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**Sodium alanate thin films grown by
reactive sputtering**

Alانات

Promising storage material

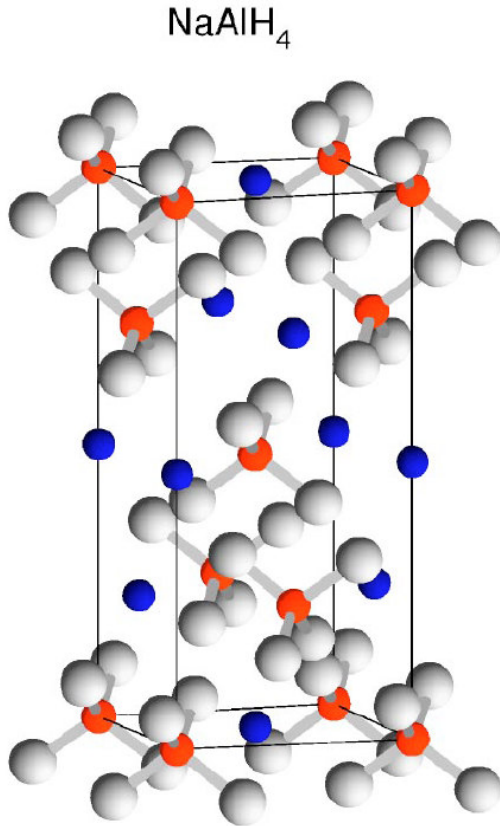
- High capacity (5.6%)
- Suitable thermodynamic stability
- Part of AlH_3 cycle

Open questions

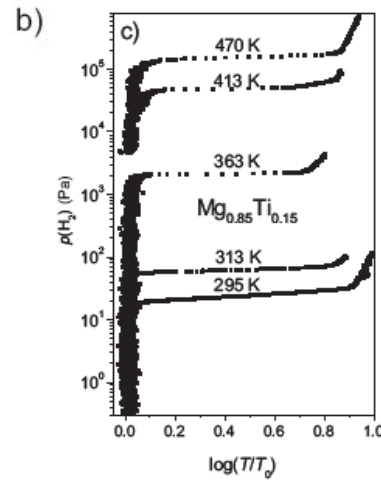
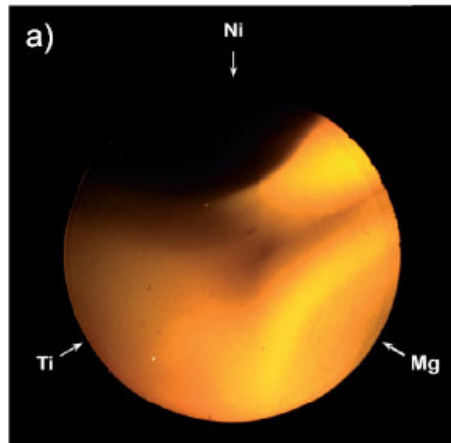
- Rehydrogenation conditions still severe (10-100 bar; 60-150 °C)
- Correlation among catalytic role, structure and location of the Ti for (de-)hydriding catalysis

Why thin films?

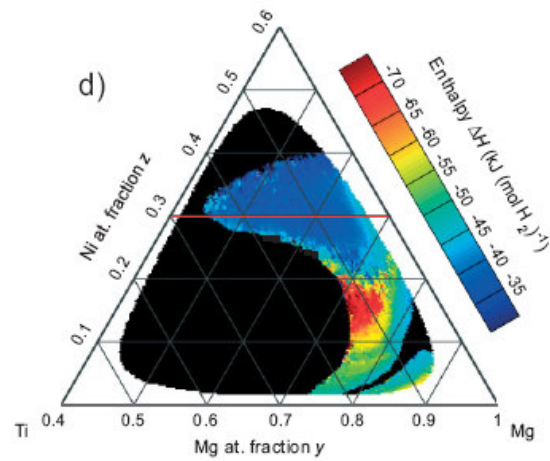
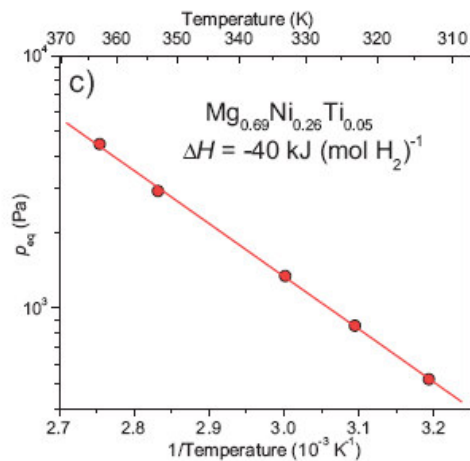
- MODEL SYSTEM: Use of combinatorial method (HYDROGENOGRAPHY)
- Dopant amount and distribution decided *a priori* (new artificial heterostructures)



