

# Materials for the hydrogen economy: (from smart windows) to hydrogen sensors

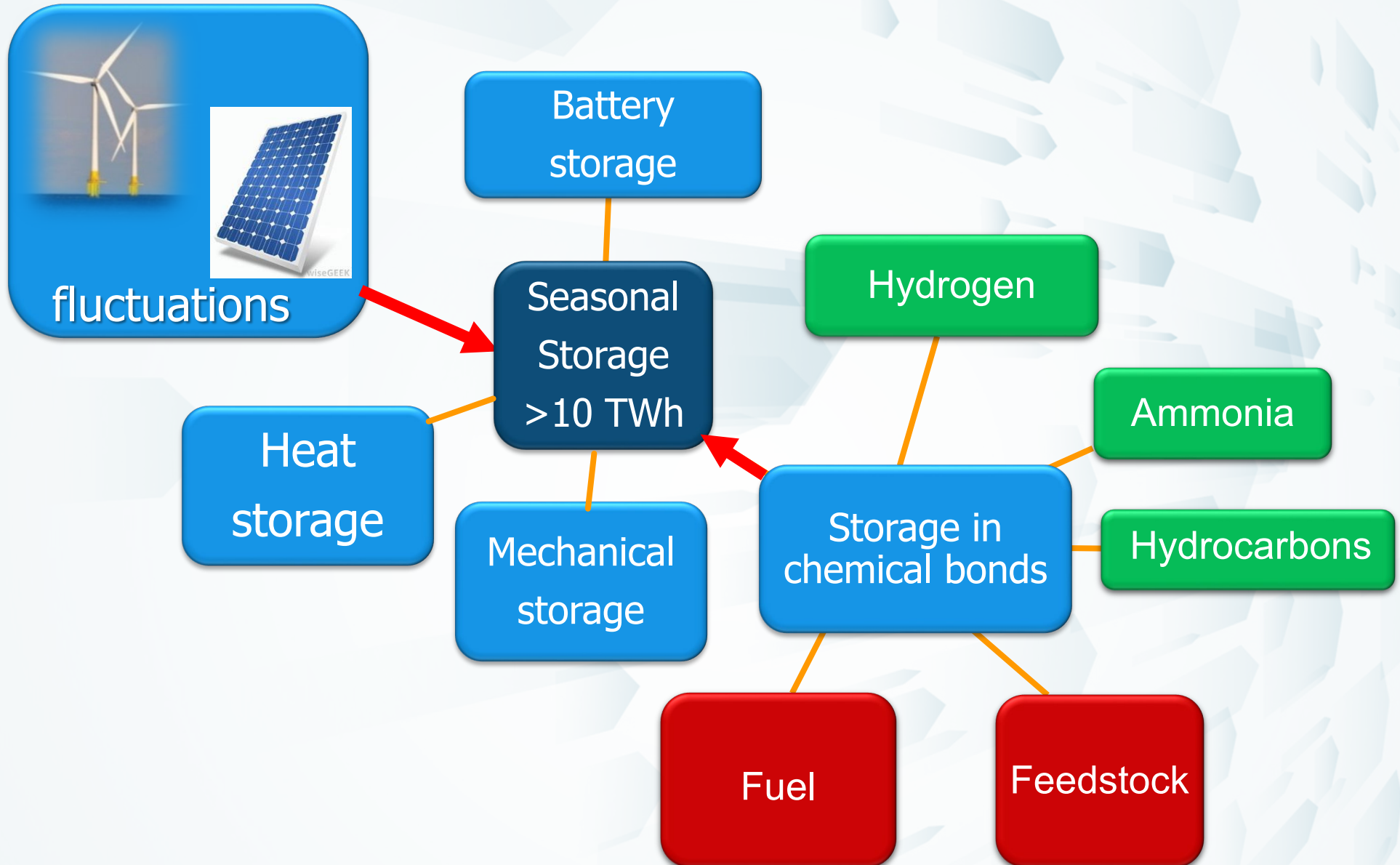
Bernard Dam, Lars Bannenberg\*, Herman Schreuders

Chemical Engineering

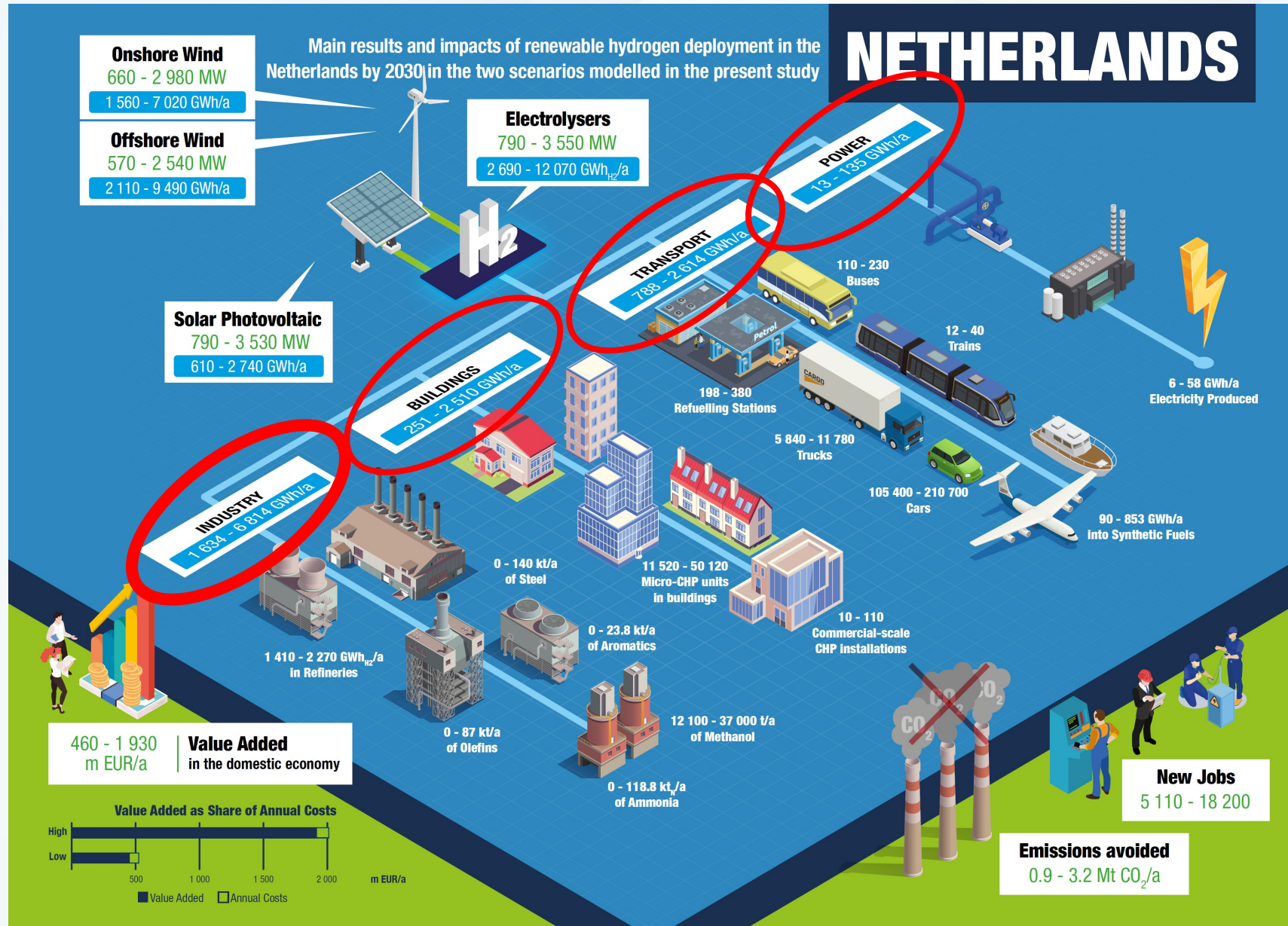
\*Radiation Science and Technology

Faculty of Applied Sciences, TUD

# A sustainable energy system



# Hydrogen for industry, buildings, transport and power

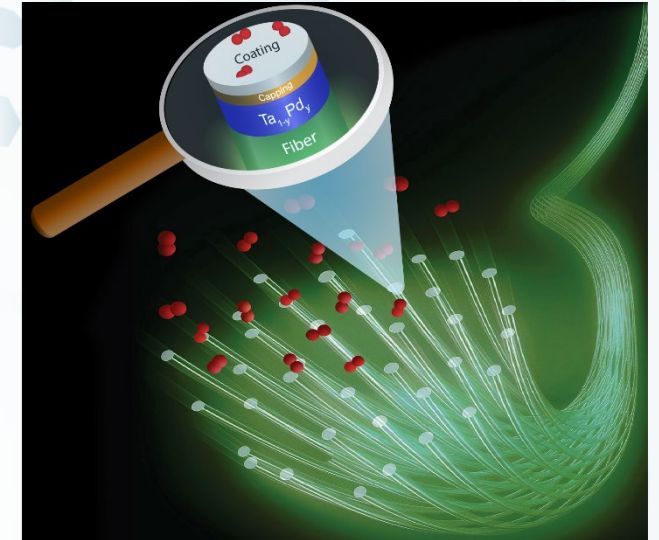


Opportunities for **Hydrogen Energy Technologies** Considering the National Energy & Climate Plans (2020)



