Cracker valve and plasma control process for reactive sputtering with Selenium & Sulphur

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thin film and pvsolutions

products. process. support

GENCOA current products cover 3 sputtering related areas

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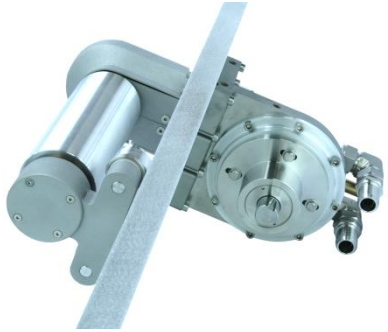


planar & rotatable
Magnetron Sputter Cathodes and Magnetic Systems

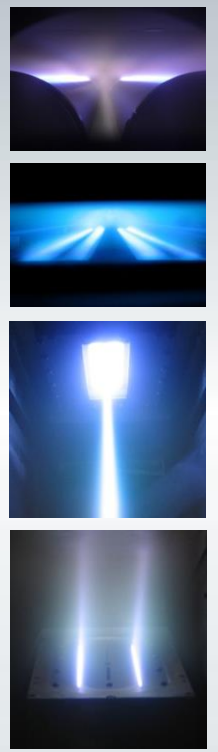
Reactive gas controller
& endpoint detector

speedflo™

Linear
ion sources

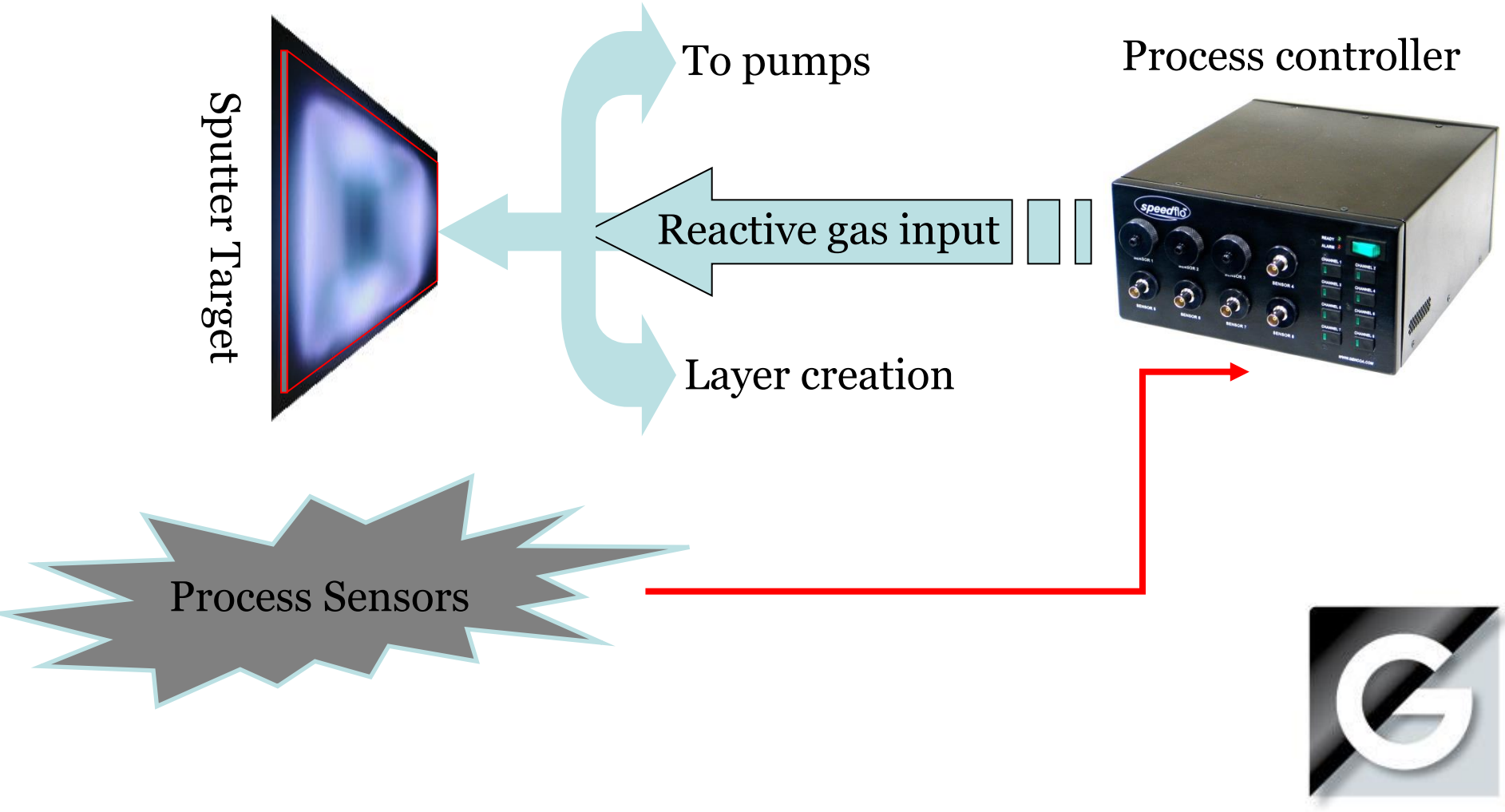
Other activities include on-site process implementation, training and tuning

Structure of presentation



- Introduction to reactive sputtering
- Existing CIGS processing routes and one system concept
- Feedback control and cracker design
- Reactive sputtering of sulphur and selenium based layers with Cu, In & Zn target materials
- Conclusions

Reactive Sputtering is highly unstable, but advanced control makes widespread production process in many sectors



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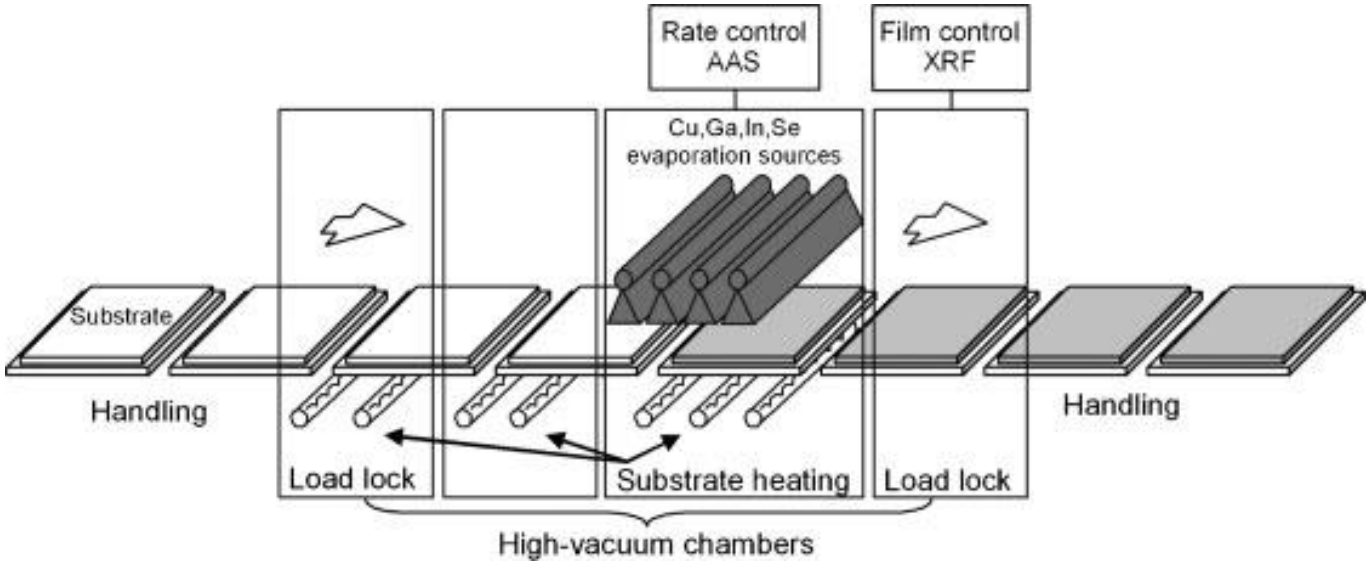
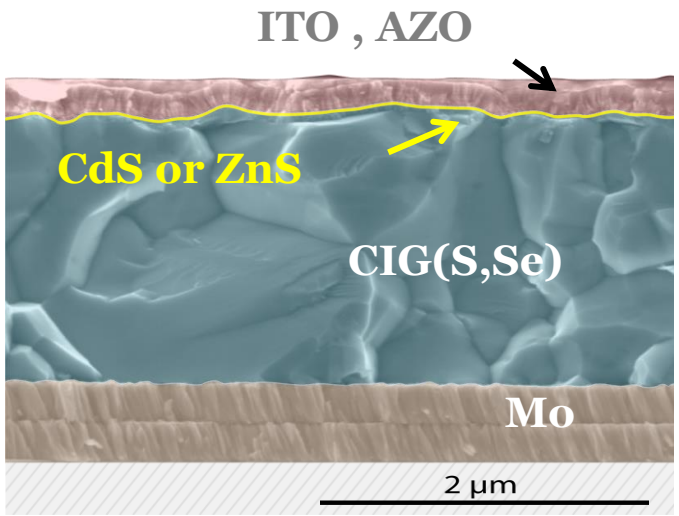
Objective is to bring established high volume flexible process to delivery of calcogens for CIGS layers

Key technology requirement in order to implement this is the delivery of the solid Se & S species to the reactive process environment at high speed - in the vapor phase - main topic of this presentation.

The attraction of the reactive sputtering route has been recognised and several companies have sought success

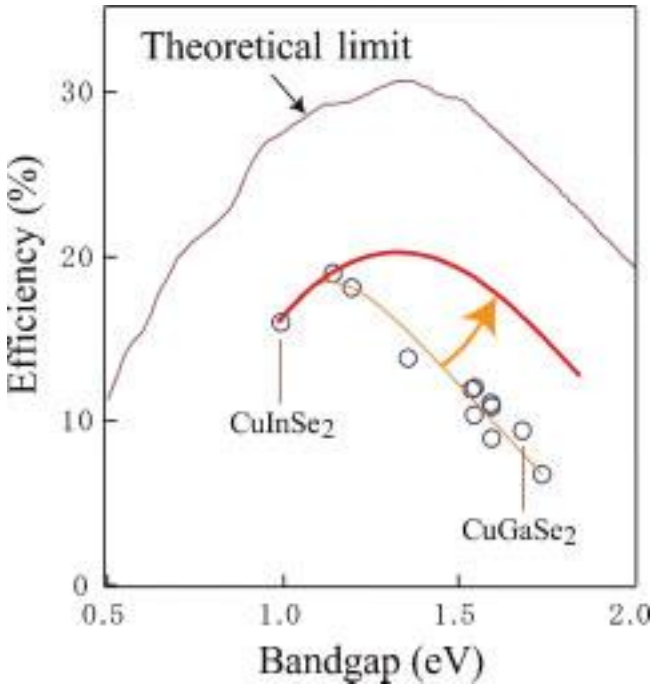




Solyndra, Miasole, Daystar have all pursued and implemented the reactive sputtering method, but due to technical and commercial challenges all have failed.

