Direct mass analysis of water absorption onto ceria and urania thin films

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14th Apr, 2016
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Plutonium storage

- ~250 tonnes of separated Pu currently stockpiled worldwide.
- ~50% in long-term storage in UK whilst the Government develops its options
- Interim storage of PuO_2 involves sealing in inert steel containers.
- Under certain circumstances, these gas cans may pressurise; this must be avoided in practice.
- Need to understand how the structure and properties of PuO_2 change with time under storage conditions (e.g. in the presence of H_2O).

Plutonia interaction with water

- 5 routes to gas production have been suggested:

  (i) Helium accumulation from α decay
  (ii) Decomposition of polymeric packing material;
  (iii) H_2O desorption (steam) from hygroscopic PuO_2
  (iv) Radiolysis of adsorbed water
  (v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

- The last 3 processes all involve PuO_2/H_2O interactions and are complex, inter-connected & poorly understood.

- Haschke has suggested a reaction: $PuO_2 + H_2O \rightarrow PuO_{2+x} + H_2$
  This has been disputed on thermodynamic grounds.

- Experimental methods have been employed to determine extent of H_2O adsorption, typically through measurement of pressure changes and use of the ideal gas equation to indirectly determine water adsorption at the plutonium oxide surface.

Aims

Current models suggest water is initially absorbed onto metal oxides as a chemi-absorbed monolayer followed by multiple, physi-sorbed layers (with possible intermediate layers of differing binding energies).

- Study the interactions of plutonium oxide and analogues with water.
  - Ceria
  - Urania
  - Thoria
  - Plutonium oxide
- Use of quartz crystal microbalance methodology to experimentally determine:
  - The number of monolayers of water bound to the surface
  - The enthalpy of binding of the different layers.

Quartz crystal microbalance (QCM)

- The QCM measures in-situ mass changes at the surface of a piezoelectrode. Changes in mass, due to oxide formation or dissolution at the electrode surface or adsorption/desorption of gases, result in resonant frequency changes of the quartz crystal.
- Changes in frequency can be related to changes in mass through the Sauerbrey equation:

$$\Delta f = -\left(\frac{n {f_0}^2}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

- Knowing the surface area of the metal oxide layer and the mass of water absorbed allows the number of layers to be accurately calculated.
- The differences in temperature at which water absorption/desorption occurs allows the thermodynamics to be determined, indicating which layers are chemi- or physio-sorbed.

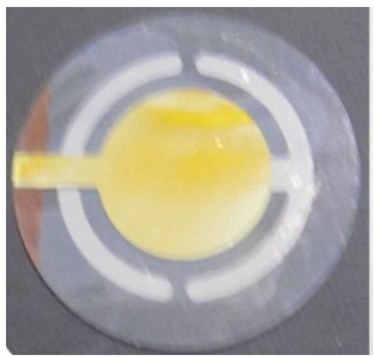
Ceria films on quartz crystals: SEM

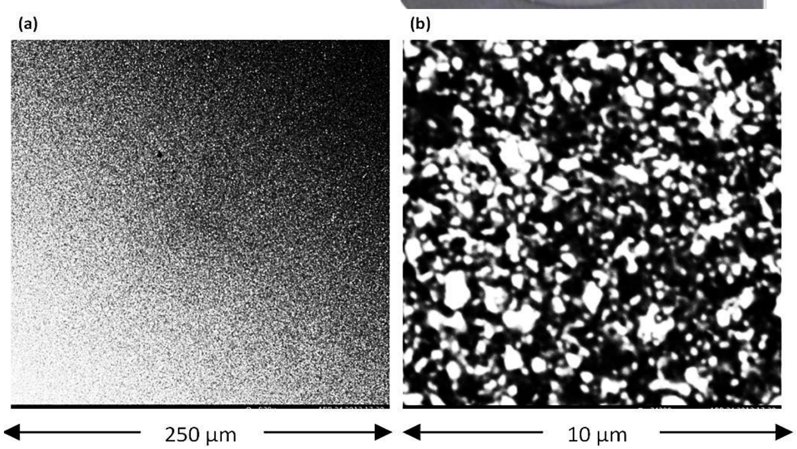
Thin films of ceria were coated onto QCM crystals *via* spin-coating of a cerium(III) nitrate precursor solution followed by calcination at 300^{o}C.

Layers of differing depth and porosity could be produced by altering the spin-coating duration and precursor / surfactant concentration.