# Why optical fiber hydrogen sensors?

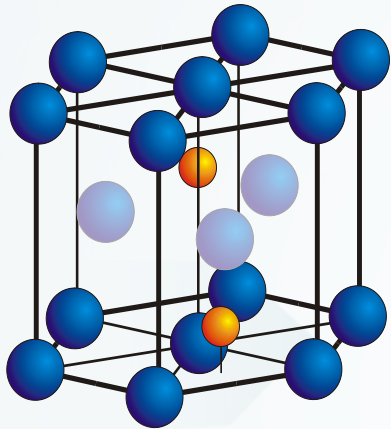
- Readout can be separated from the sensing area.
- No electric currents near the sensing area
- No presence of oxygen required
- Relatively small
- Potentially a large sensing range



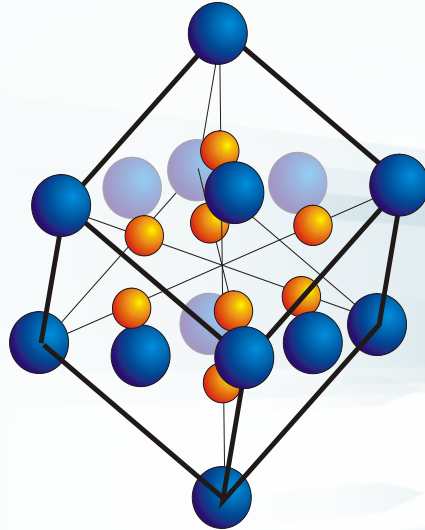


# Our basis: Optical changes in RE-hydride thin films

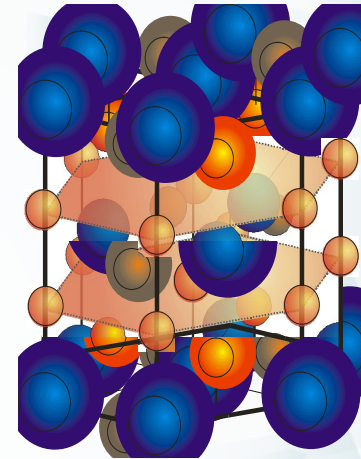
hcp  $\text{YH}_0$



fcc  $\text{YH}_{1.9}$ - $\text{YH}_{2.1}$

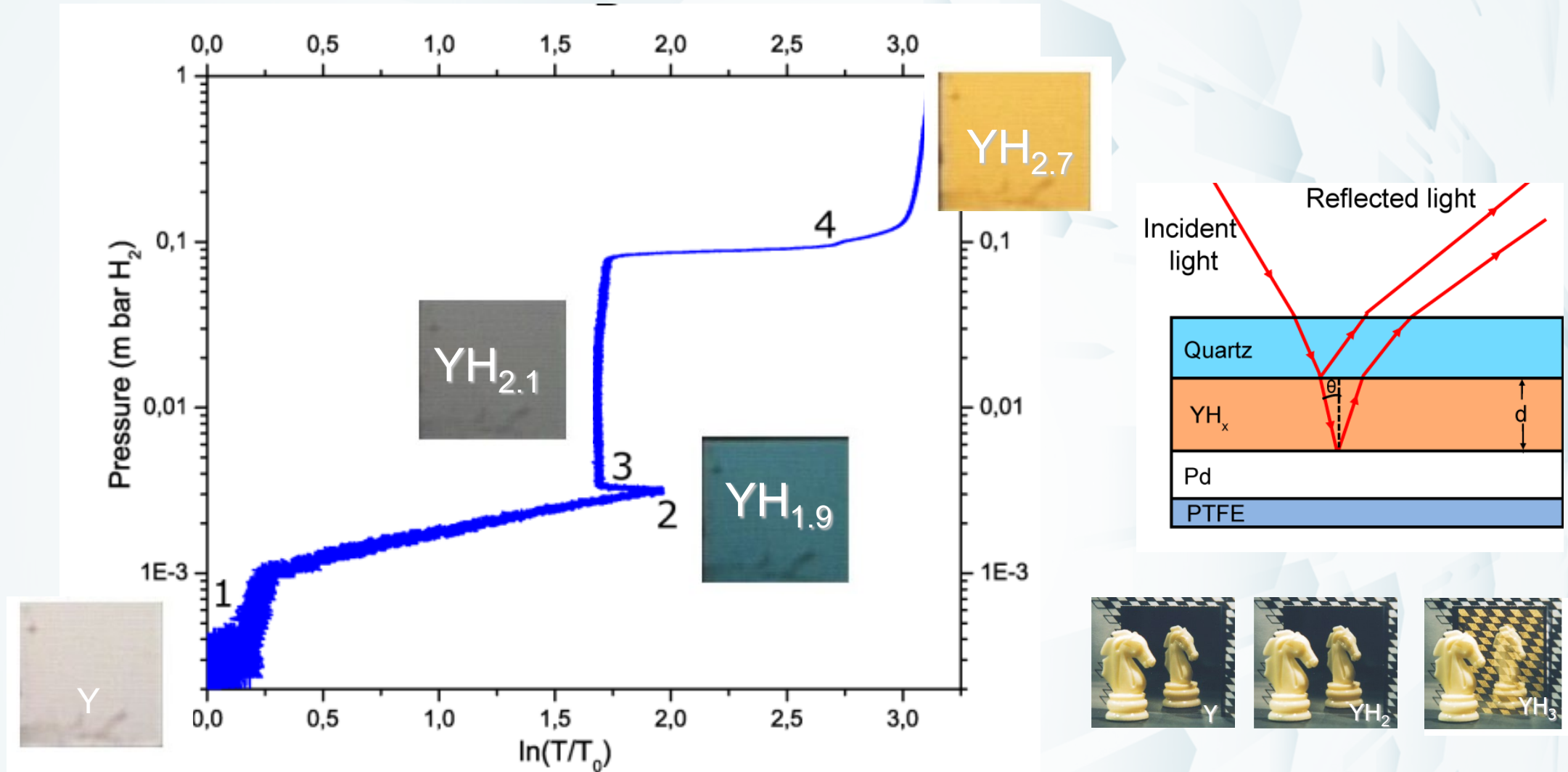


hcp/fcc  $\text{YH}_{2.7}$ - $\text{YH}_3$

