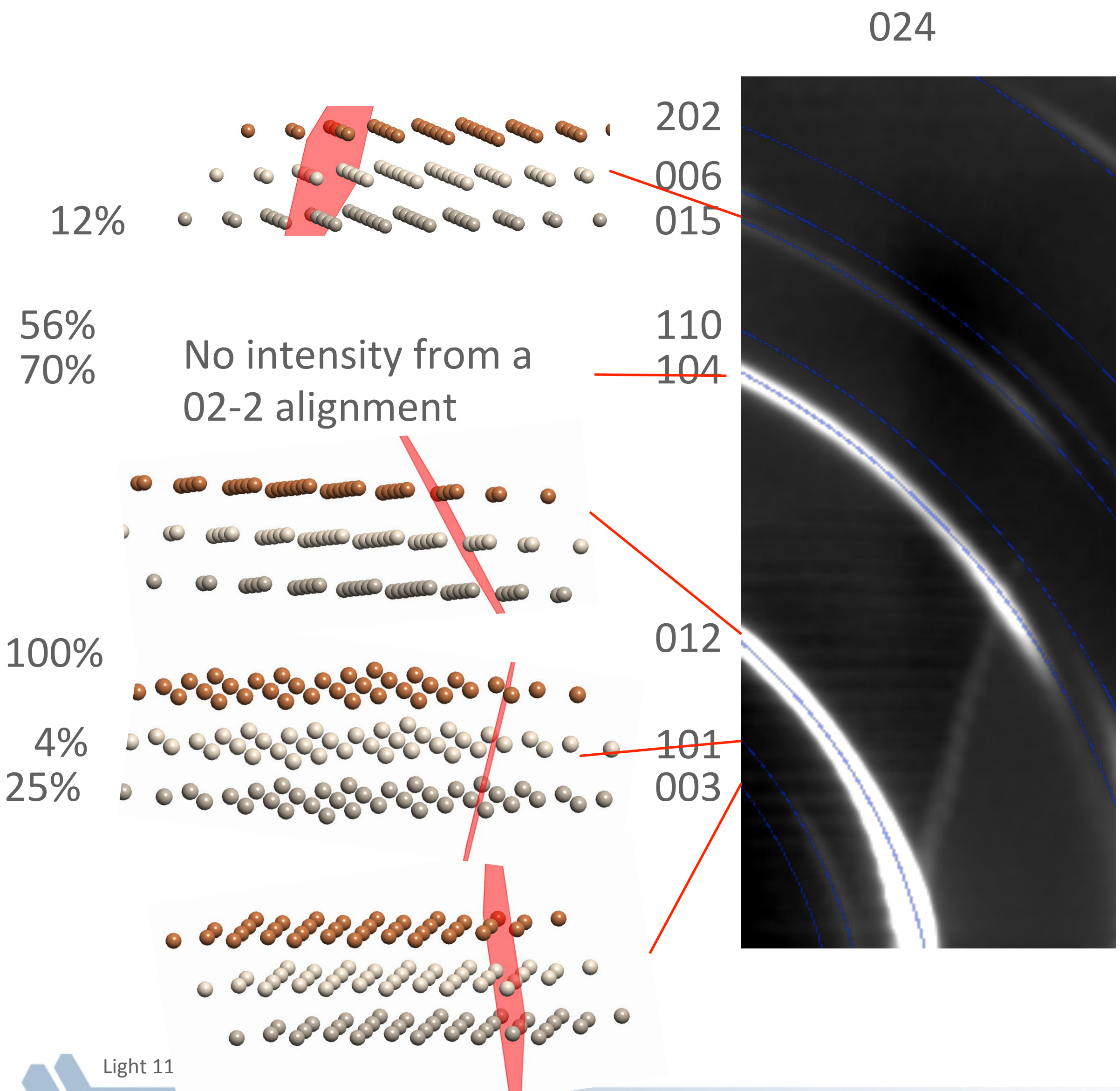
2θ	intensity	h k l
46.99	15	0 2 4
41.00	26	2 0 2
38.55	35	0 0 6
37.49	12	0 1 5
33.48	56	1 1 0
32.01	70	1 0 4
23.00	100	0 1 2
20.18	4	1 0 1
19.02	25	0 0 3

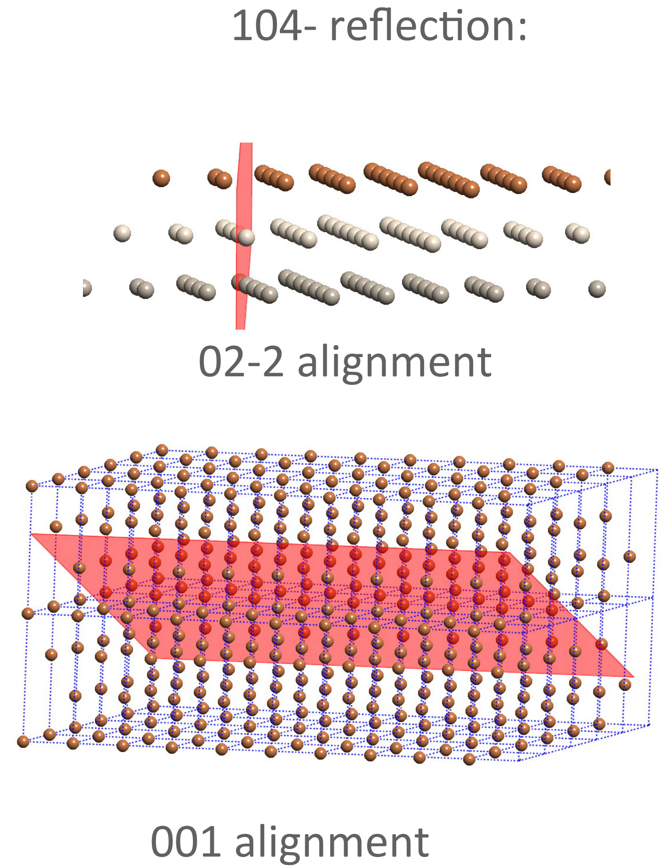
- Preliminary analysis:

  Crystallites grow with 010-plane on the substrate



The Sb-Film and the Substrate

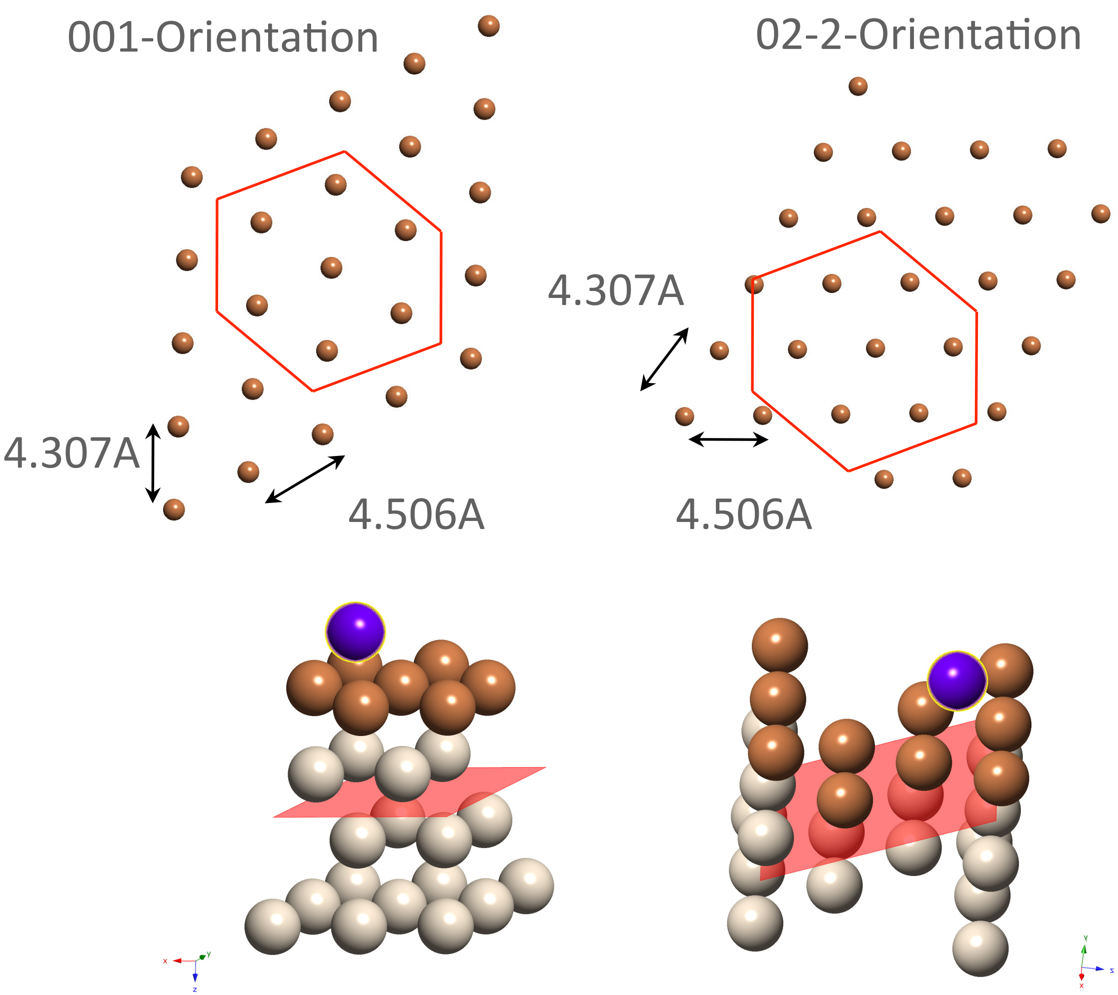




Crystal-interface is most likely a combination of 02-2 and 001 crystallites

Some Properties of the two Crystallite Orientations

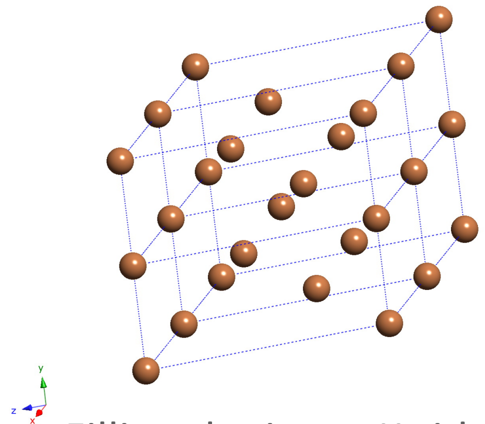
First layer between cathode and substrate:



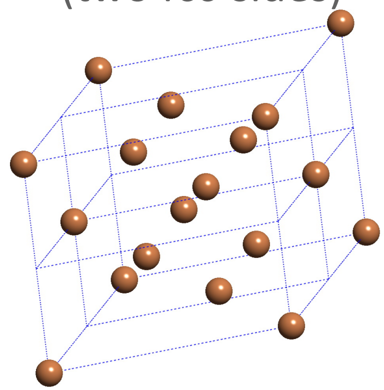
- Both crystallites give similar growth conditions
- Ionic radius of K is larger as the “open” area -> no easy inter-diffusion
- Steps may play a major role for start of inter-diffusion
- Explains initial amorphous growth (after 6nm crystalline)
- In first order:
  - substrate can not influence the growth ratio
  - Two crystallite-types determine grain boundary condition
  - Grain-boundary are important for K-inter-diffusion?

How can you get from Sb-Metal to K_3Sb

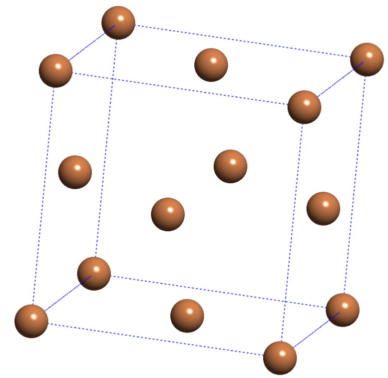
4 unit cells of Sb



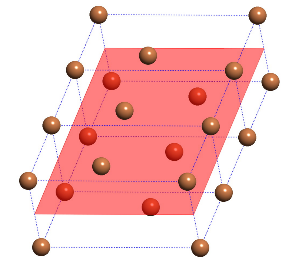
Removing 8 atoms (two fcc-sides)



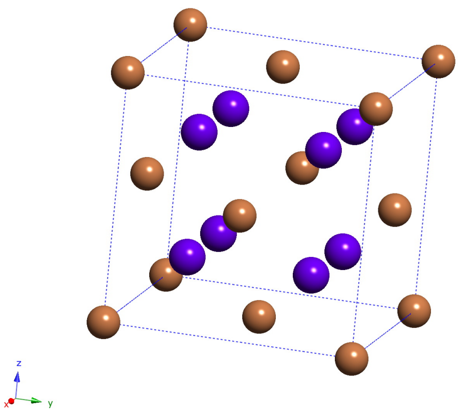
Moving the rest of the atoms to the FCC side



