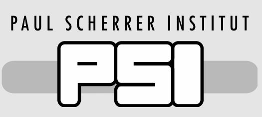


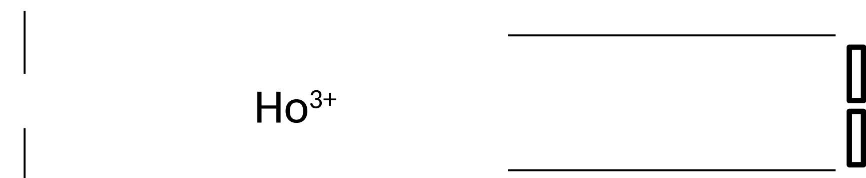
Noemi Cerboni :: PhD :: Paul Scherrer Institut

Preparation and Characterization of Holmium Sources for the HOLMES Experiment

Seminar, 12.05.2022

Motivation

Goal: prepare sources for the measurement of the electron neutrino mass from the electron capture decay of ^{163}Ho



Ideal source

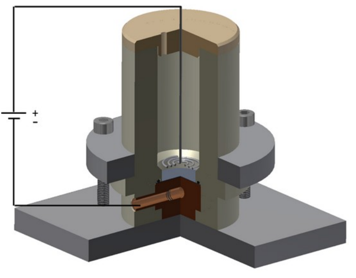
1. Chemically pure
2. Homogeneous distribution of Ho ▭ slow and constant Ho release
3. Obtained with high yield

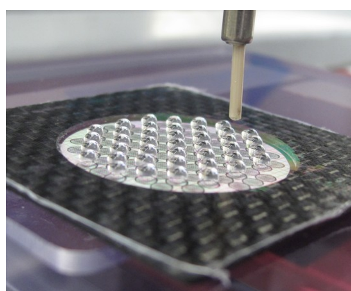
Outline

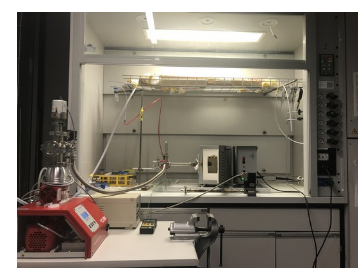
Molecular Plating (MP)

Drop-on-Demand Inkjet Printing (DoD)

Coupled Reduction (CR)







Molecular Plating

Molecular Plating (MP): deposition of Ho complexes in an organic solvent at high voltages

+
Ho^{3+}
Ho^{3+}
Ho^{3+}
–
MP
bath
$Ho(OH)_3$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$3OH^- + Ho^{3+} \rightarrow Ho(OH)_3 \downarrow$$

Investigation of influence of solvent’s vapor pressure on morphology

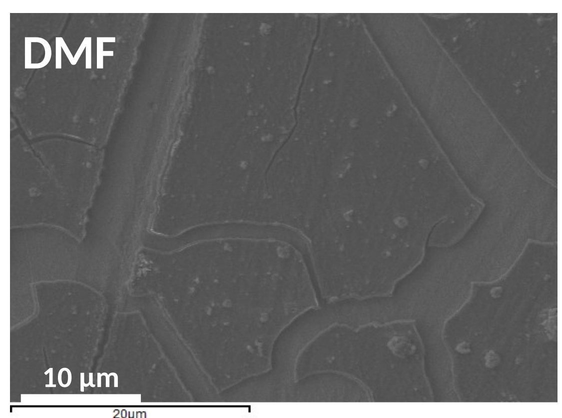
Effect of Solvents on the Yields

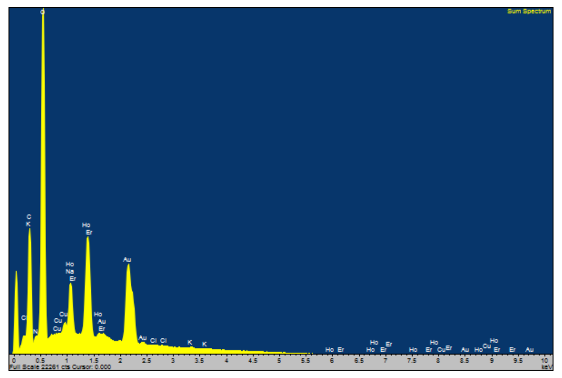
Measured by γ-spectroscopy with ^{166m}Ho as radiotracer

