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MAGNETRON SPUTTERED YHO THIN FILM OXYDATION DYNAMICS AND OPTICAL PROPERTIES

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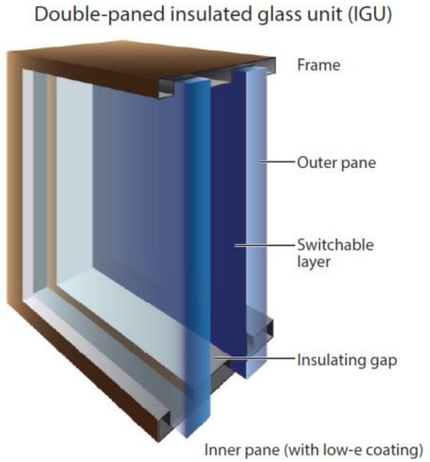
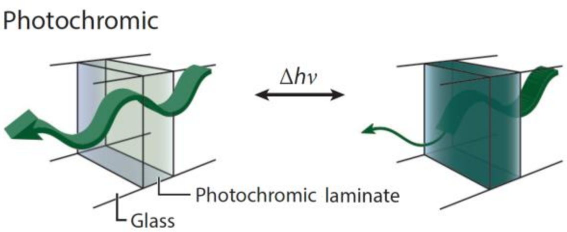
OUTLINE

- Motivation
- Introduction in rare-earth oxyhydrides
- Experimental details
- Results:
  - *In-situ* transmittance measurements
  - X-ray diffraction
  - Electron microscope images
  - Spectroscopic ellipsometry
  - X-ray photoelectron spectroscopy (depth profiling)
- Conclusions

MOTIVATION

- Yttrium and other rare-earth (RE) metal oxy-hydrides (YHO, REHO) are a new class of inorganic **mixed-anion materials** [1]
- They exhibit a **photochromic effect and a light-induced resistivity change** at room temperature and ambient pressure [2]
- Photochromic YHO thin films can be prepared by the simply exposing reactively ($Ar+H_2$) sputtered metallic β-YH_2 films to air [3]. **However, it has not been directly measured when the oxidation mostly occurs – after or during (due to residual oxygen) the deposition of YH_2 films?**
- The aim of this presentation to show the oxidation dynamics of yttrium hydride films during and after deposition process, as well as optical properties.
- Latvian Council of Science FLPP project: **Thin films of rare-earth oxy-hydrides for photochromic applications**





[1] *Nature communications 9.1* (2018) 1-15
[2] *Applied Physics Letters 111* (2017) 103903.
[3] *Sol. Energy Mater. Sol. Cells* 177 (2018) 106

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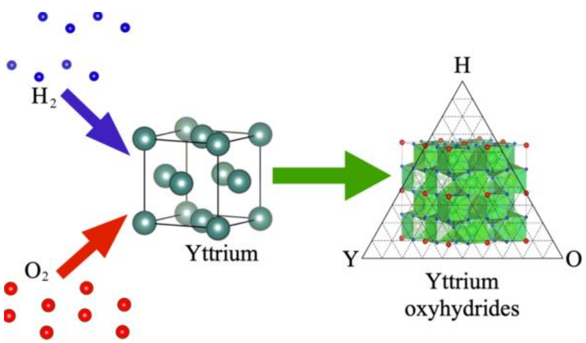
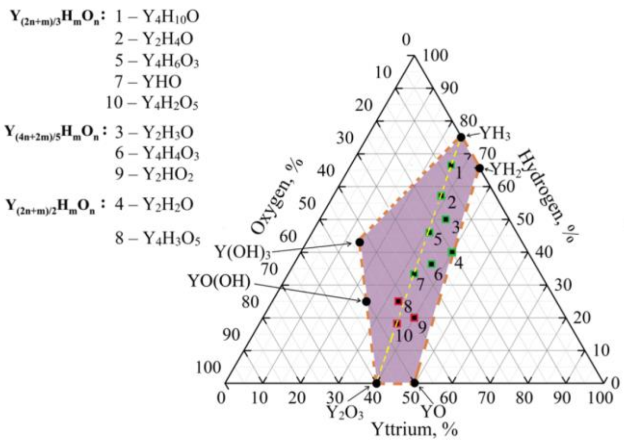
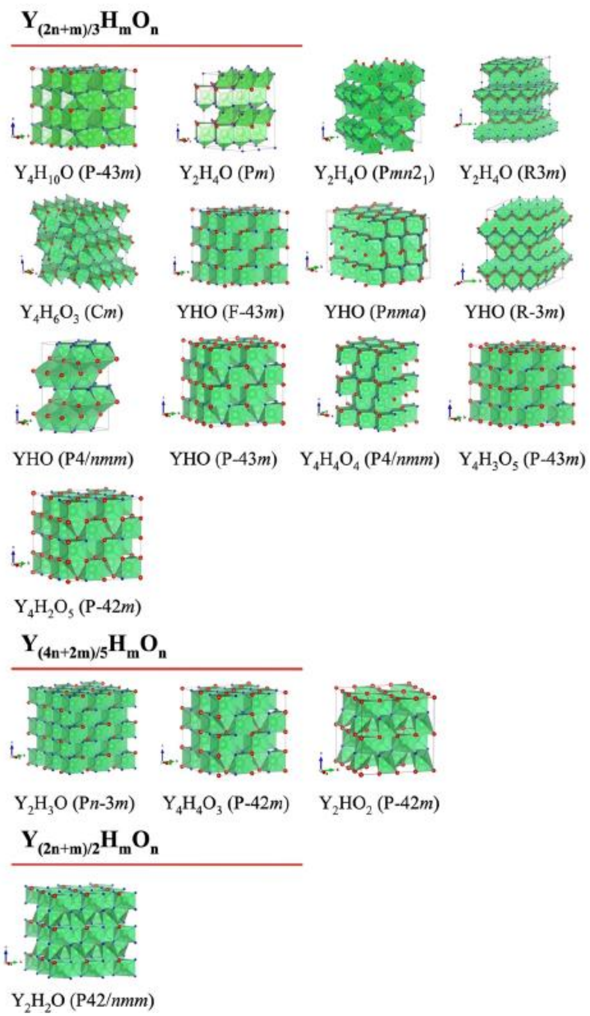
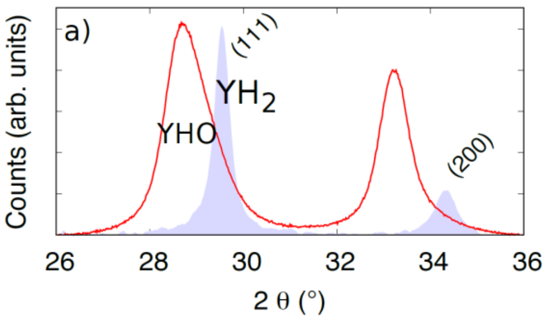
YTTRIUM OXYHYDRIDE