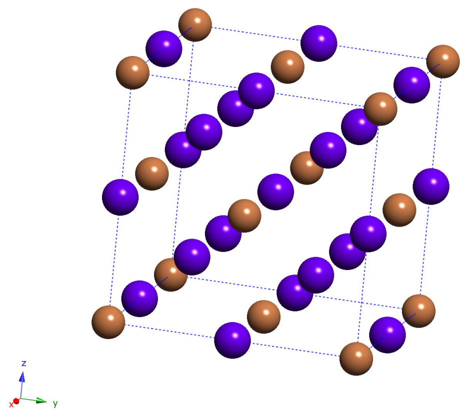
Sb-Metal surface



Filling the inner K sides



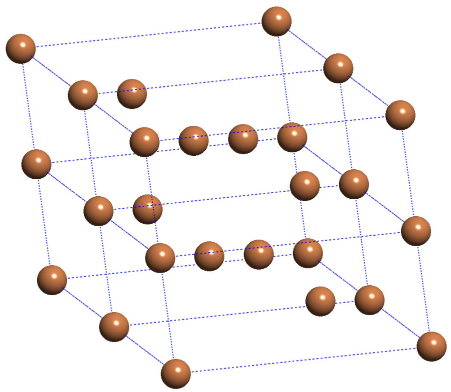
Filling the outer K sides



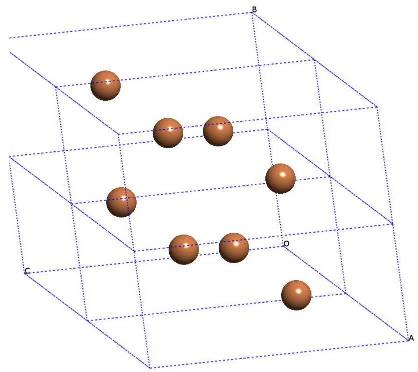
- Many Atoms have to be moved/ removed
  - Not clear where they go?
  - Does the film loose Sb atoms during K-Sb reaction?
- Inter diffusion of K will not be possible for all crystal planes!
- Is K-Sb bonding energy the “motor “ of this transition?

How can you get from Sb-Metal to KSb

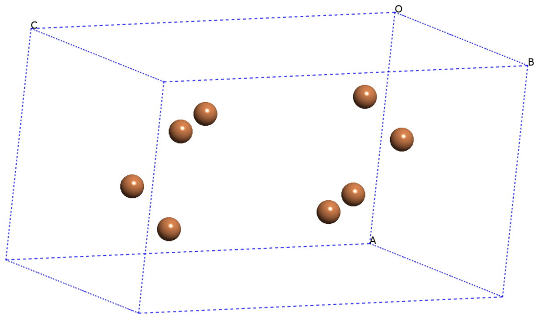
Sb-metal



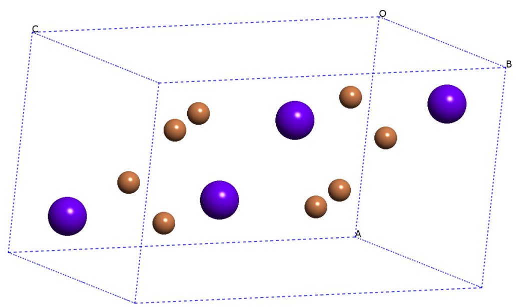
Removing of
corner atoms



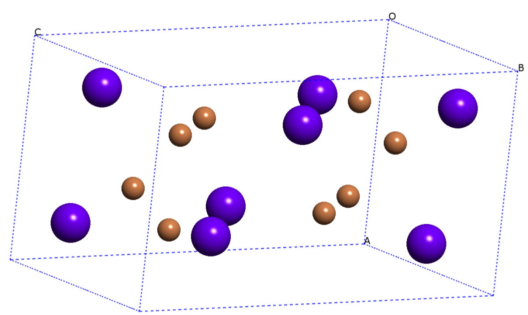
Rearranging Sb-atoms



Filling first K-position



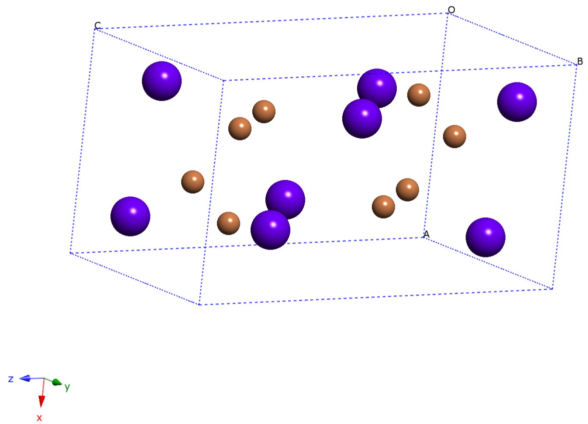
Filling second K-position



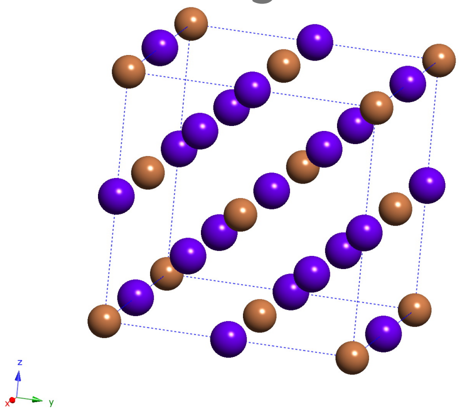
- Fewer Sb-atoms have to be removed
- Strong Sb-Sb bonds (spiral)
- K-cage holds the crystal together

No transition between KSb and K_3Sb?

KSb



K_3Sb



- No Transition between KSb and K_3Sb possible (wrong Sb-positions are occupied) without melting?
- Access K yields to lateral segregation not to a transition
- What drives the initial growth?