Older more established technologies of evaporation and sputtering with a 2nd stage selenization and sulphurization have won out – FOR NOW!

But it is accepted that the existing technologies cannot approach the theoretical maximum efficiencies of 30%



In order to achieve the higher efficiencies total flexibility to readily change layer compositions and layer combinations with a reliable process is required.

A pure sputter based approach can achieve this so long as the current challenges of the Se and S delivery are overcome.

I 'believe' that the biggest technical challenge that faced Solyndra, Daystar and possibly Miasole, was lack of good control of the Se and S gas combined with lack of a fast feedback and precise dosing method.

Principle of the gas delivery units – pulsed cracker valve – patent pending

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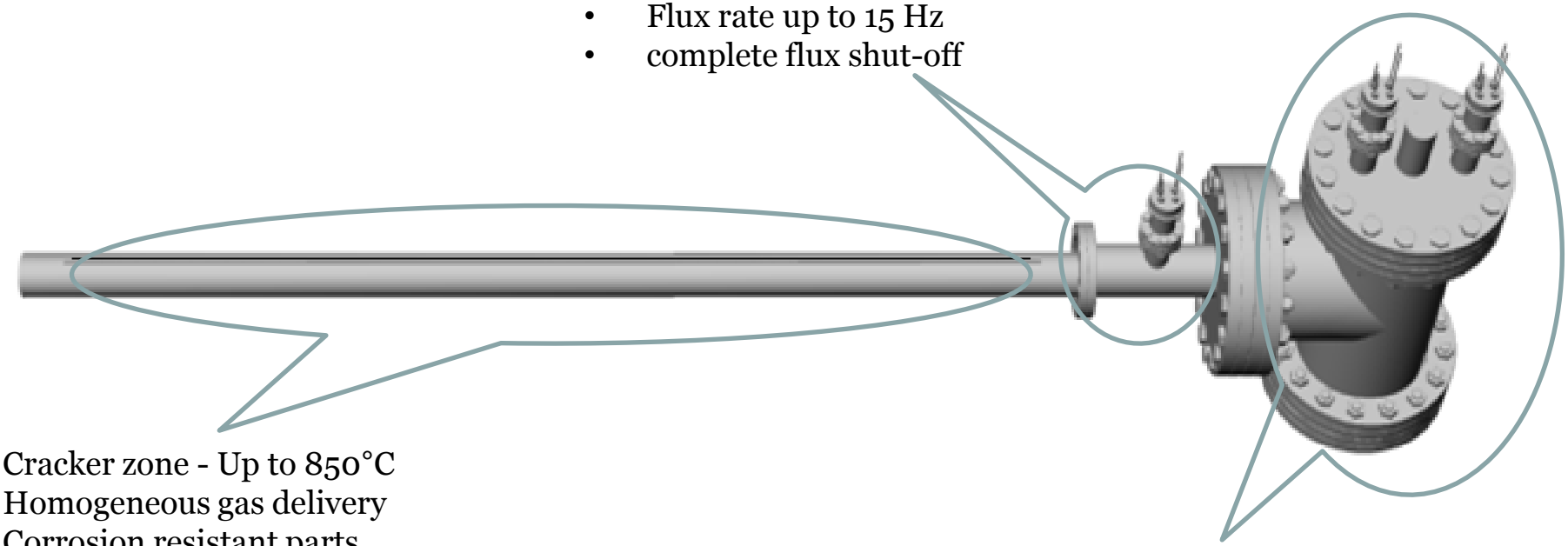
Hermetic fast actuating valve

- Fluxes from 20 msec
- Flux rate up to 15 Hz
- complete flux shut-off



Cracker zone - Up to 850°C
Homogeneous gas delivery
Corrosion resistant parts

Evaporation zone – RT to 550°C
Temperature control ±0.1°C
Corrosion resistant parts
Large capacity deposit

Operation principle: pulsed mode

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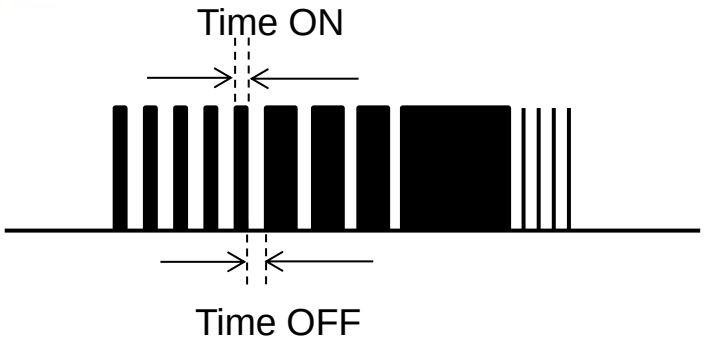
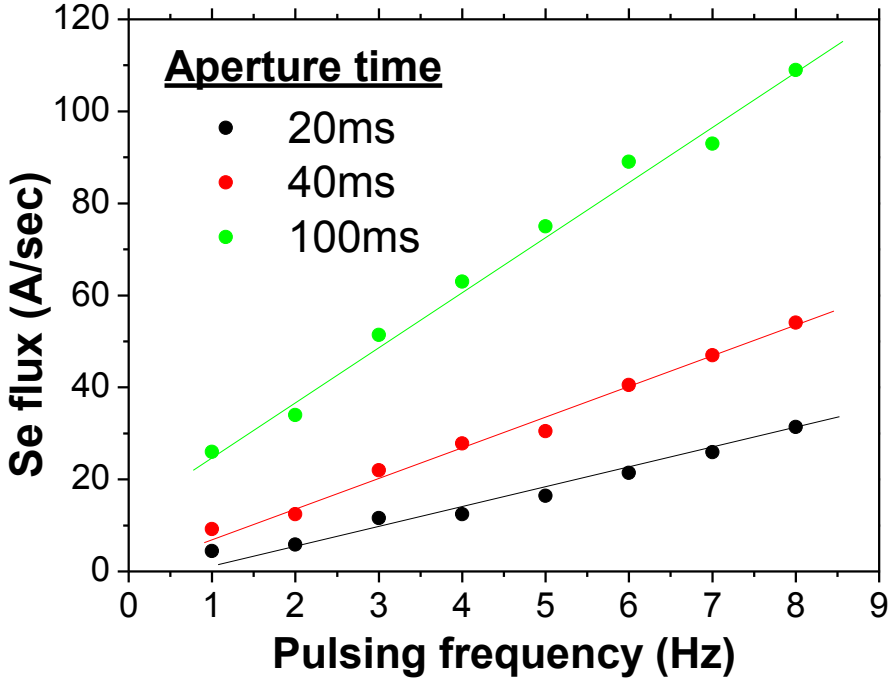
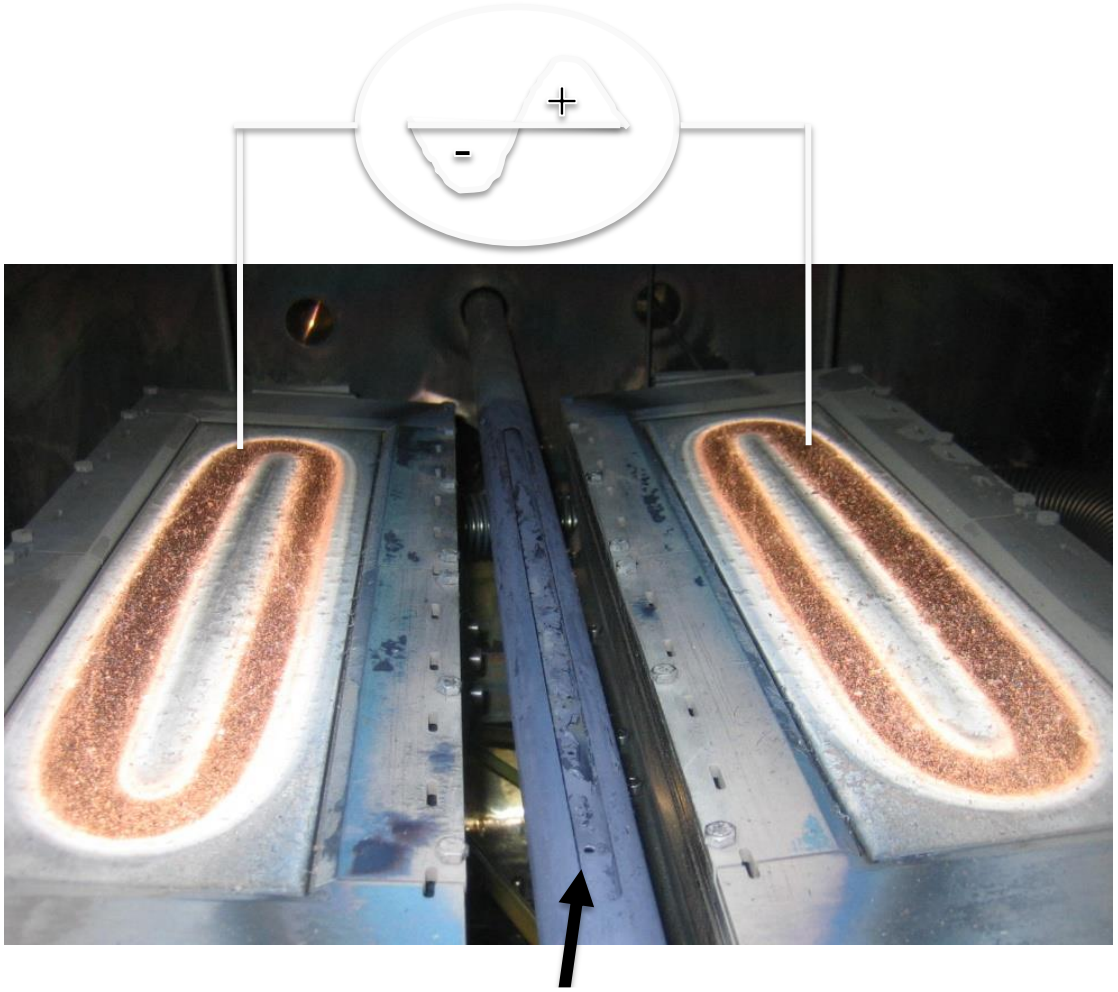


