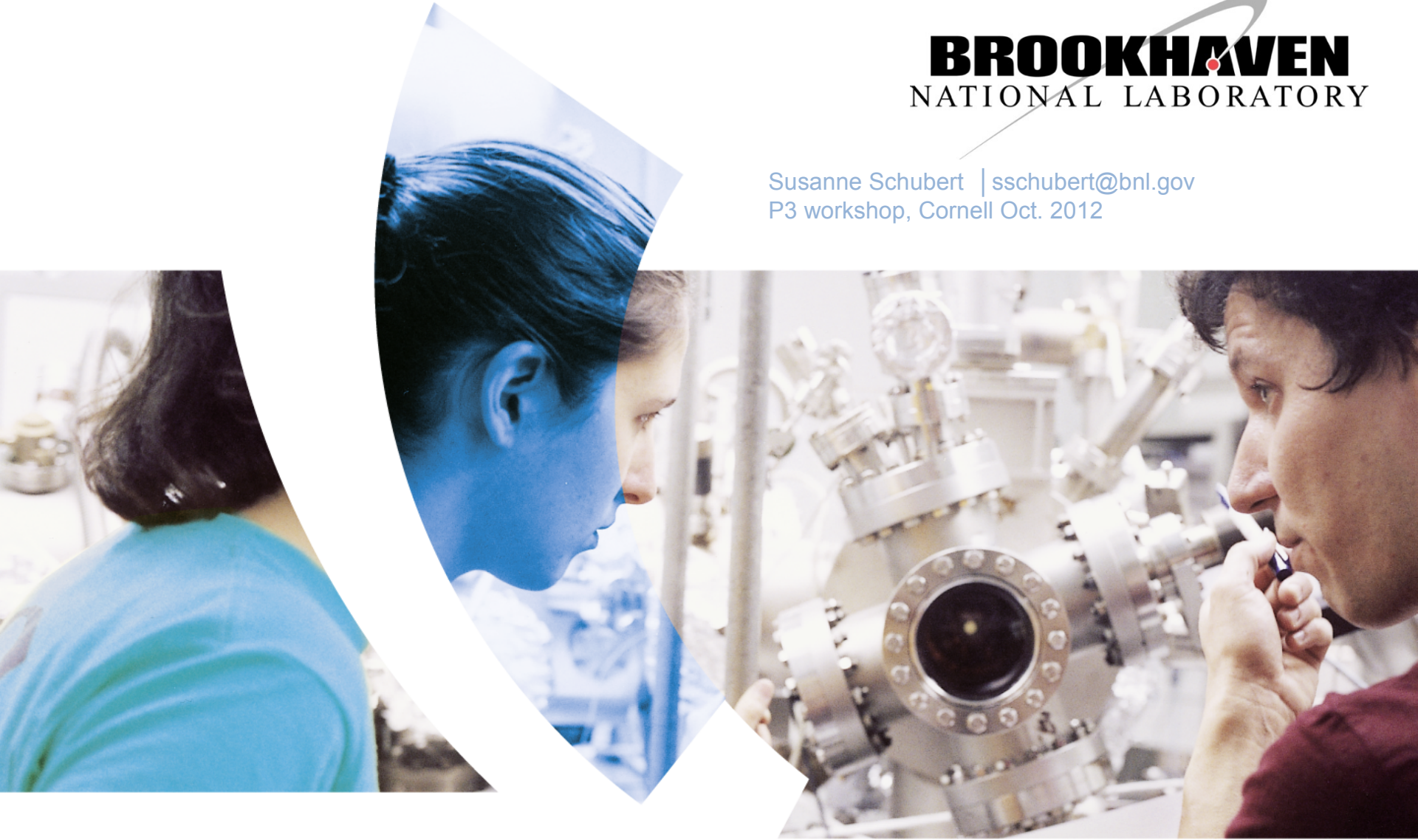
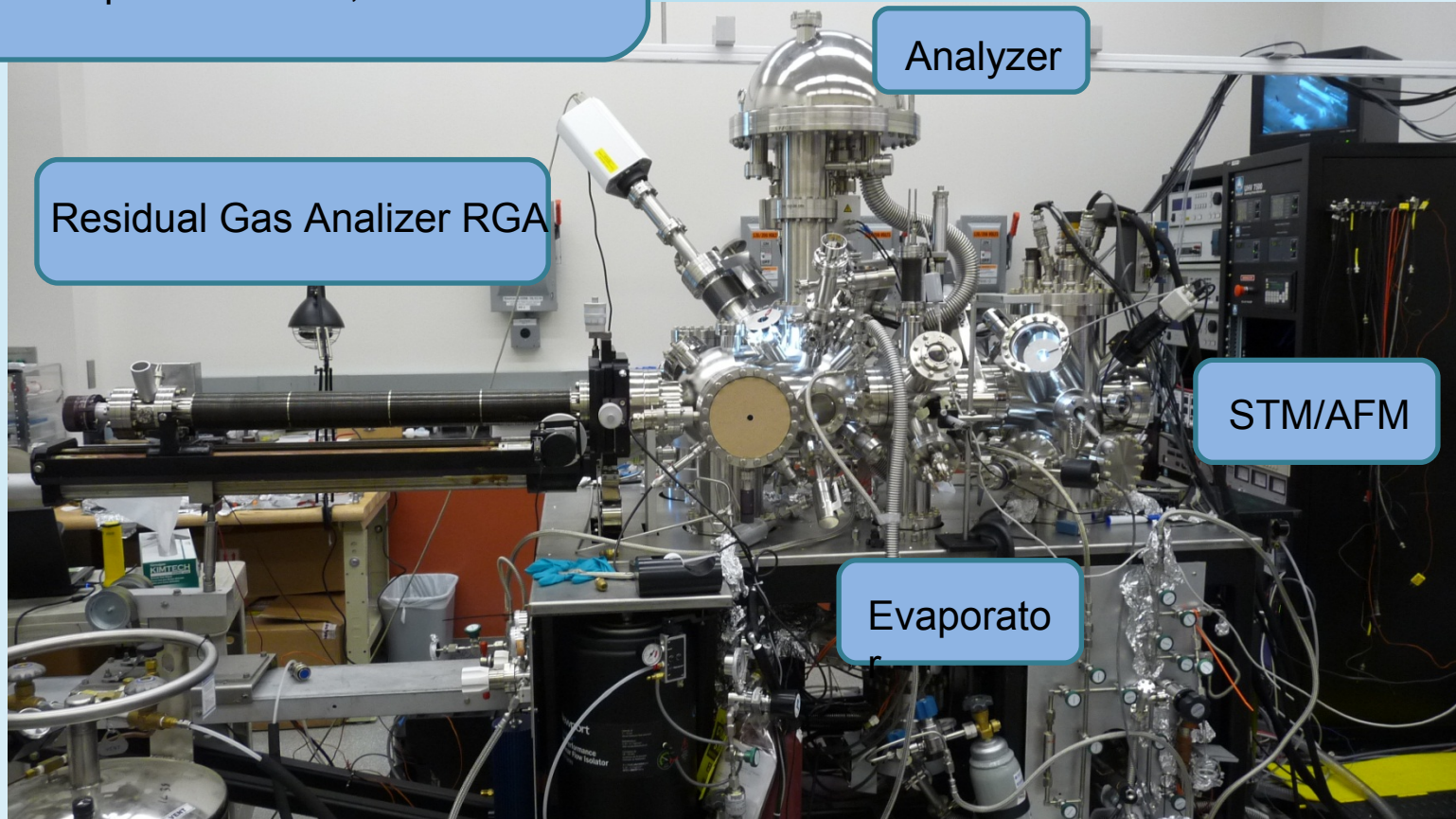