Characterization of the Full Cathode Growth

Sample 1

8 nm Sb deposition at 100 C
16 nm K deposition at 100 C
Substrate heating to 300 C
18 nm Cs deposition at 100 C
Substrate heating to 300 C
8 nm Sb deposition at 100 C
24 nm Cs deposition at 100 C
Substrate heating to 300 C

Sample 2

16 nm Sb deposition at 30 C
63 nm K deposition at 100 C
Substrate heating to 300 C
16 nm Sb deposition at 100 C
40 nm Cs deposition at 100 C
Substrate heating to 300 C

Sample	Total Sb	Total K	Total Cs
Sample 1	16nm	16nm	42nm
Sample 2	32nm	63nm	40nm

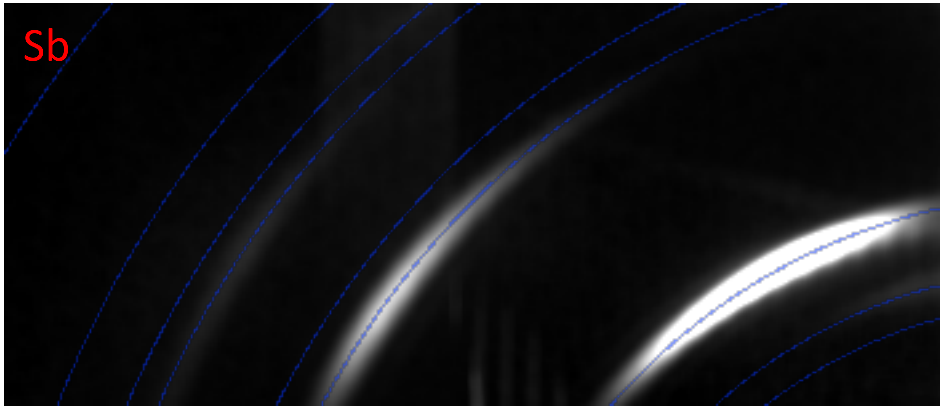
- Growth temperature of Sb-film
- Sequence of growth
- Total thickness