Flux ON

Flux OFF



Test setup – 2 x planar magnetrons 0.5m long with MF power



Effusion cell cracker for
reactive gas injection

Response of the valve and target condition with varying pulse widths

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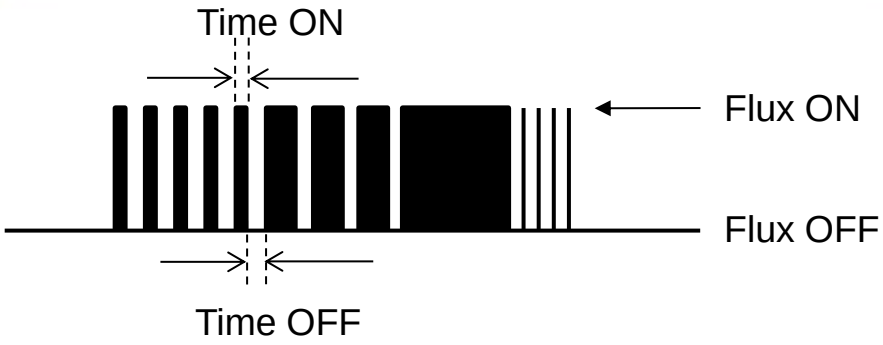
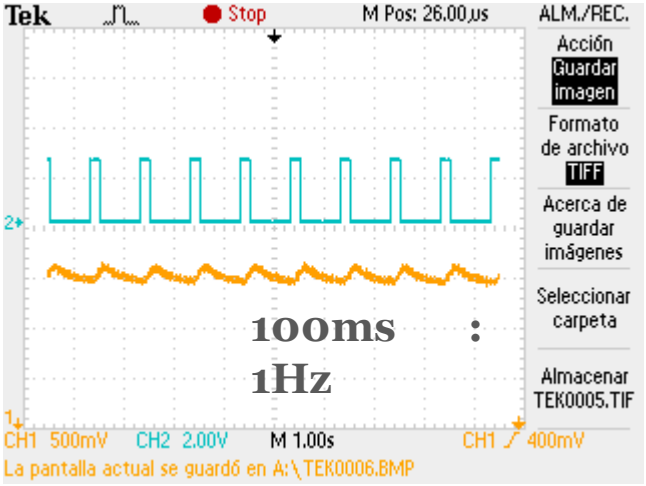
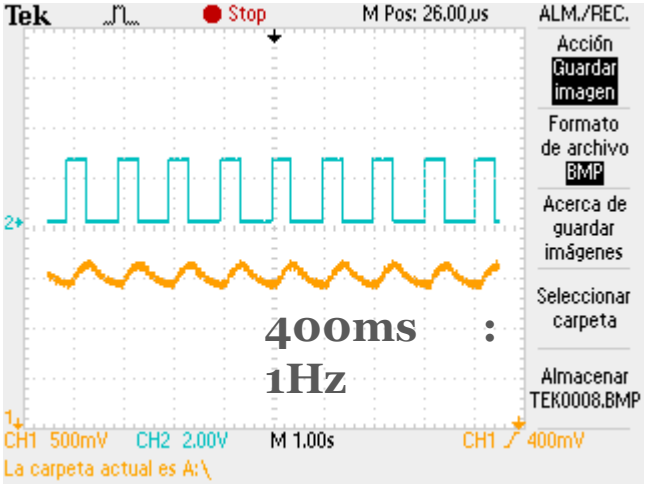


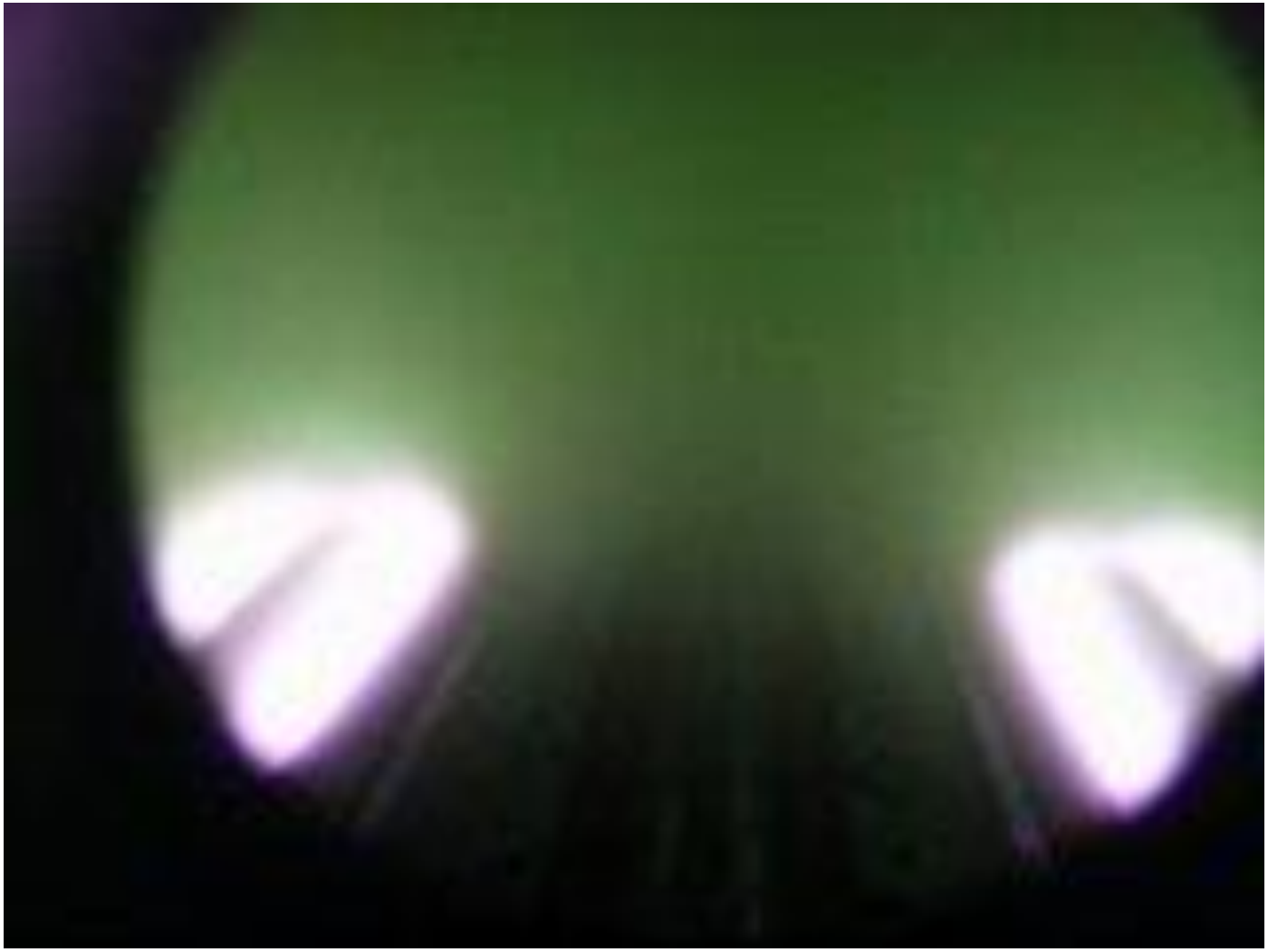
Valve actuator

Target voltage response

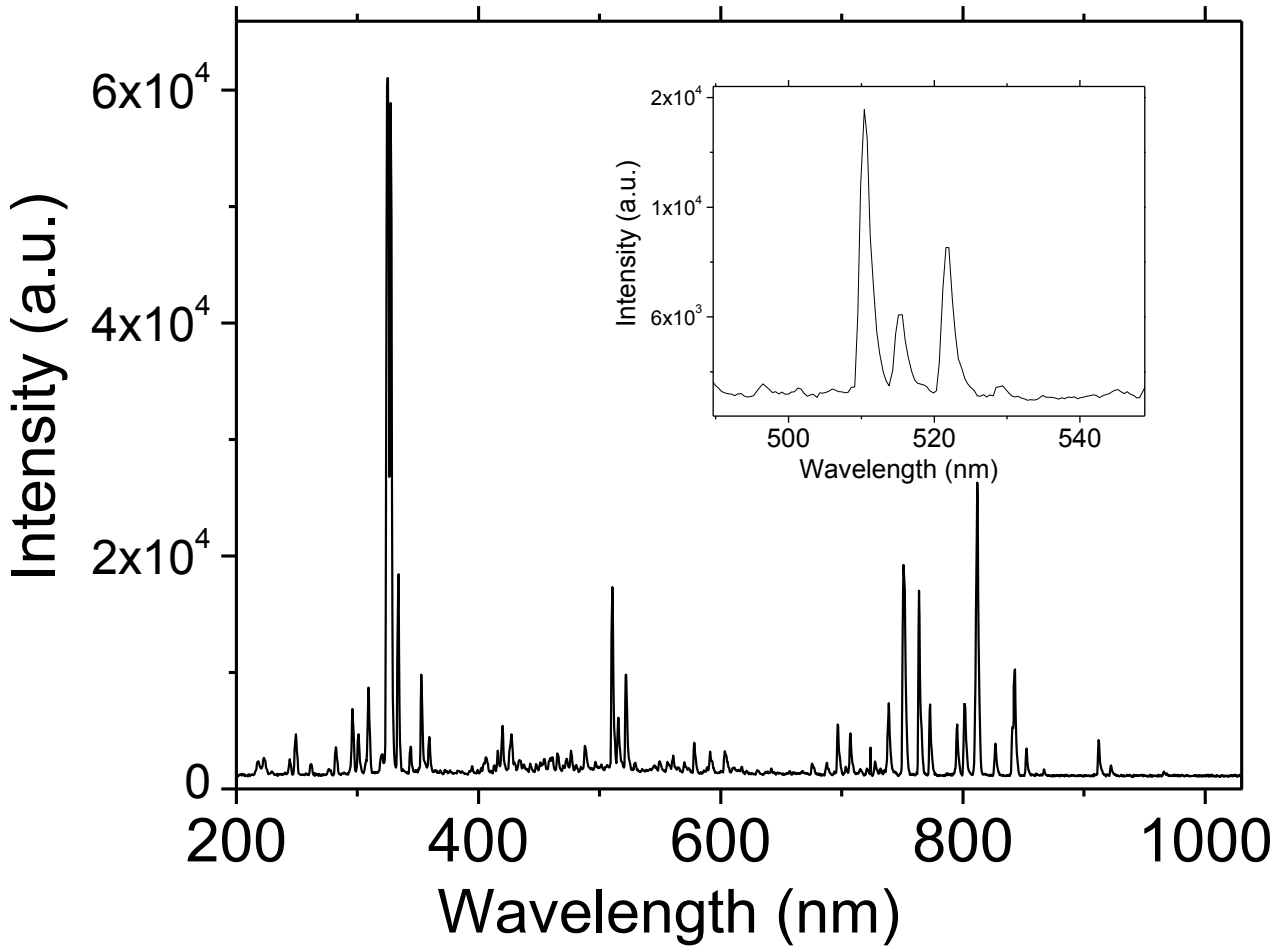




Video of plasma appearance with Se pulse gas input



Plasma optical emission spectrum with pure copper (inlaid graph) & with Cu combined with Sulphur (main graph)