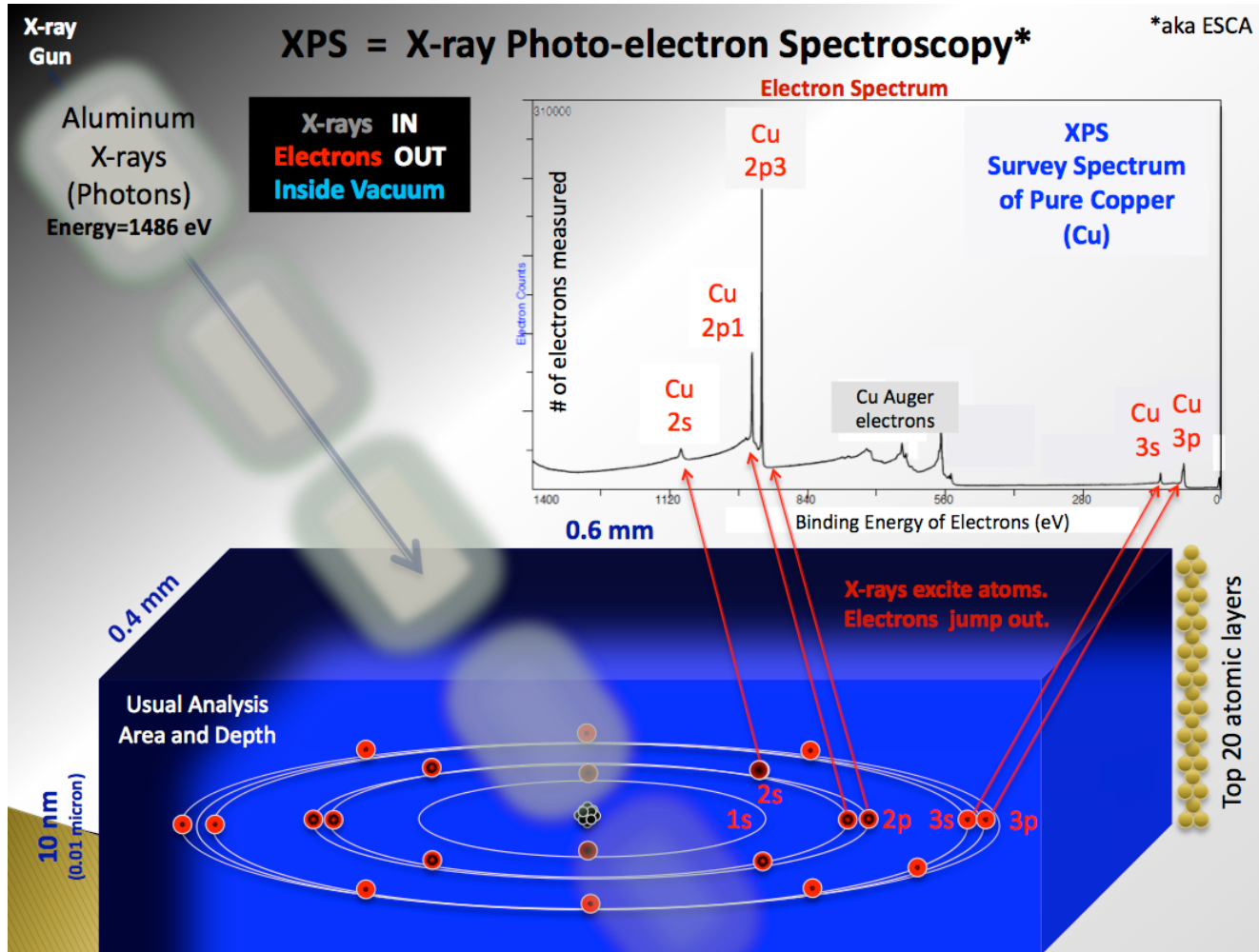
Susanne Schubert | sschubert@bnl.gov
P3 workshop, Cornell Oct. 2012



Measurement of the chemistry and growth of alkali antimonides
using **in-situ AFM** and **XPS**

UHV system (5×10^{-10} Torr base pressure)
Heating/cooling substrate/cathode
Load lock (fast exchange of substrates)
Horizontal deposition of Sb, K and Cs.





$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kin}} + \phi)$$

Pic taken from : http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy

- 10 nm Antimony layer was grown first either by sputtering or evaporation onto Si(100)
- Si-sample was HF dipped BUT traces of oxygen on the surface
- Evaporated Sb layers almost no oxide components
- Sputtered Sb layers consisted of Sb_2O_3 and Sb
- Heating of sputtered Sb layers at different temperatures to remove the oxide

Substrate Si(100):