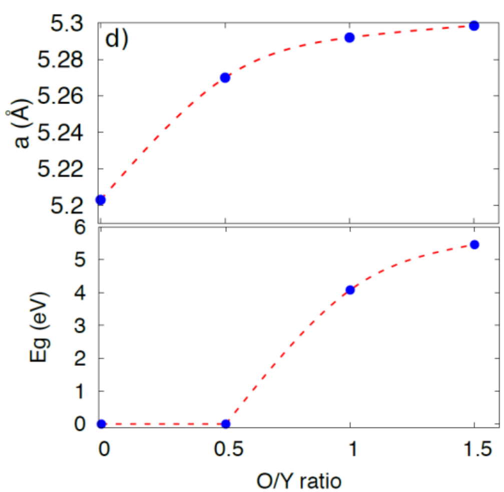






YH_2 fcc Fm-3m



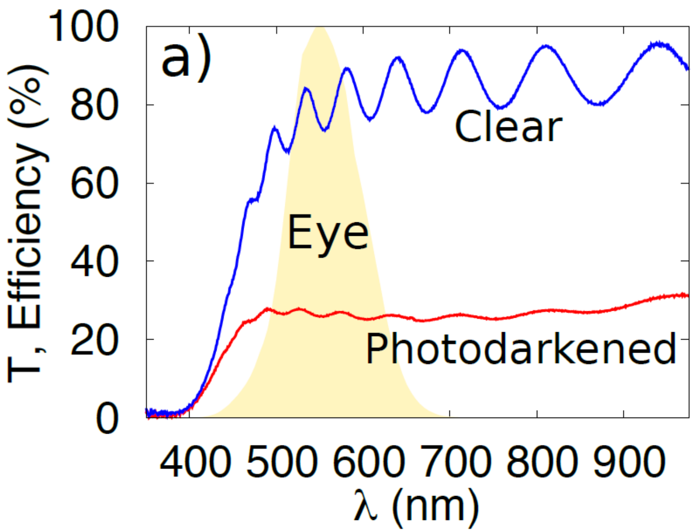


Cryst. Growth Des. 2019, 19, 2574−2582

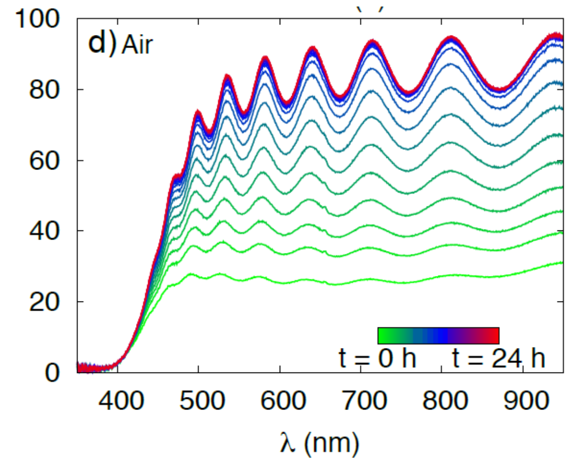
Physical Review Materials 4.2 (2020): 025201.

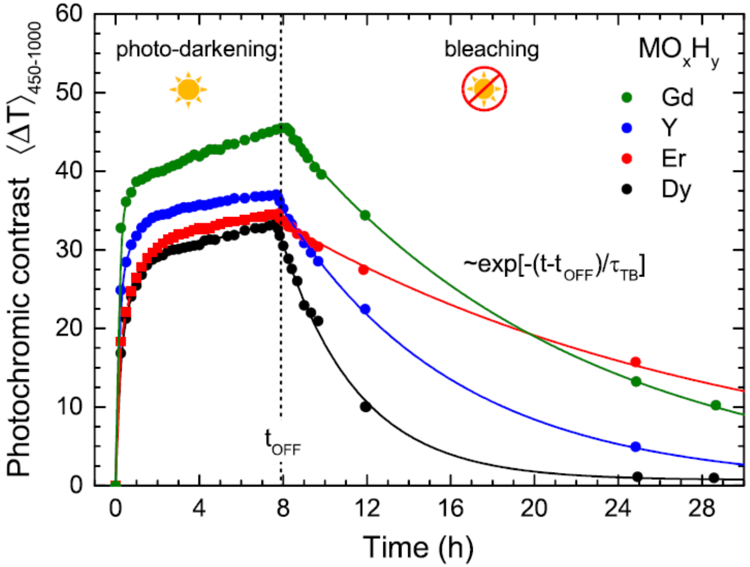
PHOTOCHROMIC EFFECT

UV-Blue light irradiation



***Physical Review Materials*, *4*(2), 025201 (2020)**





***Appl. Phys. Lett.* 111, 103903 (2017)**

EXPERIMENTAL DETAILS – YHO DEPOSITION

Vacuum coater Sidrabe G500M

Sputtering conditions:

- rectangular magnetron: balanced;
- target:
  - Y (99.95 purity);
  - dimensions 150 mm × 75 mm × 2 mm thick.
- working pressure **3 - 20 mTorr (changed by a throttle valve):**
  - Ar flow 30 sccm;
  - H_2 flow 16 sccm.
- constant average power regime (200 W);
- pulsed-DC power supply **P-DC-EP05 EnerPulse 5 kW:**
  - **frequency - 80 kHz;**
  - **Off time - 2.5 μs;**
- spectrometer: CMOS detector, StarLine AvaSpec-ULS2048CL-EVO

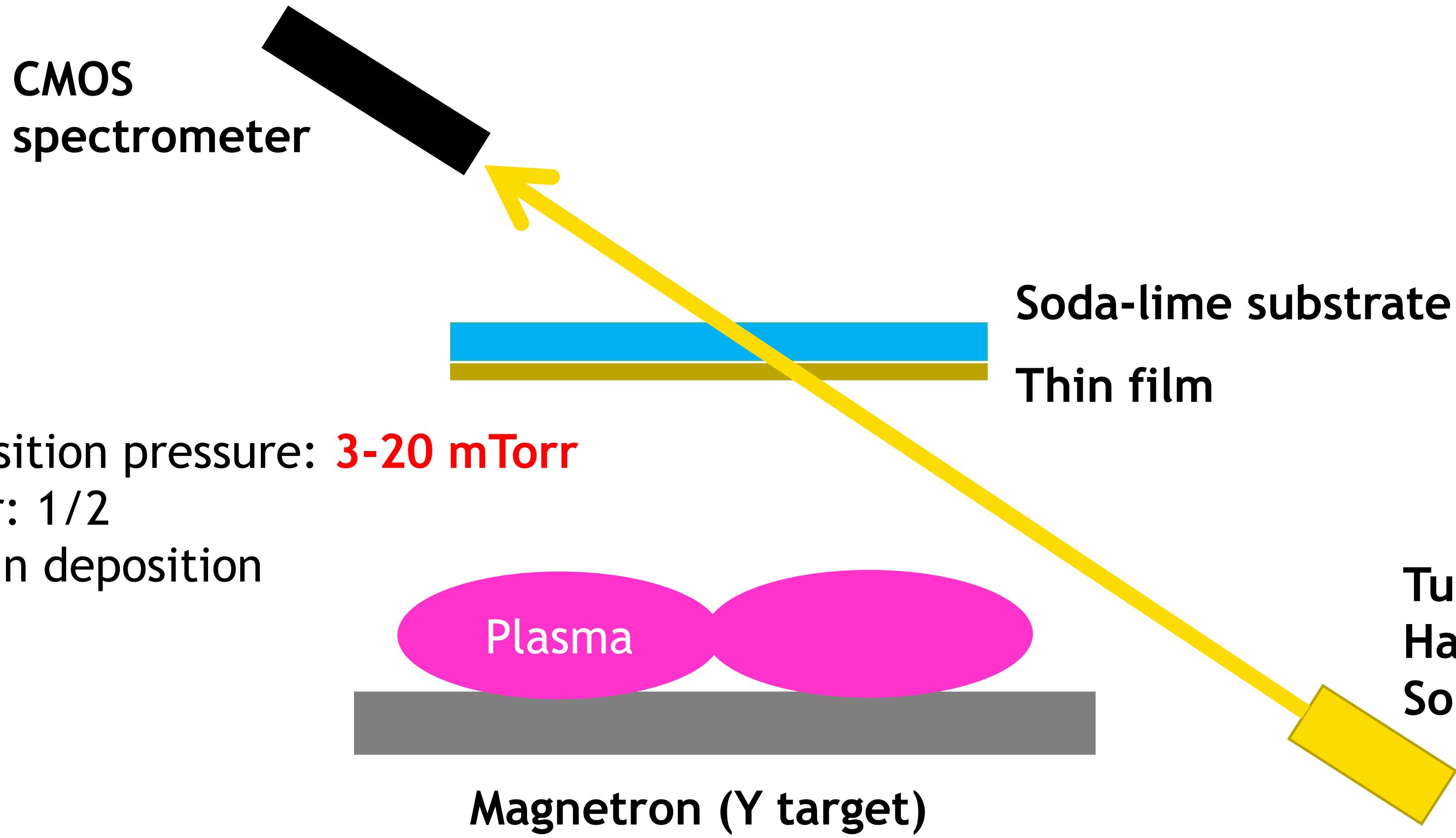
YHO deposition:

- soda-lime glass and Ti substrates;
- substrate temperature: **RT (without intentional heating);**
- deposition time: **20 min;**
- distance from target to substrate: ≈10 cm (facing the target axis);

DEPOSITED YHO SAMPLES

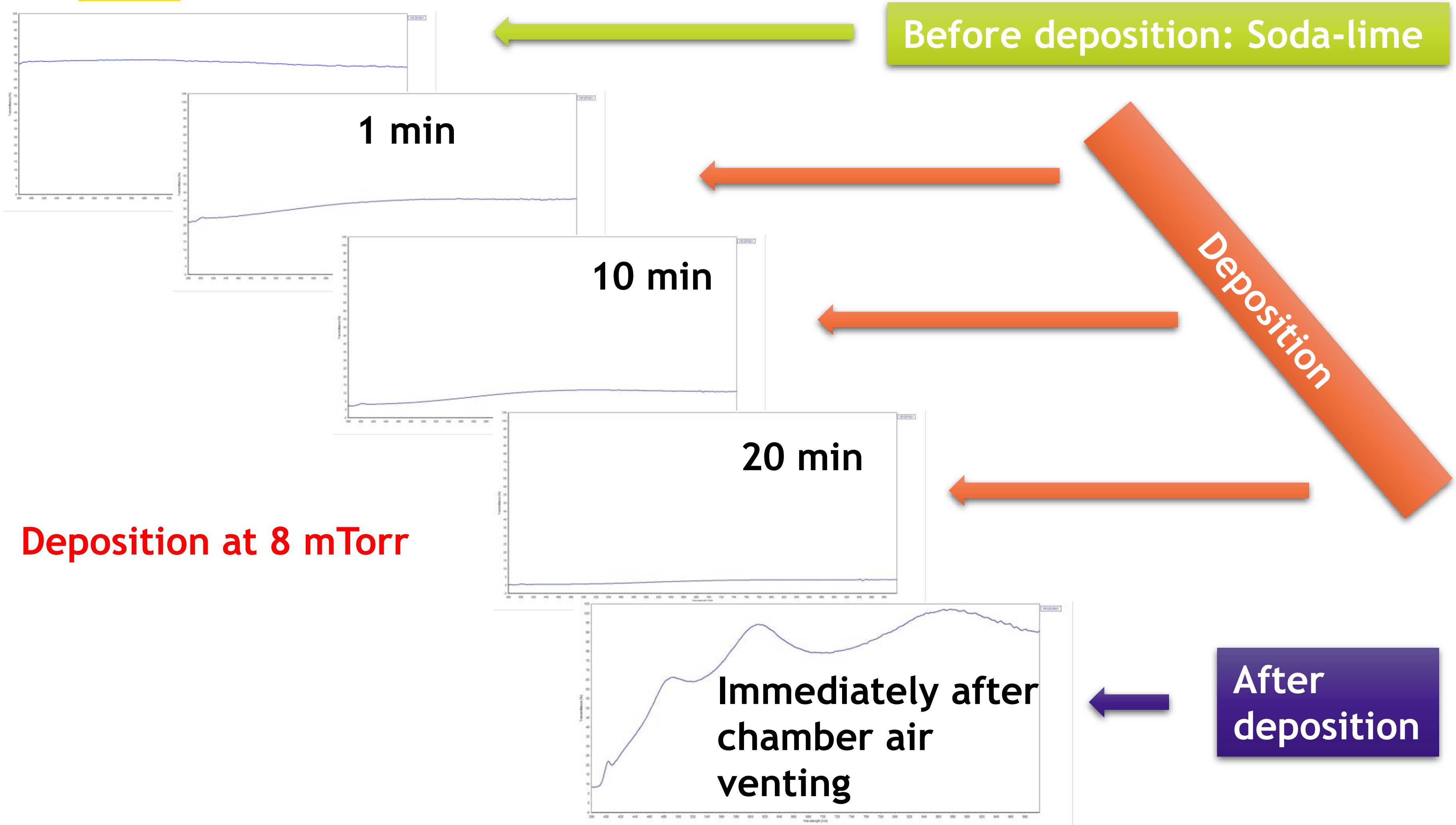
Sample No.	Sputtering pressure (mTorr)	Voltage (V)	Thickness (nm)
1	3.0	302	330
2	6.0	299	209
3	6.5	299	305
4	7.0	299	357
5	7.5	297	378
6	8.0	298	428
7	9.0	296	442
8	10.0	299	419
9	12.0	296	398
10	20.0	290	462

IN-SITU TRANSMITTANCE MEASUREMENT SETUP



Deposition pressure: **3-20 mTorr**
H_2/Ar: 1/2
20 min deposition

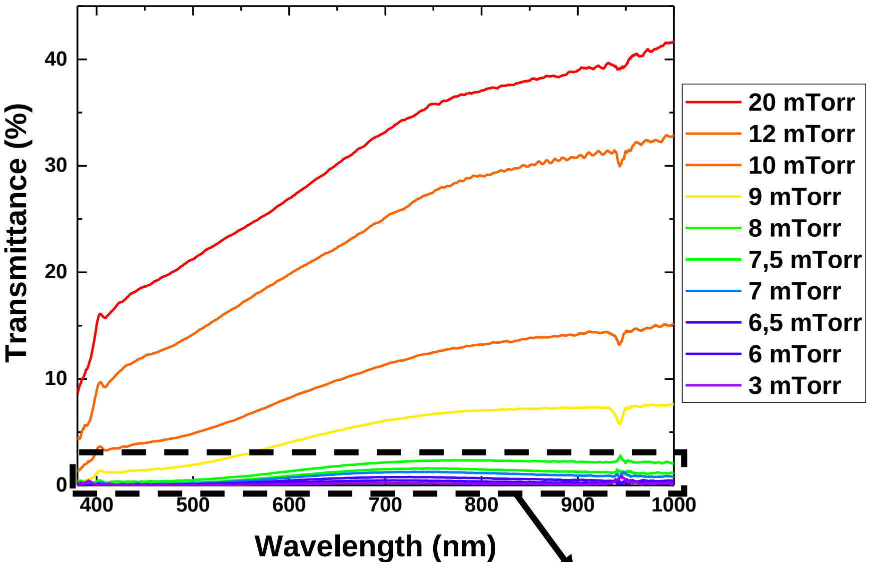
IN-SITU TRANSMITTANCE MEASUREMENT

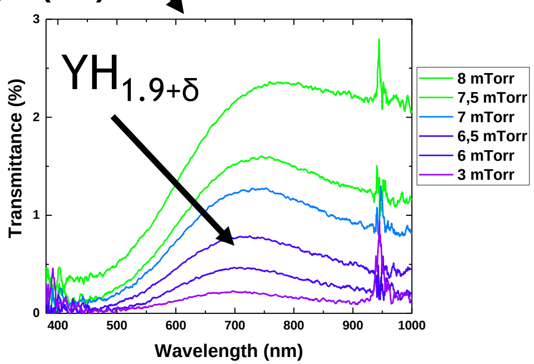


Deposition at 8 mTorr

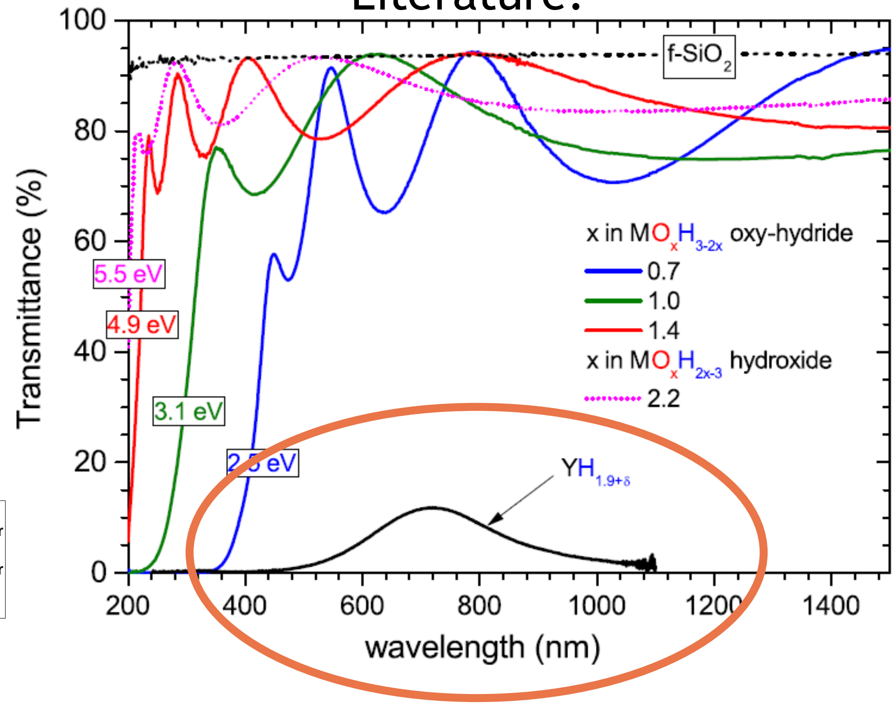
IN-SITU TRANSMITTANCE

Transmittance spectra of the deposited samples immediately after the deposition.