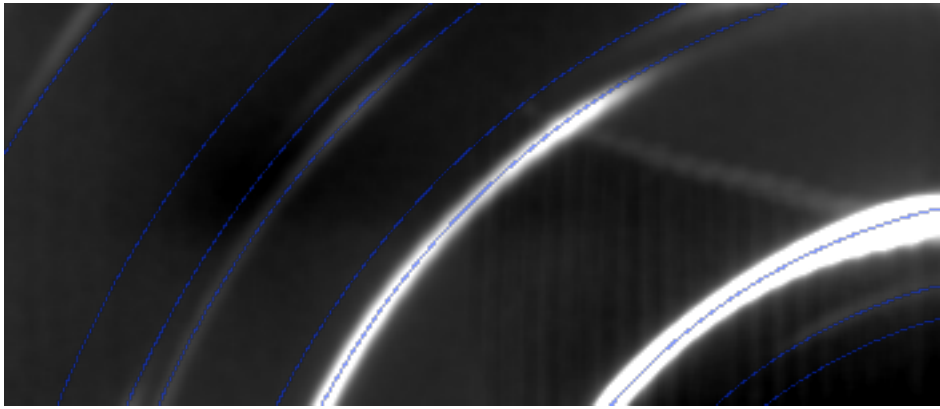
Initial Sb-Film

Thickness	8nm	16nm
Temperature	30C	100C

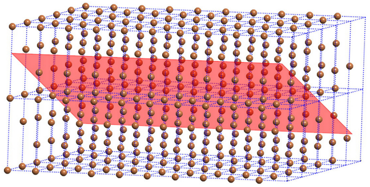
Sample 1

Sample 2

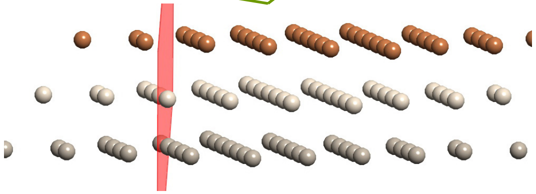




001



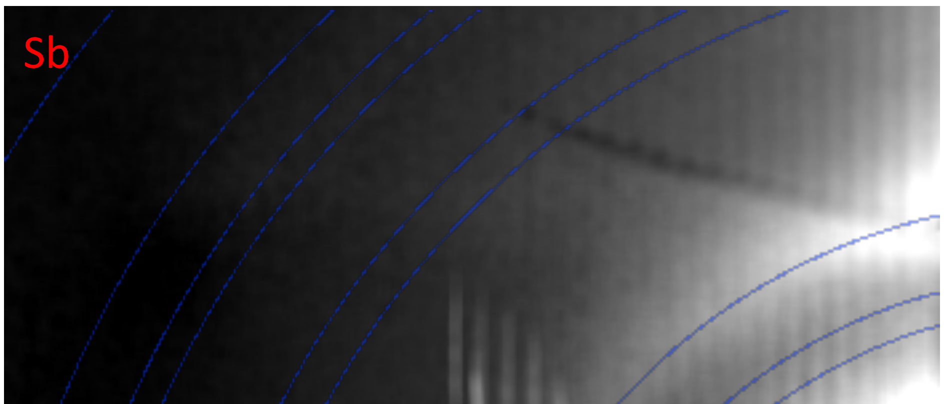
02-2



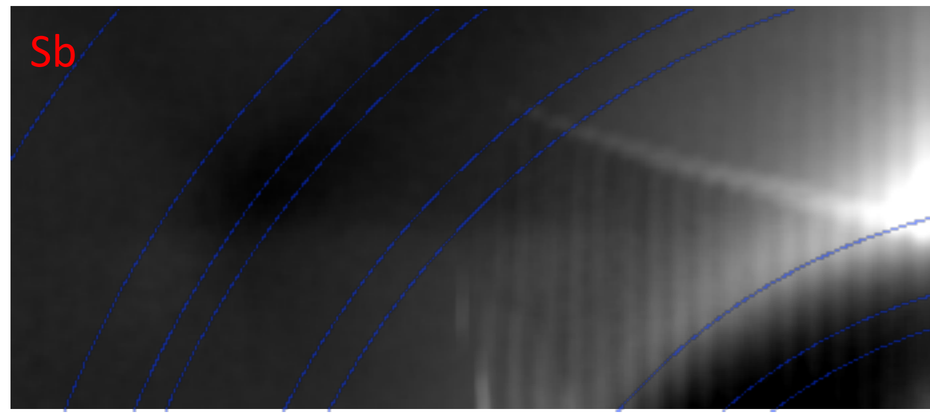
First K-deposition

Thickness	Sb 8nm/ K 16nm	Sb 16nm / K 63nm
Temperature	100C	100C

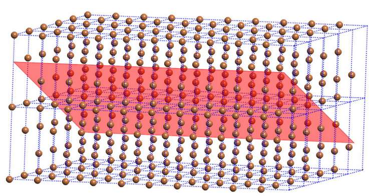
Sample 1



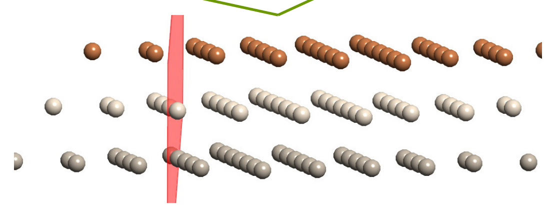
Sample 2



Reacted 001



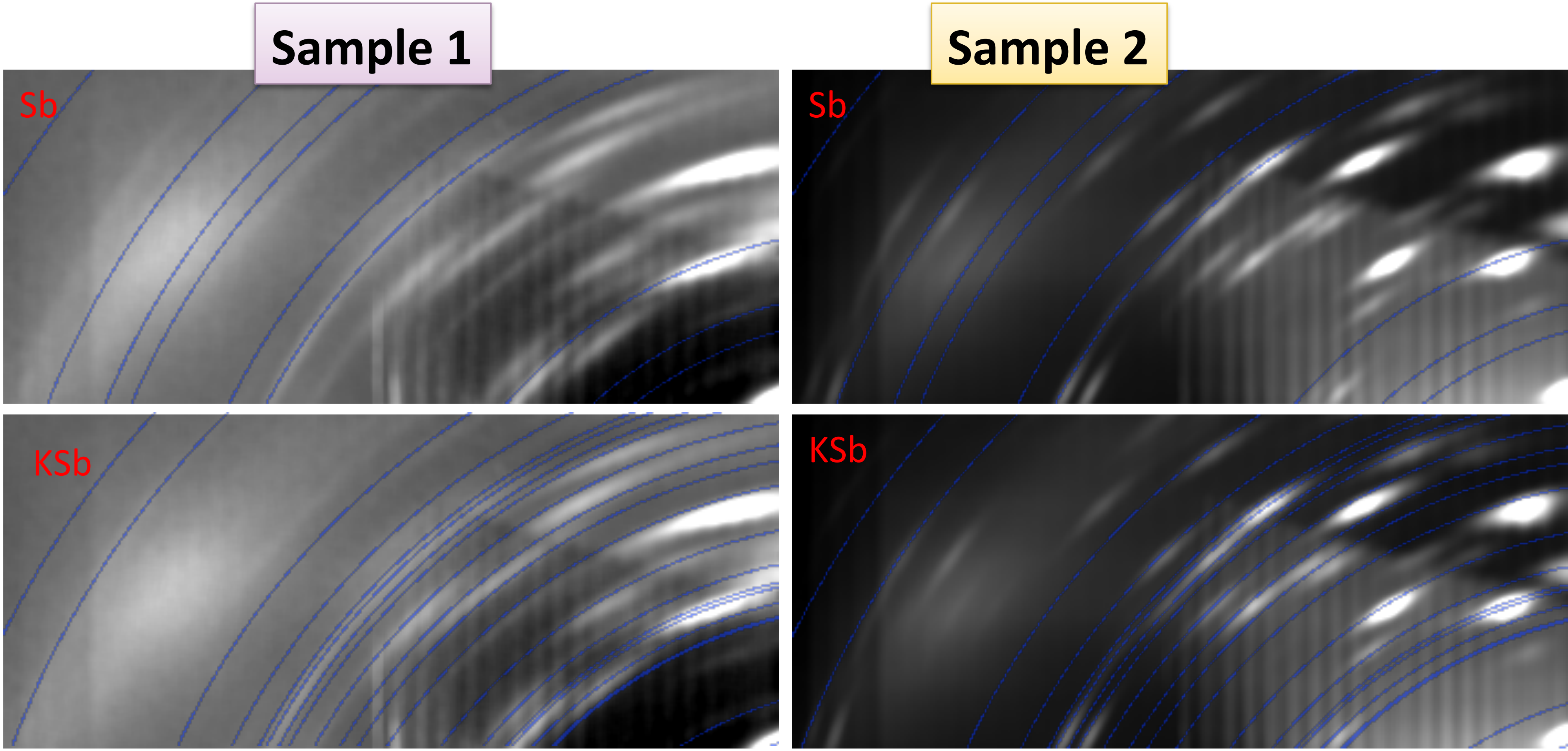
02-2



Not reacted?
Strongly strained
A specific orientation survived

Annealing of KSb-Compound at 300C

Thickness	Sb 8nm/ K 16nm	Sb 16nm / K 63nm