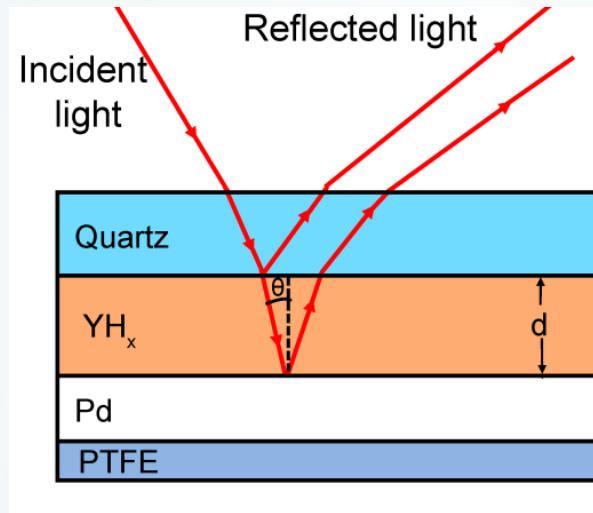


Huiberts et al., Nature 1996

# Eye-readable hydrogen detector based on $\text{YH}_x$



# Most simple approach: Eye-readable hydrogen detector based on $YH_x$



90 nm



$P_{H_2} < 10^{-3}$  mbar



Desorbing from  $P_{H_2} > 10^{-1}$  mbar



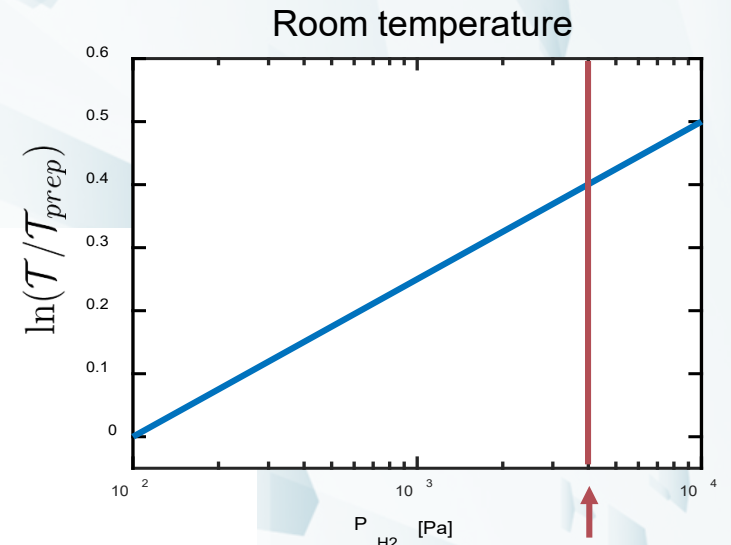
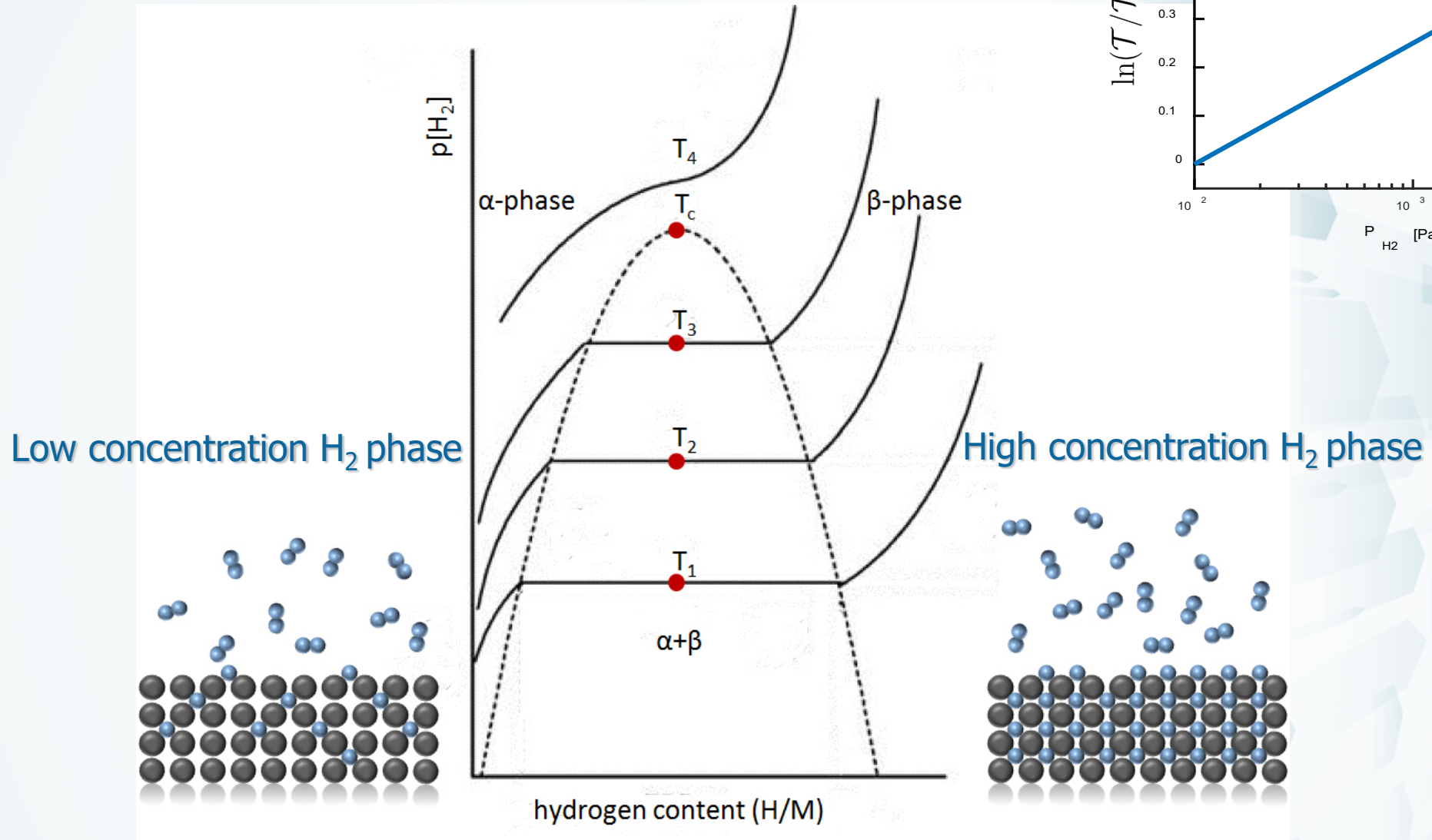
$P_{H_2} > 2 \cdot 10^{-3}$  mbar



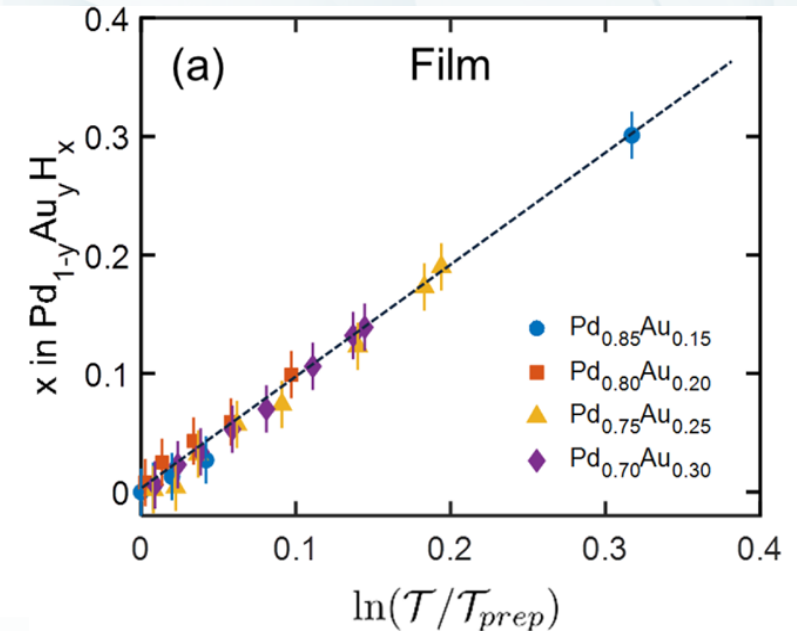
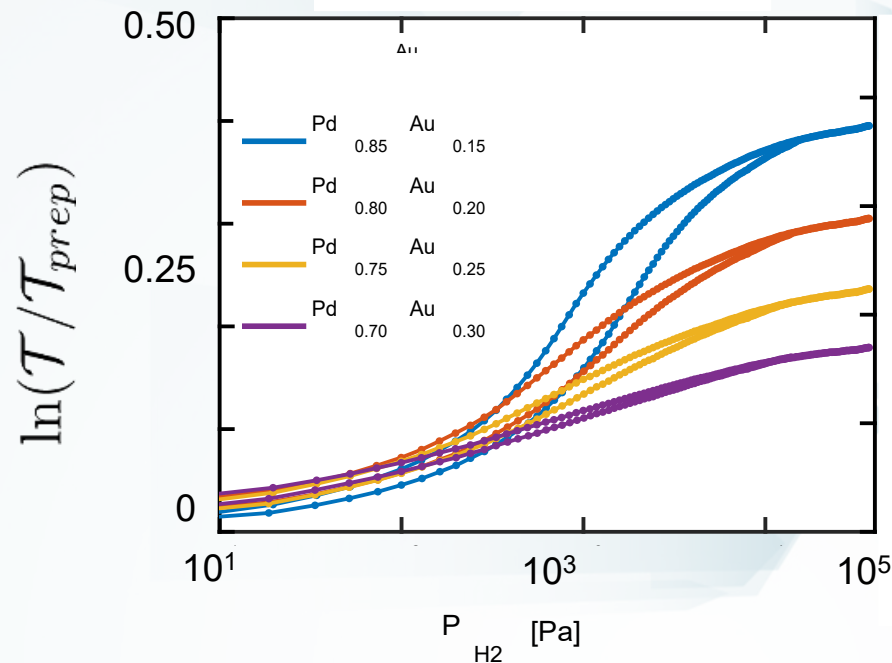
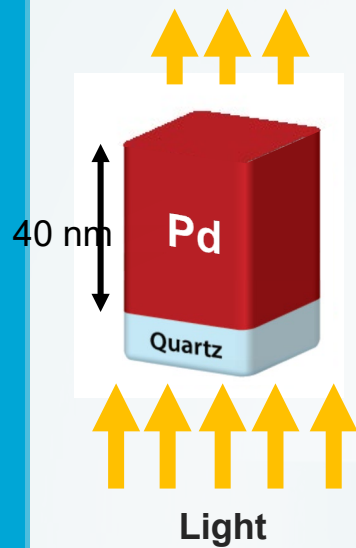
$P_{H_2} > 10^{-1}$  mbar