Cu I

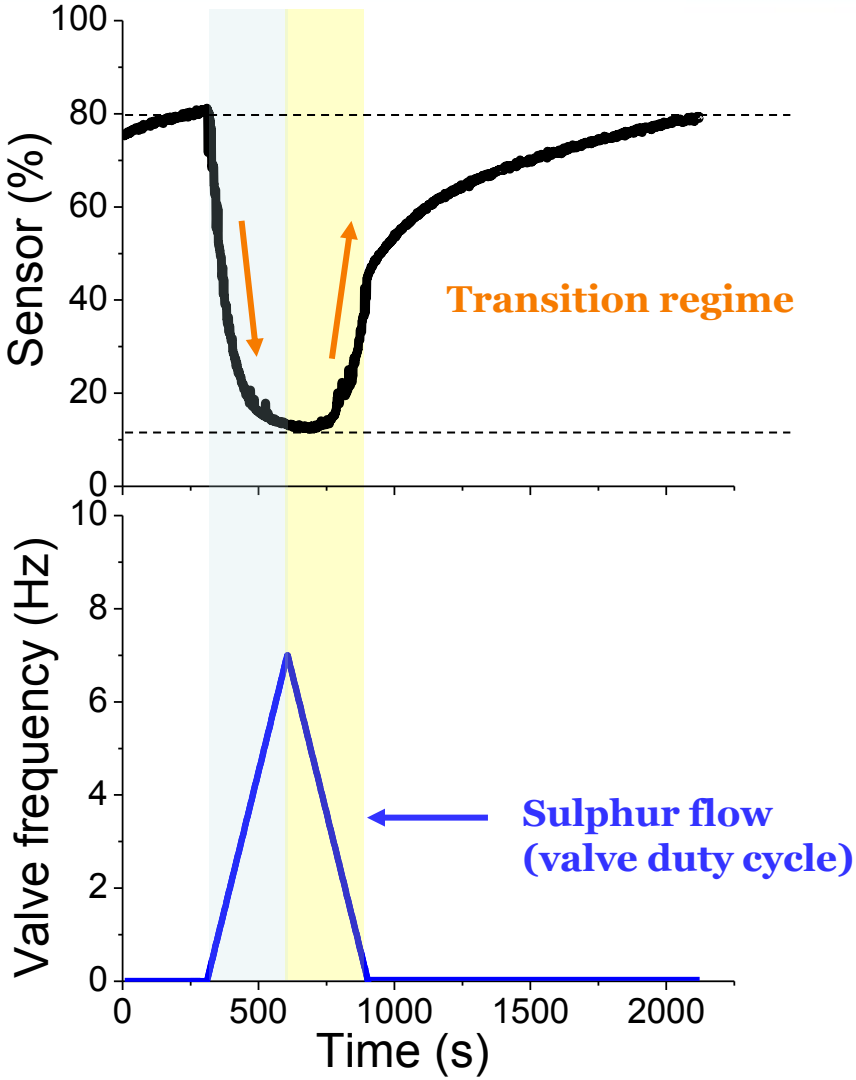
510.5 nm
515.3 nm
521.8 nm

Having a fast and stable Se & S delivery system completes the cycle required for total control of the process

SENSOR INPUTS

ACTUATOR OUTPUT

REACTIVE GAS INJECTION



'Metal'

λ Sensor (CCD)= **510.8nm (Cu)**

Fully poisoned

Hysteresis ramps: P.E.M. & target voltage, displays classic reactive sputtering behaviour which indicates needs feedback control

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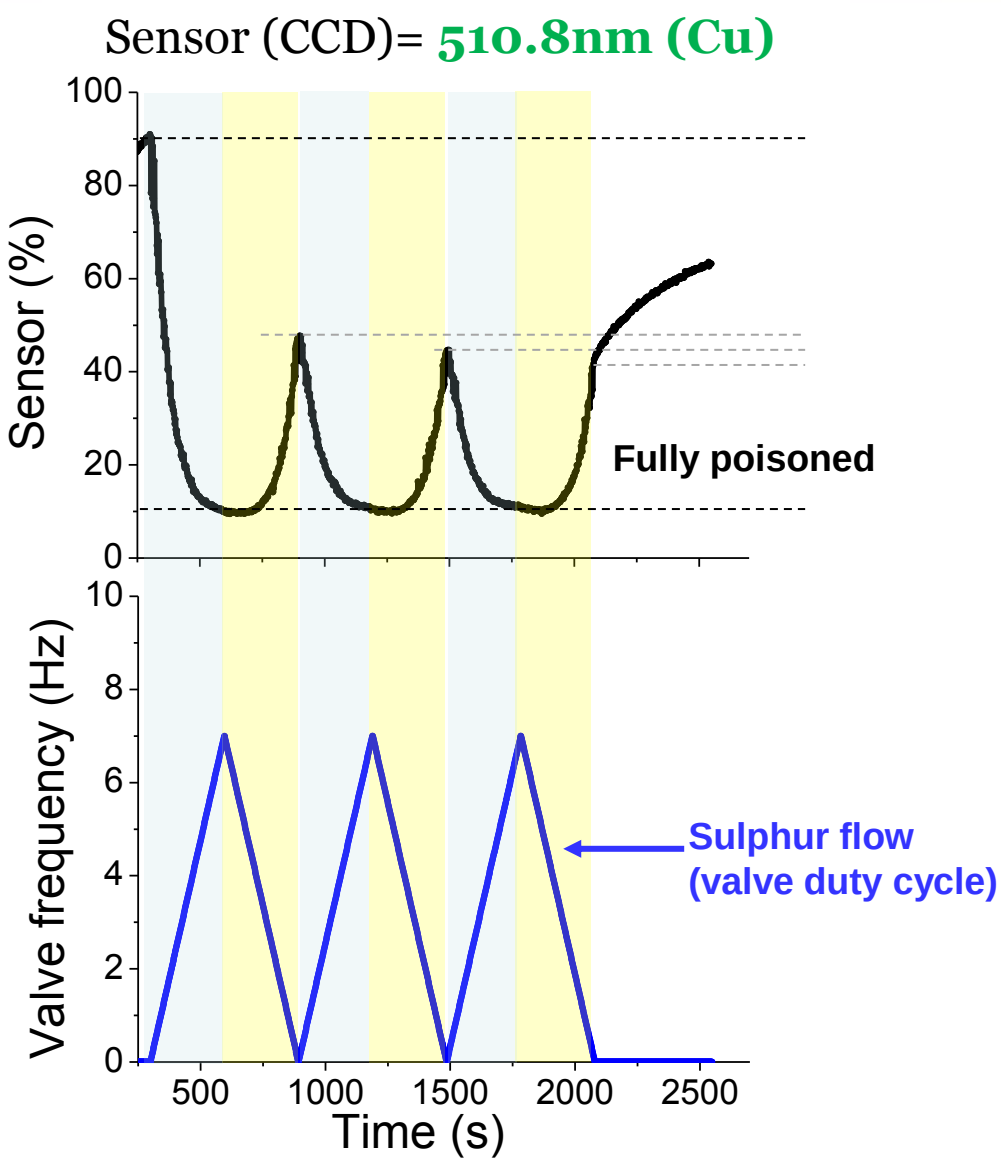

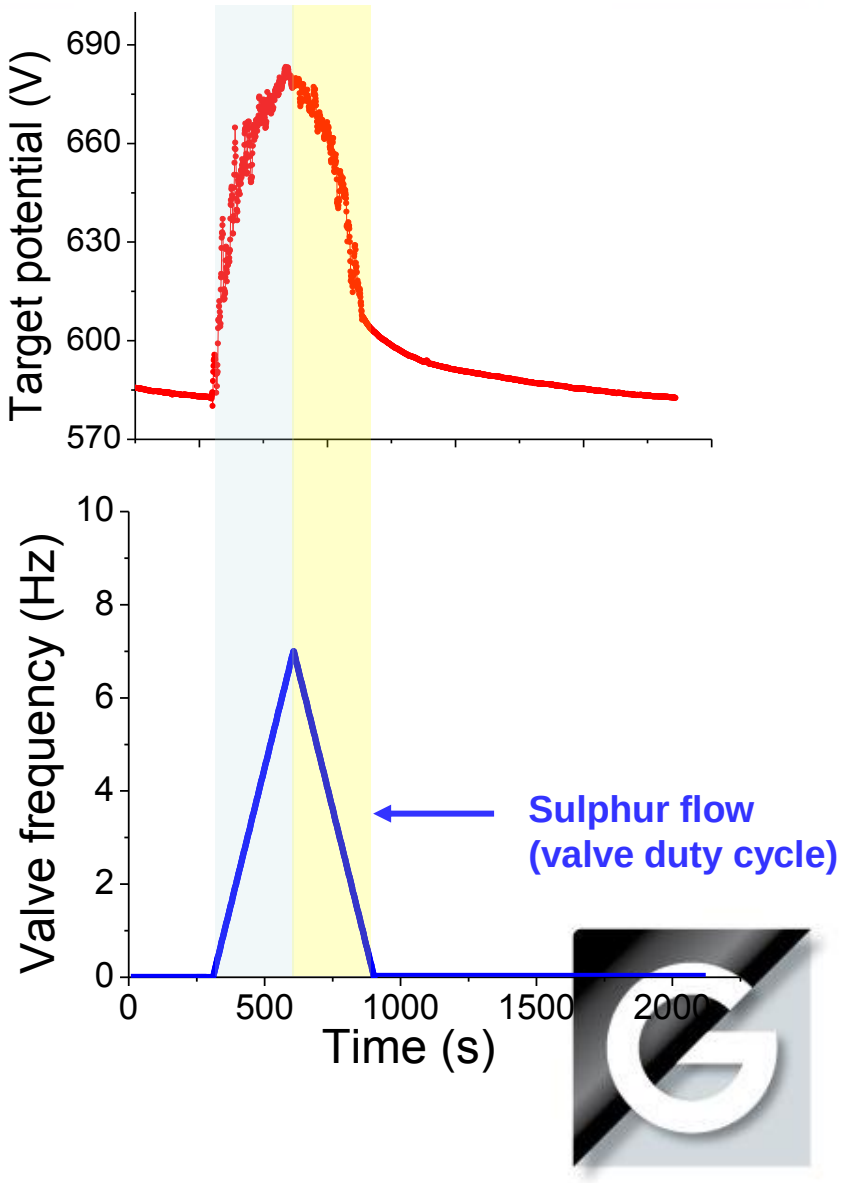

Example of Selenium flow adjustment via feedback control of the pulsed cracker valve by plasma emission sensing of Se