Hydrogenography- Looking for a needle in the haystack

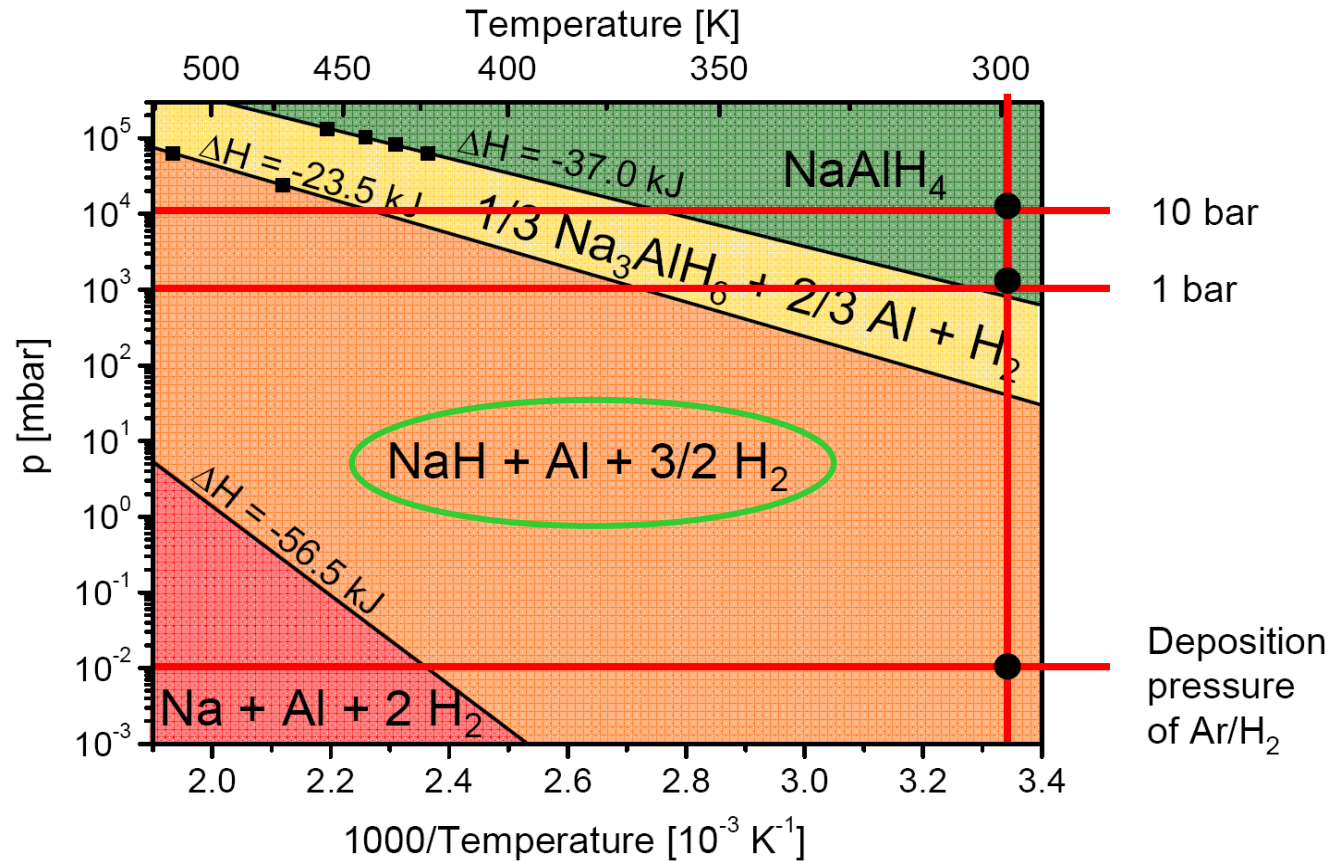


R. Gremaud et al.
Adv. Mater. (2007) 19, 2813



Deposition conditions: not really UHV...

Na/Al sputtering Argon + Hydrogen atmosphere

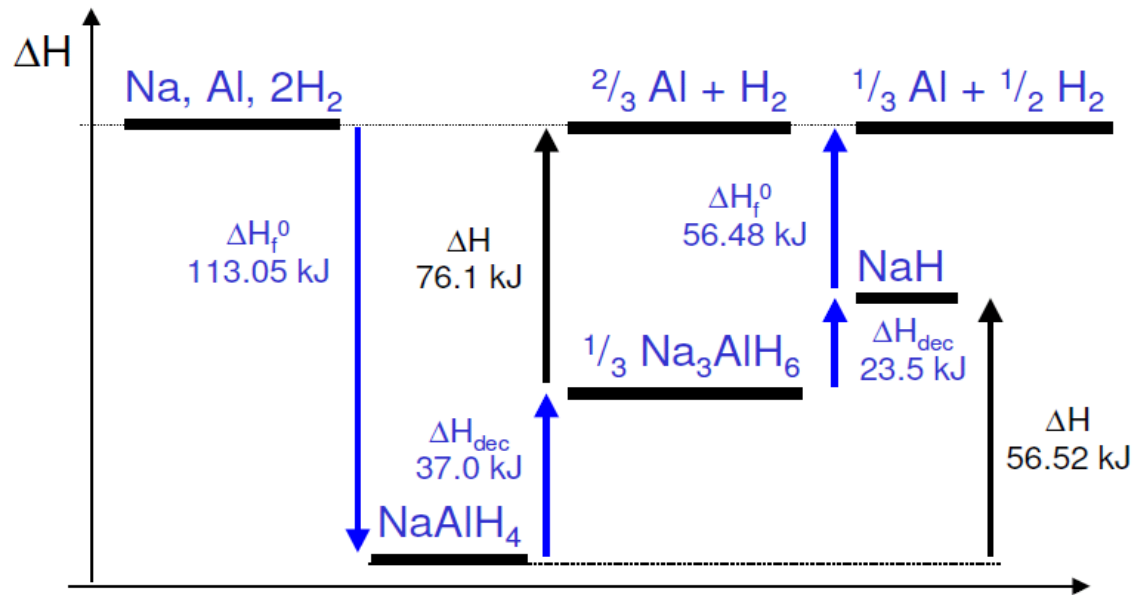
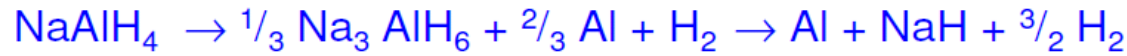
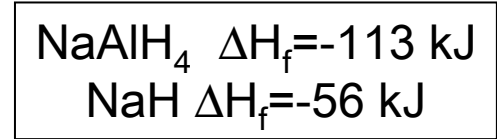