# From hysteretic detector to sensor

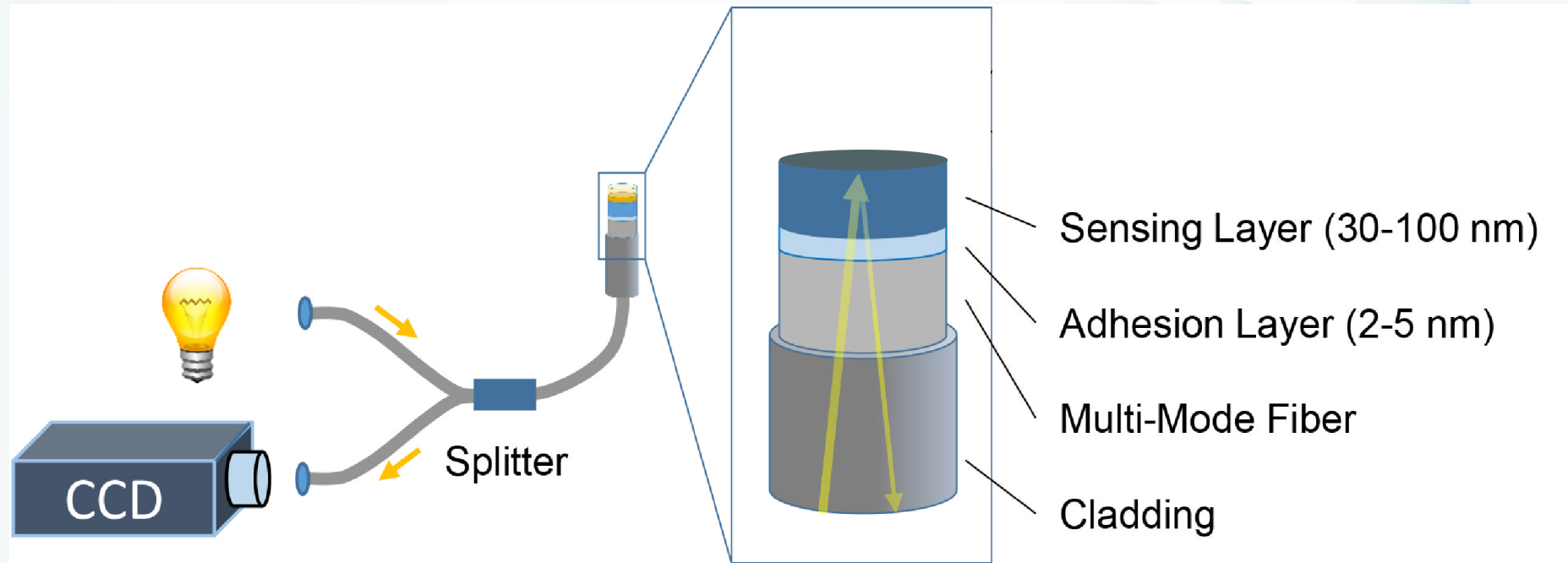


# Hysteresis suppression in Pd-based sensor



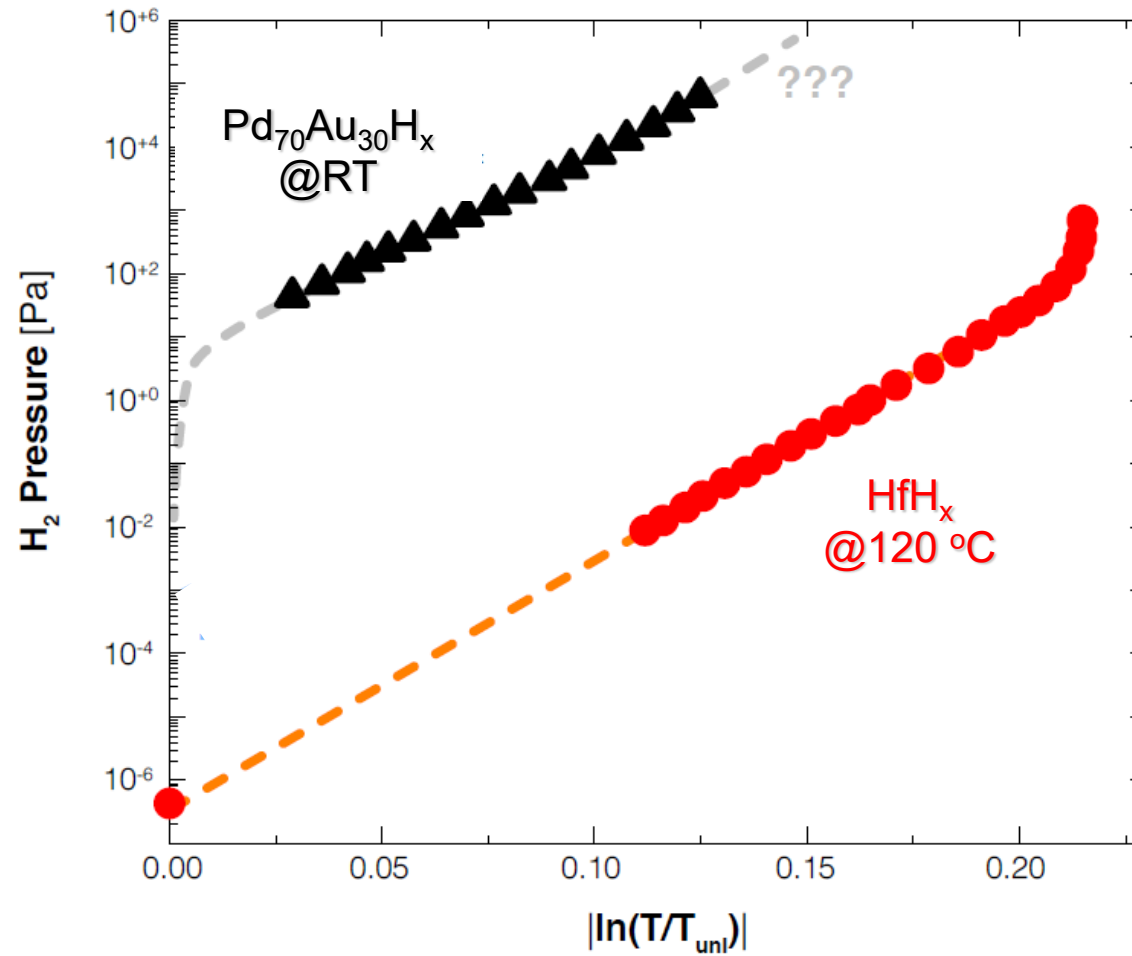
- Alloying reduces contrast and hysteresis
- H-content scales with optical contrast ( $\ln(T/T_{prep})$ )
- Alloying reduces number of available H-sites

# Optical fiber hydrogen sensors, beyond Pd



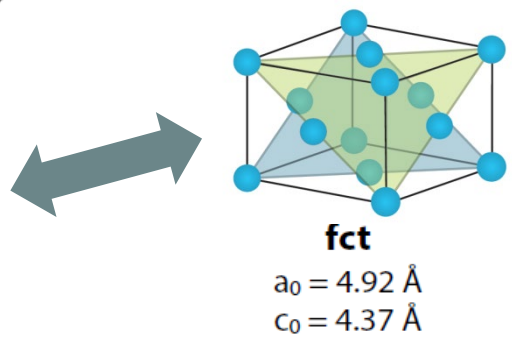
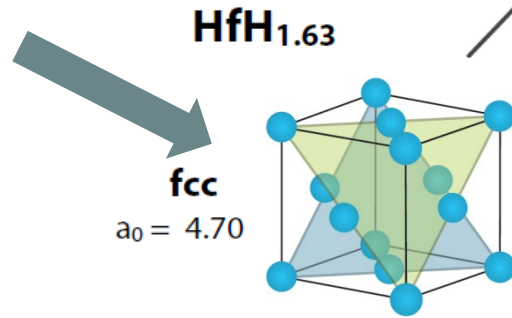
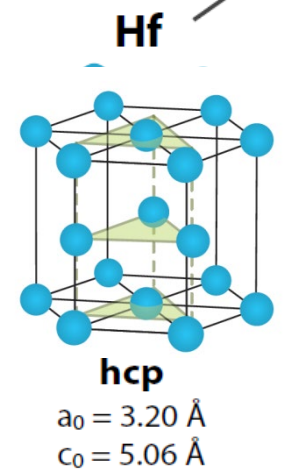
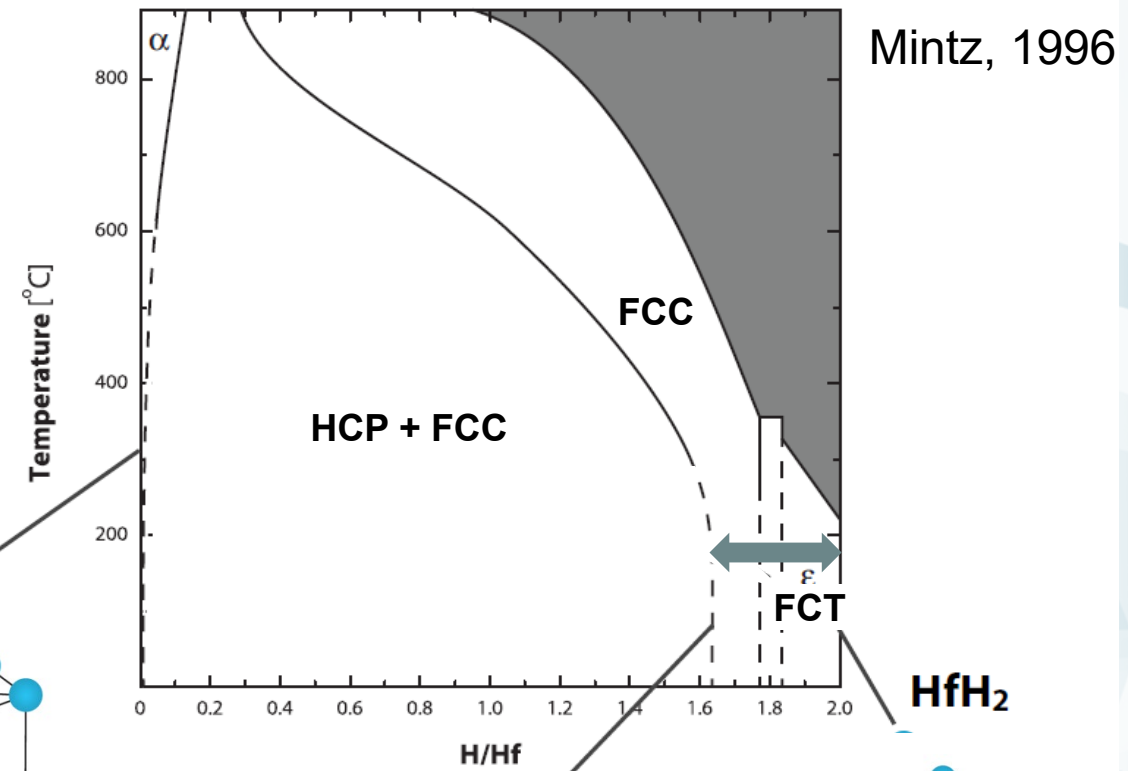