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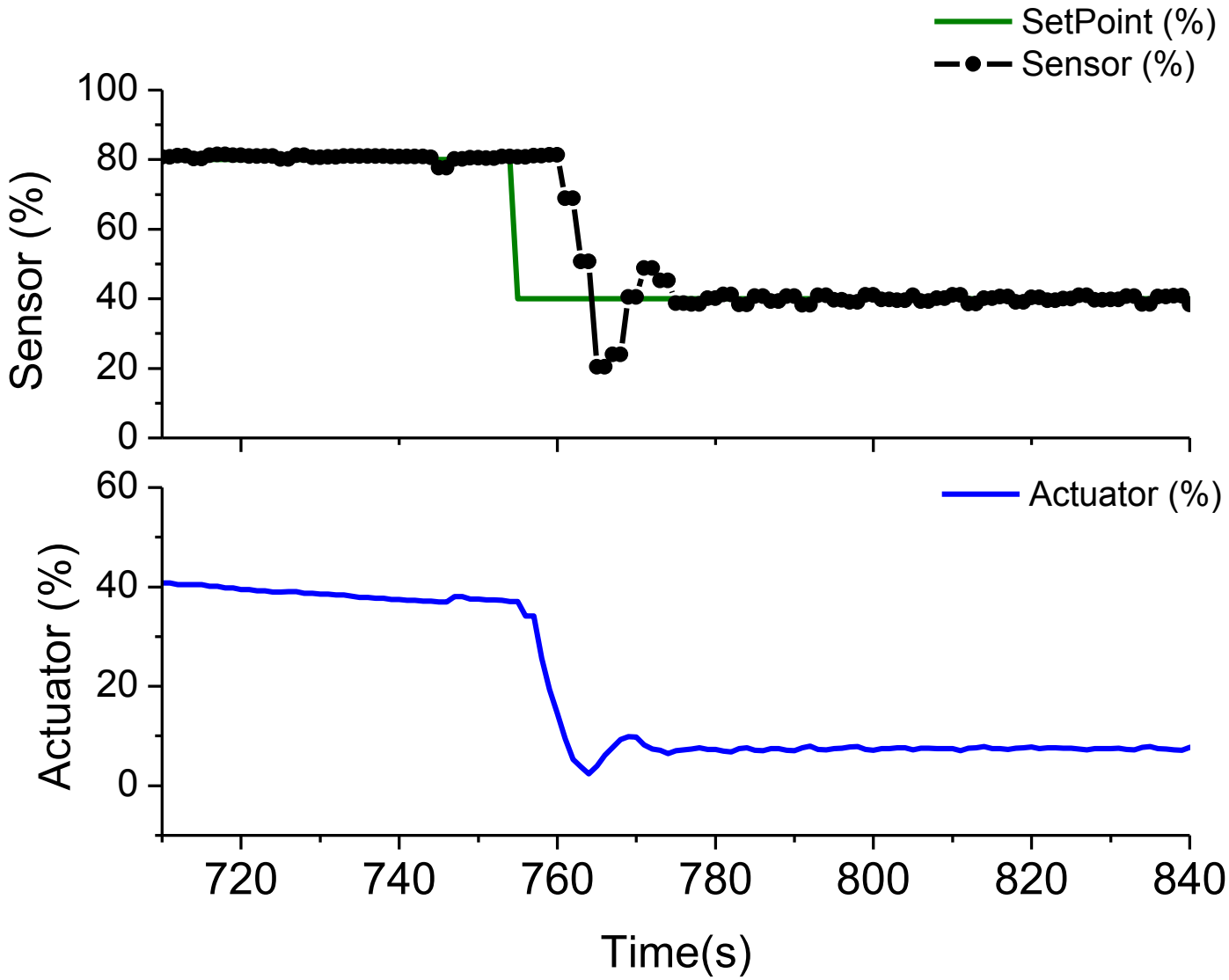
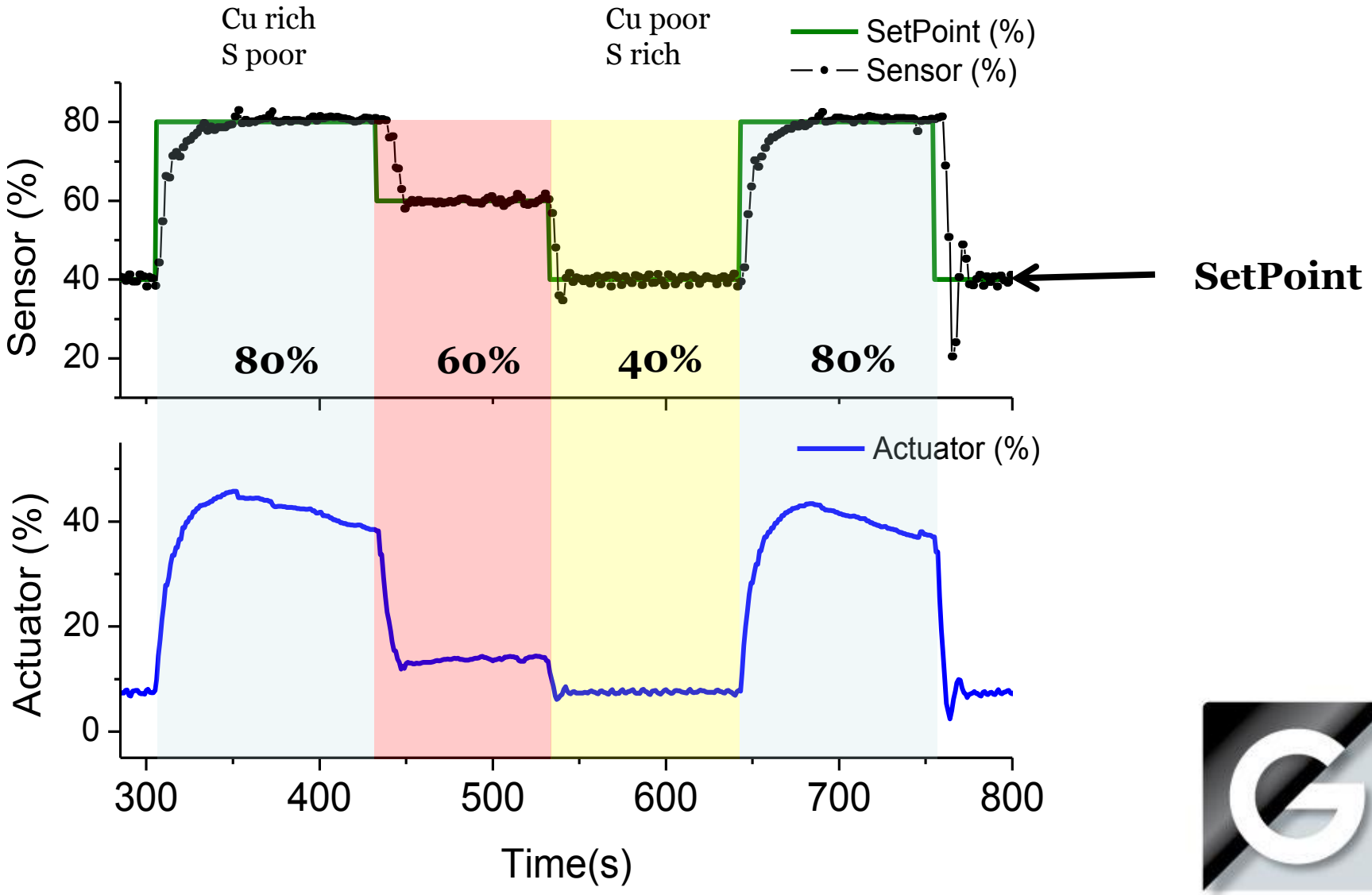


Active feedback control – changing set-points and controlling compositions at different levels to demonstrate control



Thickness and composition distribution for a Copper Sulphide combination of materials

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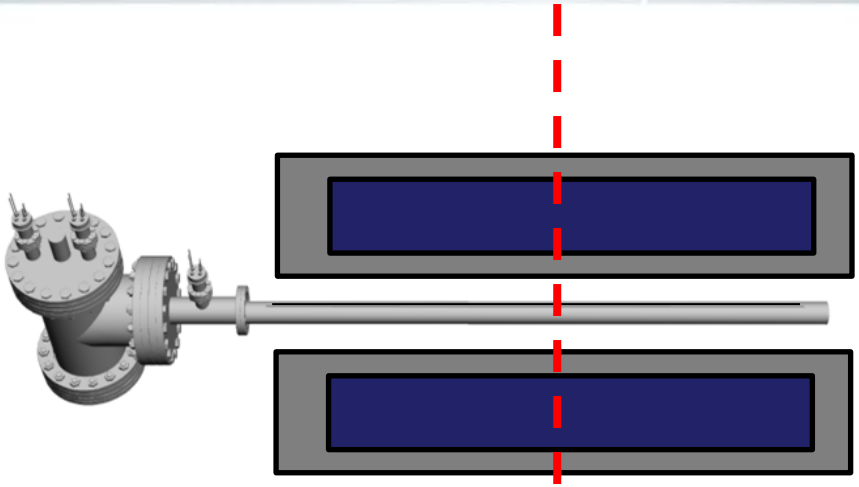