A

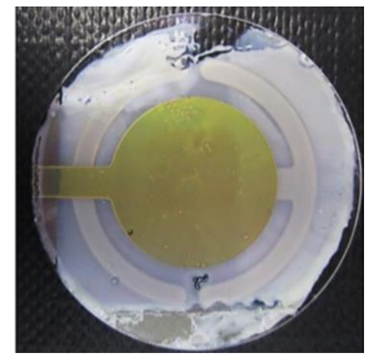
40 nm thick

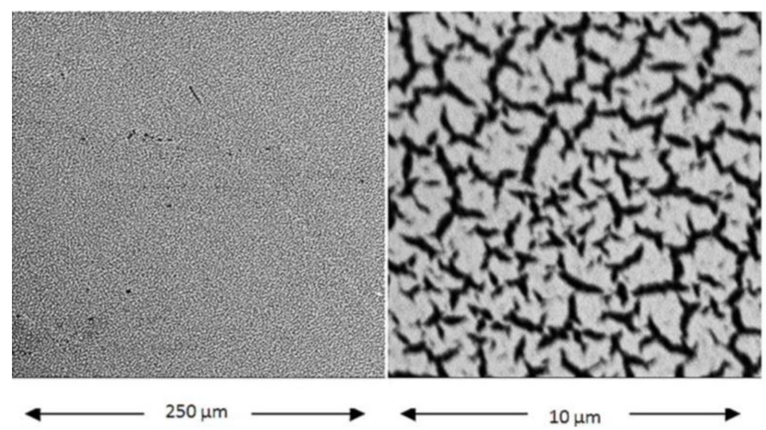




B

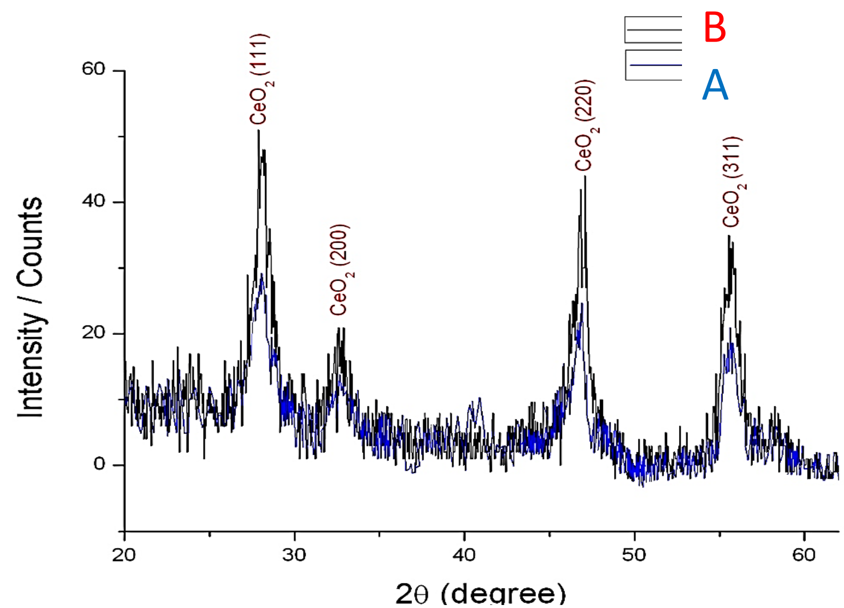
400 nm thick

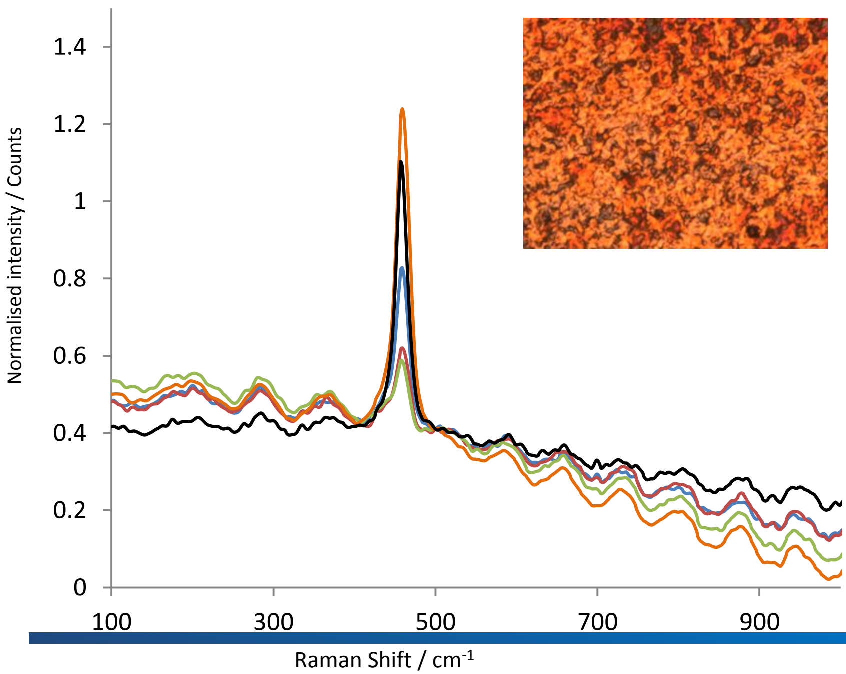


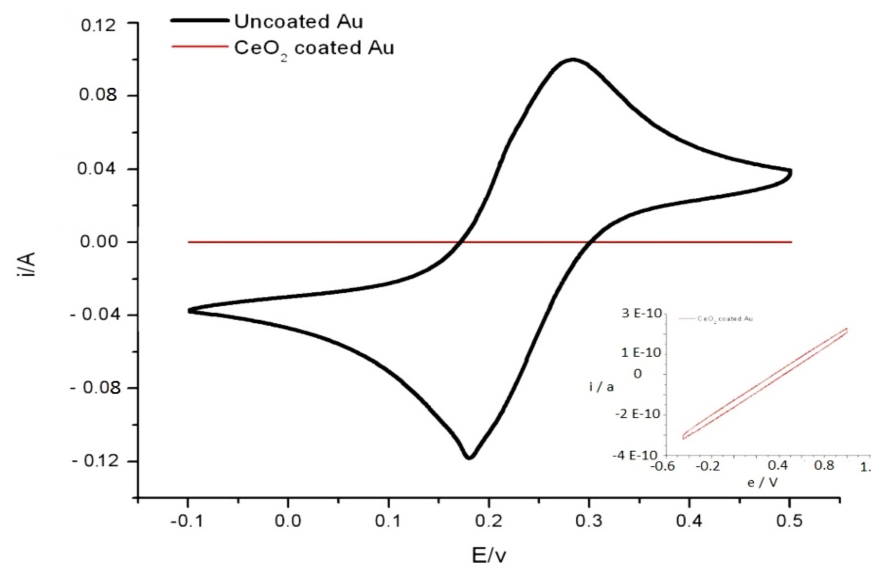


Ceria films on quartz crystals: XRD and Raman

The films were confirmed to be crystalline CeO_2 by XRD and Raman spectroscopy, which showed characteristic peaks.







Ceria films on quartz crystals: QCM and AFM

Application of the Sauerbrey to the change in frequency after coating allows the mass of ceria to be calculated:

$$\Delta f = -\left(\frac{n{f_0}^2}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

ρ_q = 3.570 g.cm^{-1} n = 1
μ_q = 2.147 x 10^{11} g.cm^{-1}s^{-2}
Coated area = 1.54 cm^2
Active area = 0.342 cm^2
d_{CeO_2} = 7.65 g.cm^{-3}

A

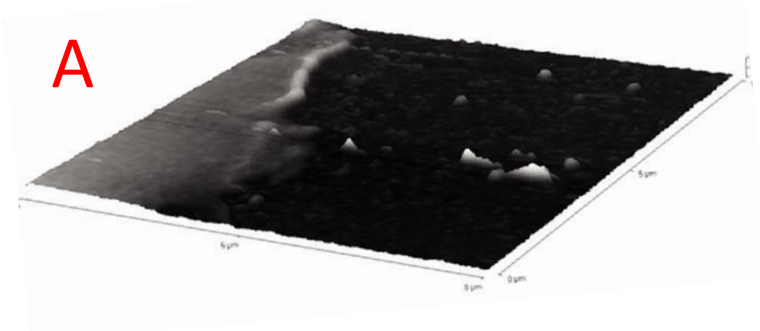
Δ F$_{25^oC}$ = –1180Hz
Δ m = 7.25 μg
h (QCM) = 28 nm