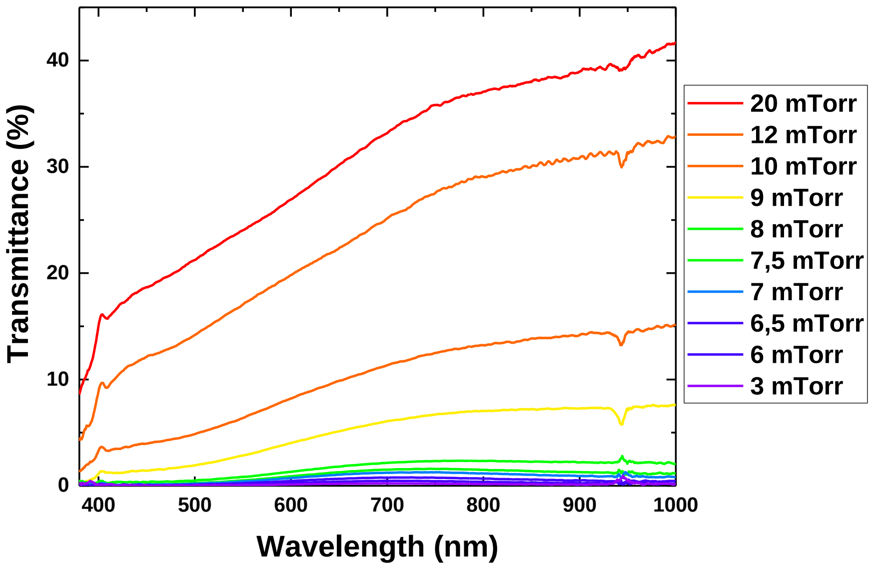
Literature:



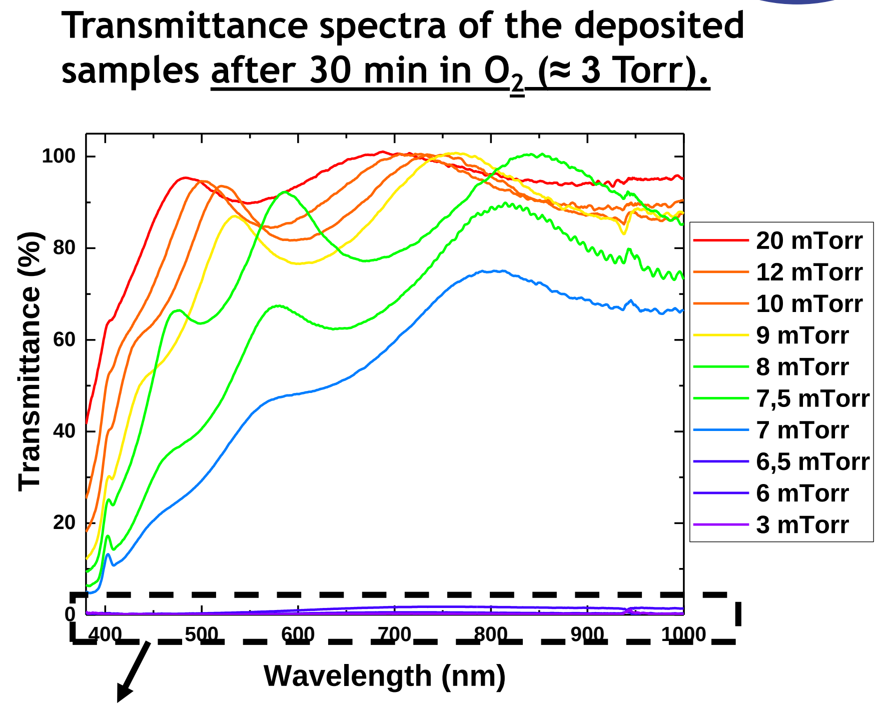
J. Phys. Chem. Lett. 2019, 10, 1342−1348

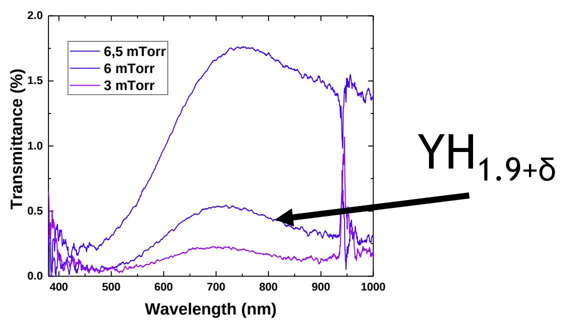
IN-SITU TRANSMITTANCE

Transmittance spectra of the deposited samples immediately after the deposition.

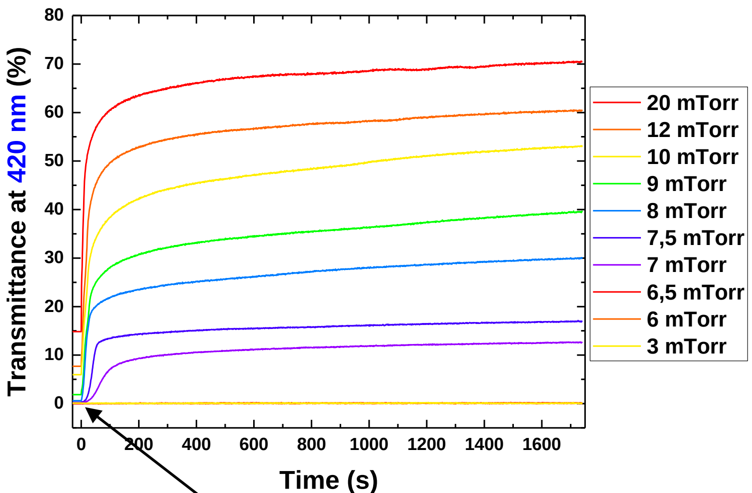


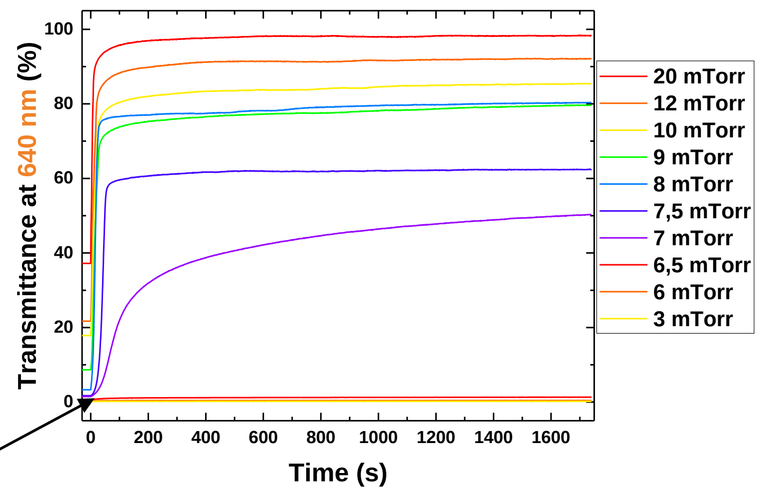
Transmittance spectra of the deposited samples after 30 min in O_2 (≈ 3 Torr).