Bogdanovic et al., J. Alloys Compd. (1996),
Phase Diagrams of binary Hydrogen alloys, Ed. F. Manchester ASM (2000)

Enthalpies of formation

ENERGY LEVELS OF NaAlH₄

A. Züttel

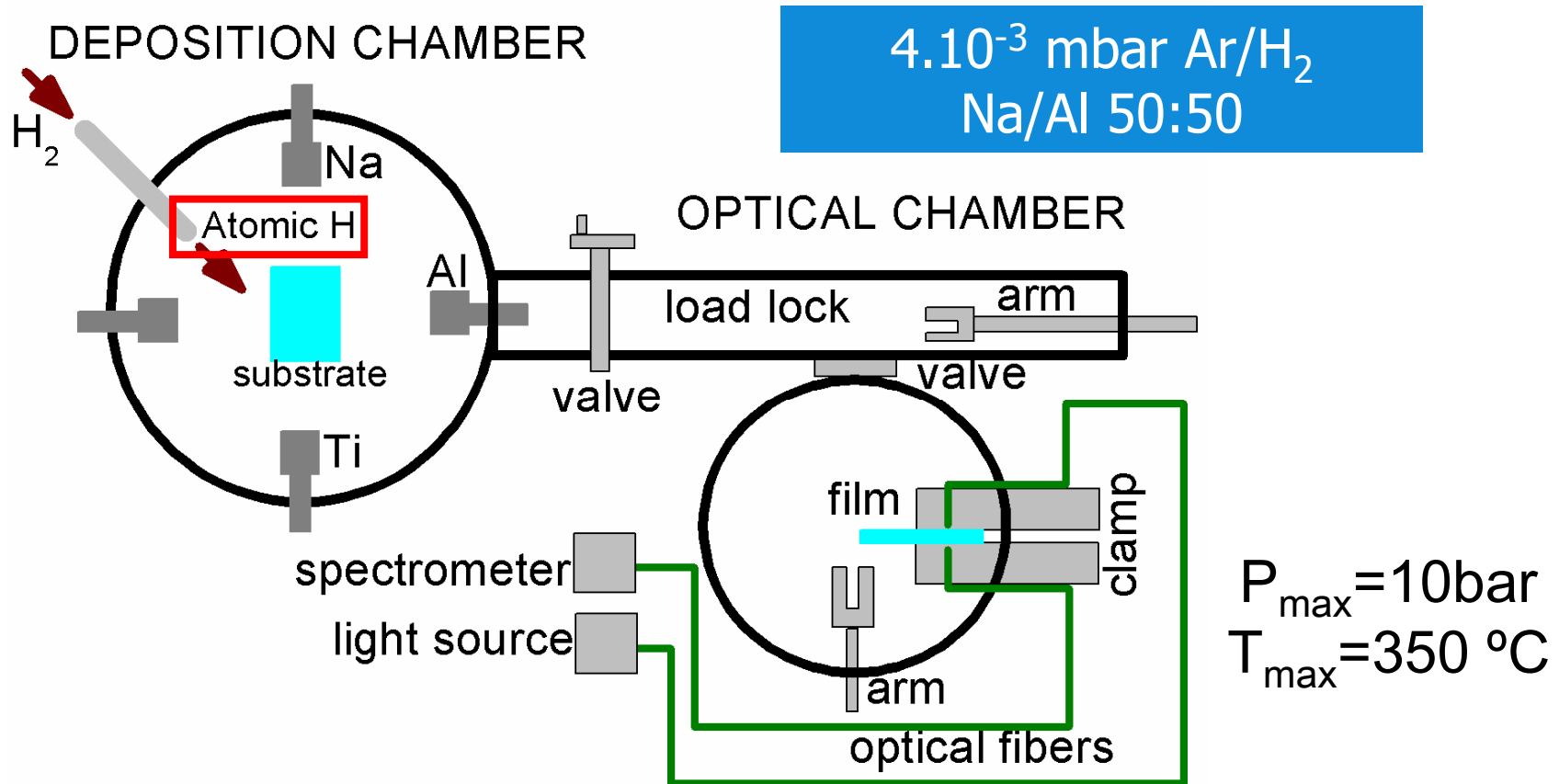


Ref.: Smith and Bass, J. Chem. Eng. Data 8 (1963), pp. 342;

Arroyo y de Dompablo M E, Ceder G, J. of Alloys and Compounds 364 (2004), pp. 6–12