B

Δ F$_{25^oC}$ = –7130 Hz
Δ m = 43 μg
h (QCM) = 164 nm

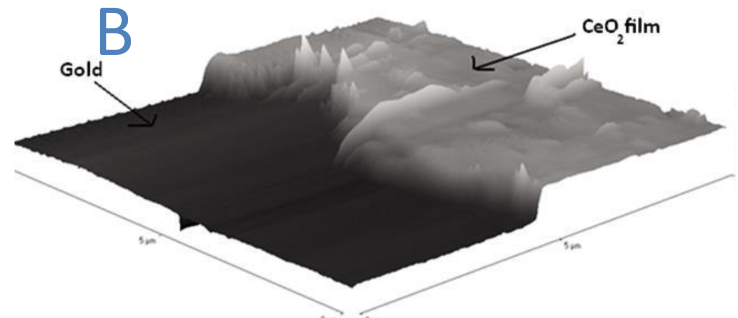
Atomic force microscopy was used to measure the film thickness experimentally:

A



h (AFM) = 40-45 nm
porosity = 30%

B



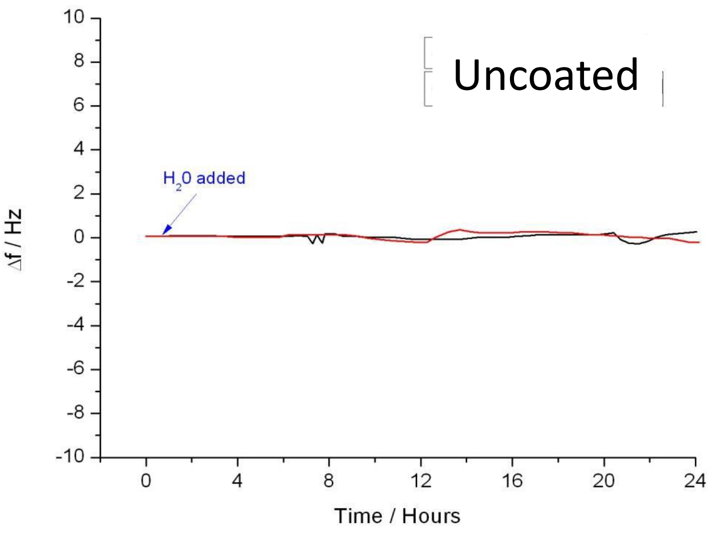
h (AFM) = 400-420nm
porosity = 60%

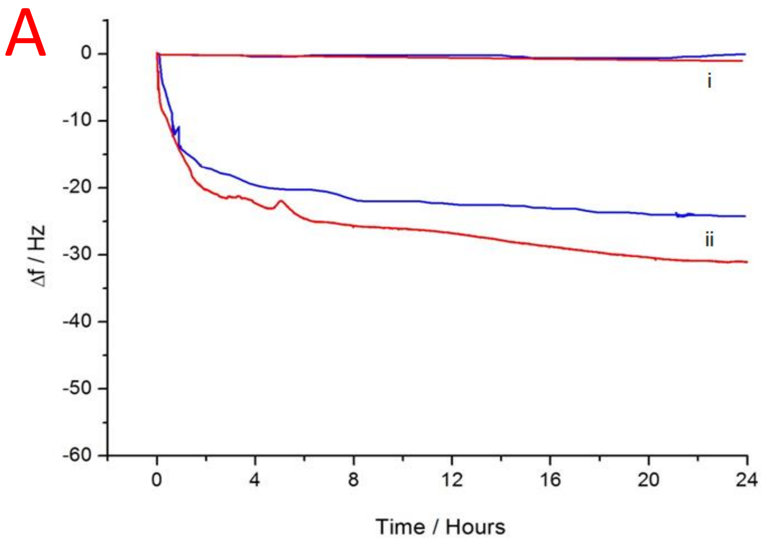
Water absorption: Pilot experiments

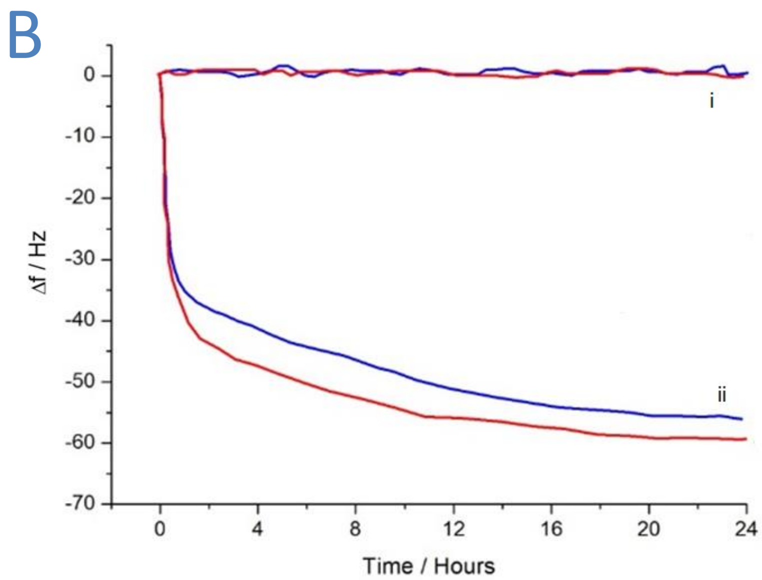
Frequency changes due water adsorption onto quartz crystals at 25°C, 100% humidity.

Uncoated crystals showed no appreciable water absorption.

Ceria coated crystals showed a reduction in frequency due to absorption of water.