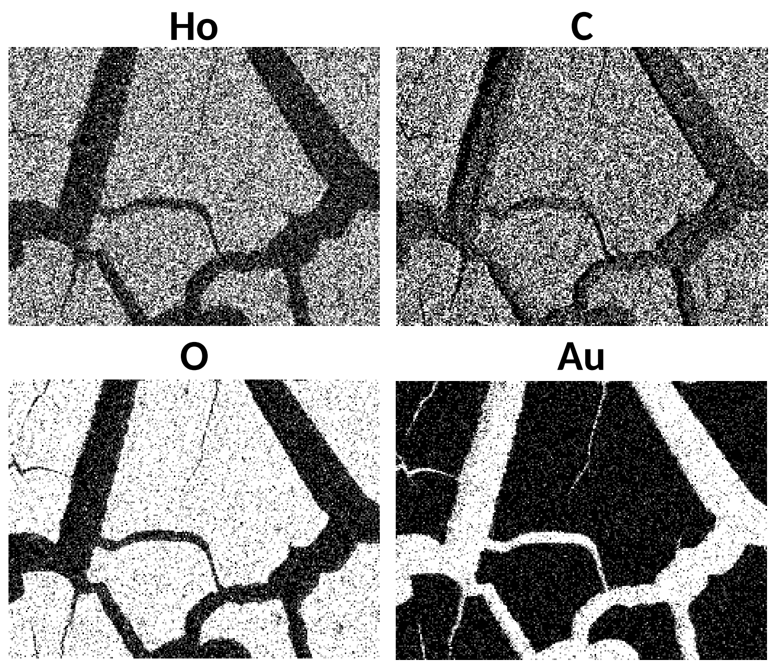
solvent	MP yield (%)	Bath losses (%)
Acetone	79	0
Isobutanol	98.1	0
Isopropanol	99.9	14.8
DMF	99.4	1.8
DMAc	96.5	0

Very high yields and good adherence to backing

Elemental Mapping *via* EDX







- Most likely deposition of $Ho(OH)_3$ and co-deposition of org. compounds
- Similar chemical composition for all solvents

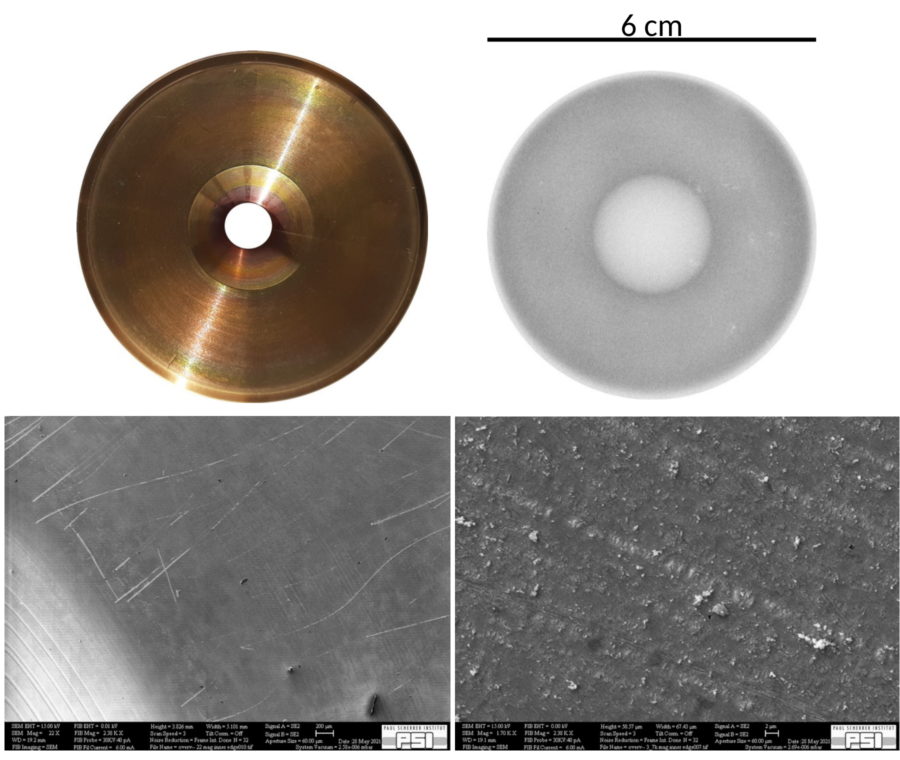
Influence of Solvent on the Microstructure