5 nm Sb sputtered at $T = RT$



Keeping $T = 200\text{ }^{\circ}\text{C}$ for 2 min

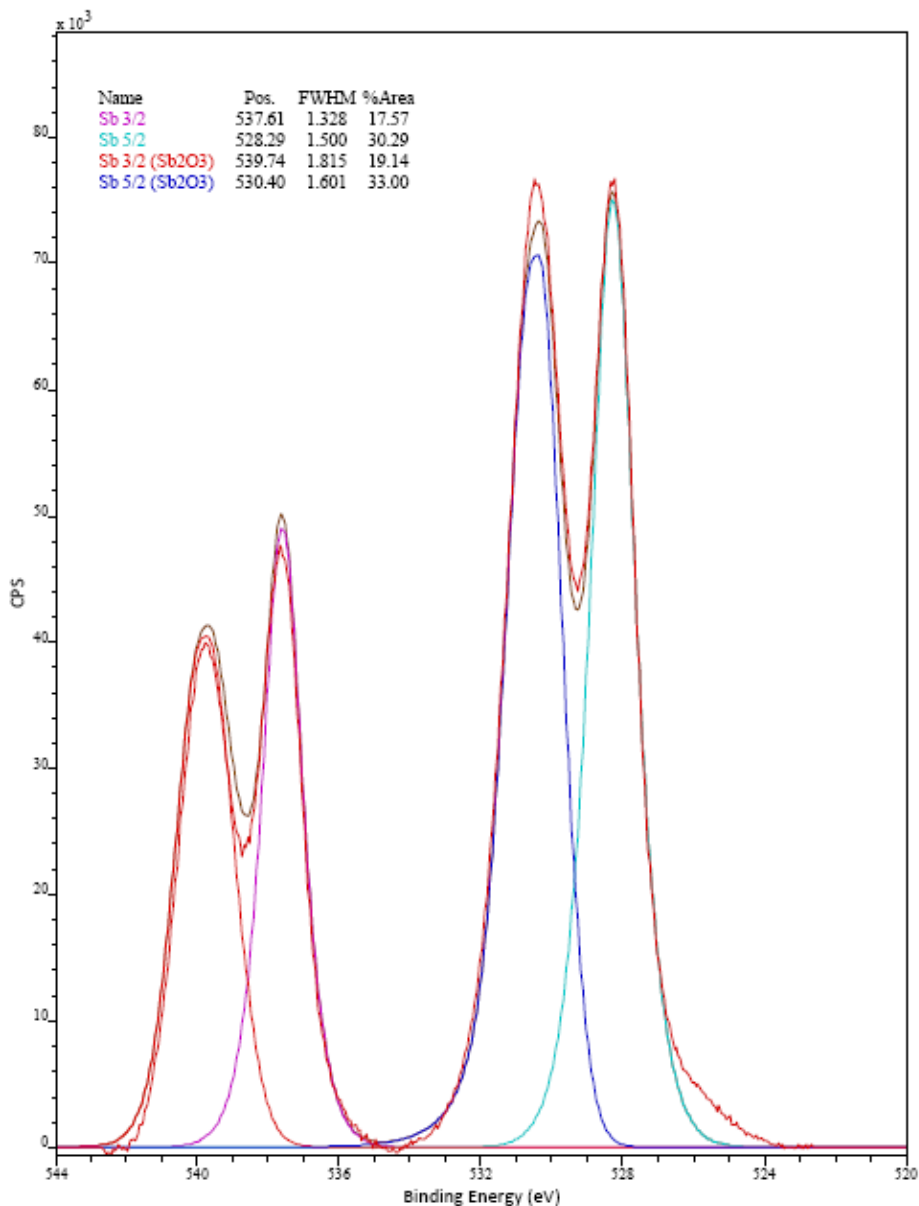


Keeping $T = 400\text{ }^{\circ}\text{C}$ for 2 min



Keeping $T = 600\text{ }^{\circ}\text{C}$ for 2 min

Sb 3d region after sputtering



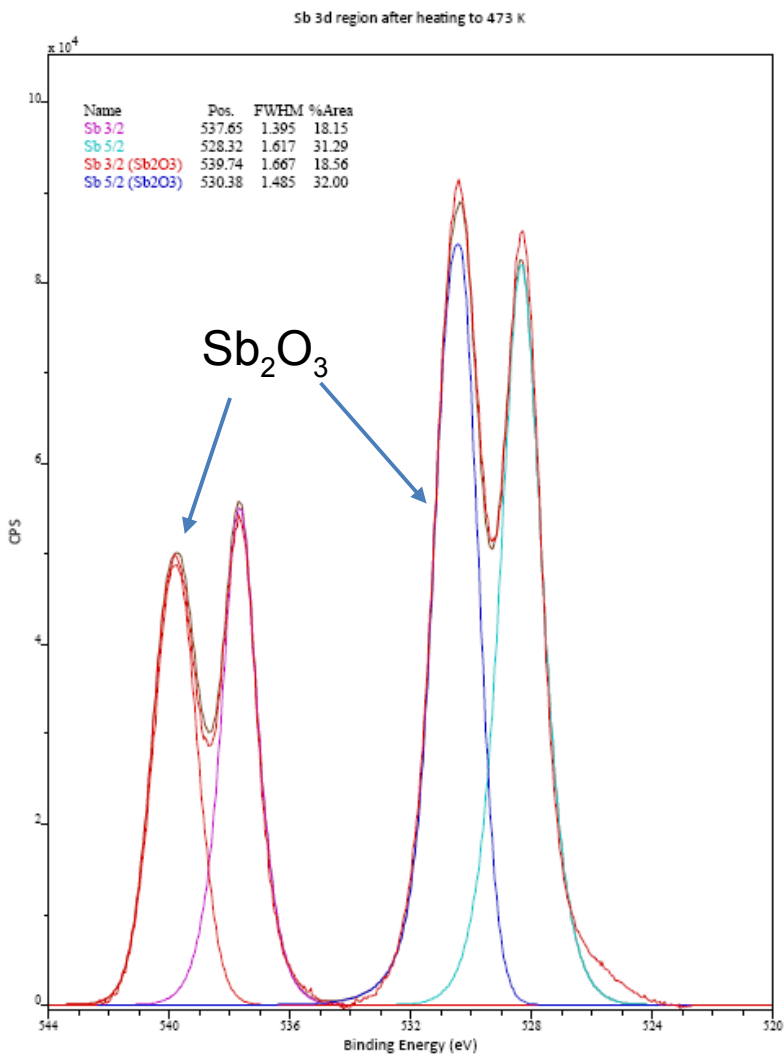
Initial situation:

Two Sb species, the doublet at 537.6 eV and 528.3 eV originates from elementary Sb [XDB].

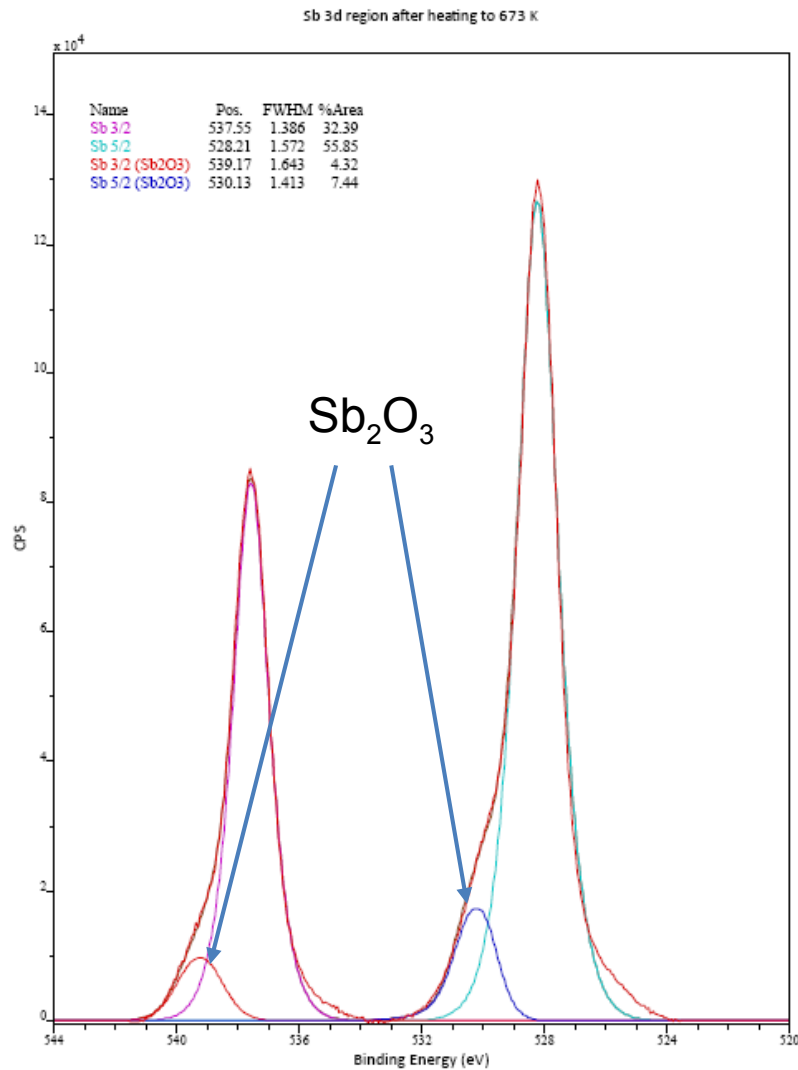
The second doublet is shifted by 2.01 eV towards higher binding energies. This chemical shift corresponds to the value found in literature for Sb_2O_3 [Wag75].

[XDB] Thompson, A. et al., X-ray Data Booklet, LBNL (2009)

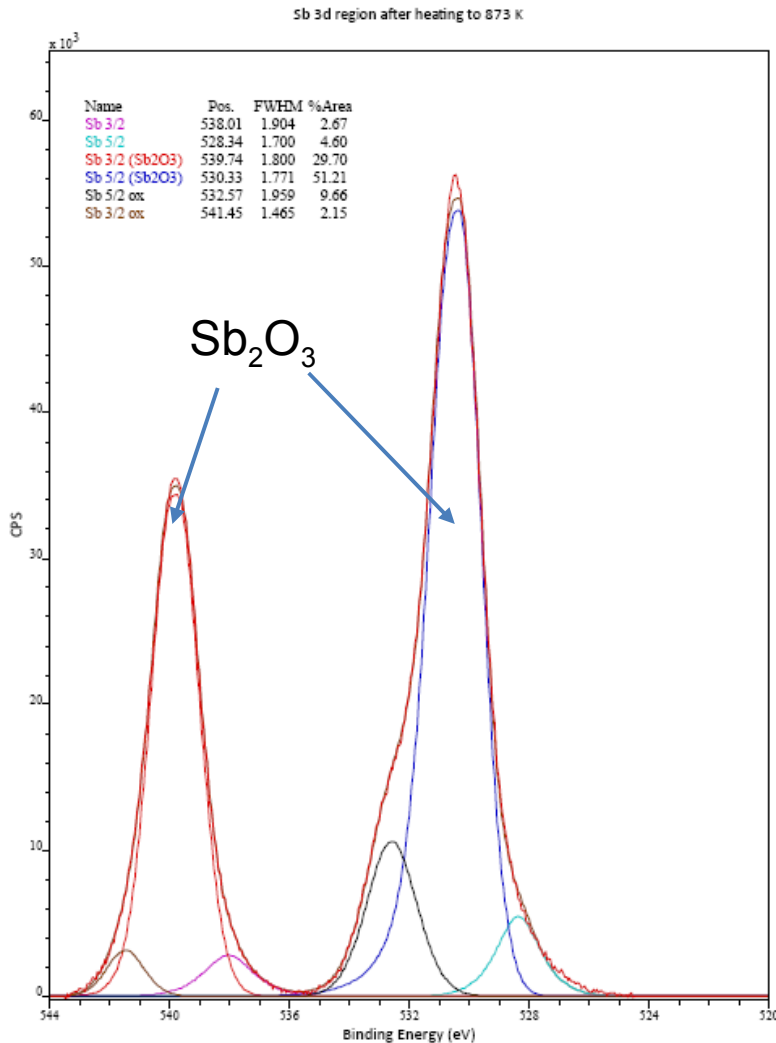
[Wag75] Wagner C.D., Discuss. Faraday Soc. 60, 291 (1975)



After heating to 200 °C for 2 min



After heating to 400 °C for 2 min



After heating the sample to 600 °C. almost 90 % of the Sb present on the surface is oxidized.

A possible explanation might be that the oxygen present at the surface before Sb adsorption get mobile and reacts with the above Sb layer building up mostly Sb₂O₃.

As well there is a loss in intensity pointing toward Sb desorption at that temperature.

After heating to 600 °C for 2 min

Traditional Recipe: substrate Si(100)

5 nm Sb evaporated on Si(100) at $T = 110^\circ\text{C}$



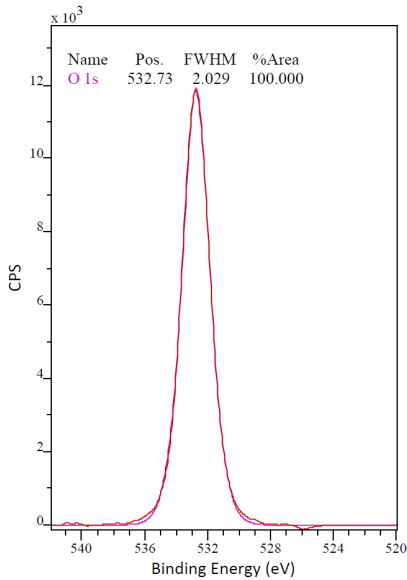
15 nm K at $T = 140^\circ\text{C}$



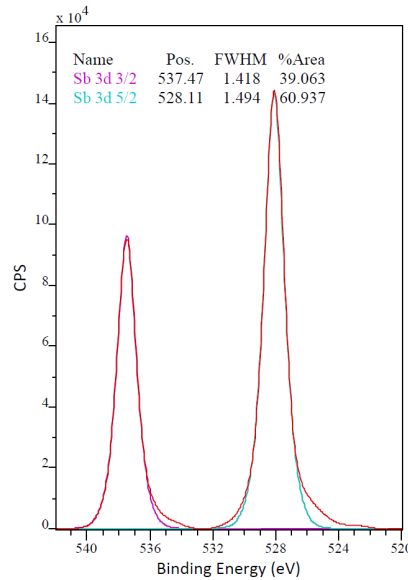
Cs at 135°C

Measured q.e. = 2.4 % at 532 nm.