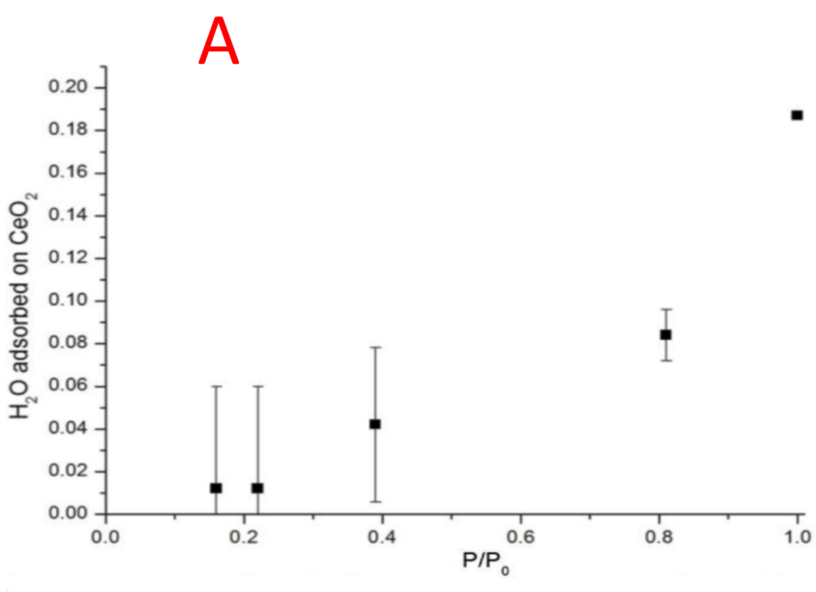


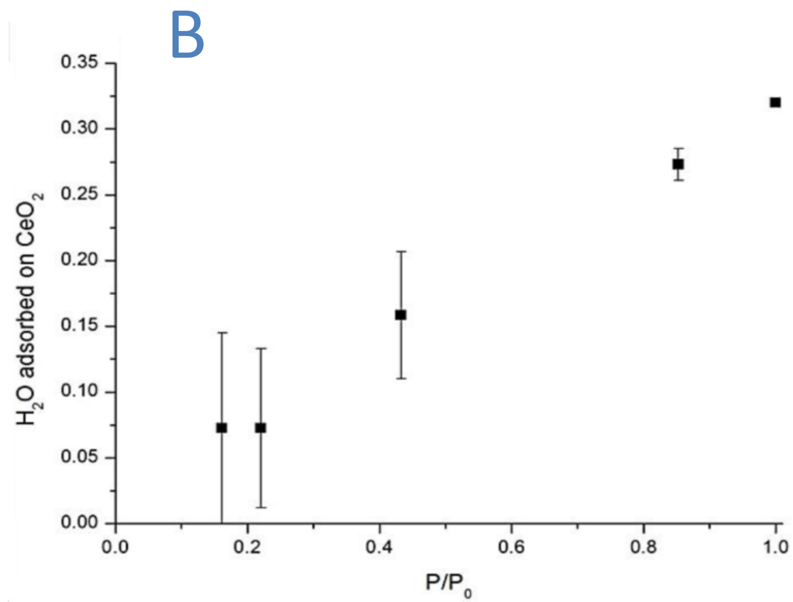


Water absorption: Humidity variation

The amount of water added to the system was varied, allowing the variation in water absorption as a function of water partial pressure / humidity to be determined.

As expected, more water was absorbed onto the ceria at higher partial pressures. At all humidities the more porous later was found to absorb more water.





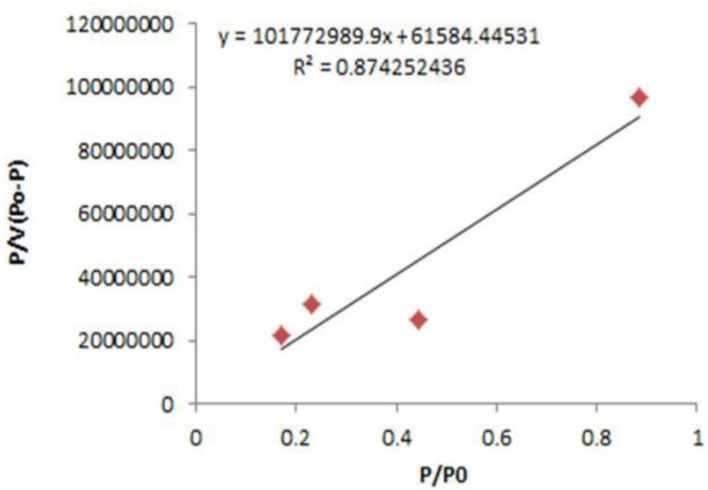
Water absorption: Surface area calculation

The BET equation can be used to calculate the enthalpy of absorption (ΔH_{ads}) and the volume of a monolayer of molecular water adsorbed onto a surface

$$1/\left[Va\left(\frac{P0}{P}-1\right)\right] = \left(\frac{C-1}{V_M C}\right)\left(\frac{P}{P_0}\right) + \frac{1}{VmC}$$

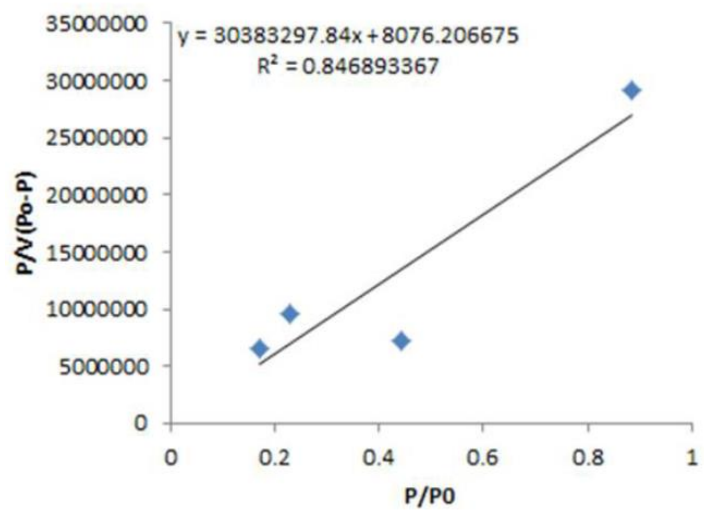
$C = \exp(\Delta H_{ads} - \Delta H_{liq}/RT)$
V_m = monolayer volume

A



ΔH_{ads} = 62 kJmol^{-1}
V_m = 9.8 X 10^{-9} cm^3
SA = 5.25 X 10^{-5} m^2
No. monolayers = 18