# Pressure range comparison

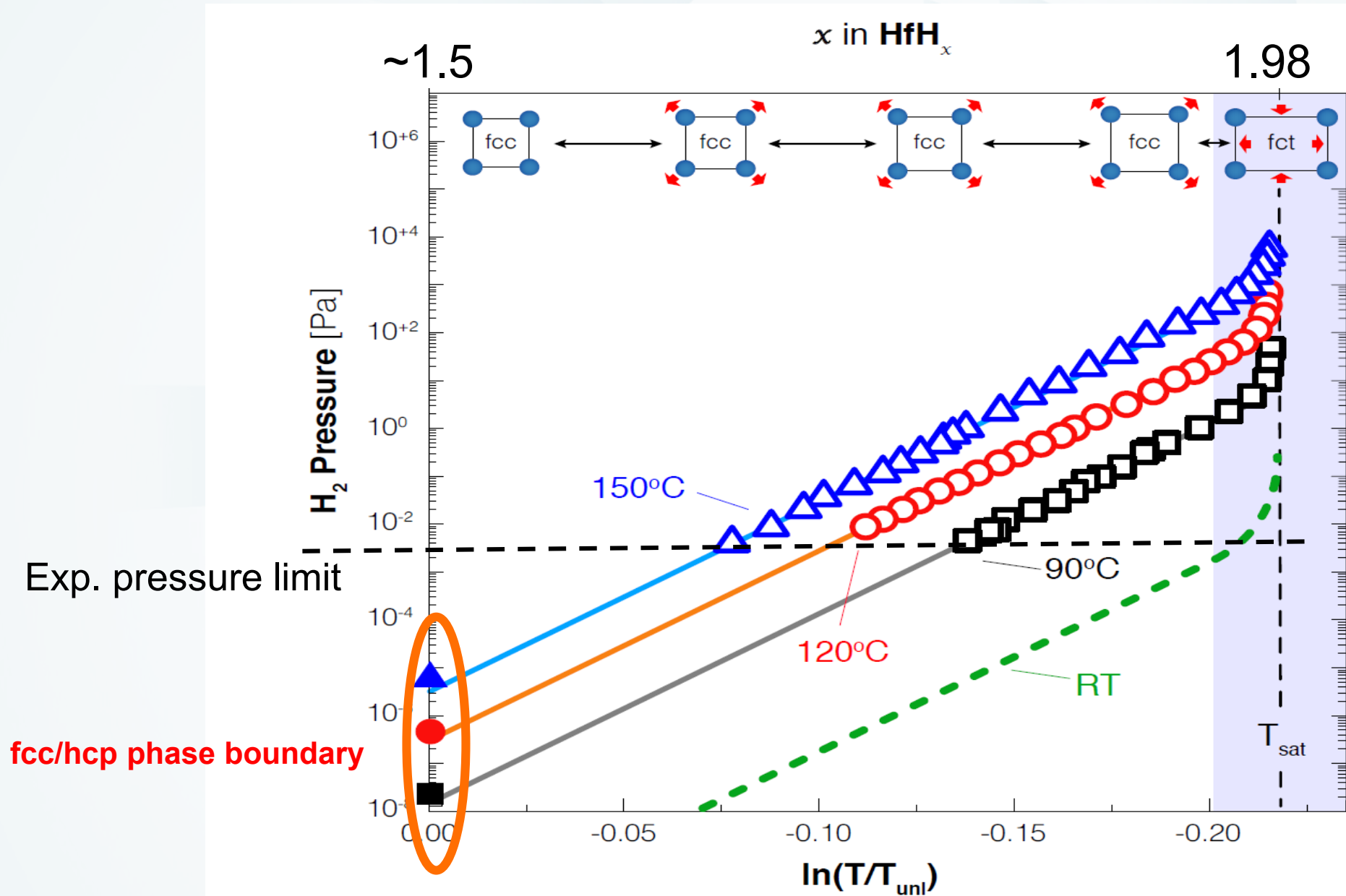


# HfH<sub>x</sub> thin films are free of hysteresis once they reach fcc

12 Mg	Group IV		Group V	
20 Ca	21 Sc	22 Ti	23 V	24 Cr
38 Sr	39 Y	40 Zr	41 Nb	42 Mo
56 Ba	57 La	71 Lu	72 Hf	73 Ta
			74 W	

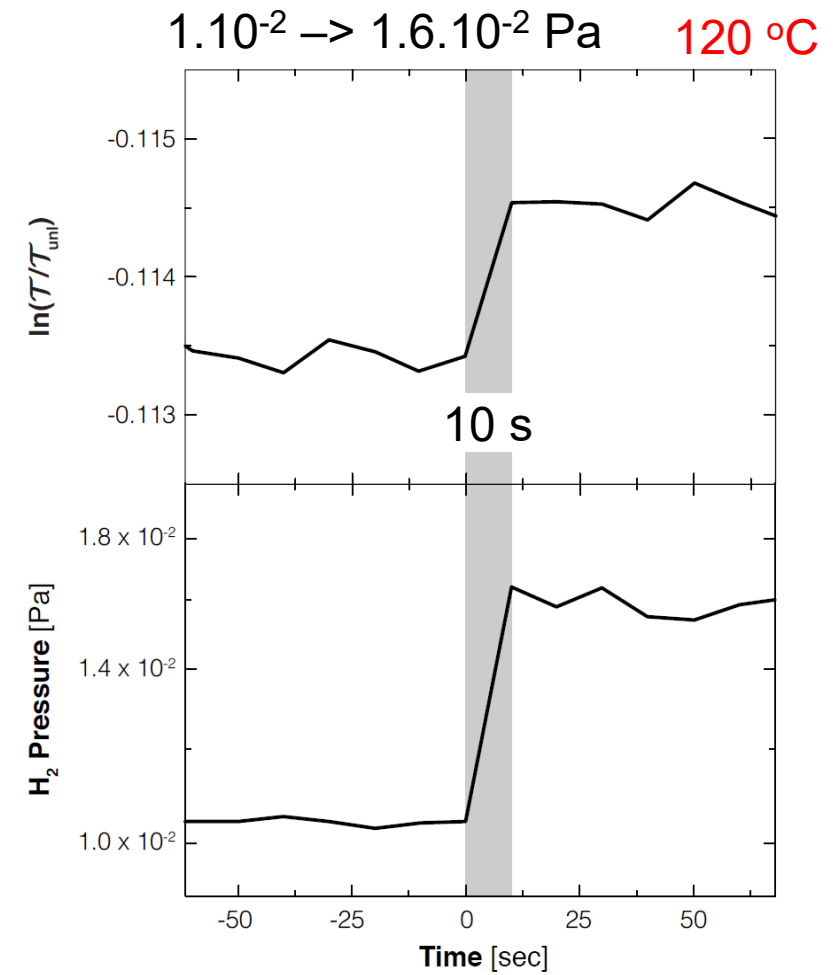
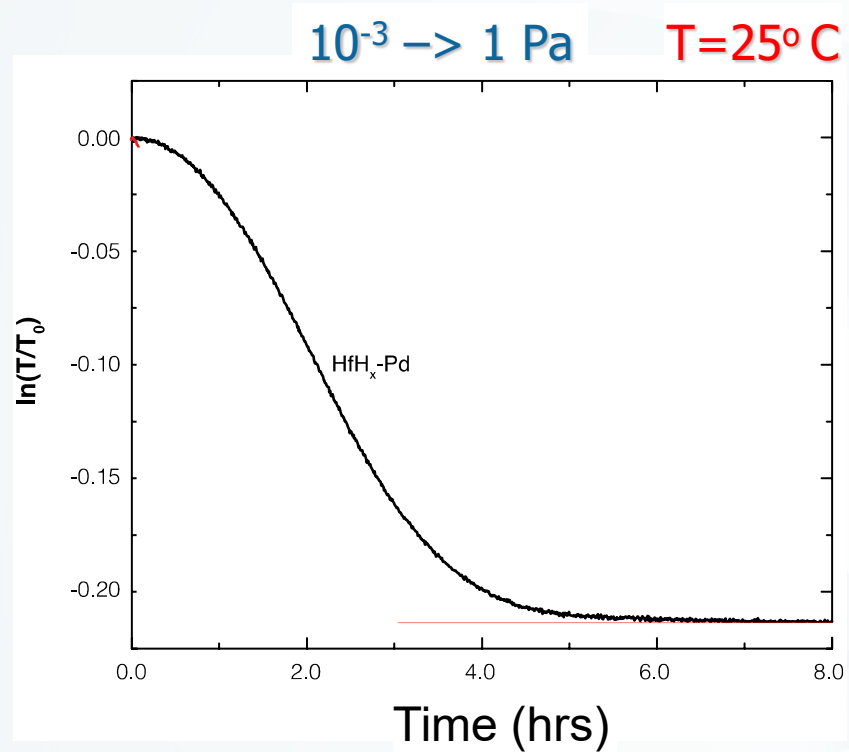