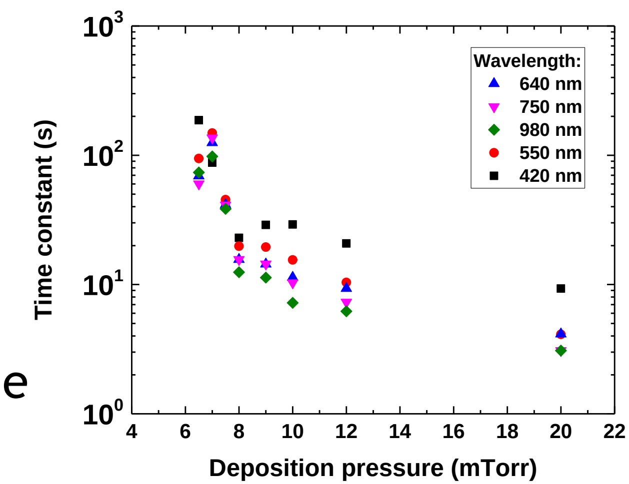


TIME CONSTANT



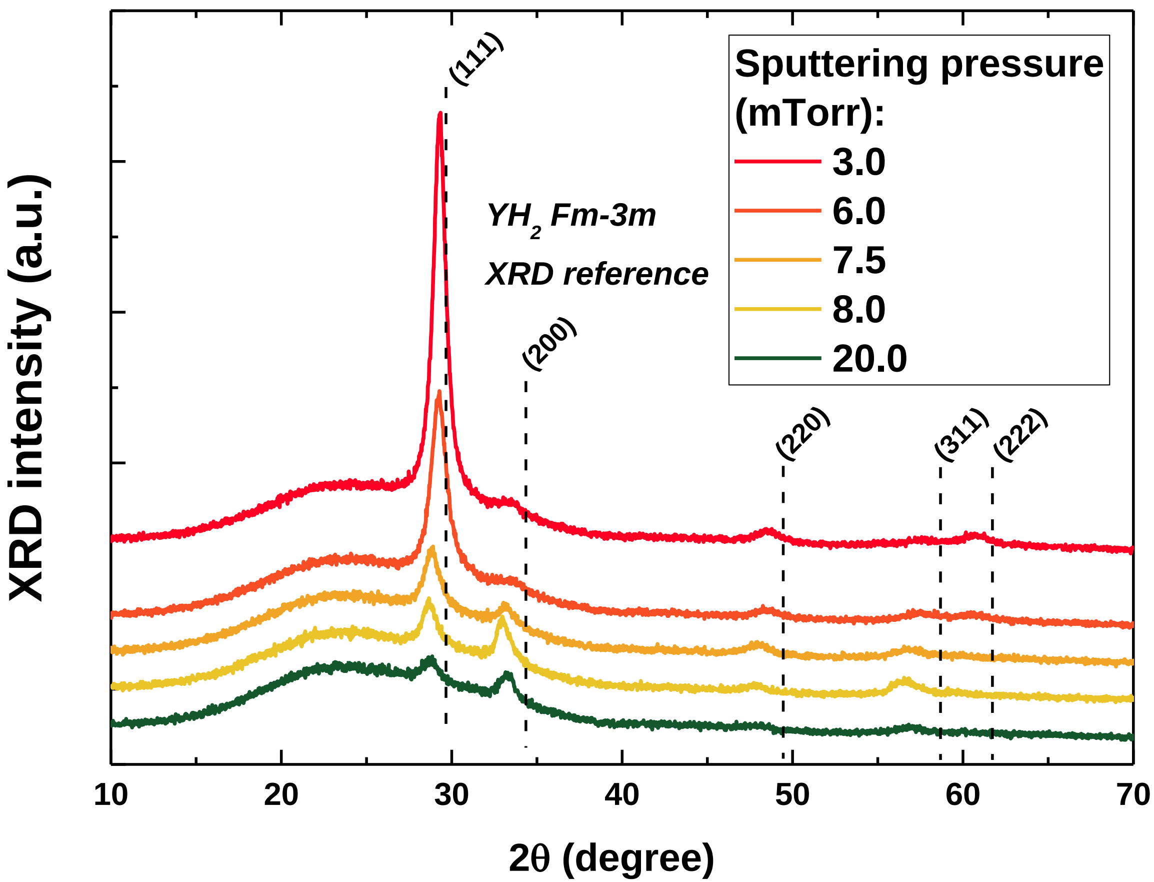


Oxygen inlet after deposition



Time constant:
Increase in transmittance value up to 50% of the final value.

XRD OF YHO

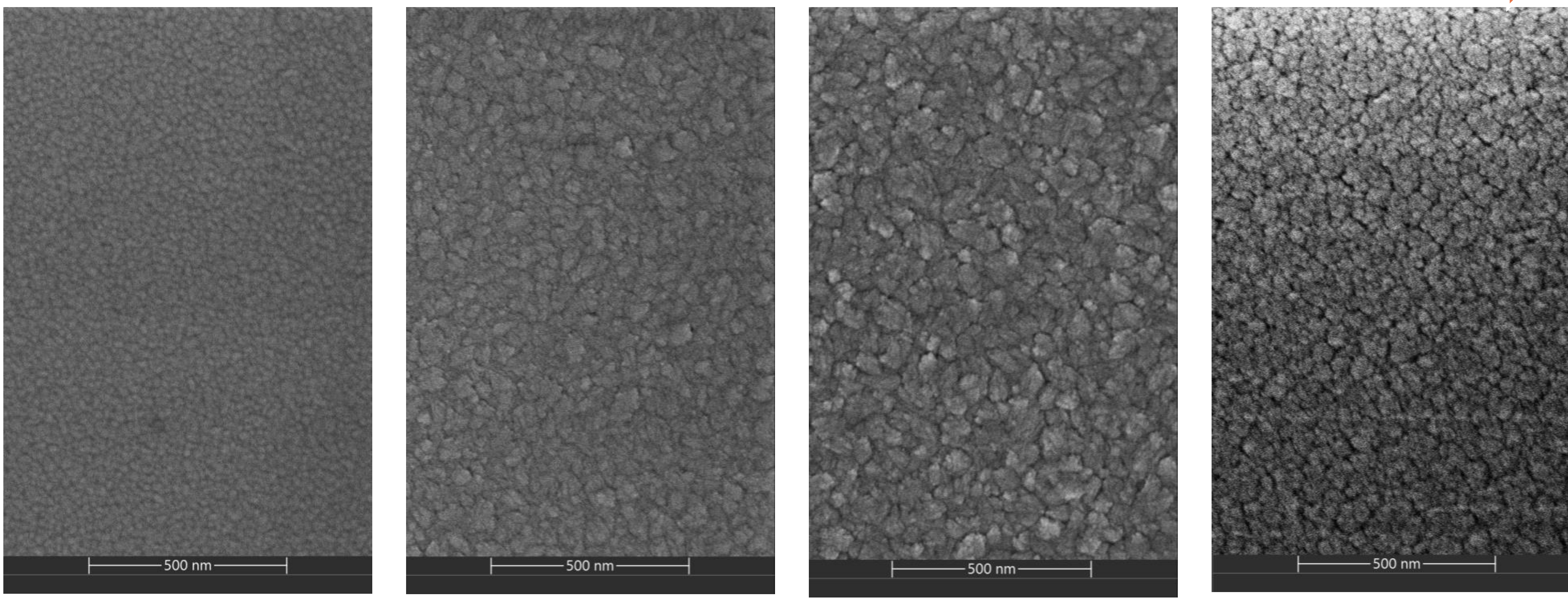


XRD intensity (a.u.)
2θ (degree)
10
20
30
40
50
60
70
(111)
(200)
(220)
(311)
(222)
YH2 Fm-3m
XRD reference
Sputtering pressure
(mTorr):
3.0
6.0
7.5
8.0
20.0