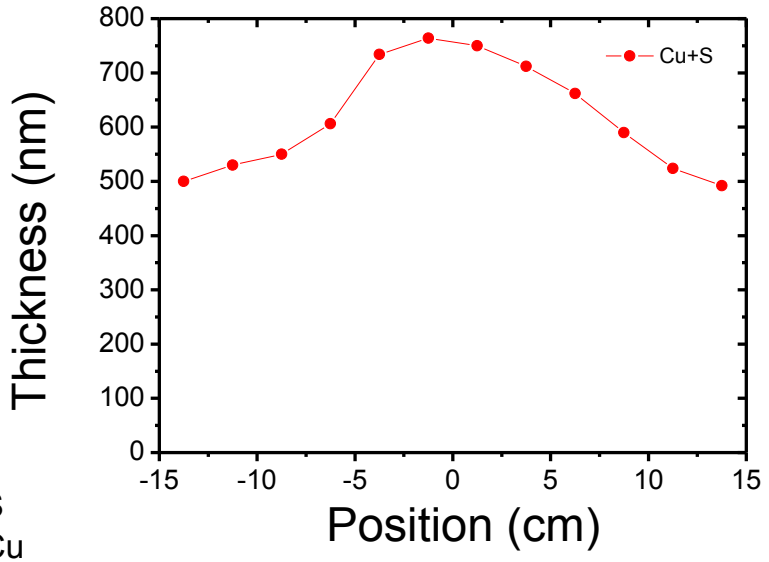

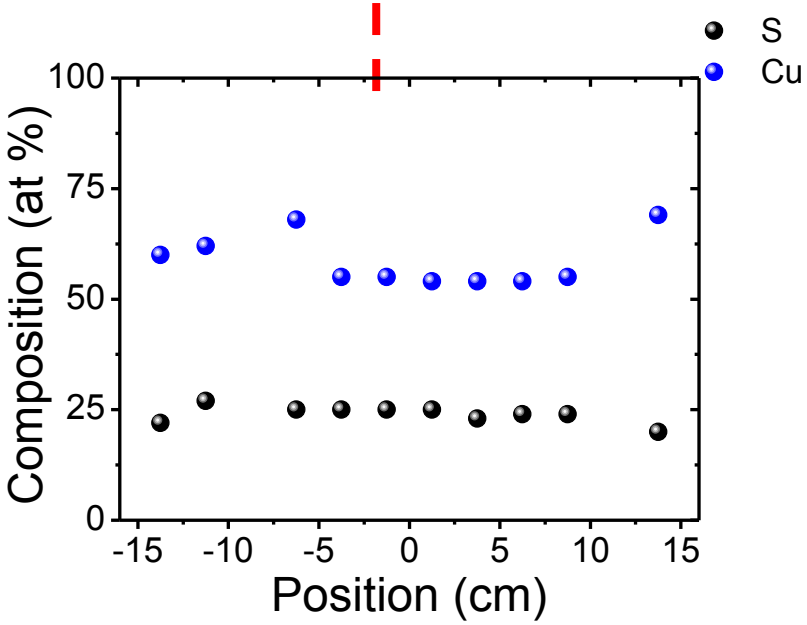

Example of reactively sputtered $CuInGaSe_2$ structure - No serious layer or cell development to be performed

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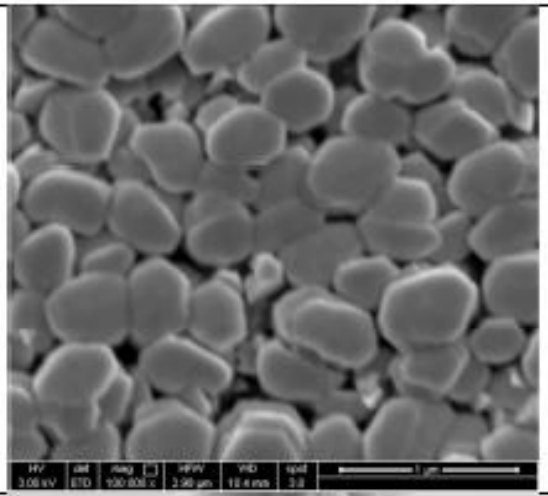
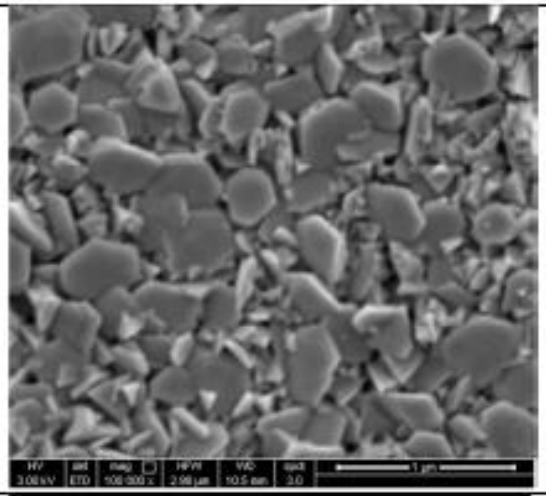
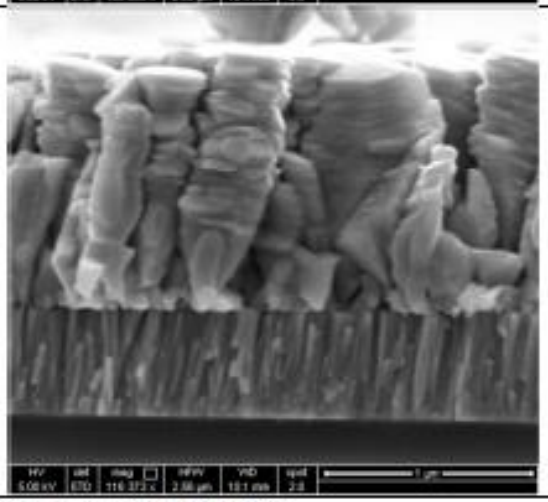
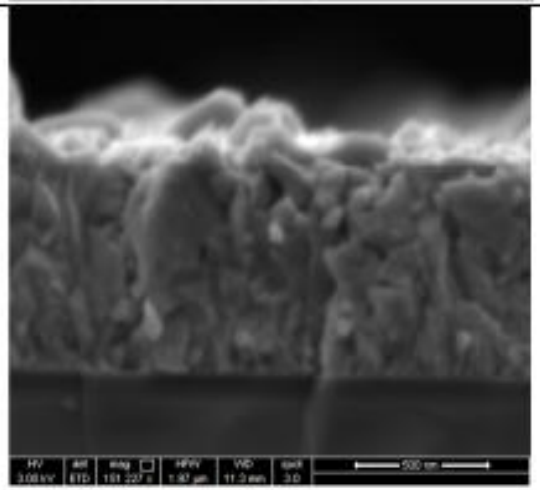
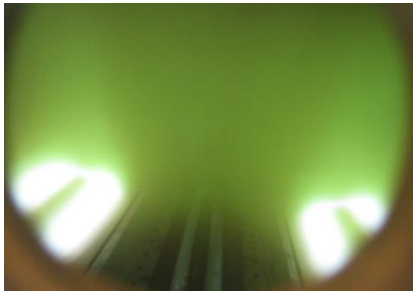
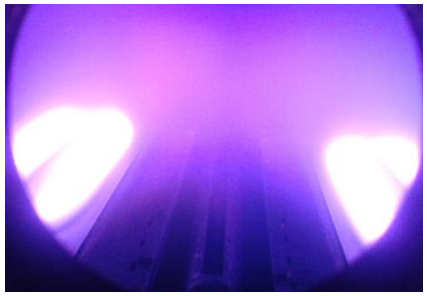
Top		
Cross-Section		
	Cu-In-Ga-Se on Mo/Glass	Cu-In-Ga-Se on Glass