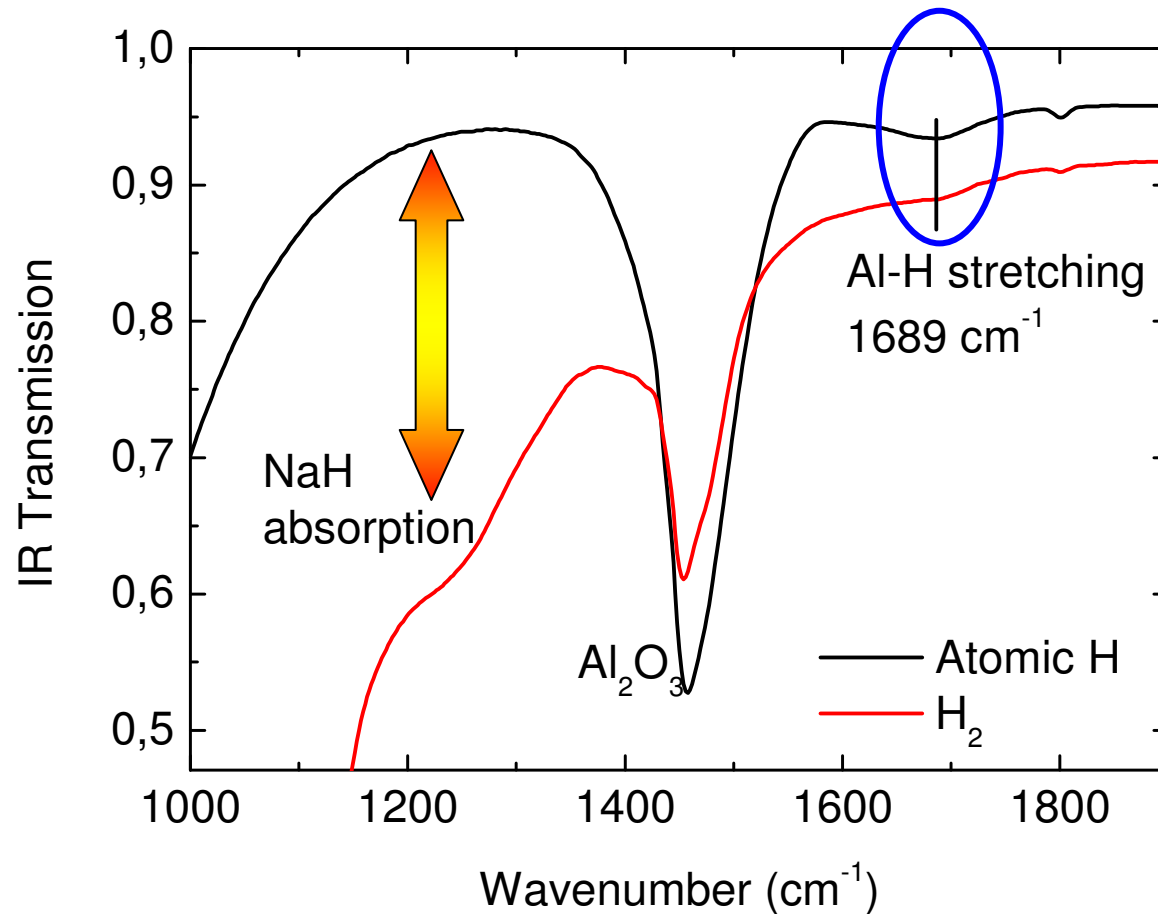
The energy gain per Na is largest for NaAlH₄

Experimental Setup



UV-VIS characterization in UHV, ex-situ IR characterization

Film deposited with/without atomic hydrogen (FTIR)