Annealing Temperature	300C	300C

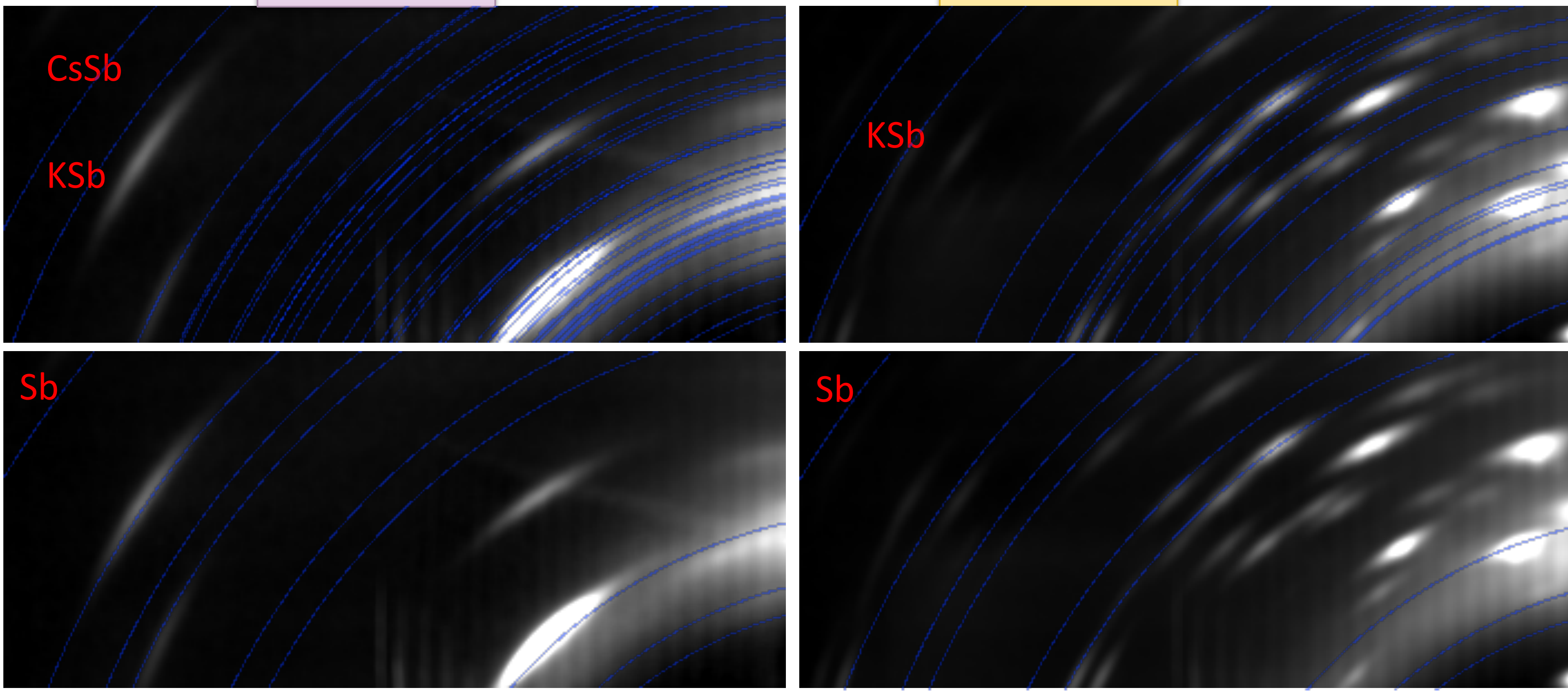


- KSb in both cases (independent from K-thick.); some systematic deviation (strain/vacancies?)
- Very strong texturing for sample 2
- May be Sb-metal phase (001-phase)

Cs-Deposition

Thickness	Sb 8nm/ K 16nm /18nm	Sb 16nm / K 63nm/ Sb 16nm / 40nm Cs
Annealing Temperature	100C	100C

Sample 1 **Sample 2**

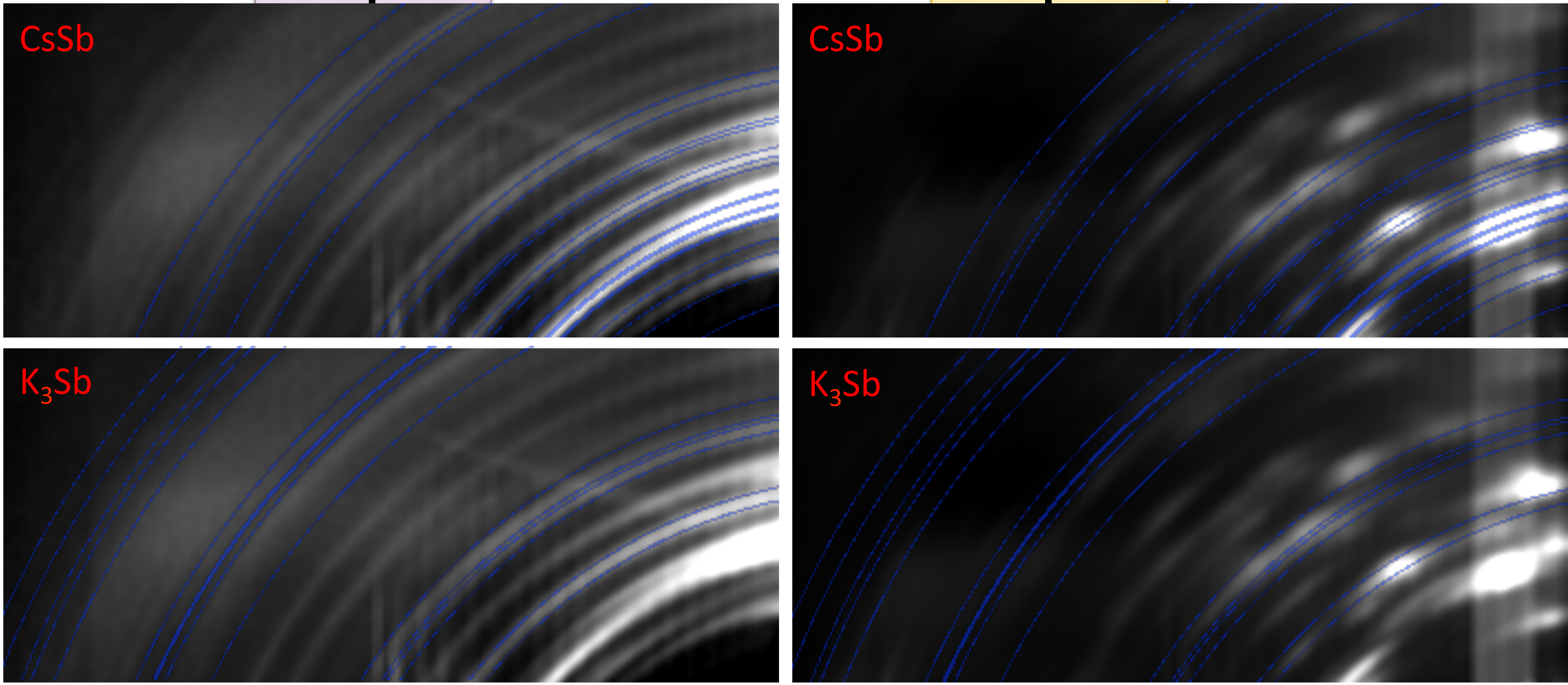


- Some metallic Sb left in both cases
- No crystalline phase of alkali-Sb for sample 1
- KSb phase visible for Sample 2

Annealing of CsKSb-Compound at 300C

Thickness	Sb 8nm/ K 16nm /18nm	Sb 16nm / K 63nm/ Sb 16nm / 40nm Cs
Annealing Temperature	300C	300C