30.80 kPa	5.78 kPa	1.53 kPa	0.44 kPa	0.17 kPa
Acetone	Isopropanol	Isobutanol	DMF	DMAc

The lower the vapour pressure the more stable the deposition (less cracks, less flaking)

Large Cathode - Results

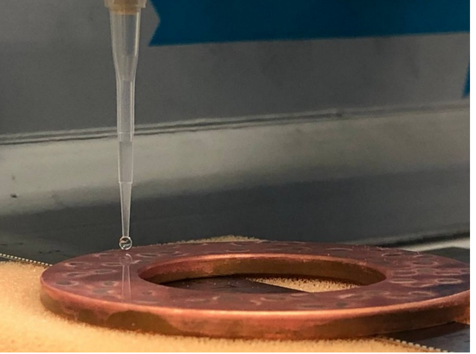
- Very high yields (> 99%)
- Homogeneous deposition
- Good microstructure (similar to small samples)
- no relevant current detected at 165 u but at 182 u in mass separator might correspond to $HoOH^+$
- Very low current sputtering of thin film at the same time



Drop-on-Demand Inkjet Printing

3D positioning system (automatic movement)

Dosage device (droplet deposition)



Deposition of droplets with identical volume (3-7 µL)

Investigate different sources produced starting from different Ho salts

SEM Imaging of Different Ho Salts on Au

5 mm

$Ho(NO_3)_3$ on Au

$HoCl_3$ on Au

$Ho(OAc)_3$ on Au

1 mm

- Different drying mechanism for $Ho(NO_3)_3$ and $HoCl_3$ versus $Ho(OAc)_3$
- In our case, more uniform deposition (and hence higher surface density) with $Ho(OAc)_3$