SURFACE MORPHOLOGY

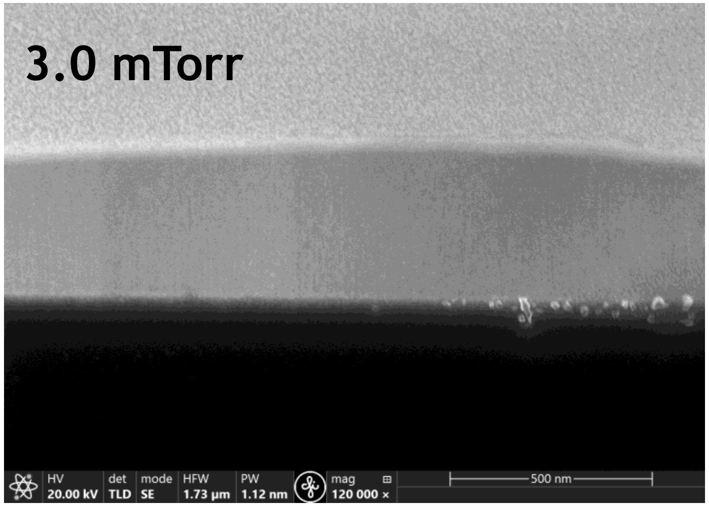
Sputtering pressure

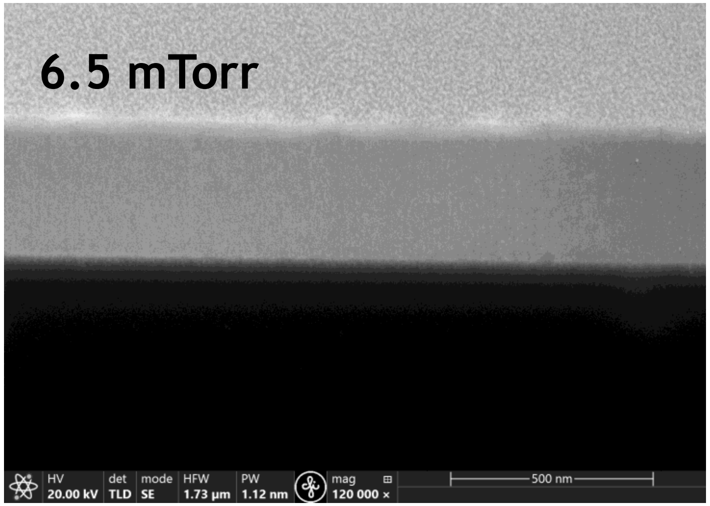
3.0 mTorr | 6.5 mTorr | 7.5 mTorr | 20.0 mTorr

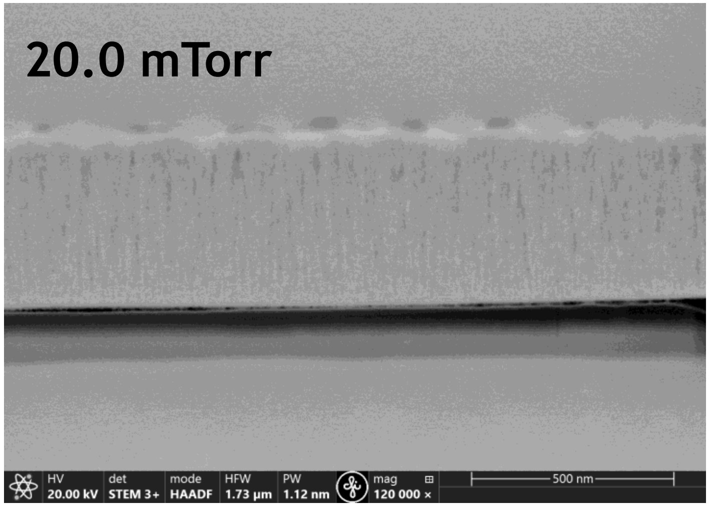


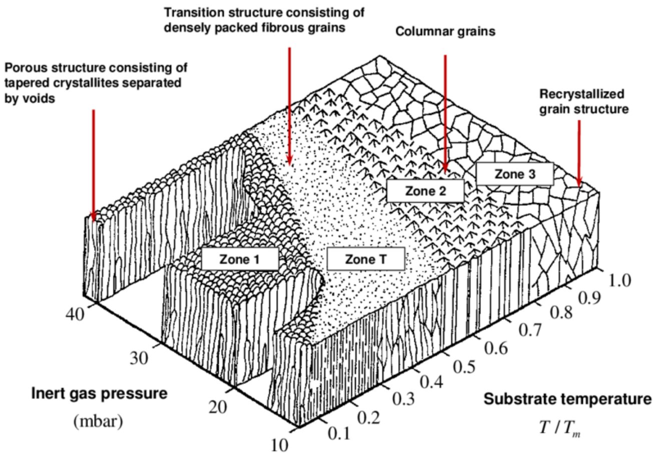
The surface morphology of the films is less dense at higher sputtering pressures.

CROSS-SECTION IMAGES OF YHO FILMS



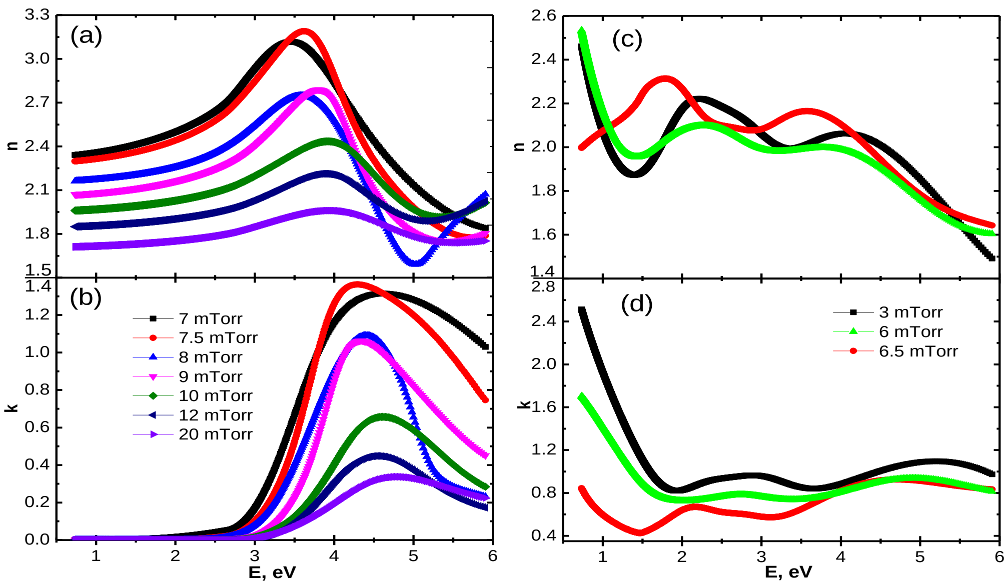




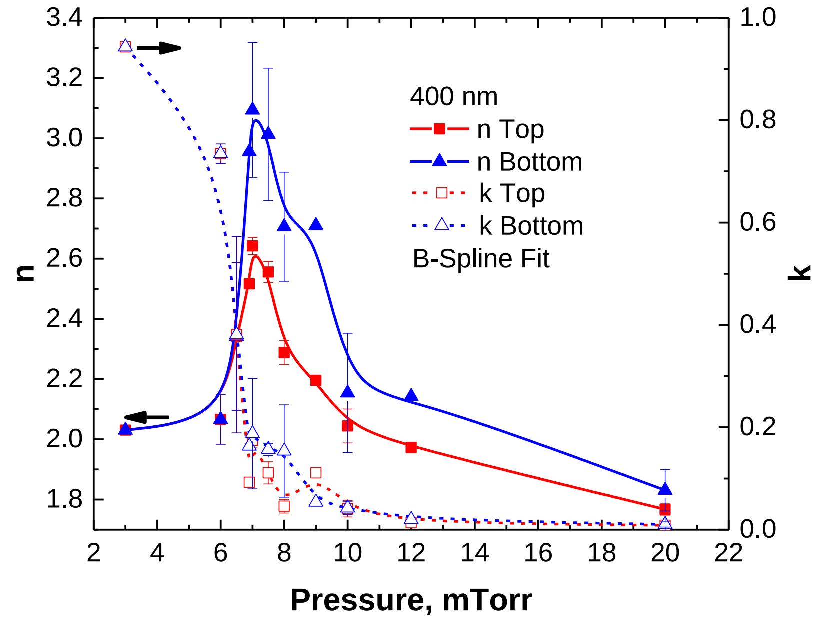


OPTICAL CONSTANTS

The refractive index n (a, c) and extinction coefficient k (b, d) as functions of photon energy and sputtering pressure.