Plasma emission spectrums for In, Cu & Zn in the presence of Sulphur

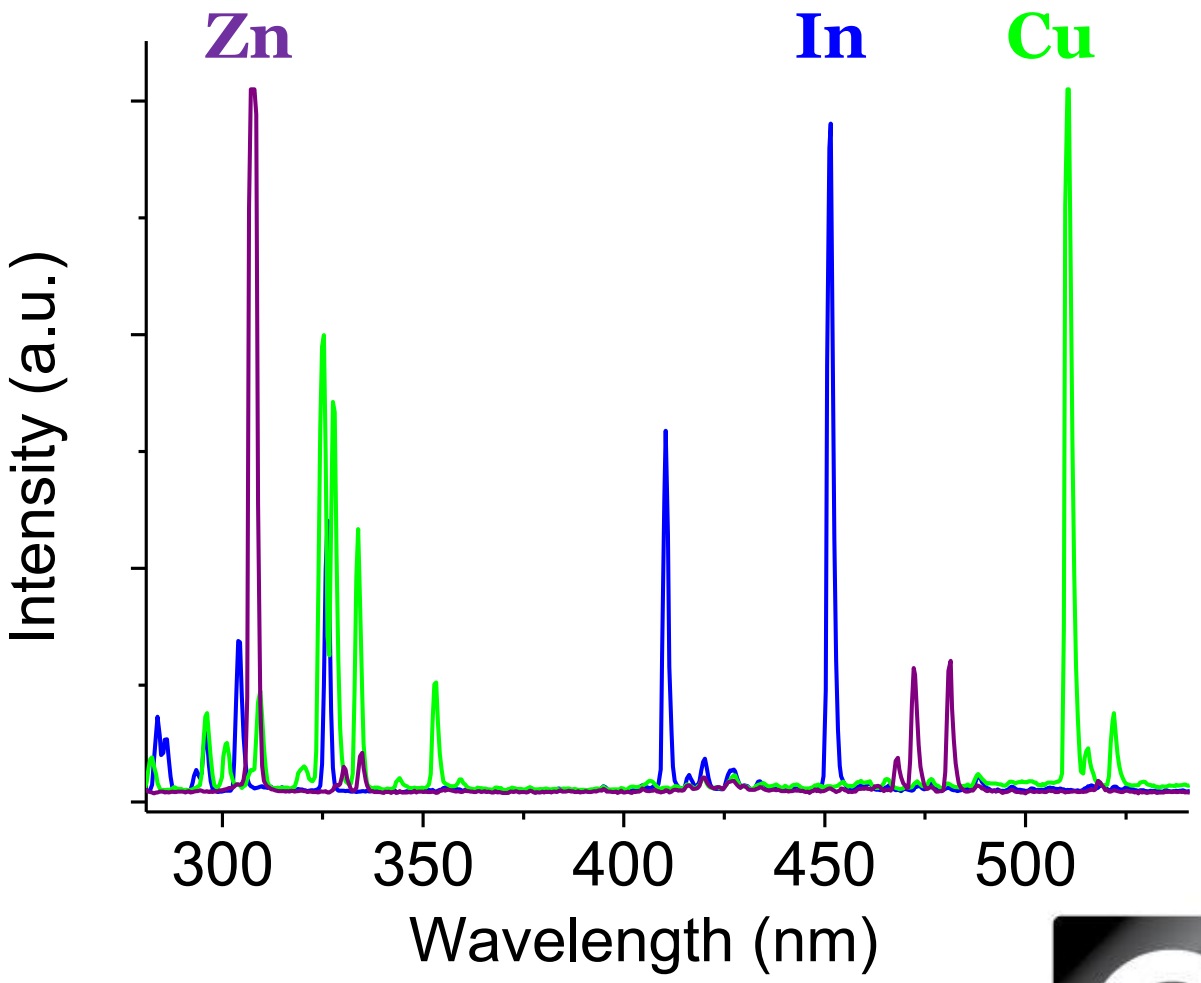
In



Cu



Zn



Hysteresis ramps: P.E.M. & target voltage for the Indium & Sulphur system

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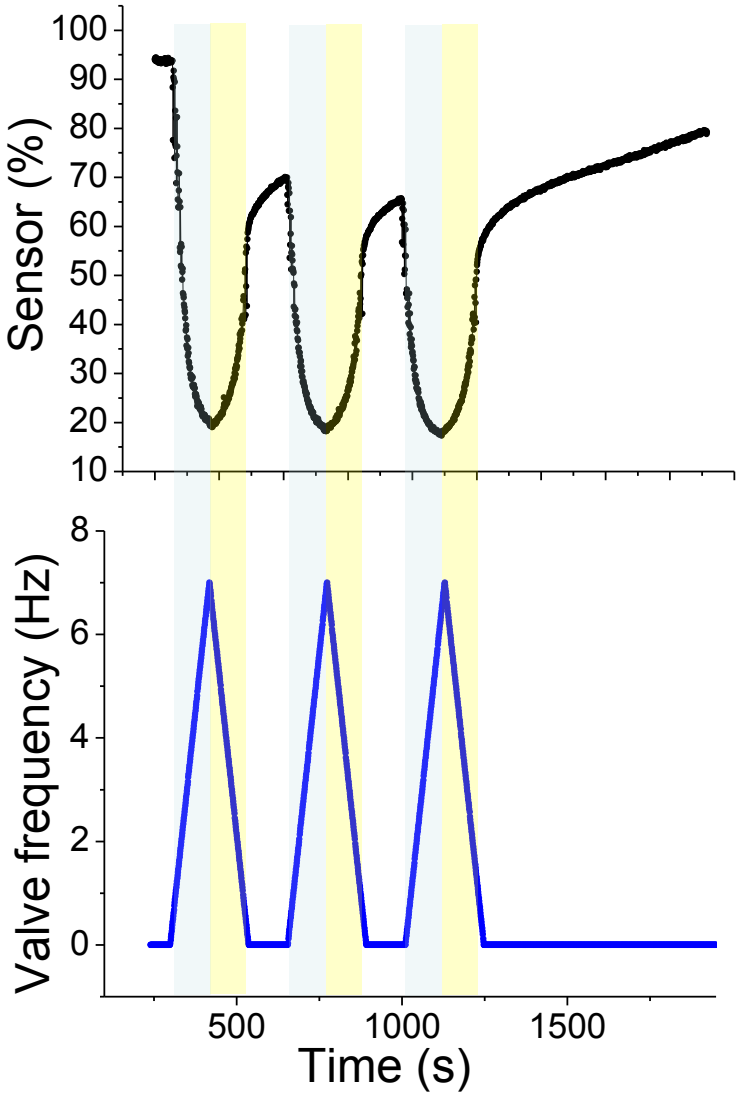
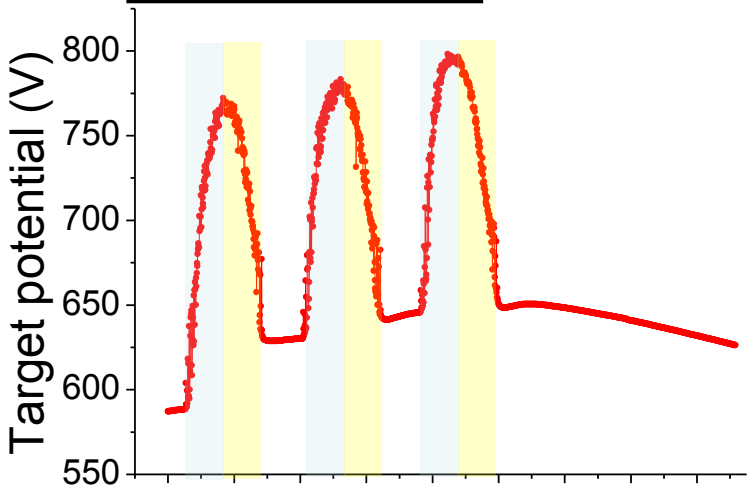
λ Sensor (CCD) = 451.7nm (In)

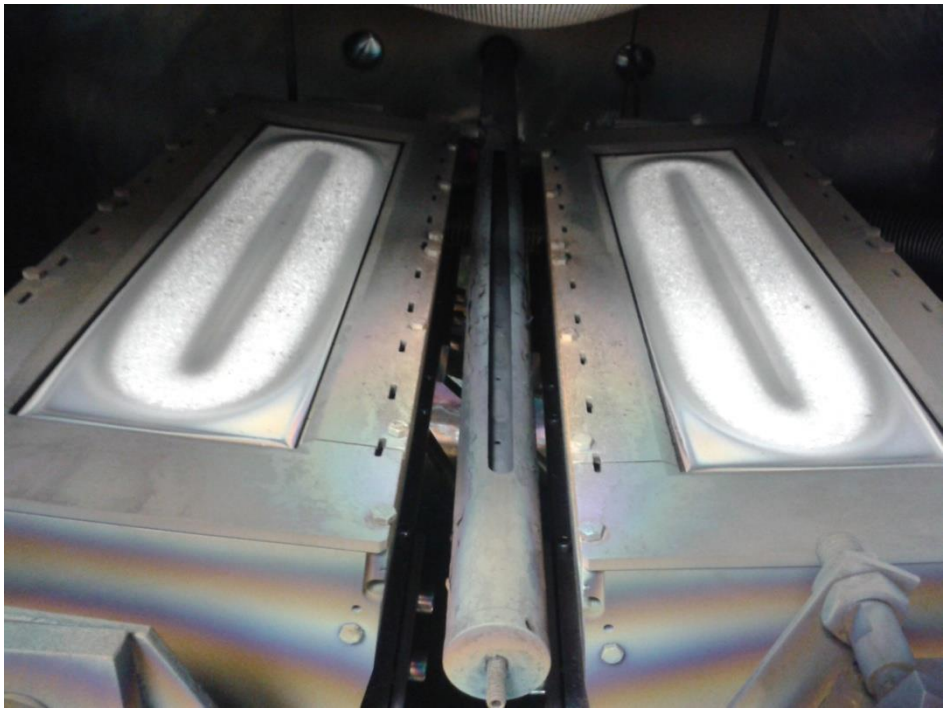


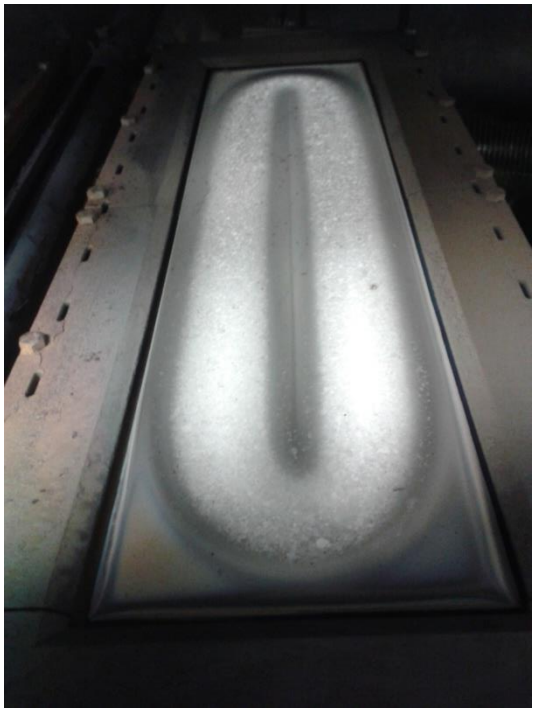
Target potential



In / S

Indium target (In) + Sulphur (S) – target displays classical transition mode appearance