B

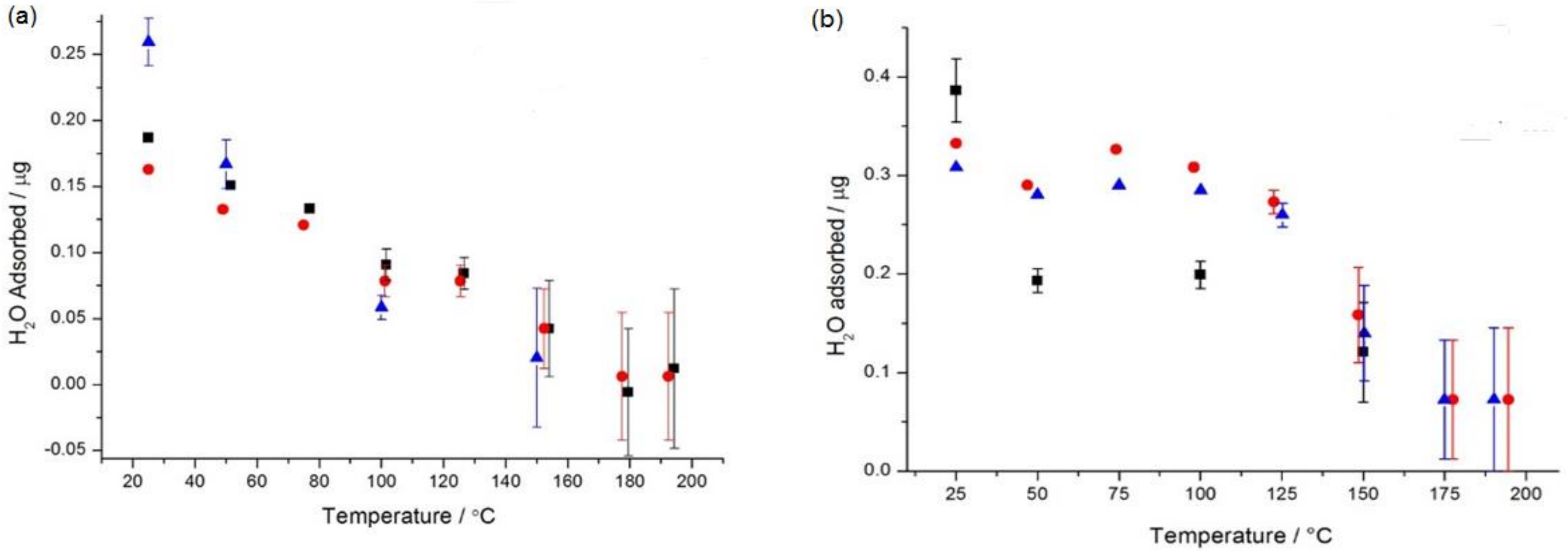


ΔH_{ads} = 64 kJmol^{-1}
V_m = 33 X 10^{-9} cm^3
SA = 17.6 X 10^{-5} m^2
No. monolayers = 10

Water absorption: Temperature variation

The temperature of the system was increased, while maintaining a fixed amount of added water.

As the temperature increased, the amount of water absorbed onto the surface decreased.

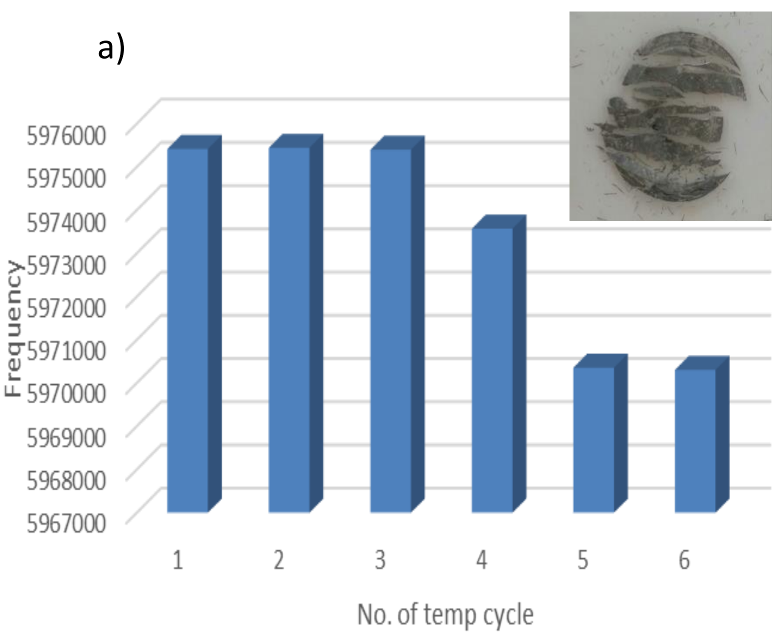


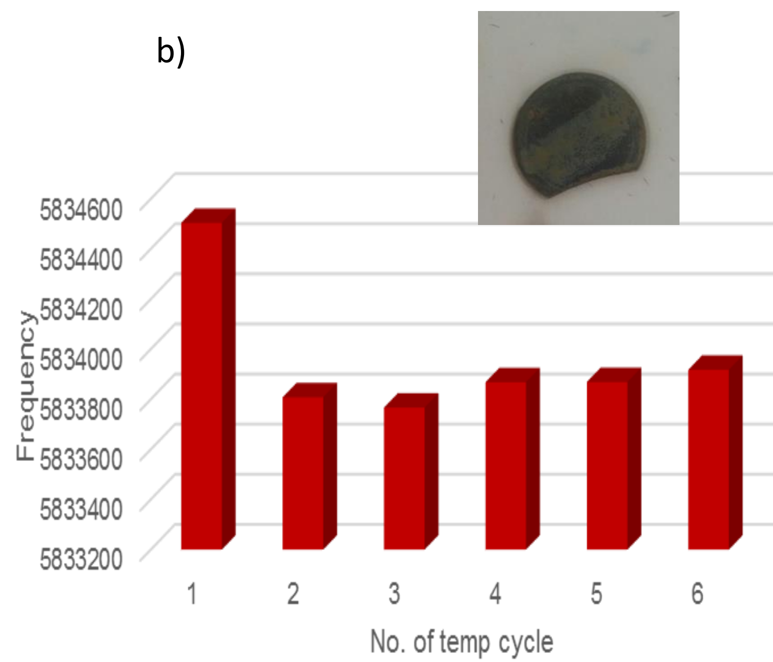
The maximum operating temperatures was approximately 200°C. At this temperature, a significant amount of water of water was still absorbed onto the ceria surface. For the 400 nm thick ceria layer, this equates to ~90 ng, the equivalent of ~3 monolayers of water.

$GaPO_4$

$GaPO_4$ crystals have a higher piezoelectric limiting temperature, allowing for higher calcination temperatures of metal oxide coatings (up to ~900ºC), reducing porosity.

Redesign of system to use metal sensor head in place of teflon.