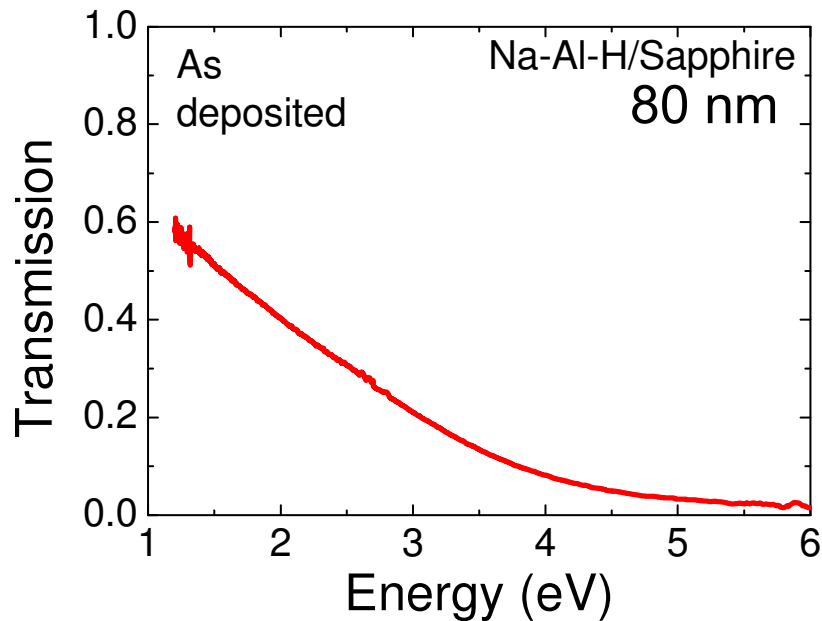


Molecular H₂:
-NaH is preferred
-NaAlH₄ phase
already formed

Atomic H:
-NaAlH₄ formed
-No NaH

As deposited film

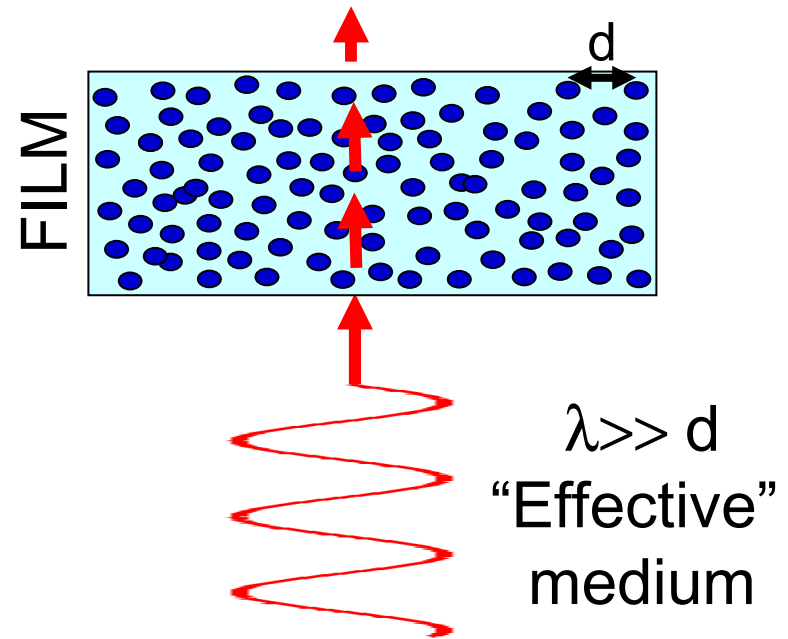
Optical response Vis-UV



As deposited film:
Transparent material+metallic impurities (7%) $\ll 200\text{nm}$

Transparent matrix (NaH? NaAlH_4 ?)

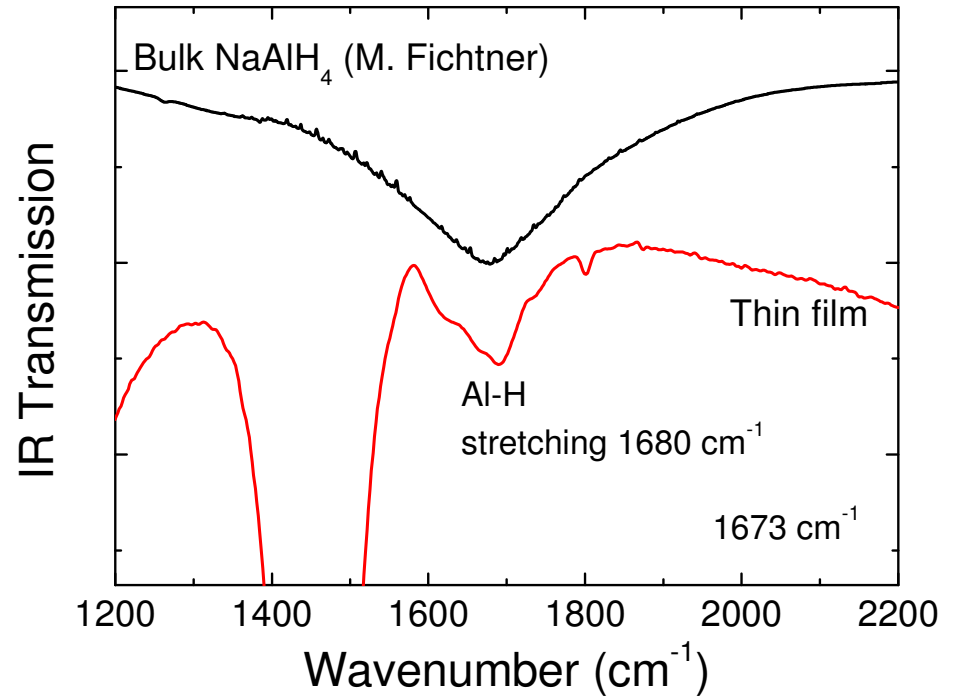
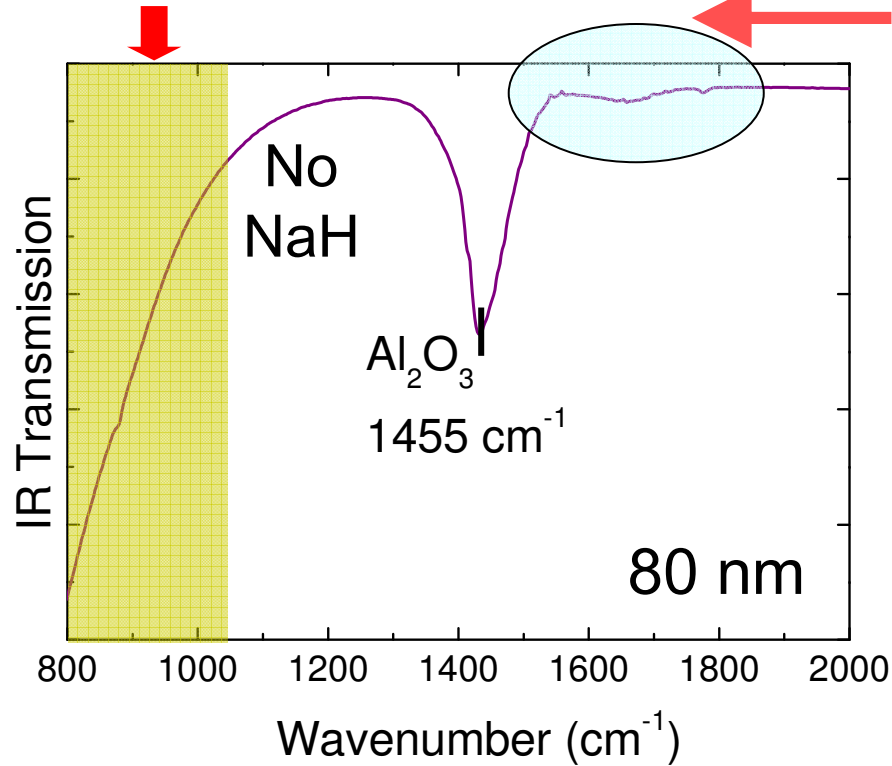
• metallic impurities