Si (100)



after Sb adsorption

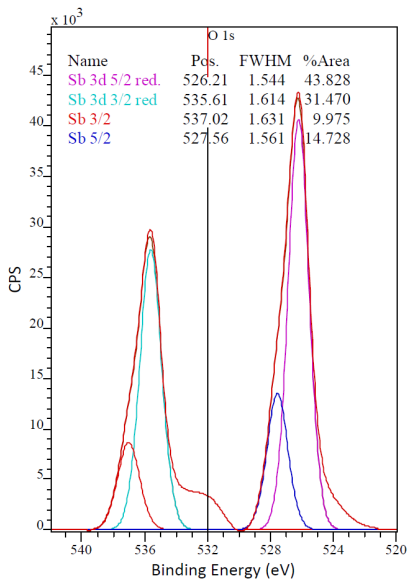


Cathode 1:

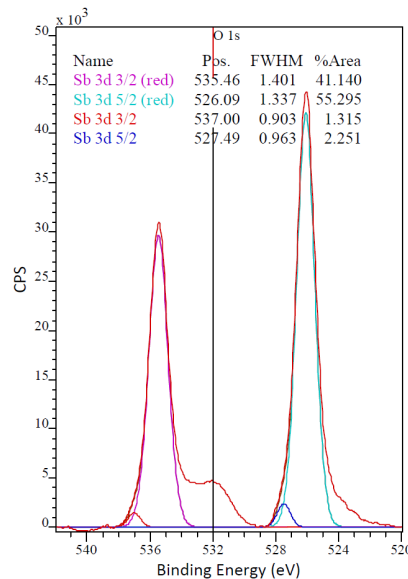
Sb on Si(100) – only one species which corresponds to Sb in ground state.

After K adsorption some of the Sb has reacted with the K, shift of 1.9 eV towards lower binding energies.

after K deposition

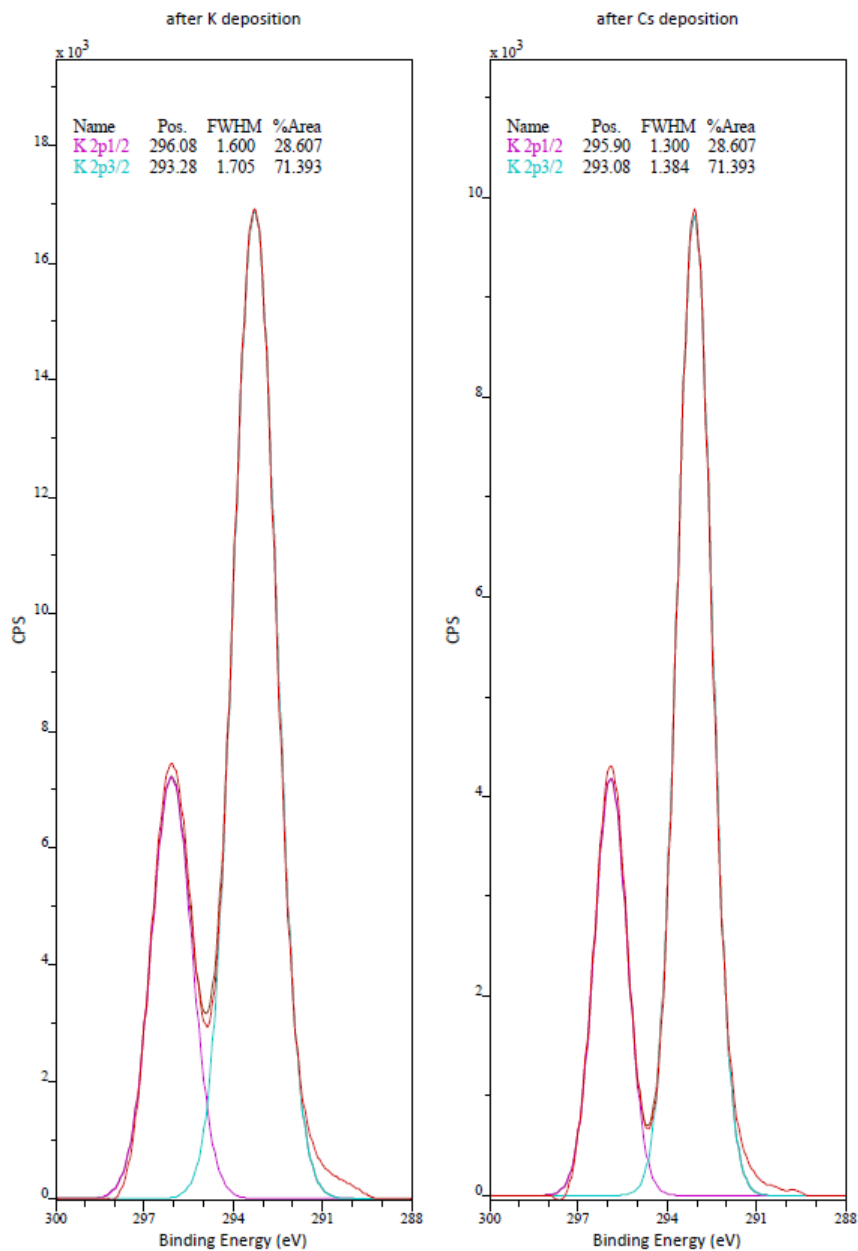


after Cs deposition



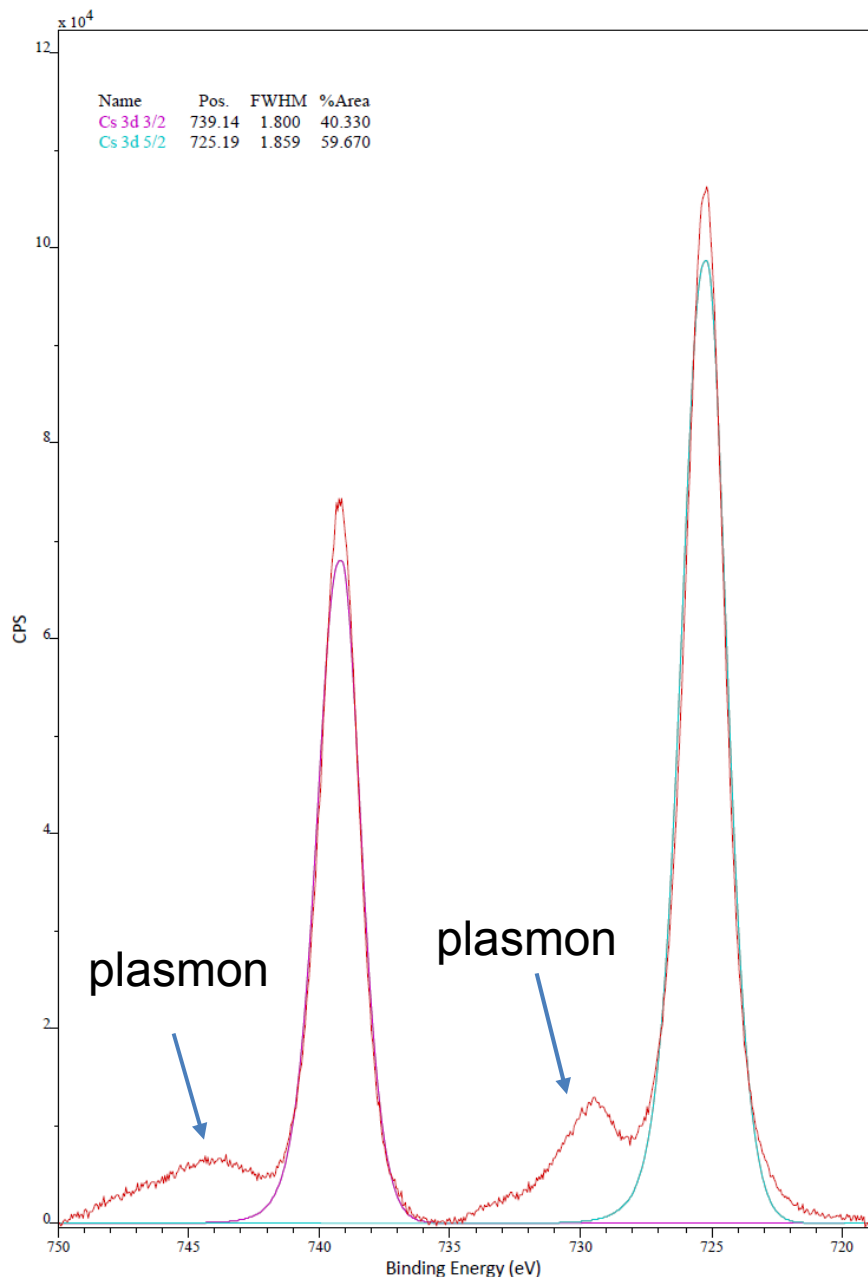
After Cs adsorption almost all Sb has reacted, only small amount of unreacted Sb.