# Large range, linear temperature dependence

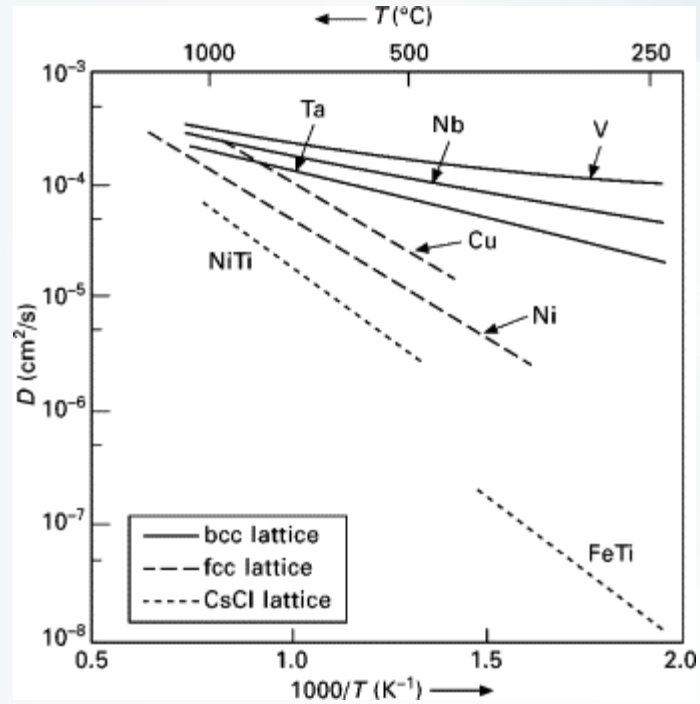




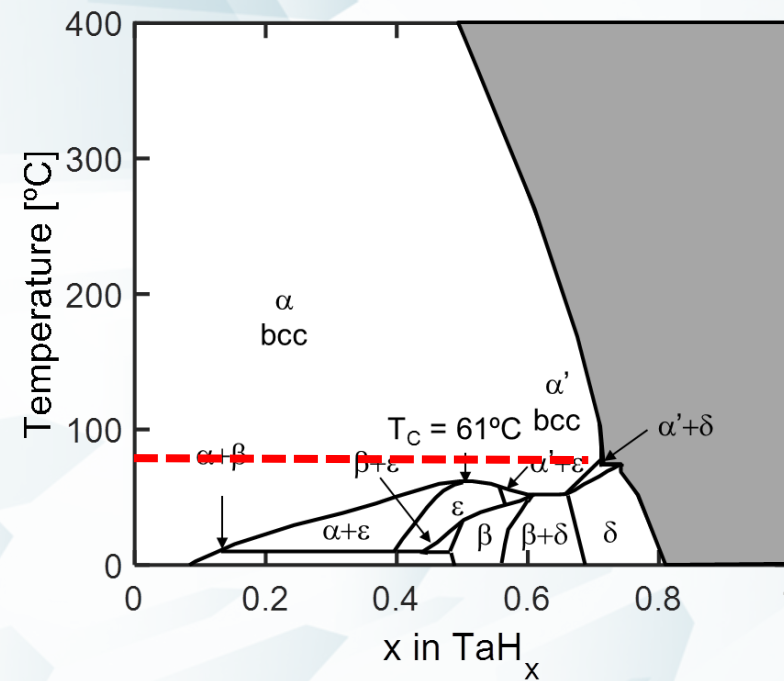
# Optical response Pd-capped Hf



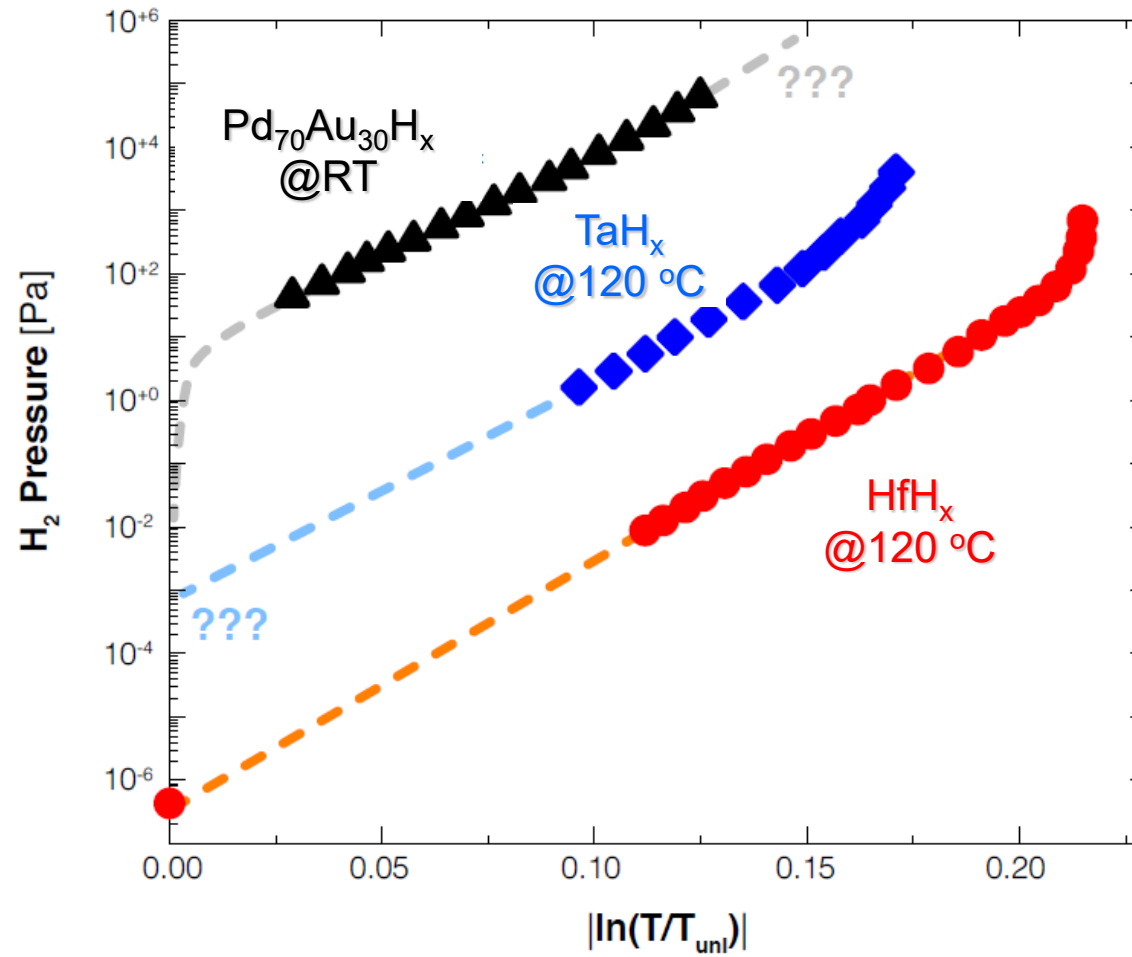
# Tantalum: bcc lattice implies very fast diffusion



12 Mg					
		Group IV	Group V		
20 Ca	21 Sc	22 Ti	23 V	24 Cr	
38 Sr	39 Y	40 Zr	41 Nb	42 Mo	
56 Ba	57 La	71 Lu	72 Hf	73 Ta	74 W