Sample 1 **Sample 2**

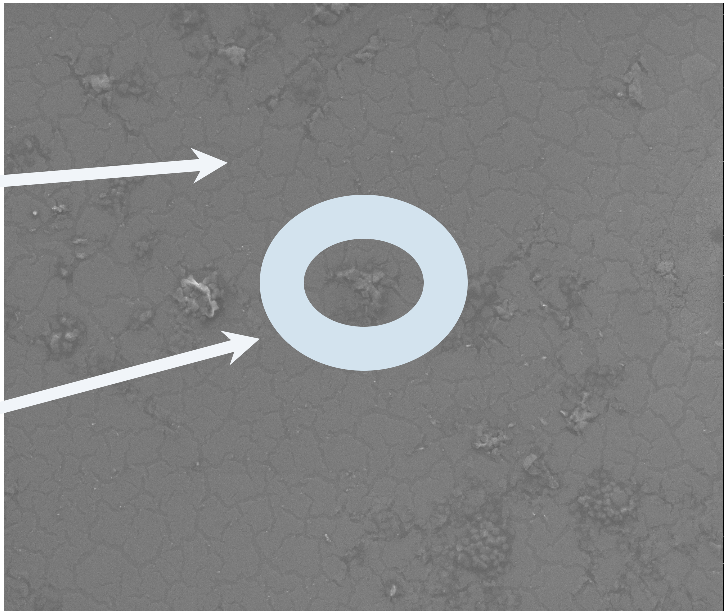


- In both cases mixture of AlSb (Al=Cs/K)
- Unlikely a Al_3K-phase! (Al=Cs/K)

Summary of In-situ Growth Experiment

Sb K Cs on Si X21 Oct 2011 Samp 3 1Date:10/5/2011 4:31:31 PMHV:15.0kVPuls th.: 17.27kcpsCenter Average

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K-series	0.54	0.56	1.35	0.9
O	8	K-series	3.69	3.85	6.90	1.1
Si	14	K-series	84.15	87.79	89.71	3.5
K	19	K-series	0.52	0.54	0.40	0.1
Sb	51	L-series	3.88	4.05	0.96	0.6
Cs	55	L-series	3.08	3.21	0.69	0.3
		Total:	95.86	100.00	100.00	

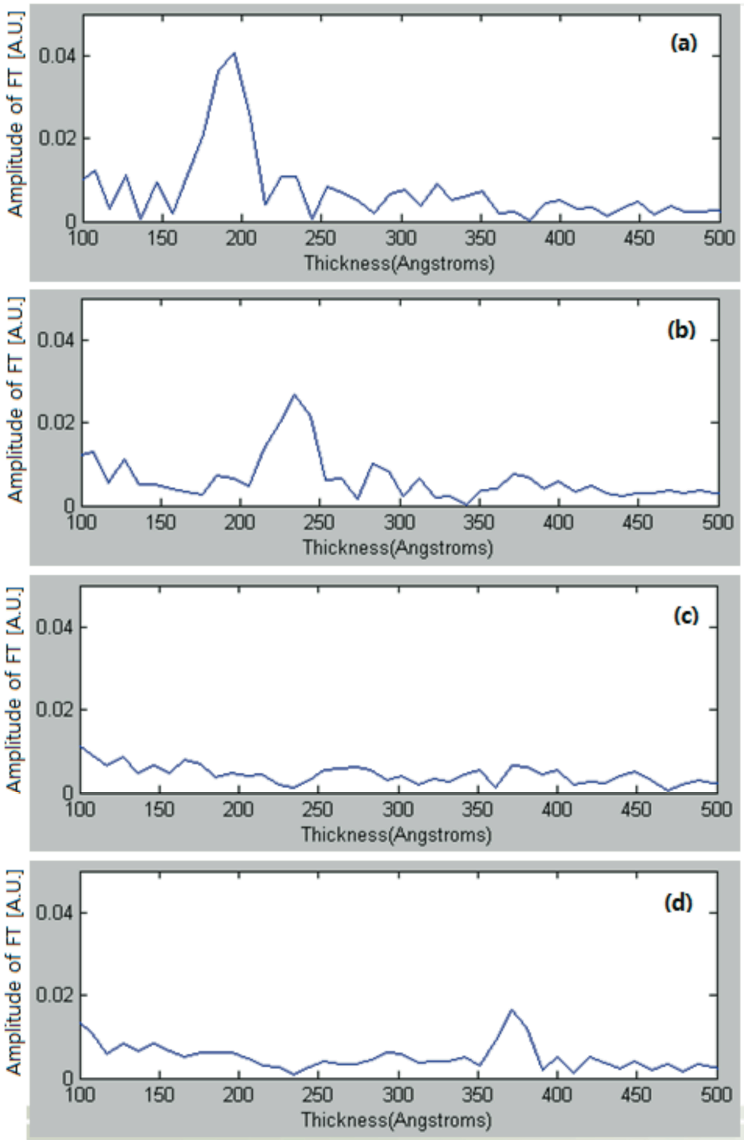


Very K-rich (K-metal?)

- Observations:
  - Sb-metal film growth often strongly textured
  - K-evaporation onto of Sb-metal yield to an amorphous material or glass (no long range order)
  - Formation of islands are unlikely since this would favorite crystalline phases which cannot be detected!
  - K-Sb mixture crystallizes at 300C (dynamics, activation energies are currently not known but can be extracted from existing data set)
  - Crystallized K-Sb film is mainly KSb with strong texturing (orientation and crystal size can be concluded from existing data set)
  - Cs behaves very similar to K
  - Produced cathode was not homogeneous: largely a CsSb-phase and a crystalline non identified CsKSb-phase

The Transition from Sb-Film to K_3Sb-film

Surface Roughness during the Processing



Sb-Metal

- Nice smooth film with 19nm thickness
- Height distribution ~3nm

K-evaporation started

- Decrease of peak height indicates fraction of surface don't contribute to signal
- Height distribution ~5-7nm
- No double layer structure

K-evaporation ended

- No reflectivity signal detectable
- Very rough!

heating

- Reflectivity signal comes back
- Not all surface has recovered
- Goes ahead with crystallization!