As well visible the influence of oxygen, with an increase of intensity around the oxygen 1s region, which cannot be usefully resolved with peak fittings.



Decrease in intensity upon Cs adsorption

Position and spin orbit coupling remains the same (+/- 0.2 eV)



The binding energy is slightly shifted towards lower b.e. as reported in literature for Cs compounds.
Spin-orbit coupling for Cs metal = 14 eV [Ebb79]

The determined Cs 3d coupling is 13.86 eV.

[Ebb79] Ebbinghaus, G. et al., Chem. Phys. 43, 117 (1979)

Stoichiometric ratio derived from XPS intensities:

$$n_1 / n_2 = (I_1 / s_1) / (I_2 / s_2)$$

I...intensity (height or area)

s... sensitivity factor (dependend of height or area)

$$s (\text{Cs } 3d_{5/2}) = 7.2$$

$$s (\text{Sb } 3d_{5/2}) = 4.8$$

$$s (\text{K } 2p_{3/2}) = 1.24$$

After K deposition: $\text{K}_{1.8}\text{Sb}$

After Cs deposition: $\text{Cs}_{2.5}\text{K}_{0.9}\text{Sb}$

This cathode showed a q.e. of about 2.4 % at 532 nm.

s taken from: <http://www.cem.msu.edu/~cem924sg/XPSASFs.html>

Traditional Recipe: substrate Si(100):

5 nm Sb sputtered on Si(100) at $T = RT$



Heated to 400 °C

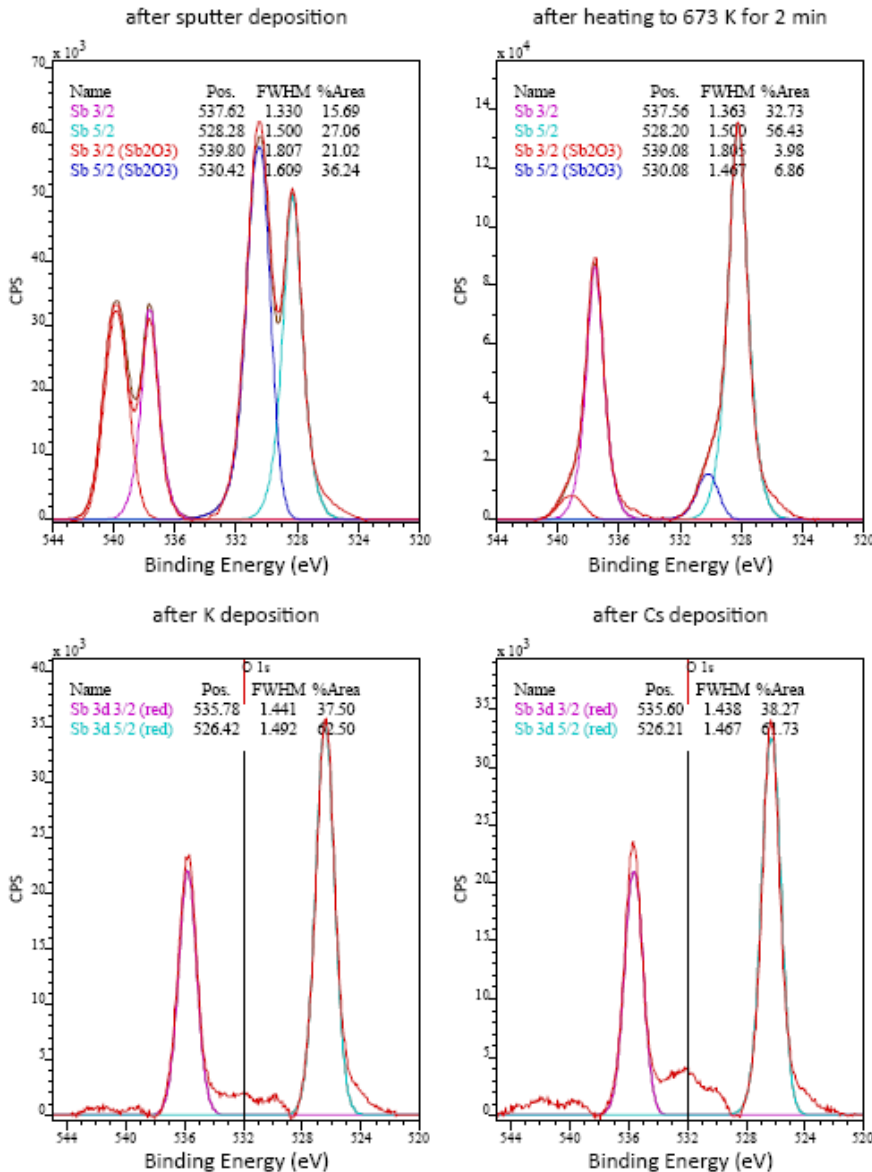


15 nm K at $T = 140$ °C



Cs at 135 °C

Measured q.e. = 1 % 532 nm.

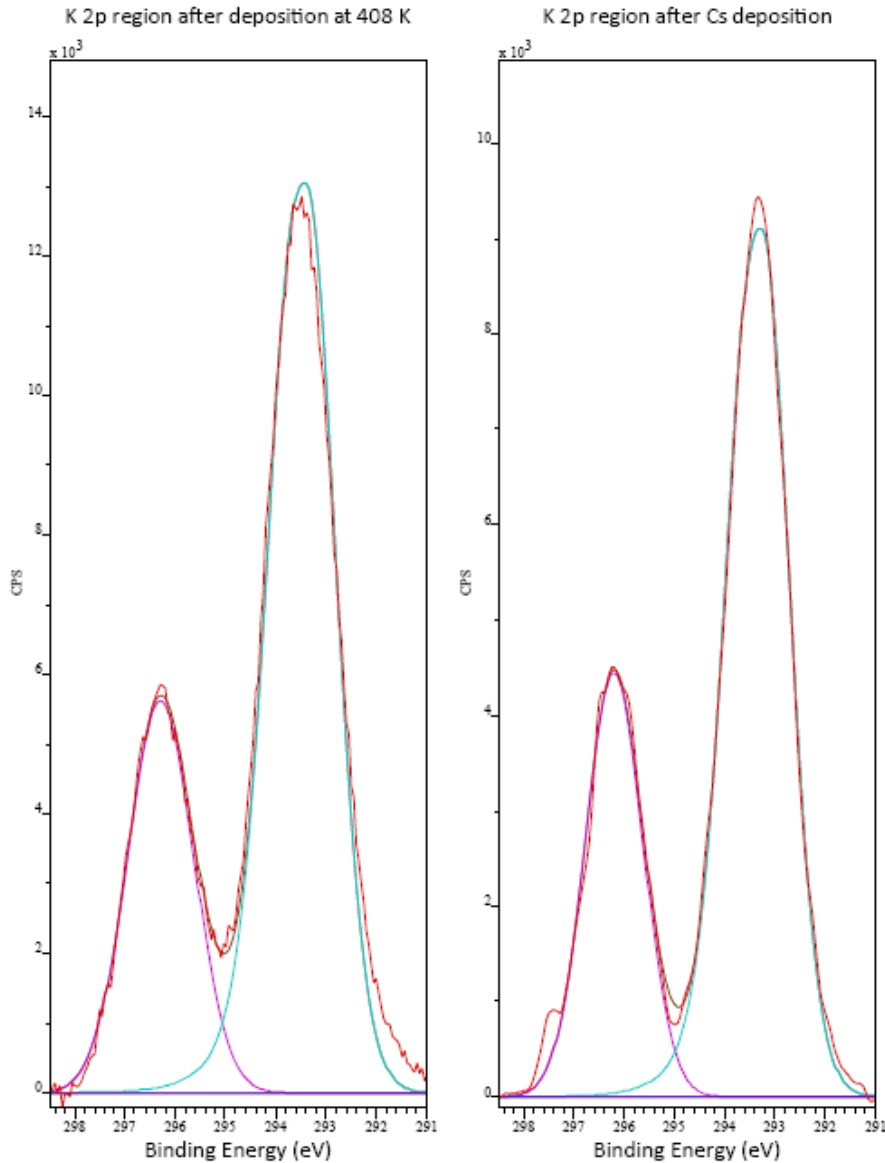


After sputter deposition again Sb₂O₃ is present in the Sb layer.