$200\text{nm} < \lambda < 1000\text{nm}$

As deposited film- FTIR

CaF₂ substrate

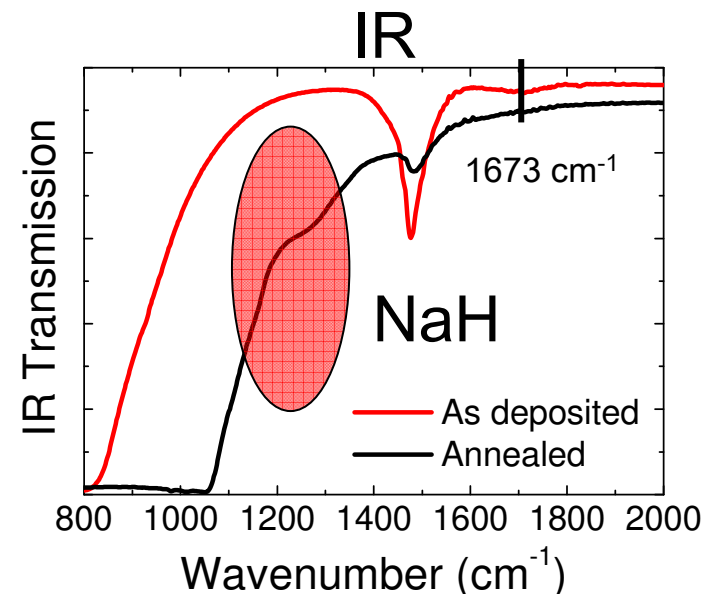
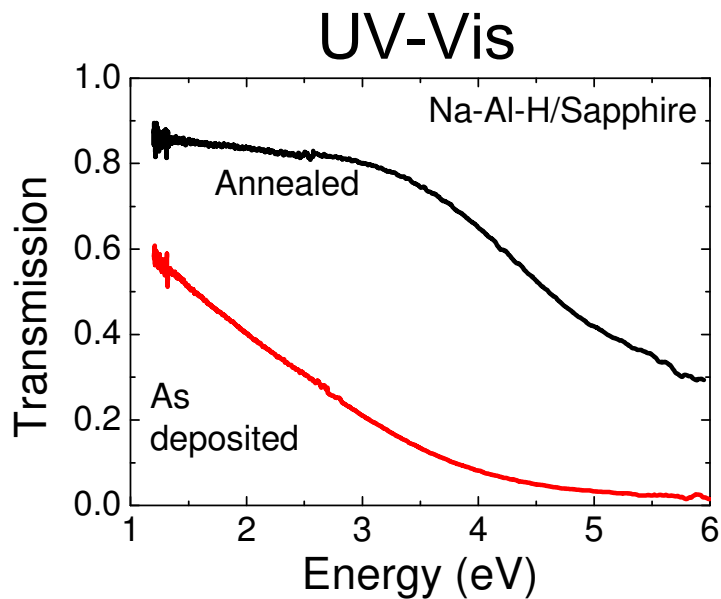


As deposited state:
NaAlH₄

Hydrogen desorption

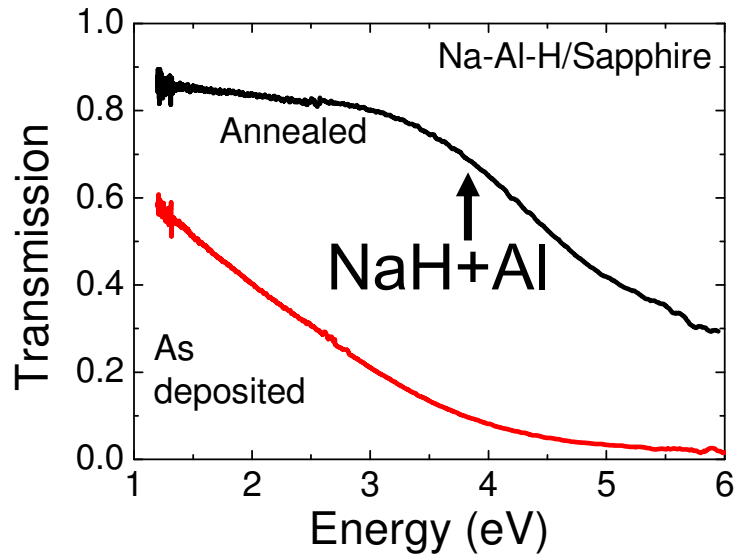
Upon annealing: $\text{NaAlH}_4 \rightarrow \text{NaH} + \text{Al}$