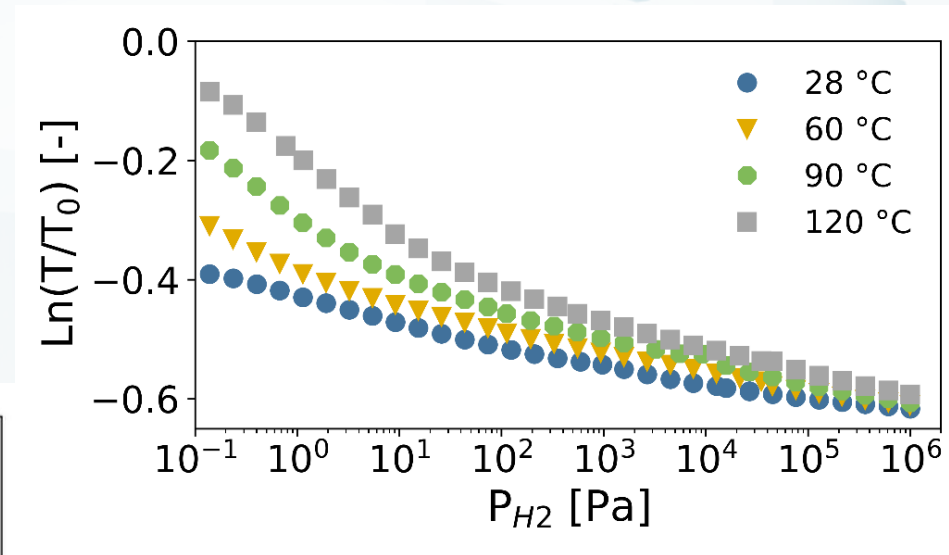
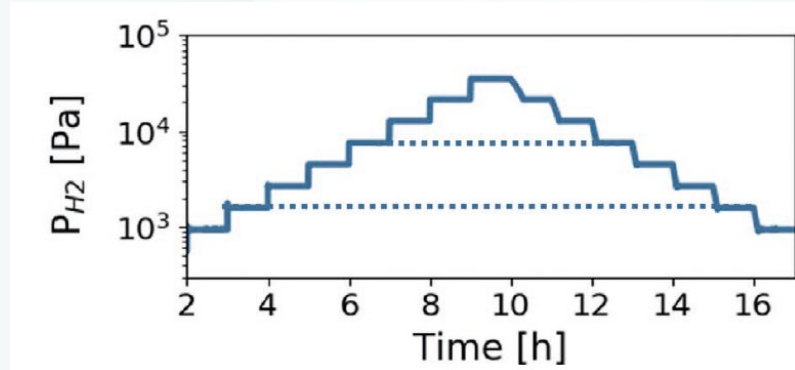


# Pressure range comparison



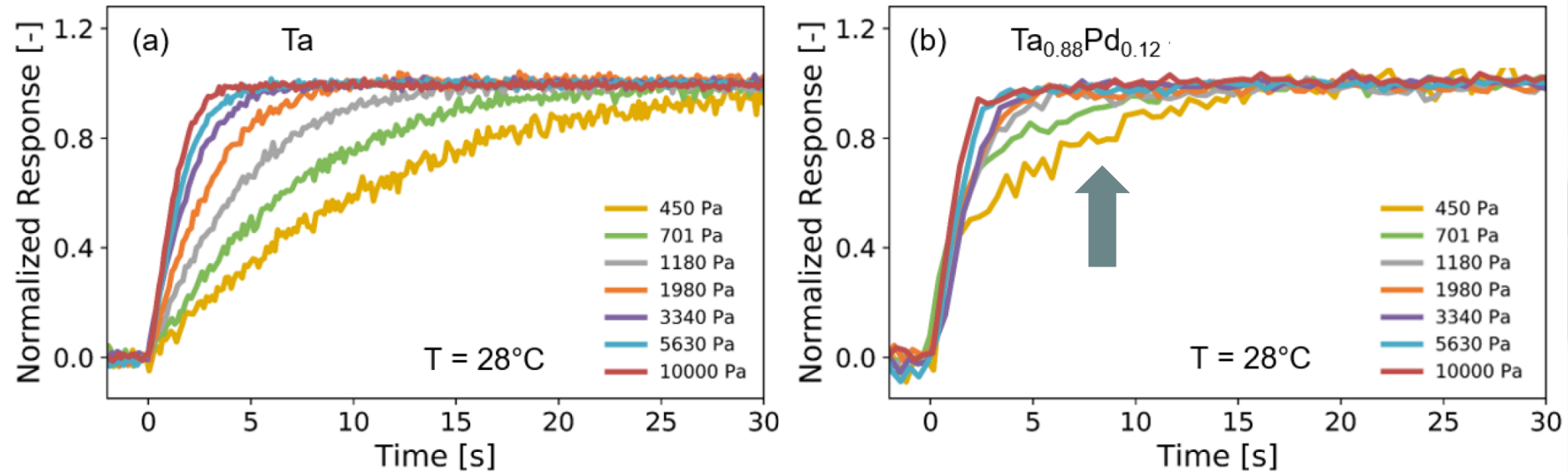
# Ta: room temperature hydrogen sensing

- Hydrogen sensing material covering 7 orders in pressure



- No hysteresis, even at room temperature

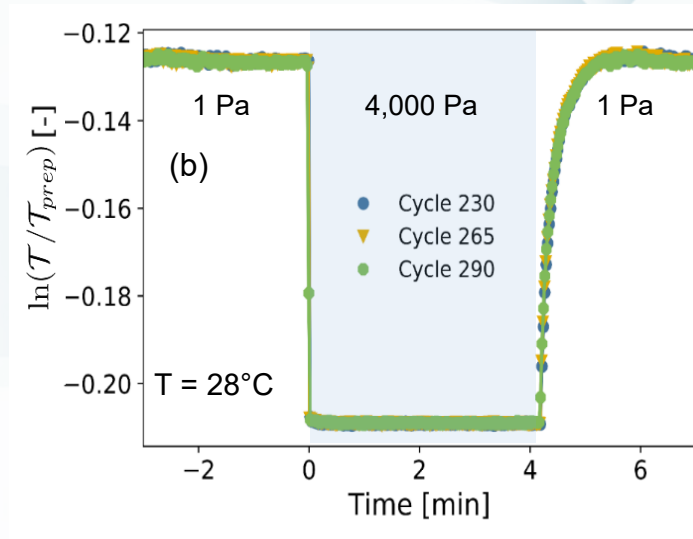
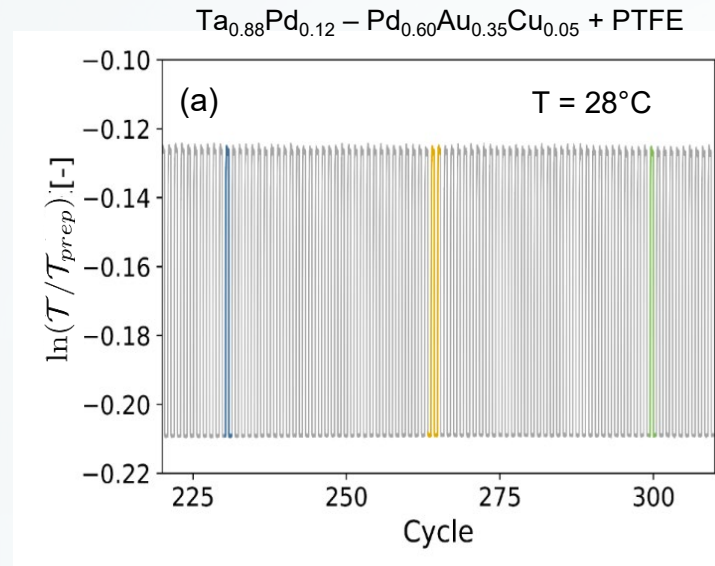
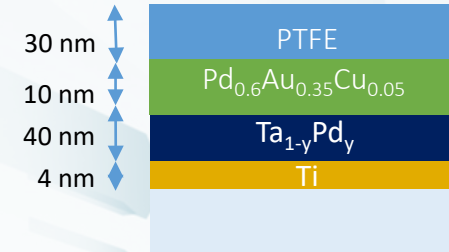
# Sensing speed improves by alloying with Pd