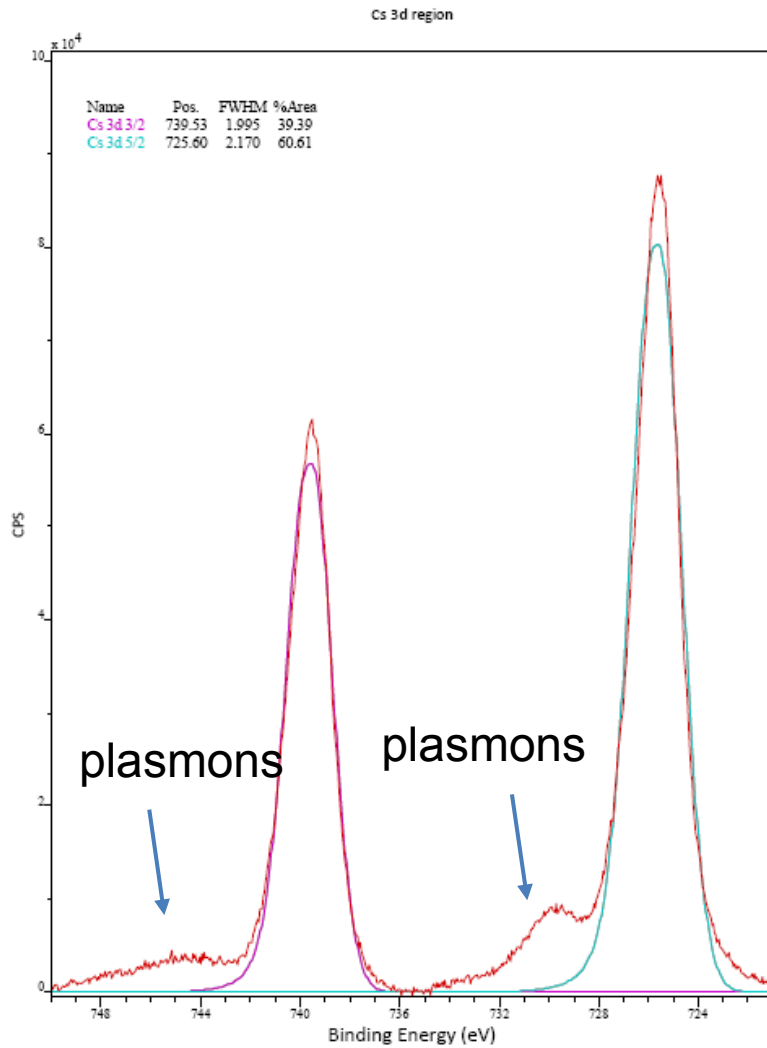
Heating the sample to 400 °C removes most of the oxide.

Due to reaction with K the peaks are shifted by 1.8 eV towards lower binding energies.

They are even shifted more when Cs is added by about 0.2 eV.



Decrease upon Cs adsorption, but spin-orbit coupling and peak position remain constant ± 0.1 eV.



Determined spin-orbit coupling is 13.93 eV.

Stoichiometric ratio derived from XPS intensities:

$$n_1 / n_2 = (I_1 / s_1) / (I_2 / s_2)$$

I...intensity (height or area)

s... sensitivity factor (dependend of height or area)

$$s (\text{Cs } 3d_{5/2}) = 7.2$$

$$s (\text{Sb } 3d_{5/2}) = 4.8$$

$$s (\text{K } 2p_{3/2}) = 1.24$$

After K deposition: $\text{K}_{1.6}\text{Sb}$

After Cs deposition: $\text{Cs}_{2.5}\text{K}_1\text{Sb}$

This cathode showed a q.e. of about 1 % at 532 nm.

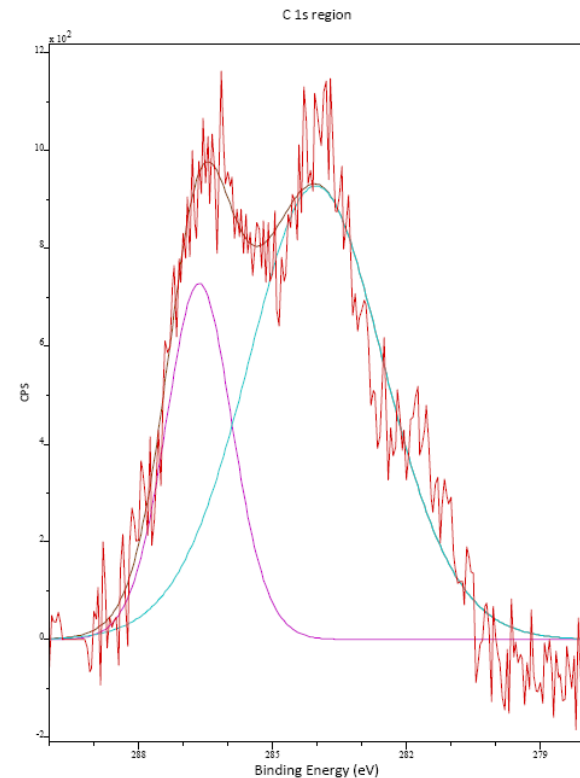
s taken from: <http://www.cem.msu.edu/~cem924sg/XPSASFs.html>

We were not successful in growing a stoichiometric CsK_2Sb cathode.

Nevertheless the cathodes showed a q.e. around 1 %. And whether the Antimony layer is sputtered or evaporated makes no difference for the outcome from the XPS side of view, IF the sputtered Sb layer is heated prior to K deposition.

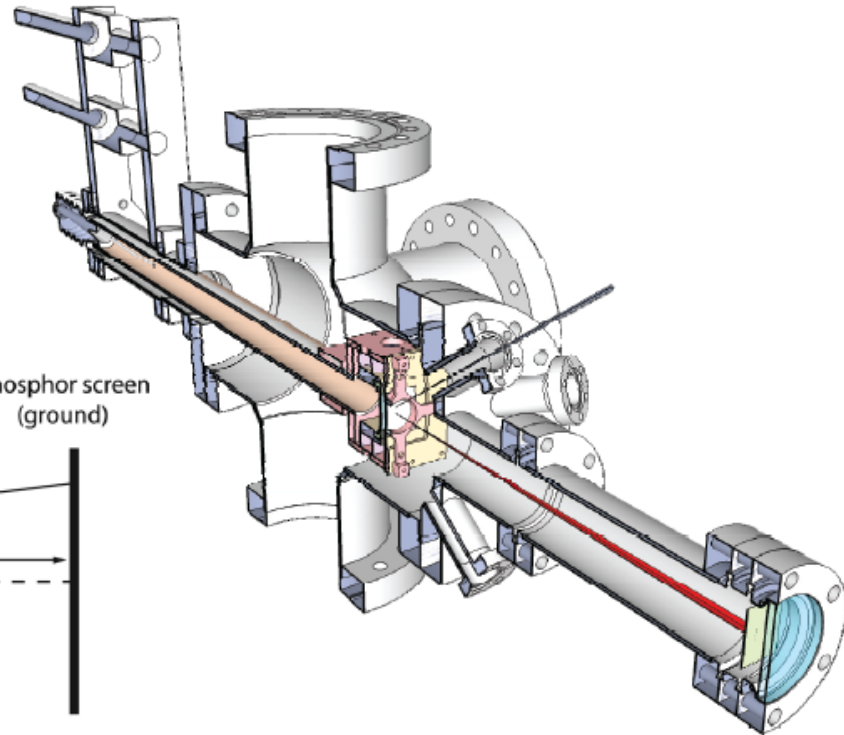
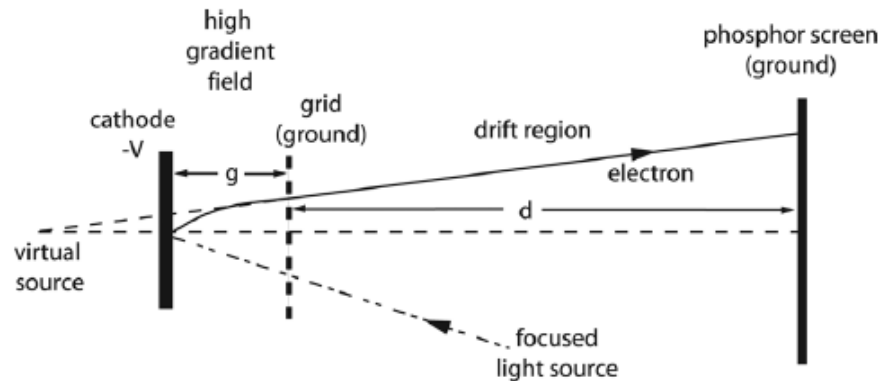
At all times was C present in the compound and oxygen clearly contributed.