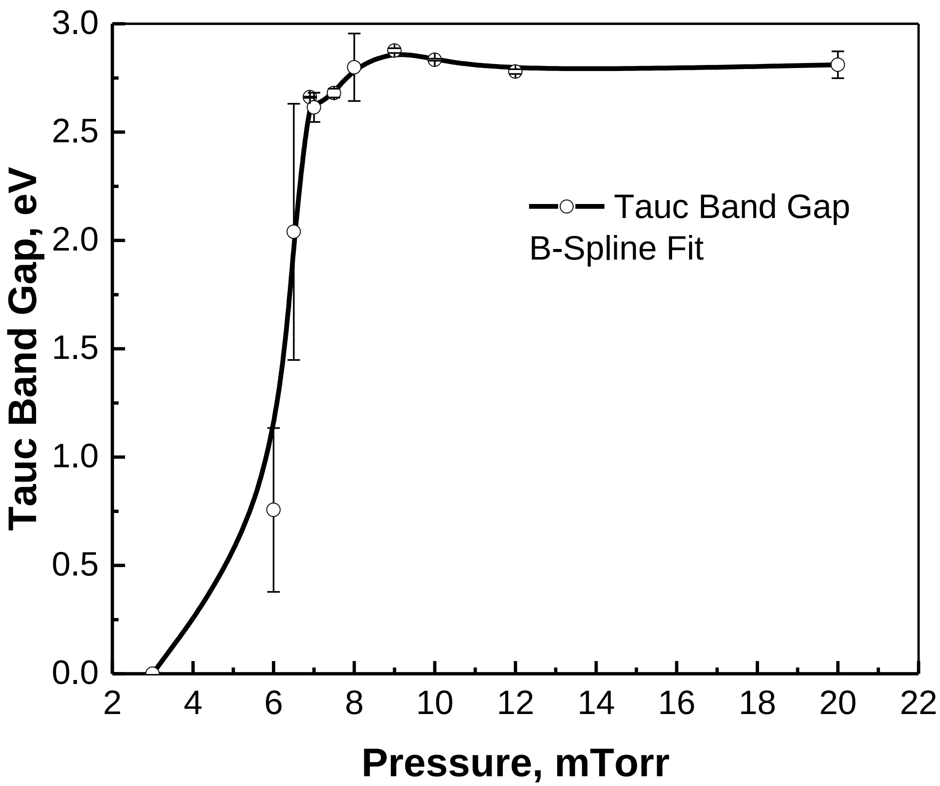


Refractive index n and extinction coefficient k at 400 nm wavelength as functions of sputtering pressure.



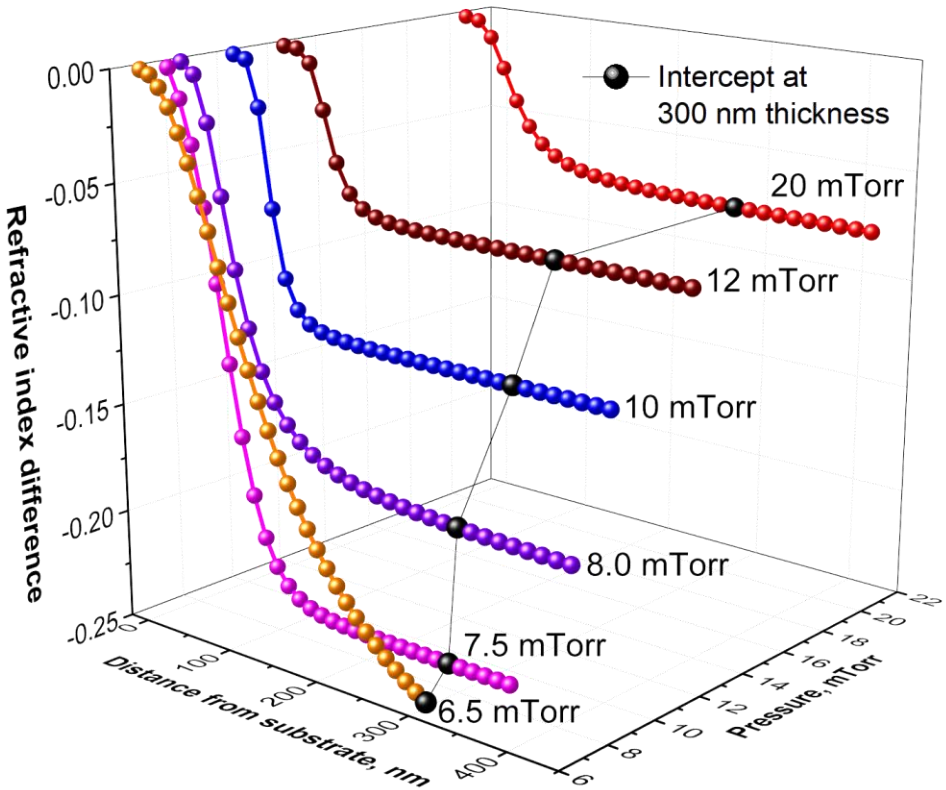
OPTICAL BAND GAP

Tauc band gap E_g (fitting parameter of TLO) as a function of the sputtering pressure.