Optical response of a 40 nm film

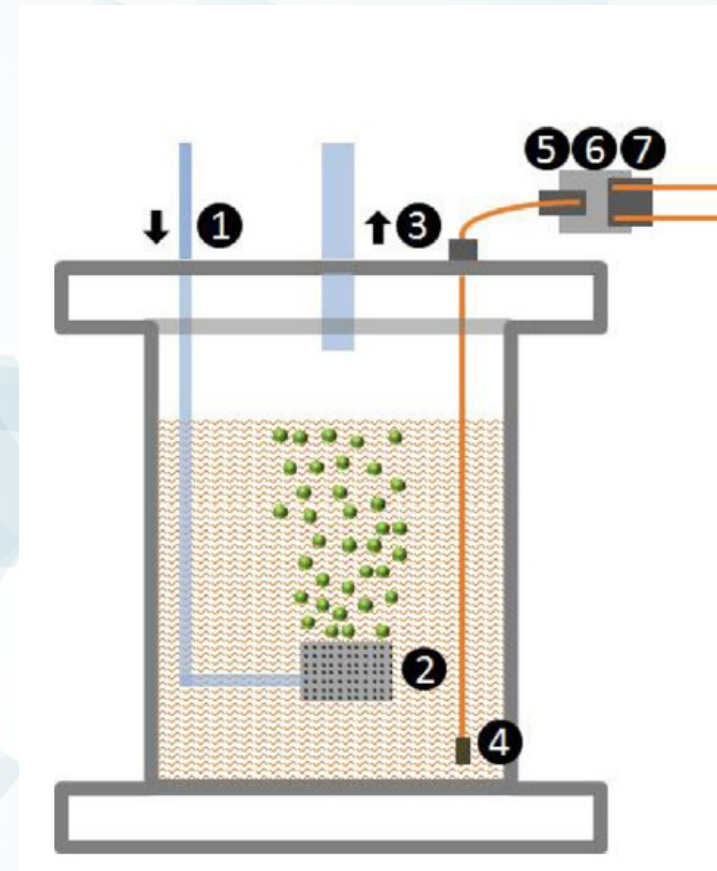
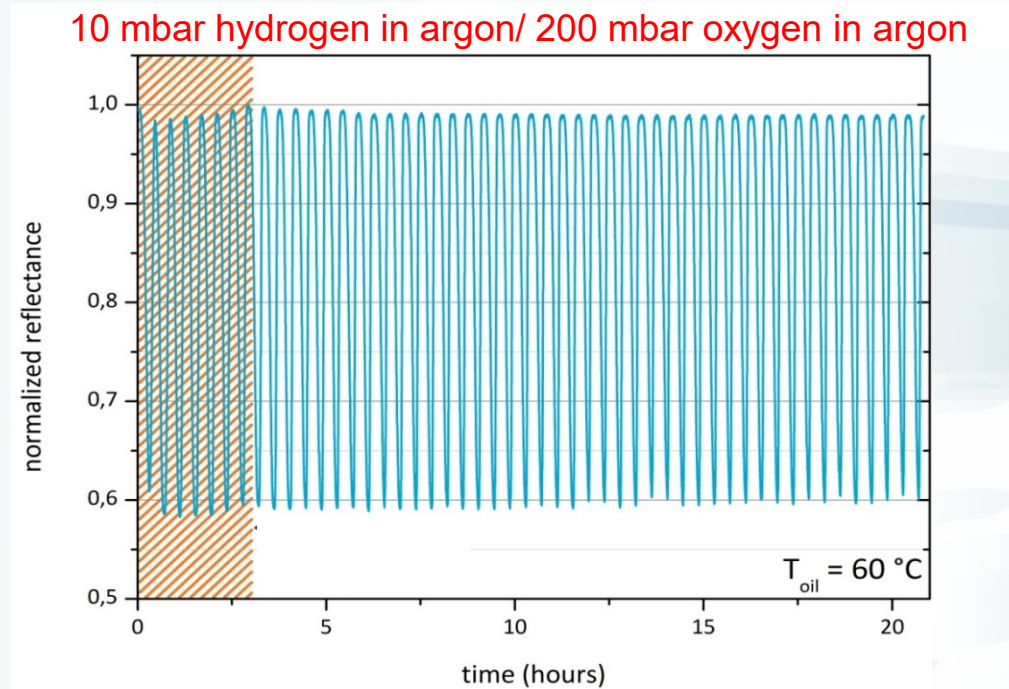


# Stability $Ta_{88}Pd_{12}$



Optical response is stable and reproducible for over at least 300 cycles.

# Measuring hydrogen dissolved in oil using a Teflon coated Pd/MH-based sensor



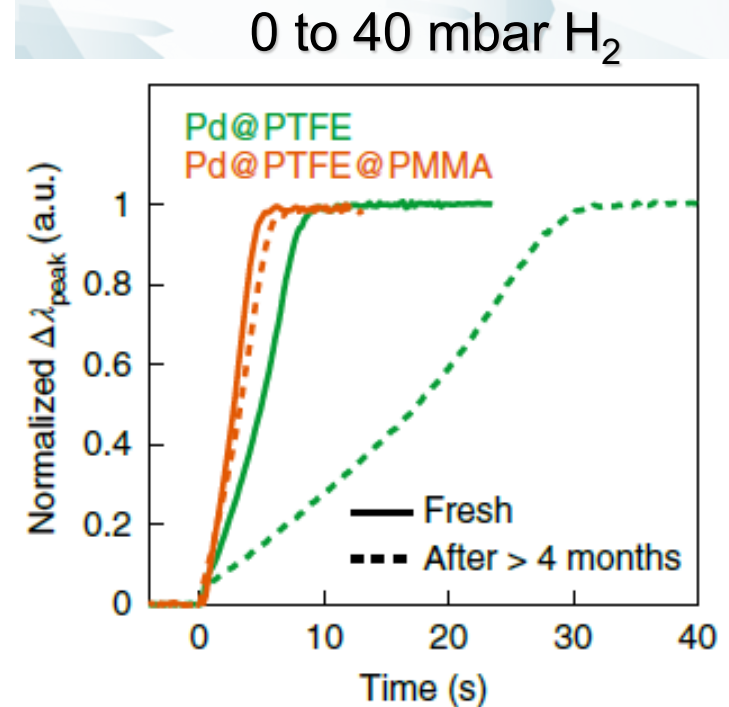
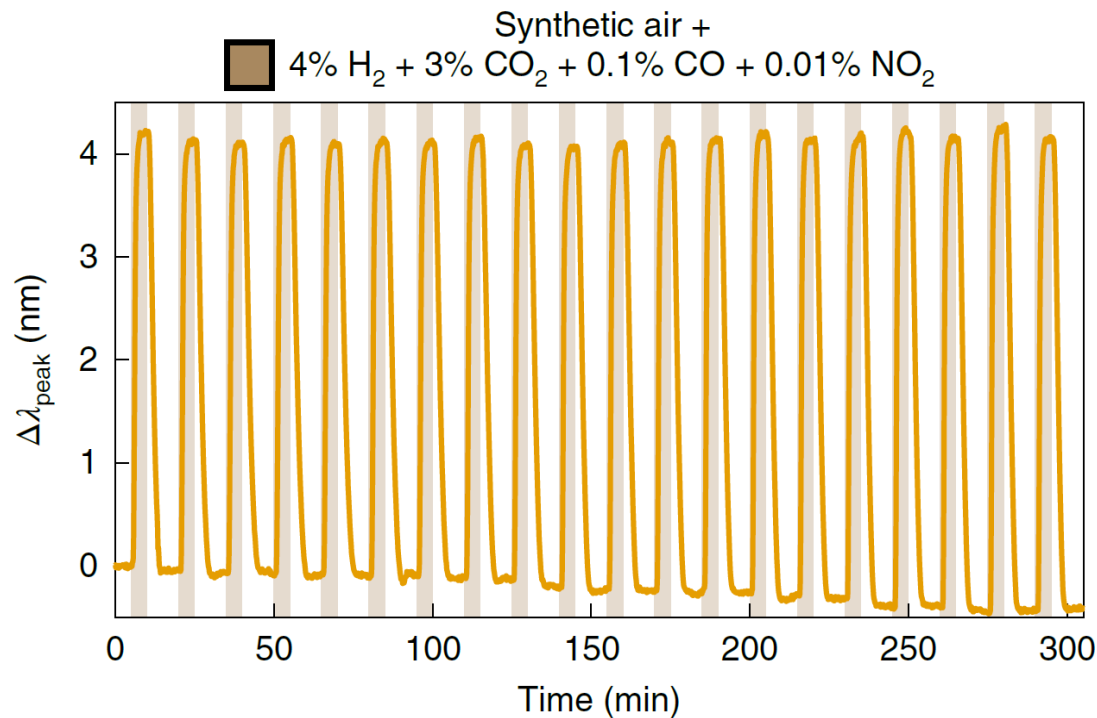
$$\text{Henry's law: } p_{\text{H}_2} = k_{\text{H}}(T) \cdot C_{\text{H}_2}$$

# PTFE and PMMA protection layers needed to prevent Pd poisoning

- PTFE shortens the response times
- PMMA provides protection against deactivation of the sensor by e.g. CO and NO<sub>2</sub>

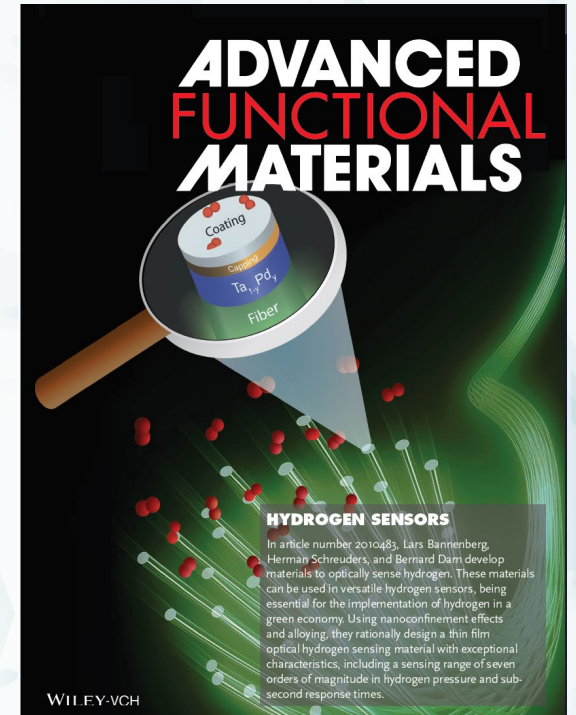


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UNIVERSITY OF TECHNOLOGY



# Conclusion

- Optical hydrogen sensors are an attractive way to reliably measure the hydrogen pressure.
- $Ta_{1-y}Pd_y$  is versatile hydrogen hysteresis-free sensing material that has a sensing range of at least 7 orders of magnitude in pressure
- $Ta_{1-y}Pd_y$  allows for sub-second response times at RT
- The Pd cap needs a protective coating to prevent poisoning in operando conditions





# Reversible photo-darkening in $\text{REO}_x\text{H}_{3-2x}$ thin films