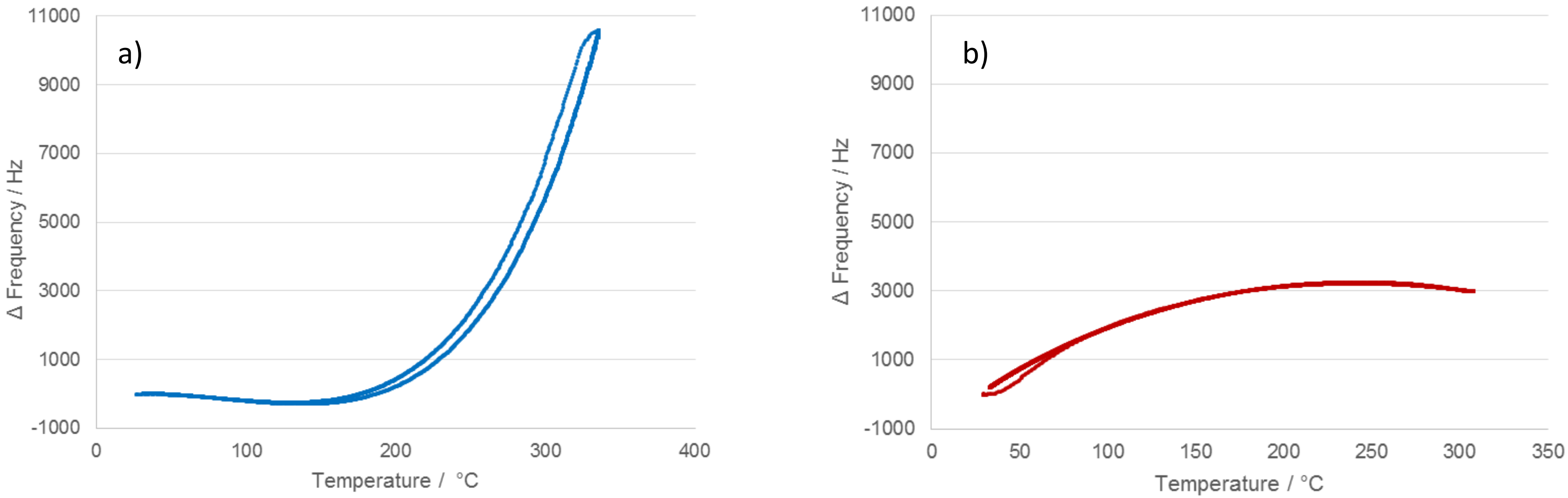




Frequency of uncoated a) Quartz and b) Galium phosphate crystals at room temperature after repeated temperaturecycling to 550ºC. Inset: photographs of crystals after heating to 950°C.

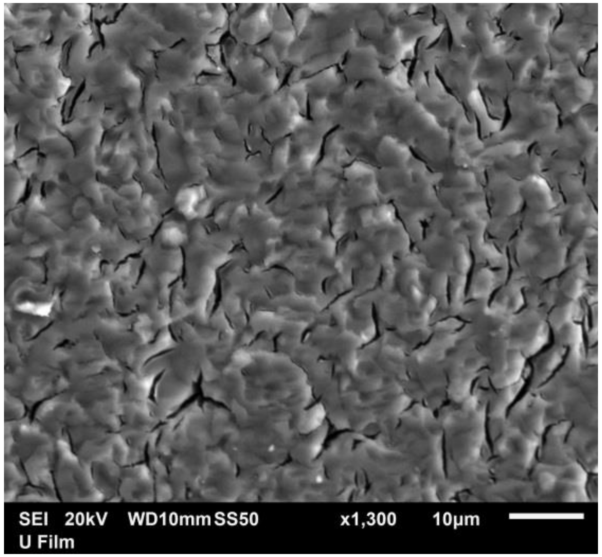
$GaPO_4$ crystals

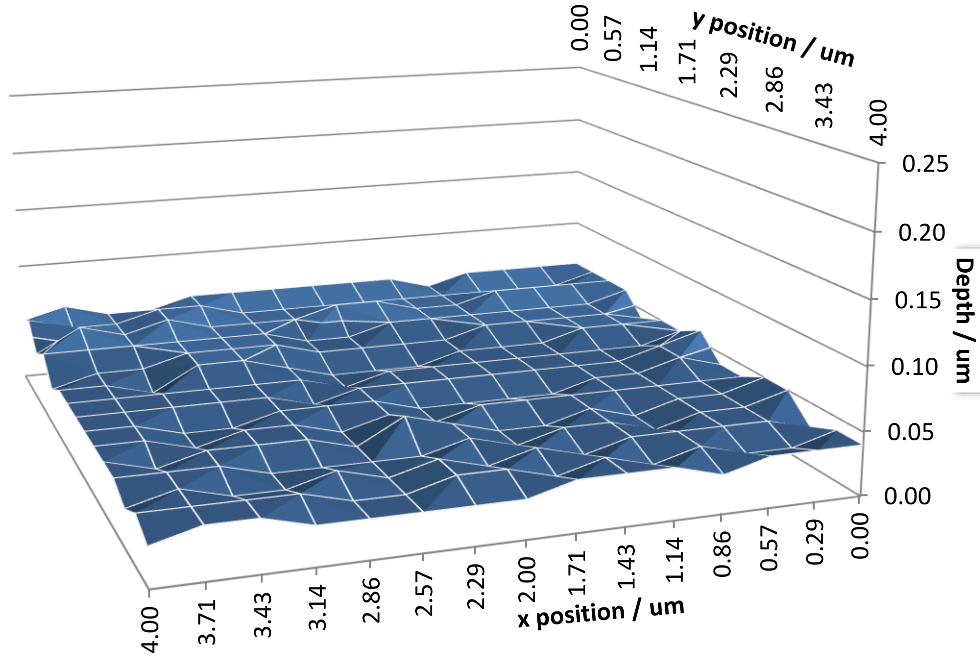
Use of $GaPO_4$ crystals, which have a linear temperature-frequency dependence, making higher temperature measurements much more accurate.



Temperature dependence of uncoated a) Quartz and b) Galium phosphate crystals, between 30 and 300°C, using high temperature QCM probe.