The Carbon peak needs to be addressed in more detail, because upon the adsorption of K the C 1s shifts to higher binding energies, pointing towards carbene generation.

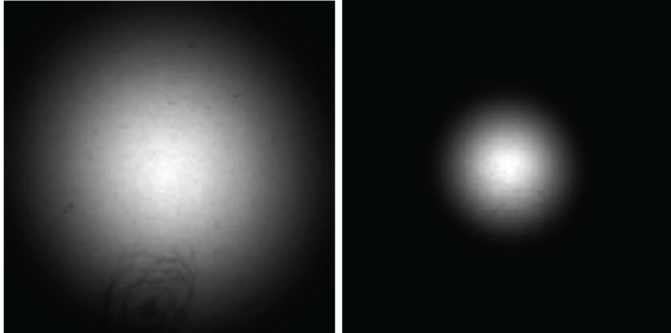


Surface roughness becomes a crucial parameter for the performance of srf electron injectors which are run with a multi-alkali photocathode, since the emittance growth is dependent on roughness and applied field.

Emittance vs. roughness studies performed by Theo et al..
See measurement setup [Vec11]:



[Vec11] T. Vecchione et al., Appl. Phys. Lett., 99, 034103 (2011)

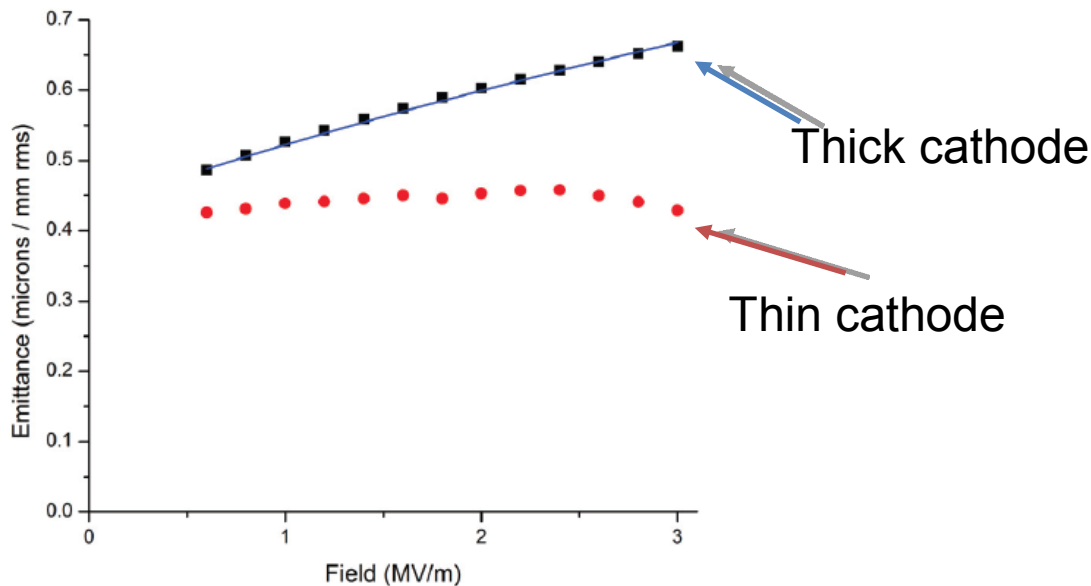


Transverse momentum distribution of bi-alkali photocathode as recorded by means of a CCD camera: left 0.6 MV/m and right 3 MV/m (473 nm wavelength) [Vec12]

Effects that contribute to the transverse energy spread:

- c) Initial energy spread due to difference in photon energy and threshold energy for emission
- b) Geometrical effect due to local tilting of the surface
- c) Bending of the field lines around curved surface (dependend on surface roughness and field gradient)
- d) A cross term of b and c

[Vec12] T. Vecchione et al., Proceedings of IPAC12, MOPPP041



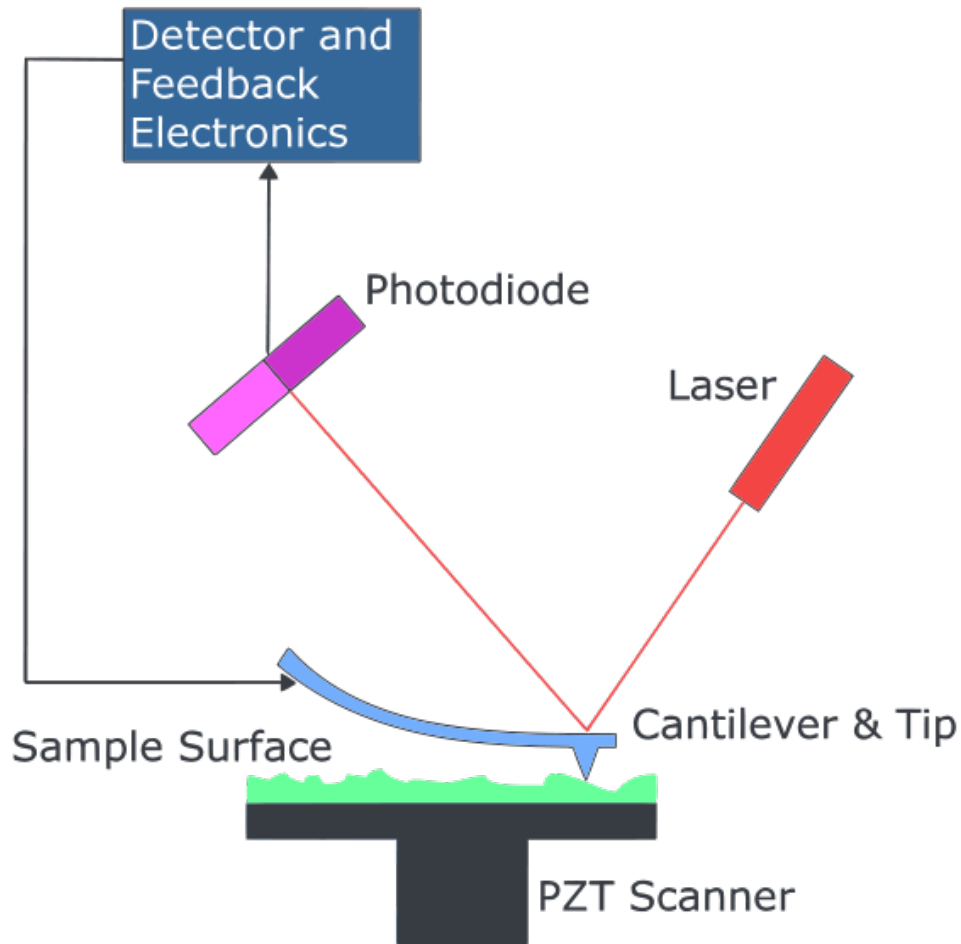
Solid line derived from simple model shows excellent agreement with measurements → knowing the roughness = prediction of emittance

Thin cathodes show almost **no emittance change** upon field gradient enhancement, whereas the emittance of **multi-layer cathodes** has a **strong field dependence**.

The higher the field the higher the emittance.

From SEM measurements we know that the multi layer cathodes are much rougher than the thinner cathodes.