Influence of Interface Layer

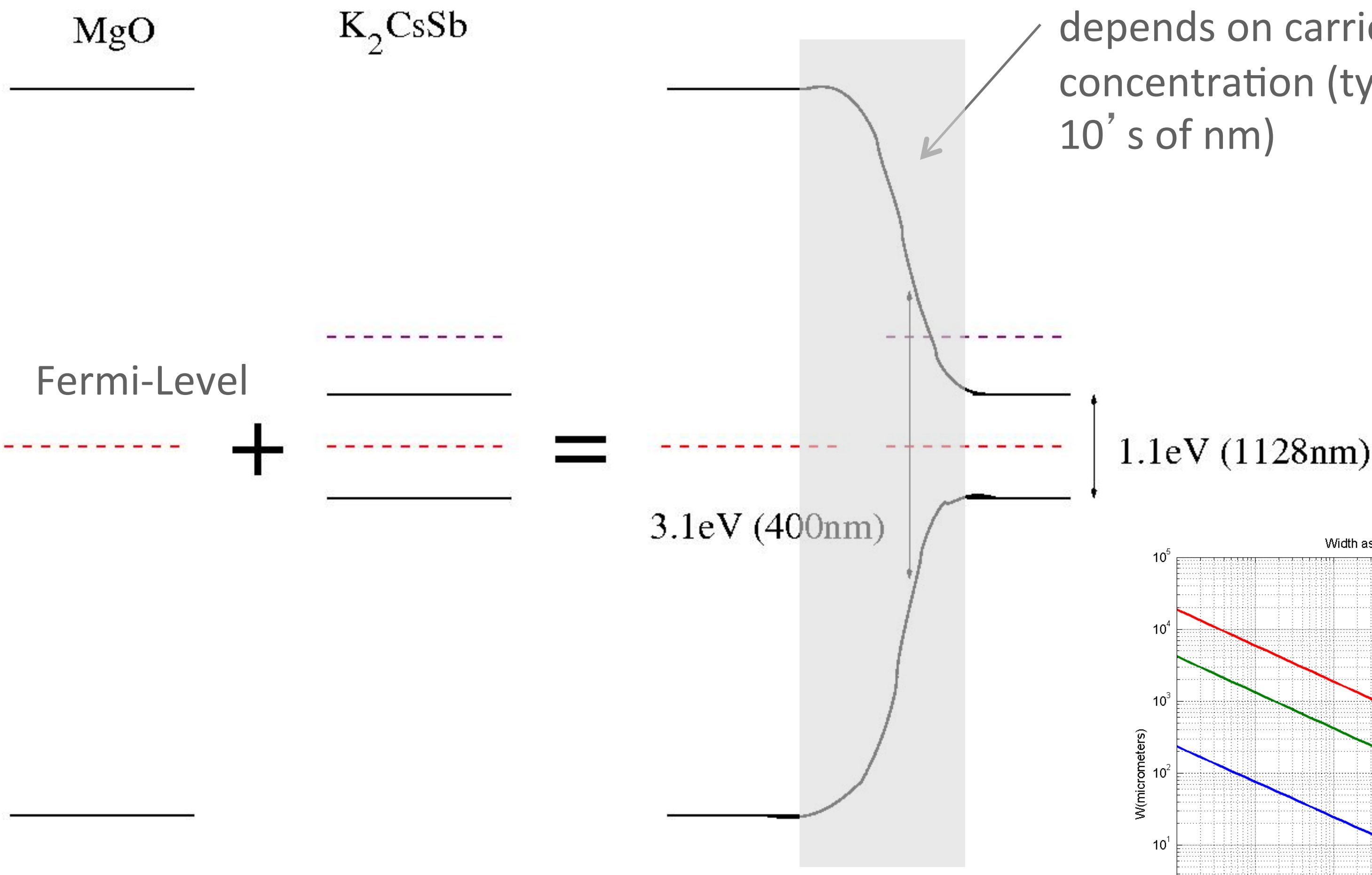
- Commonly used materials:

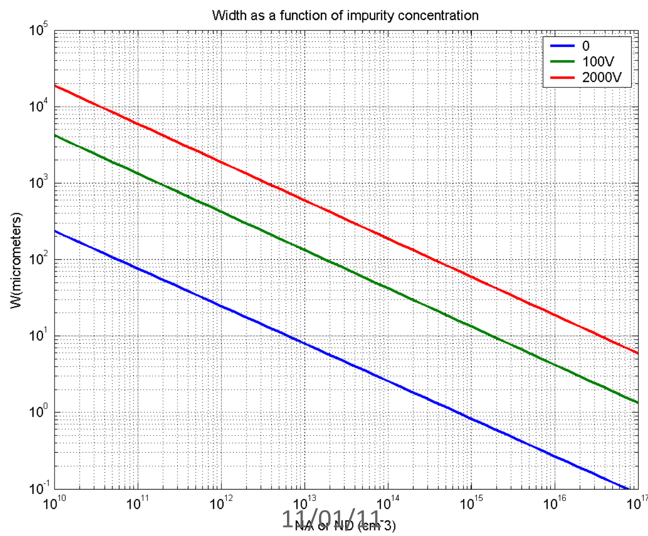
Material	Crystal group	Lattice parameter	Match with K_3Sb	Band gap
Sb_2O_3	Fd-3m	a=11.152A	yes	3.7-3.9eV
Sb_2O_4	Fd-3m	a=10.26A	yes	?
MgO	Fm-3m	a=4.2117A	excellent	4.7-7.8eV
BeO	$P6_3mc$	a=2.698A c=4.3772A	no	10.7eV
K_3Sb	F m -3 m	a=8.493		1.4eV
CsK_2Sb	F m -3 m	a=8.61		1.0-1.2eV

BeO is used to produce super-bialkali cathodes!

Combining Wide-Band-Gap Materials with Alkali Systems

Width of depletion zone depends on carrier concentration (typically 10's of nm)





The Next Steps

- Instrumentation:
  - Development of miniature evaporator system with defined growth conditions (high q-range, easy to transport, can be implemented in various beamlines)
  - Data-quality improvement: calibration standard & background reduction
- Data-analysis, simulation, & theory:
  - Automatic data analysis using script languages
  - Quantitative analysis of texture information
  - Peak-width simulation based on strain, size and defect-structure
  - Data base for known compounds (alkali-Sb and oxides/fluorids)
  - Calculation of potential surface for Alkali inter diffusion (at least important areas)
- Program:
  - Influence of Oxide layer on growth and band bending
  - Understanding of KSb versus K_3Sb growth

Conclusion

- In-situ X-ray diffraction and reflectivity was applied and provides:
  - Compound composition during the processing
  - Structural information on crystallinity, size and orientation of crystals
  - Temporal evolution of these parameters
- Results of the presented experiment:
  - Alkali-evaporation at 100C substrate temperature yields to amorphous or glassy material
  - No transversal but lateral segregation is observed.
  - Crystallization can be achieved at 300C heating (necessary time can be extracted from data)
  - Grown cathode is more of the CsSb and some non-identified CsKSb-compound (not CsK2Sb)
  - Crystallinity (and texture) of the final film is independent from the Sb-structure but may depend on the KSb-crystallinity and the influence of the substrate layer?
- Next goals
  - Improve in-situ experiment so that many cathode recipes can be investigated.
  - Influence of the substrate on the crystallization process of the Alkali compound
  - Determination of activation energies and rate constants of the crystallization process (for the different compounds).