Urania films on $GaPO_4$ crystals: SEM and XRF





$\Delta\ F_{25ºC} = -2352$ Hz

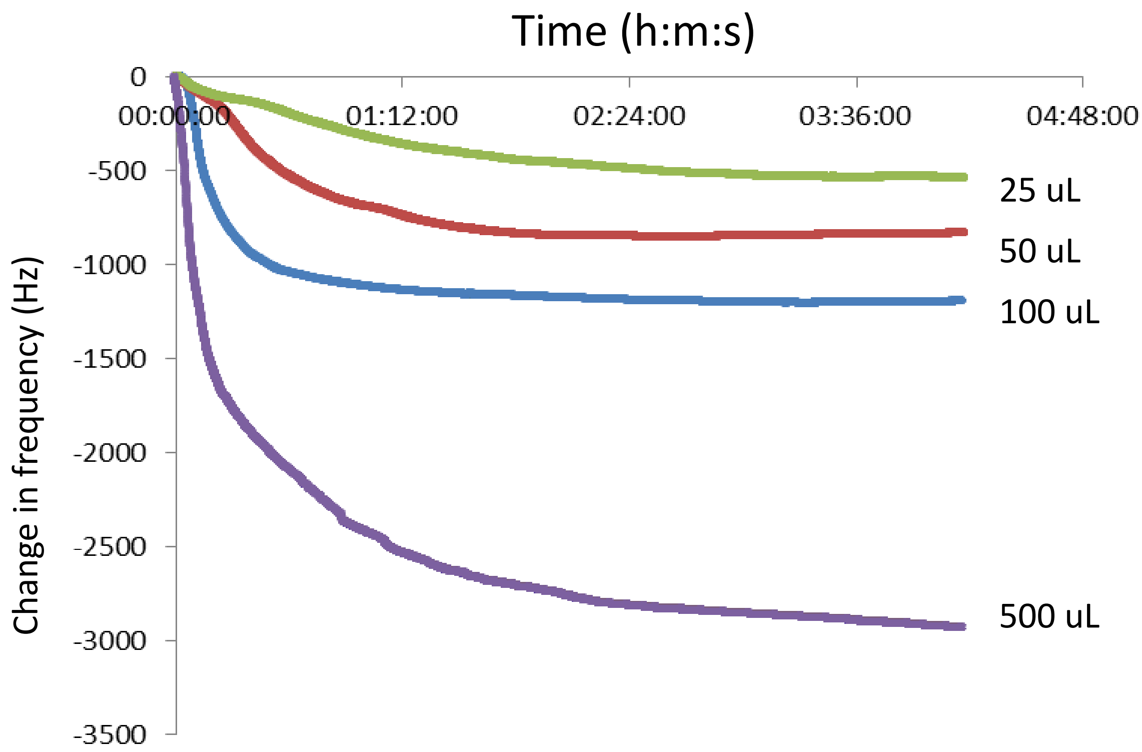
$\Delta\ m = 18\ \mu g$

h (QCM) = 27 nm

XRF map in a 15 x 15 grid (225 points) gives an average urania thickness of 42 nm (SD = 9 nm).

This gives a volume of $2.52 \times 10^{-6}\ cm^3$ and therefore a porosity of 35%.

Urania films on $GaPO_4$ crystals: RT water absorption



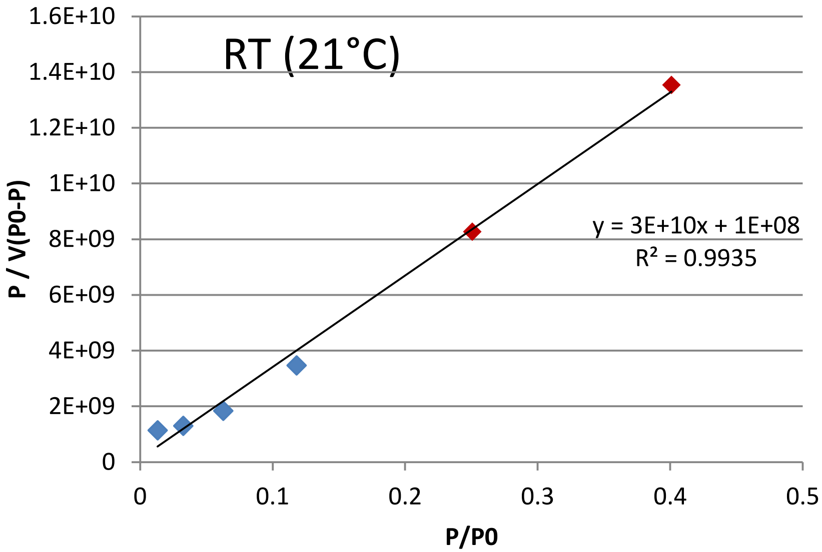
Different amounts of water were added to the pre-dried system at RT and equilibrated for 4 hours.

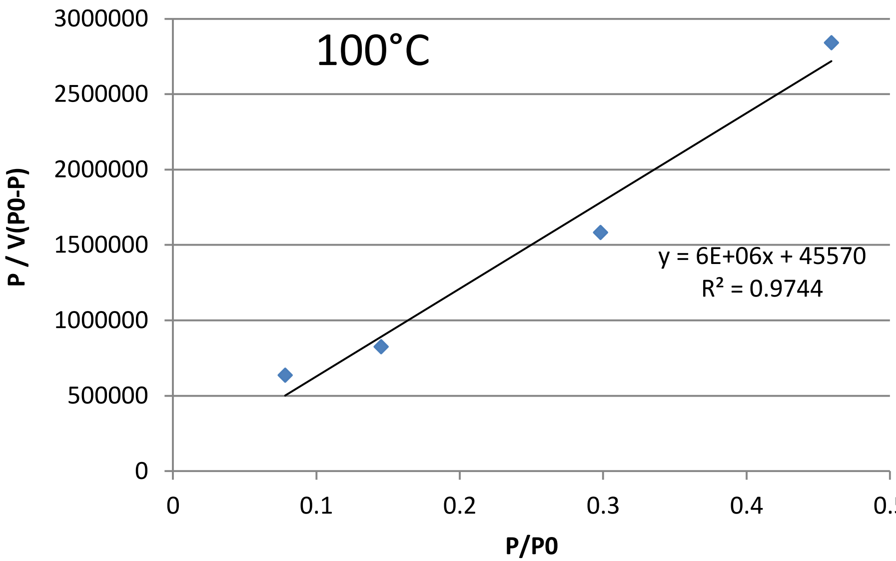
The change in frequency is proportional to the mass of water absorbed onto the urania, and increased as the amount of water increased.