Elemental Mapping *via* EDX

$Ho(NO_3)_3$ on Au

$HoCl_3$ on Au

Au

Ho

O

N

20 µm

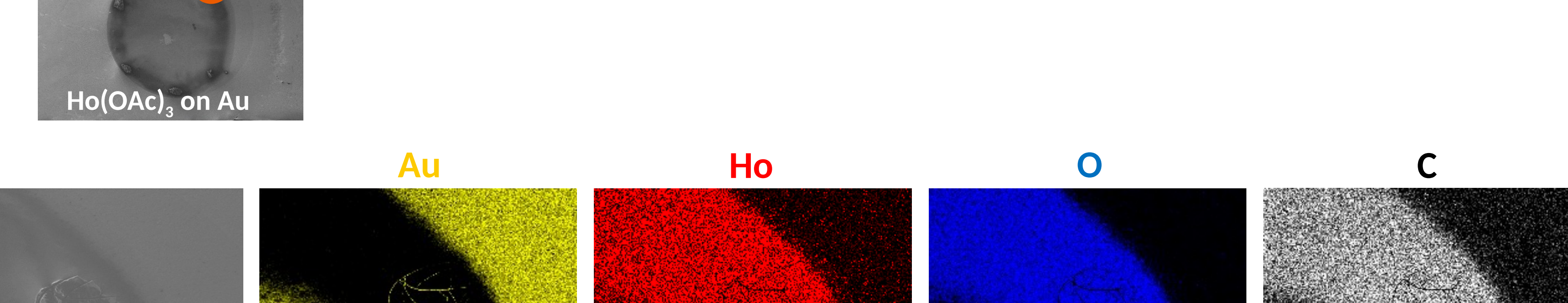
Au

Ho

O

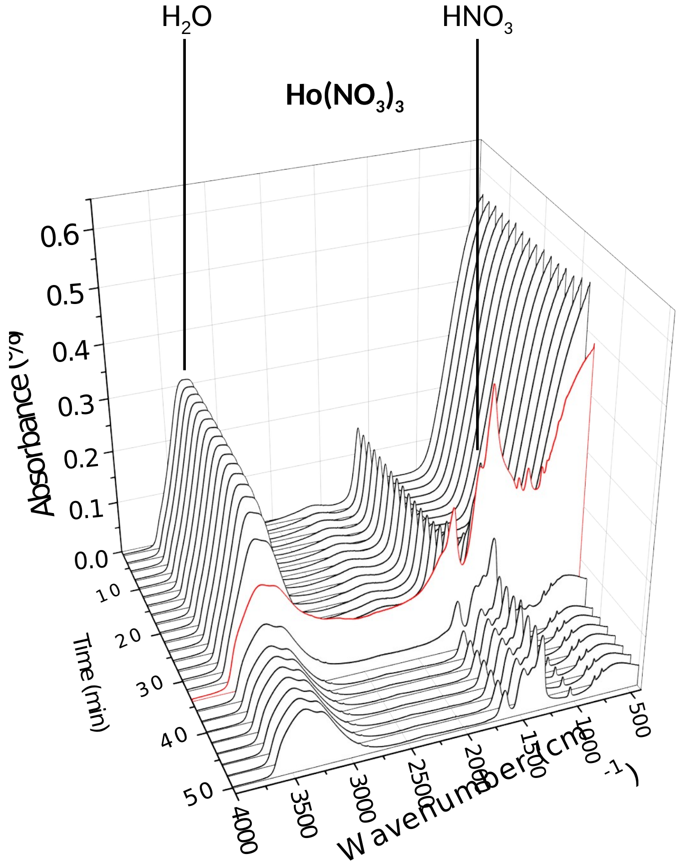
Cl

Elemental Mapping *via* EDX



Indicate elemental composition of dried substances does not change upon drying (with unknown ratio)

Time-Resolved Infrared Spectroscopy



- *In-situ* monitor drying mechanism: start from IR spectrum of H_2O and finish with spectrum of dried product
- Here: scan every 2 min for 1h