AFM ... Atomic Force Microscopy enables us to scan the topography of the sample

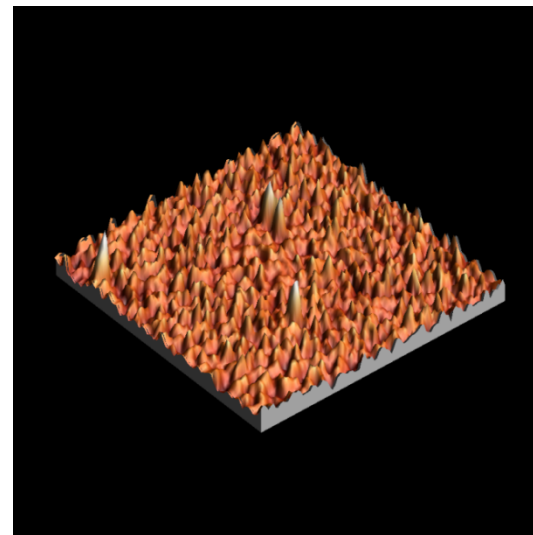
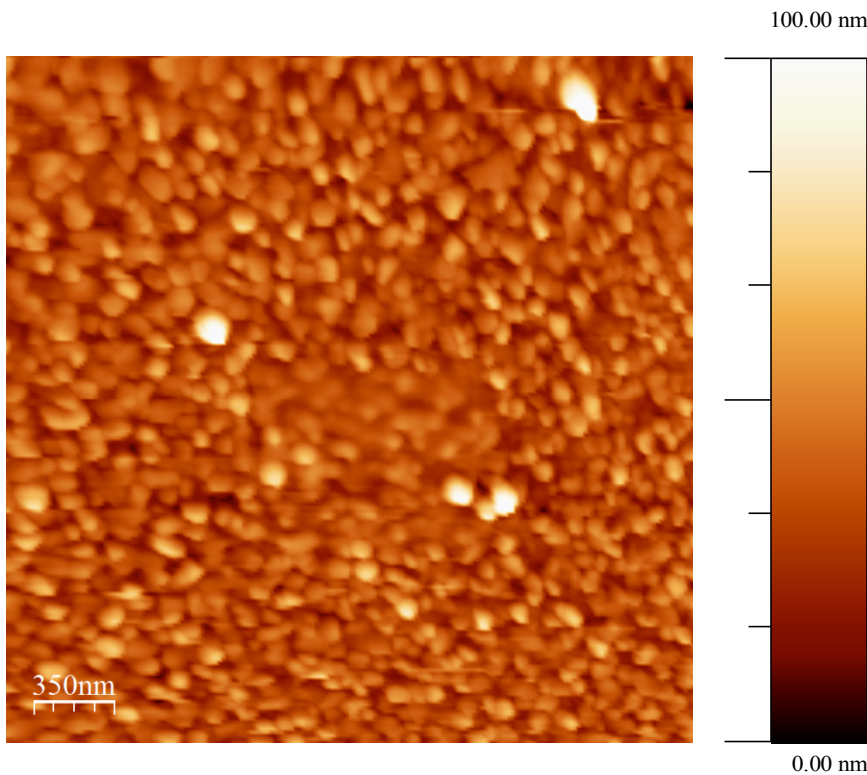
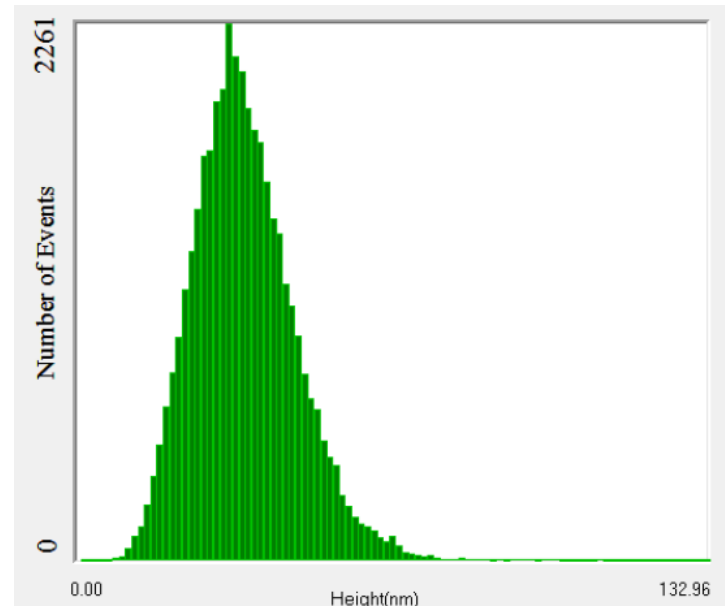


Pic taken from: http://en.wikipedia.org/wiki/Atomic_force_microscope

The surface appears quite rough.
Islands of different height are found.

The average height is about 34.73 nm.

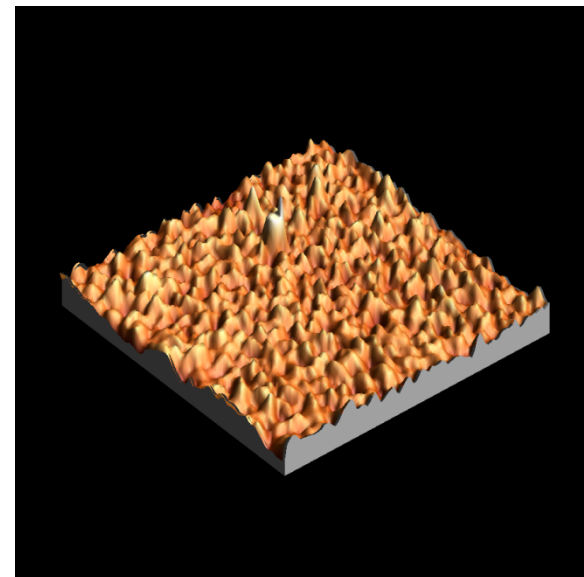
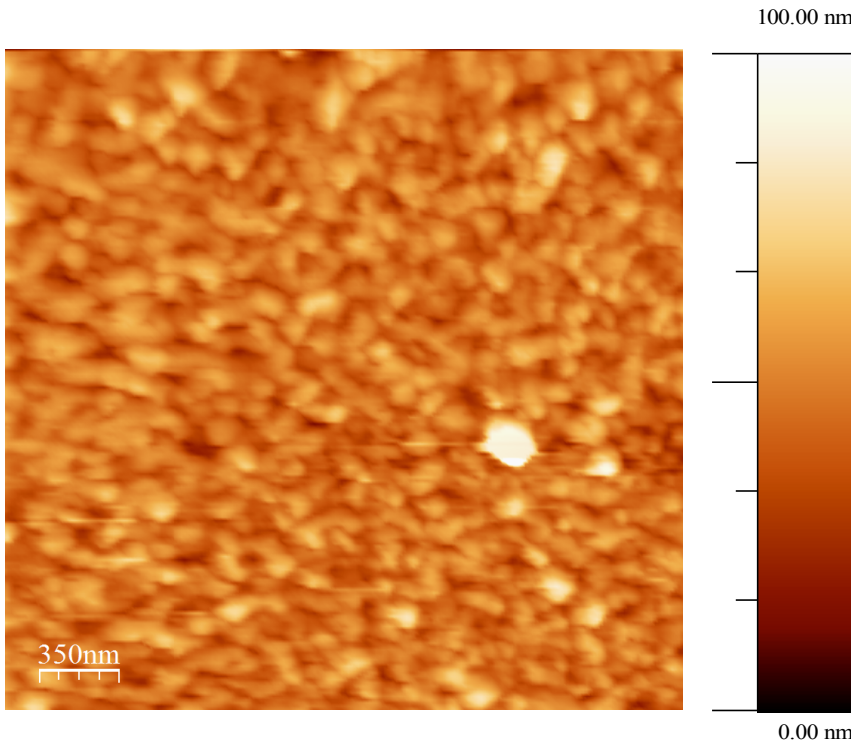
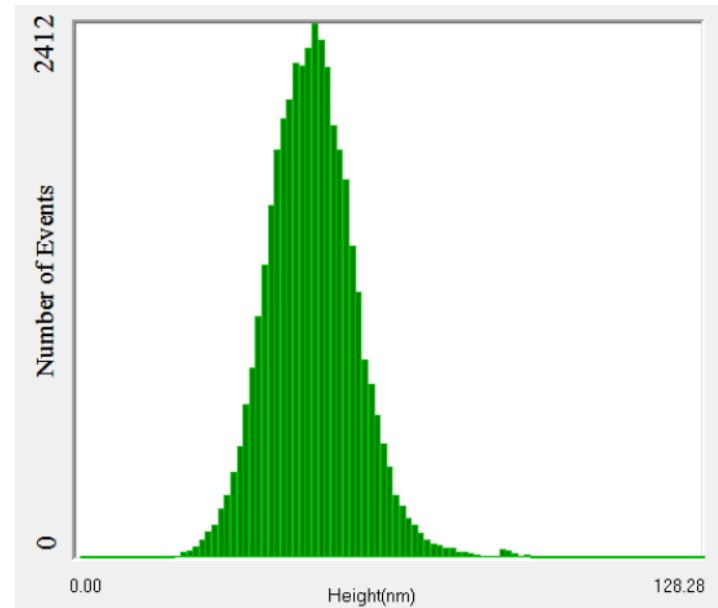
Determined average roughness is 11.5.



On top of the first cathode an new layer of Cs-K-Sb was grown.

The height range is smaller than before, and the average height is about 47.63 nm.

The overall roughness is smaller than the one determined for the “single” layer cathode (9.2).



The work was performed in the Center of Functional Nanomaterial at BNL within the combined effort of BNL, LBNL, Stony Brook University and HZB.

The work is financially supported by DOE.

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Triveni Rao
Howard Padmore
Theodore Vecchione
Susanne Schubert



THANK YOU FOR YOUR ATTENTION!