Urania films on $GaPO_4$ crystals: BET

The BET equation allows the volume of a monolayer and the enthalpy of absorption to be calculated:

$$1/\left[Va\left(\frac{P0}{P}-1\right)\right] = \left(\frac{C-1}{V_M C}\right)\left(\frac{P}{P_0}\right) + \frac{1}{VmC} \qquad C = e^{(\Delta H_{ads} - \Delta H_{liq}/RT)}.$$





A plot of $P/V(P_0\text{-}P)$ against P/P_0 gives an intercept of 1/VmC and a gradient of $(C-1)/(V_M C)$, therefore we can calculate:

V_m =	1.26 / 0.98 x 10^{-11} m^3	1.68 x 10^{-11} m^3
ΔH_{abs} =	48.0 / 50.0 $kJmol^{-1}$	49.6 $kJmol^{-1}$

No. monolayers at :

100% rel. humidity:	13	25
100 abs. humidity:	13	11

Conclusions

- Coated quartz piezocrystals with ceria and urania layers of different porosities. Analysed the morphology and thickness by SEM, AFM, XRF.
- Measured the absorption of water onto the ceria and urania films by direct mass analysis at different humidities.
- Calculated the surface area of the ceria and urania films, and the volume and number of absorbed monolayers at room temperature.
- Varied the temperature of the ceria-water systems, showing the desorprtion of water up to 200°C.
- Synthesis of thoria-coated $GaPO_4$ crystals.
- Increase the temperature of the systems, showing the desorprtion of water up to 500°C.

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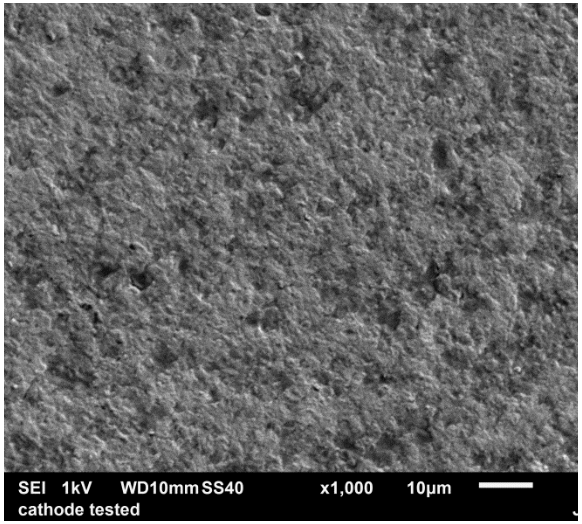
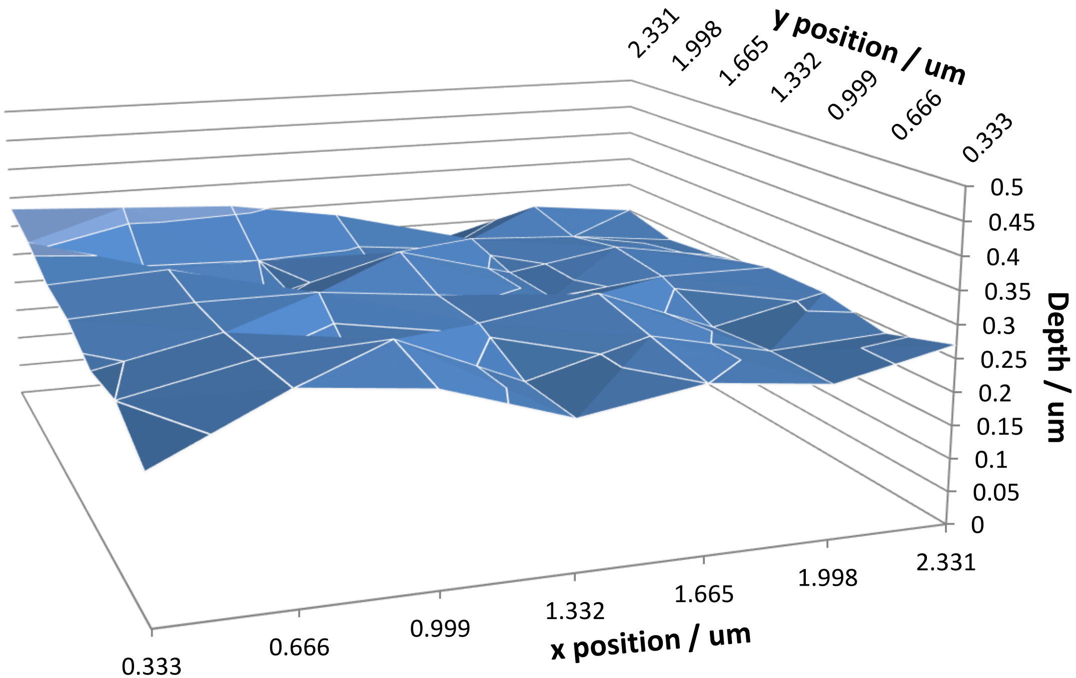
Thanks for your attention

Ceria films on $GaPO_4$ crystals: SEM and XRF





$\Delta\ F_{25ºC} = -7450$ Hz

Δ m = 33 µg

h (QCM) = 71 nm

XRF map in a 7 x 7 grid (49 points) gives a average ceria thickness of 261 nm (SE = 29 nm).

This gives a piezoactive volume of 8.9 x 10^{-6} cm^3 and therefore a porosity of 54%.

Ceria films on high temperature crystals: QCM

Uncoated crystal $F_{21ºC}$ = 5833918 Hz

Coated crystal $F_{25ºC}$ = 5826468 Hz

$$\Delta f = -\left(\frac{n{f_0}^2}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

$\Delta F_{25ºC} = -7450$ Hz

$\Delta m = 42\ \mu g$

$\rho_q = 3.570\ g.cm^{-1}$ n = 1

$\mu_q = 2.147 \times 10^{11}\ g.cm^{-1}s^{-2}$

Coated area = 1.33 cm^2

Active area = 0.46 cm^2

$d_{CeO_2} = 7.65\ g.cm^{-3}$

$nF_0^2 = 3.409 x 10^{13\ Hz2}$

$(Pgxug^{0.5}) = 8.755 \times 10^{5\ gcm-1s-1}$

$Cf = 3.89 \times 10^7$

vol = 5.5 x 10^{-6} cm^3

Thickness = 125 nm

A_{Pu239} = 210 KBq

A_{Pu240} = 768 KBq

(A_{Pu241} = 350 MBq)

$$A = N_A \frac{M}{m_r} \cdot \frac{\ln(2)}{t_{1/2}}$$

$A_{Pu239\text{-}240(70:30)}$ = 377 MBq

$N_A = 6.022 \times 10^{23}\ mol^{-1}$

Pu^{239} $t_{1/2}$ = 24100 yrs = 760 x 10^9 s

Pu^{240} $t_{1/2}$ = 6560 yrs = 207 x 10^9 s

Pu^{241} $t_{1/2}$ = 14.4 yrs = 0.454 x 10^9 s