Characterization: Infrared Spectroscopy

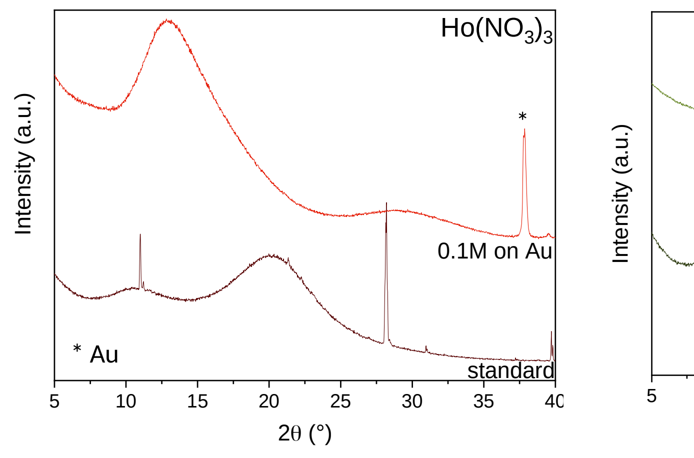
Dried droplet

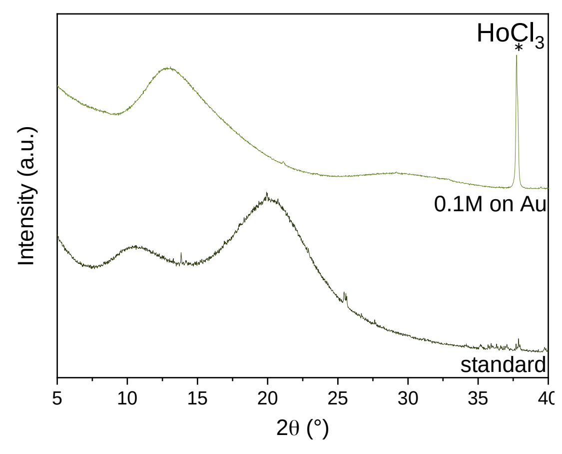
Reference

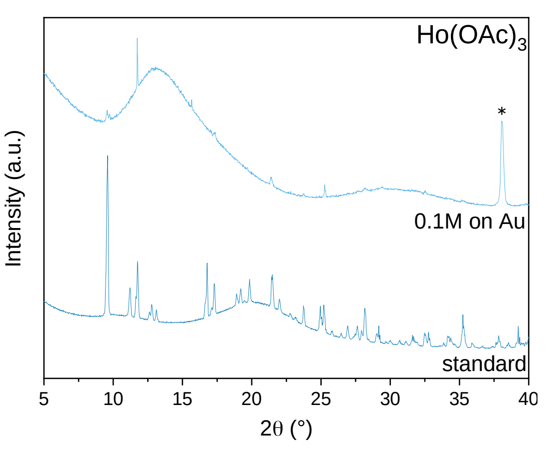
$Ho(NO_3)_3$	$HoCl_3$	$Ho(OAc)_3$

- Likely change in coordination geometry visible from change in peak intensity
- Still, dried product correspond to dissolved Ho salt

Characterization: X-Ray Diffraction





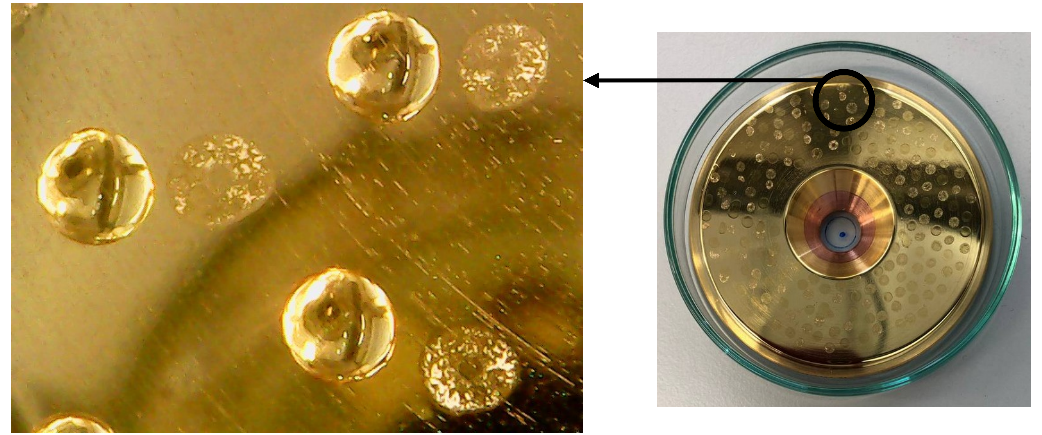


- No reflection signals in drops on substrate
  - Either deposit an amorphous material
  - or impossible detection of the actual drop

- Preferentially orientated crystallisation

- Other studies with high-intensity synchrotron radiation required (under evaluation)

Large Cathode - Results



190 droplets of 3.5 µL each

Weak peak detected at 165 u but it significantly decreases over time ▭ too fast sputtering

Coupled Reduction

Coupled Reduction (CR): Ho reduction and diffusion into backing material due to thermodynamically favourable formation of intermetallic compound

M = Pd, Pt

Ho^{3+}

MP

$Ho(OH)_3$

H_2

CR

Ho_xPd_y or Ho_xPt_y

Study two different backing materials and different Ho concentrations

Yield of Molecular Plating

Pt	Pd				
0.25 wt%	0.25 wt%	0.5 wt%	1.25 wt%	2.5 wt%	5 wt%
99.4 %	99.6 %	99.2 %	99.2 %	92.8 %	84.9 %

- Uniform surface distribution
  - 5 wt% Ho on Pd → deposited layer too thick to be stable

- Increase of thickness of deposited layer visible from color

Ho-Pt before and after CR

Before CR

After CR

- Similar morphology as before CR → no Ho diffusion
- After CR: very small O peak → Ho reduction

Ho-Pd before and after CR

Before CR

After CR

- Grain boundaries of Pd visible → Ho diffusion
- After CR: no Ho and O peak → successfull Ho reduction and diffusion

Preparation of Ho/Pd intermetallic → to be measured

Conclusion

- MP
  - Very high yields
  - Deposition of Ho complexes → fast sputtering of $HoOH^{+}$
- DoD:
  - Very high yields
  - Deposition of one Ho complex with labile bonds → fast sputtering of Ho^{x+}
- CR:
  - High yields
  - Formation of Ho^{0} into the bulk of the backing material → constant sputtering of Ho

Wir schaffen Wissen – heute für morgen

My thanks go to

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- Georg
- Dominik
- …