After annealing at 0.1 bar and 110 °C

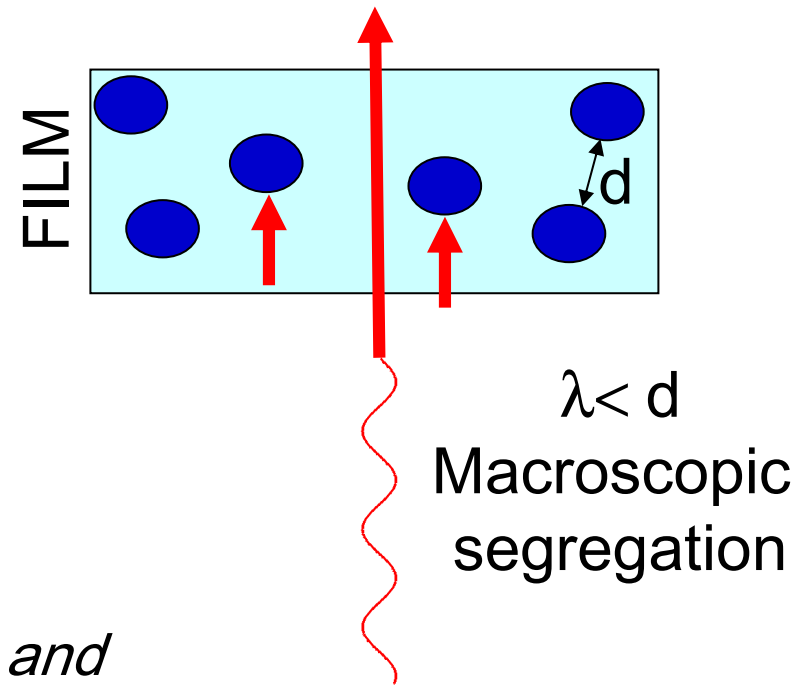


✓ $\text{NaAlH}_4 \rightarrow \text{NaH} + \text{Al}$

Phase segregation- Unloaded sample



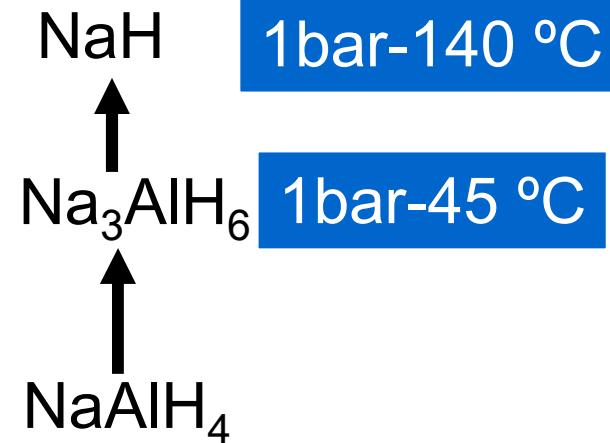
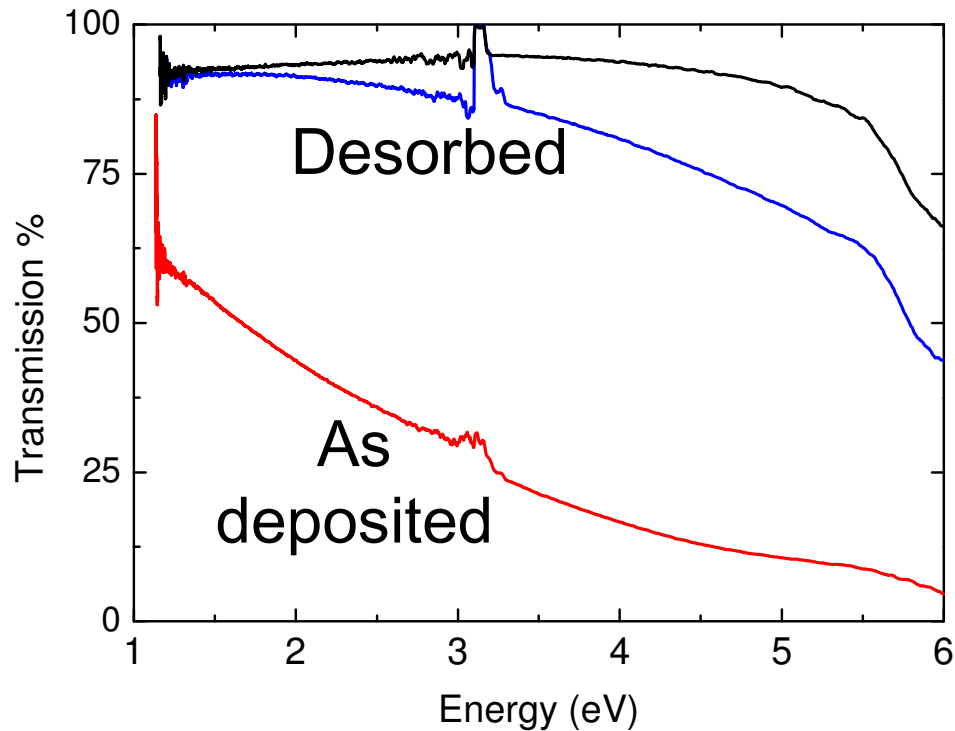
- Transparent matrix (NaH)
- Al metallic regions



No reloading up to 9.5 bar H₂. Effect of phase segregation?

We can study the hydrogen desorption and phase segregation with a thin film approach 200nm λ <math>< 1000\text{nm}</math> (IR-UV)

Hydrogen desorption-Two steps



Ti doping

Ti containing species:

Catalytic effect

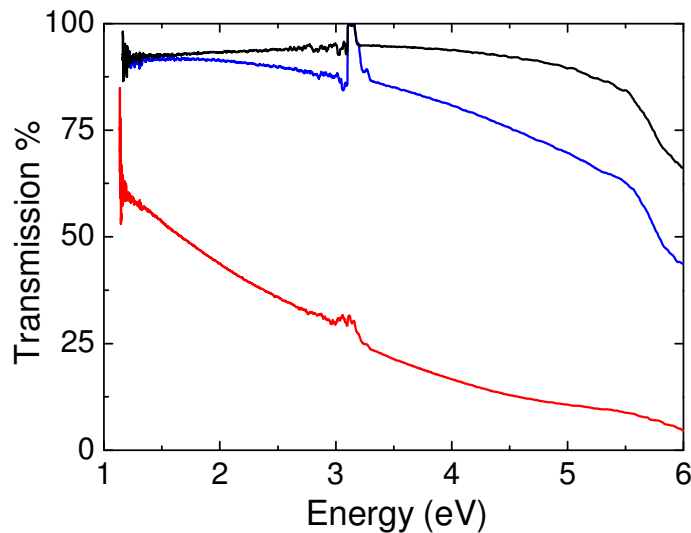
Grain refining

Correlation among catalytic role, structure and location of the Ti for (de-)hydriding catalysis