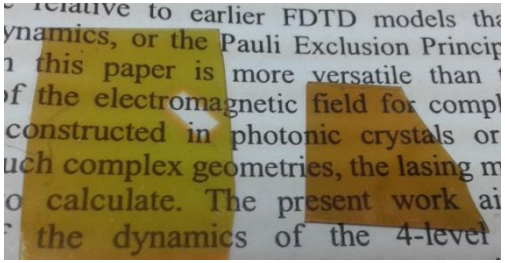




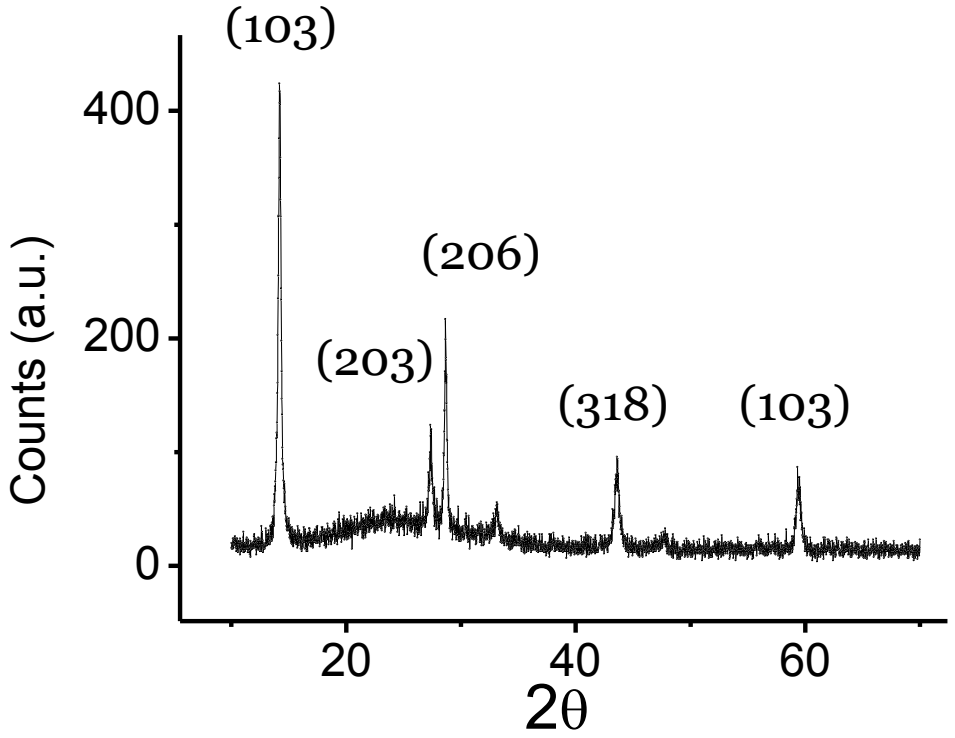
In

In_2S_3 deposition

Tetragonal β-In_2S_3 on glass at 250°C

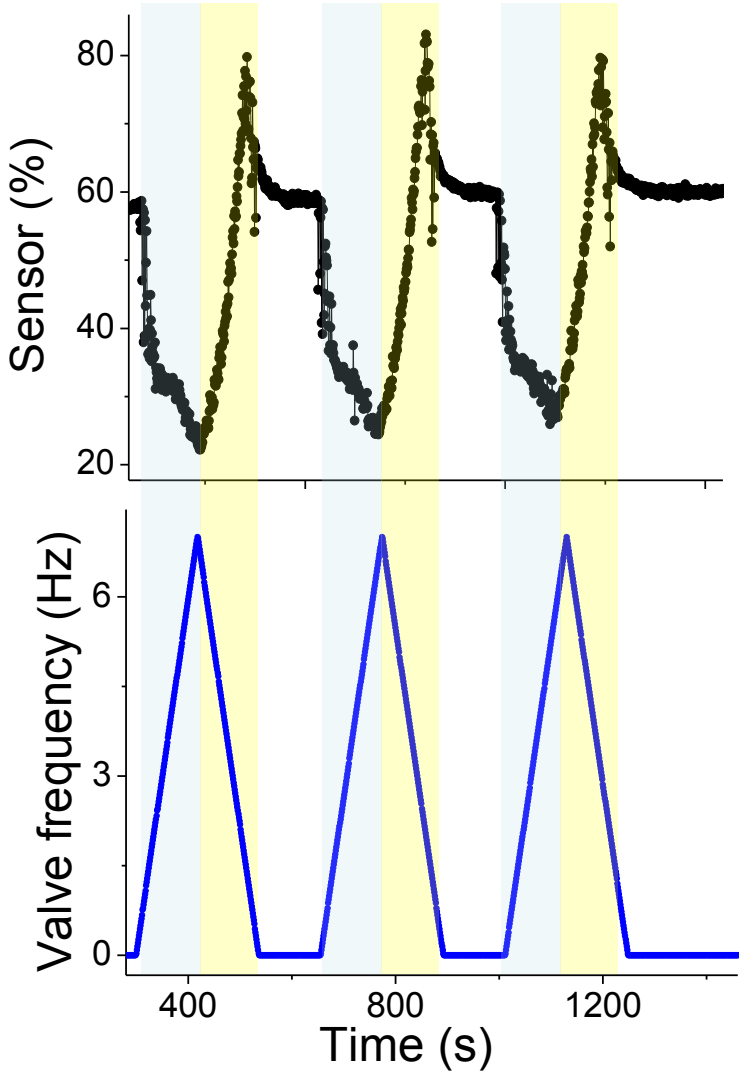


In_2S_3 In_2S_3:V

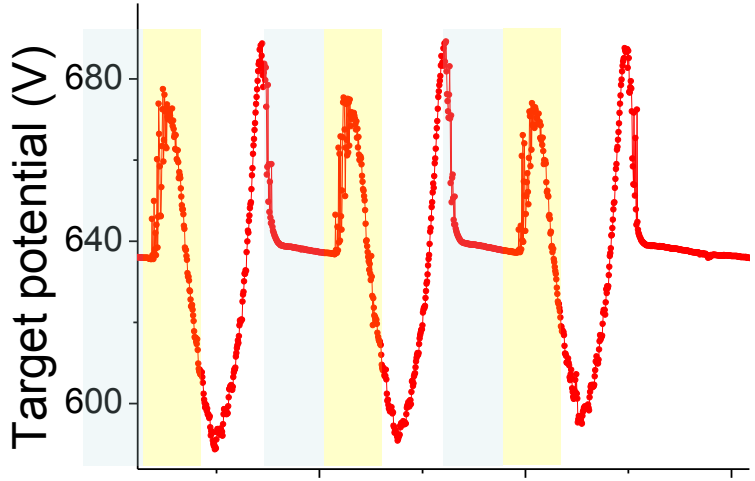


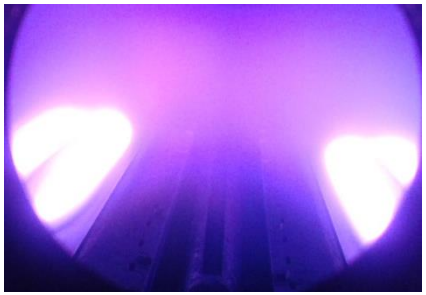
Hysteresis ramps: P.E.M. & target voltage for the Zinc & Sulphur system

λ Sensor (CCD) = **307.4nm (Zn)**



Target potential





Zn / S

The control process is good and rotatable magnetrons are better for cleanliness and productivity

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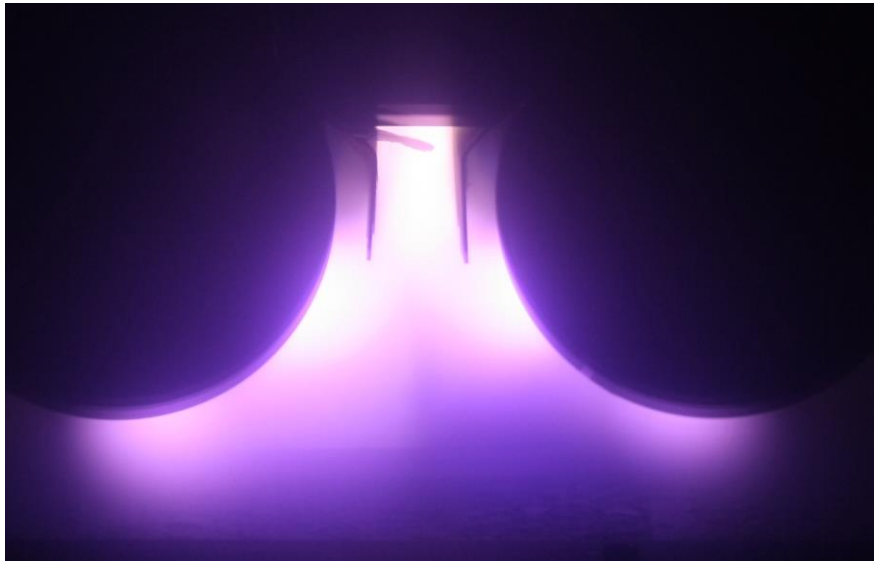
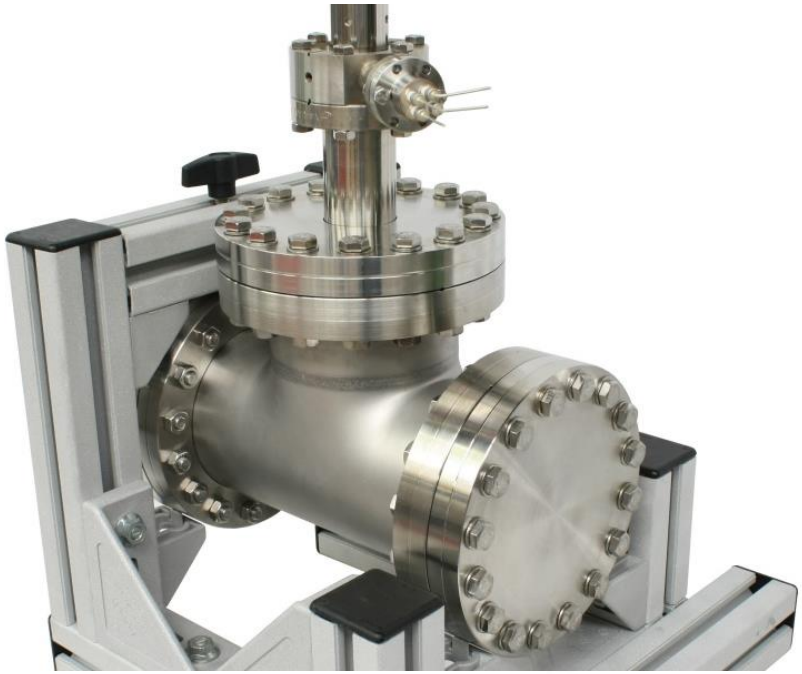


- A rotating target is self-cleaning so is an easier process to control compared to planar type targets
- Rotating targets offer higher rates and longer lifetimes
- CuGa, CuIn, CuInGa, In, Zn rotatable targets are readily available

- A fast feedback process for reactive sputtering of several layers in a CIGS cell has been shown
- CuInGa, Zn, In elements can be combined with both S and Se with a high degree of control and in varying combinations
- This technology makes the highly developed graded structures possible that will be required to improve cell efficiency
- The 2nd stage selenization / sulphurization can be removed
- A single stage purely sputtered cell is readily achievable with non-reactive and reactive sputtering



References attributed to Niki et al, Prog. Photovolt. Res. Appl. 2010 **18** 453-466

Thank you for listening and acknowledgments

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Victor Bellido-González
Dermot Monaghan
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Fernando Briones

Raquel Gonzalez,
Pedro Melgar

Ambiörn Wennberg
Ivan Fernandez

Employment opportunities exist at Gencoa for people with good scientific backgrounds or with plasma knowledge.