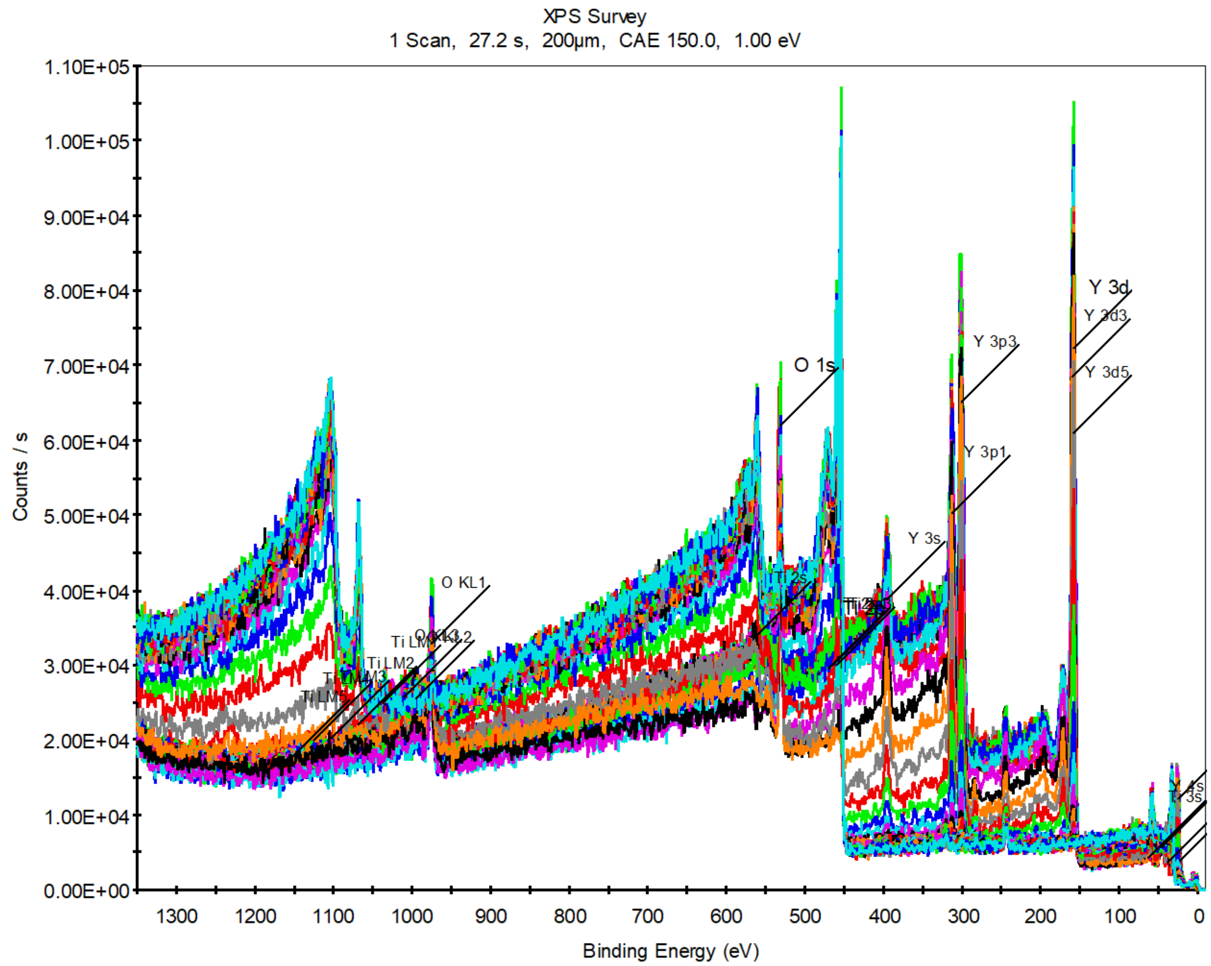


OPTICAL GRADIENT

Optical depth profile (at 1.669 eV or 742.8 nm) of thin films sputtered at different pressures.



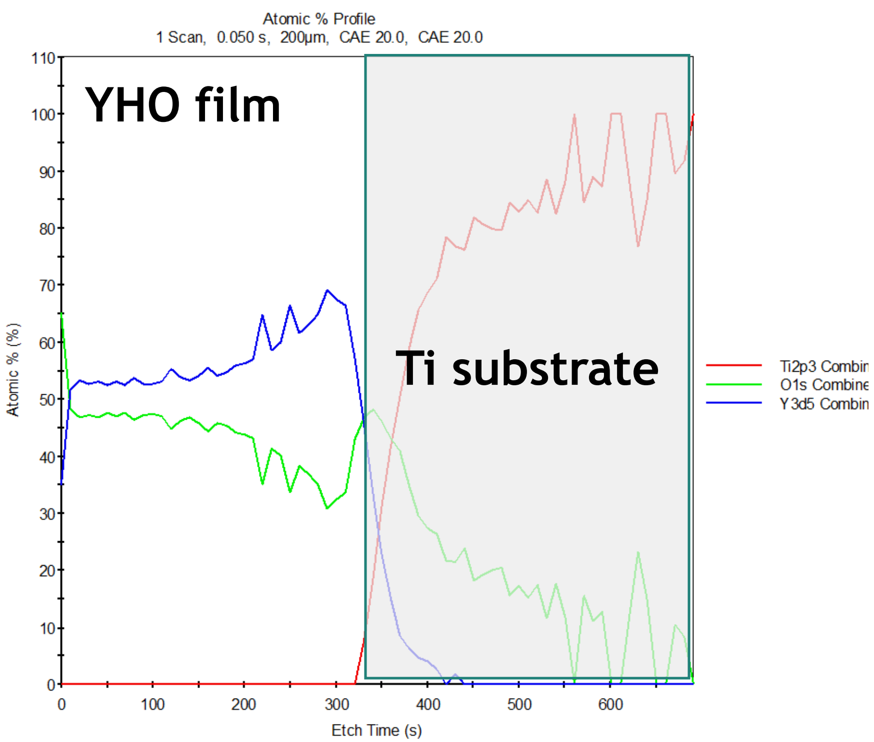
XPS – DEPTH PROFILING



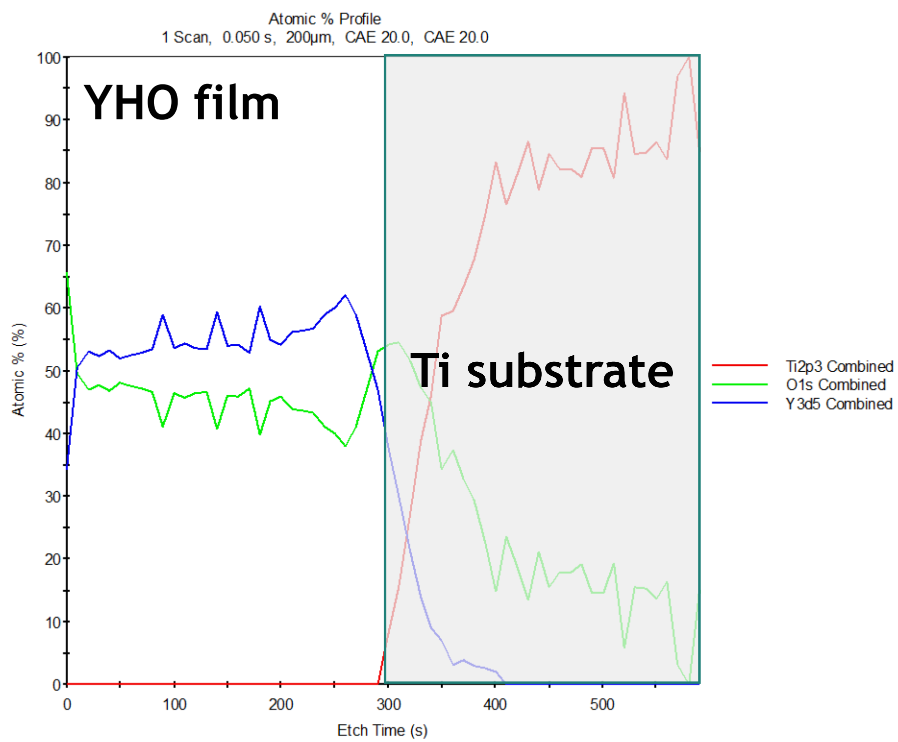
DEPTH PROFILING

YHO films on the Ti substrates

7.0 mTorr



8.0 mTorr

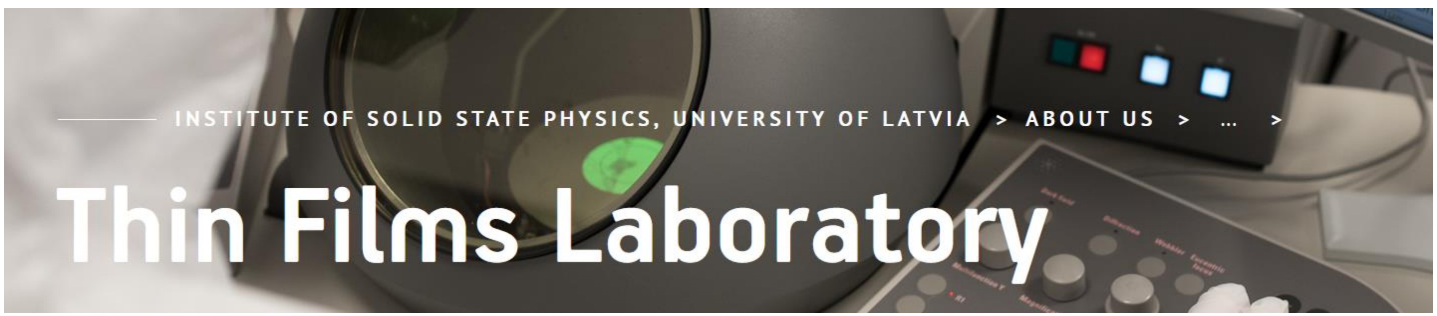


The film composition (O / Y) is not uniform throughout the thickness of the films.

CONCLUSIONS

- The oxidation of YH_{2-x} films during and after deposition occur more rapidly when the higher sputtering pressure is used.
- The most of the oxidation happens when oxygen (or air) is introduced into a vacuum chamber intentionally.
- The lattice of YHO films expands with the deposition pressure due the higher oxygen concentration which is promoted by the less dense structure.
- There is the transition from metallic to semiconducting/insulating YHO films when the deposition pressure is increased (at 7.0 mTorr in our case).
- The transparent films in the visible light range exhibit an optical gradient throughout the thickness of the films due to the nonhomogeneous composition.

Thanks for Your attention !!!



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