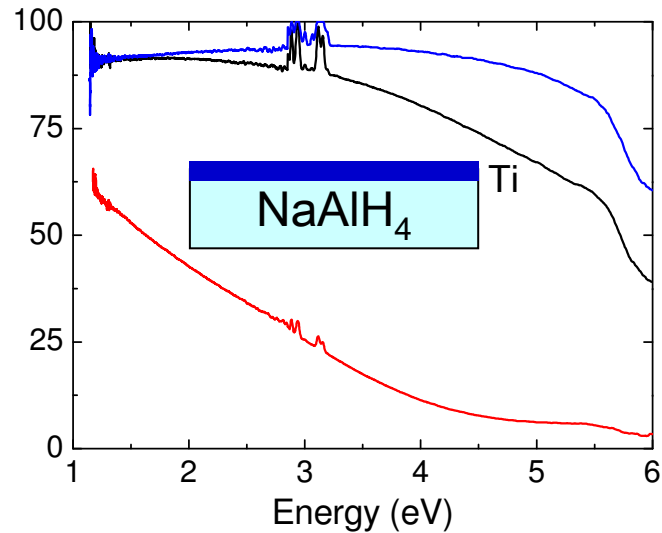
Thin film study: New artificial NaAlH_4/Ti heterostructures mixed at the nanoscale

Ti is believed to be in the zerovalent state:
Metallic Ti doping

Metallic Ti on top



Undoped



3nm Ti/80 nm NaAlH₄

1bar-140 °C

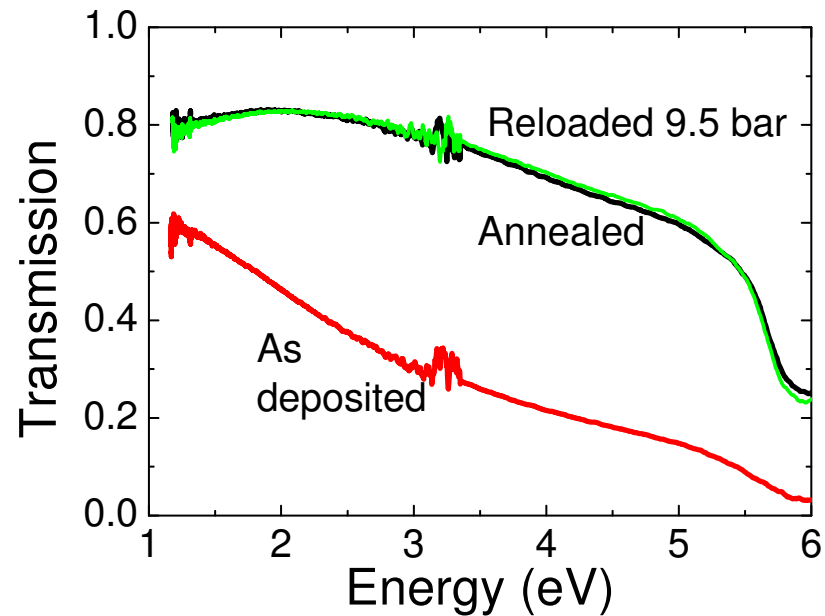
1bar-45 °C

Macroscopic Al segregation in both samples
Ti present as TiH₂

Ti on the bottom



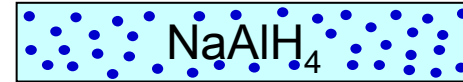
3nm Ti on the bottom



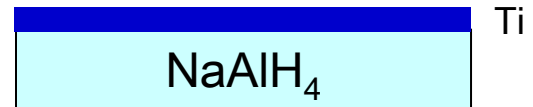
Macroscopic Al segregation
Ti remains metallic

Metallic Ti doping

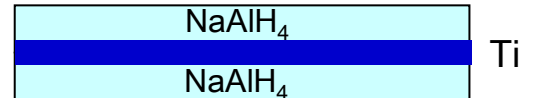
-Co-sputtered 2.5% 5% 8% 30%



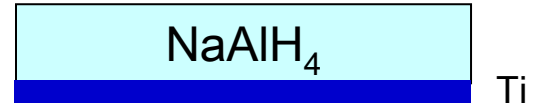
-3nm Ti on top



-3nm gradient Ti (0-100%) on top



-“Sandwiched” Ti layer (3nm)



- 3nm Ti on the bottom



- Multilayer (8nm NaAlH₄+1nm Ti)x11

Metallic Ti is not preventing the macroscopic NaH and Al segregation
Dopant remains inert (TiH₂ or Ti)

Summary and future work

- Successful reactive sputtering of NaAlH_4 thin films
- Study of the hydrogen desorption, phase segregation and role of dopants (metallic Ti)

Thin film approach can be used for a model study of technologically relevant lightweight metal hydrides

M.F. et al. *Applied Physics Letters* **95**, 121904 (2009)

Future:

- Study of the mechanism of catalysis (TiCl_3)
- Other alanates (LiAlH_4 , KAlH_4)
- Hydrogenography on compositional gradients