The Hydrogenation Kinetics of a Magnesium Thin Film: An in-situ Neutron-Reflection and Optical-Transmission Study of a Two-Phase System

L.J. Bannenberg, H. Schreuders, L. van Eijck, J.R. Heringa, N.J. Steinke, R. Dalgliesh, B. Dam, F.M. Mulder, A.A. van Well

Bannenberg *et al.*, JPhysChemC **120** (2016) 10185

OUTLINE

- Introduction

  - Nano structuring of insertion materials
  - Hydrogen in Mg thin film

- Hydrogen loading and unloading kinetics studied with

  - optical transmission
  - neutron reflectometry (spec / offspec)

- Discussion

ENERGY STORAGE MATERIALS

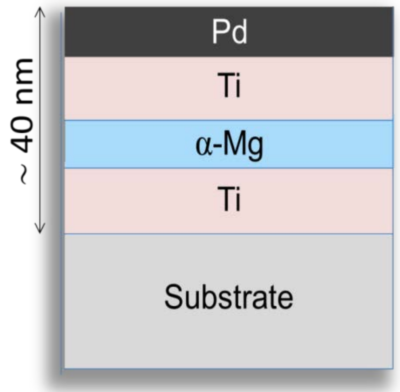
Batteries / Hydrogen storage

- Batteries: Li insertion materials (electrodes)
  - two phases: Li poor and Li rich (*e.g.* Li_xTiO_2 Li_yTiO_2) in bulk: x = 0.05, y = 1
  - improve kinetics: nanostructuring → shorter diffusion paths
  - also: change thermodynamics → changing solubility limits: $x > 0.05$, $y < 1$

- H storage: H insertion materials (e.g. Mg)
  - two phases: e.g. Mg (α-phase) and MgH_2 (β-phase)

question of this study:
what is the influence of nanostructuring for the latter system?

MODEL SYSTEM

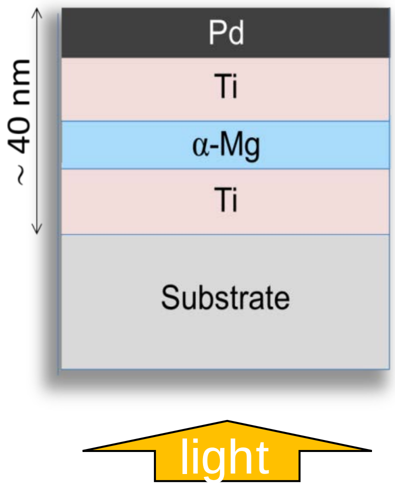


nano films (instead of nano grains)

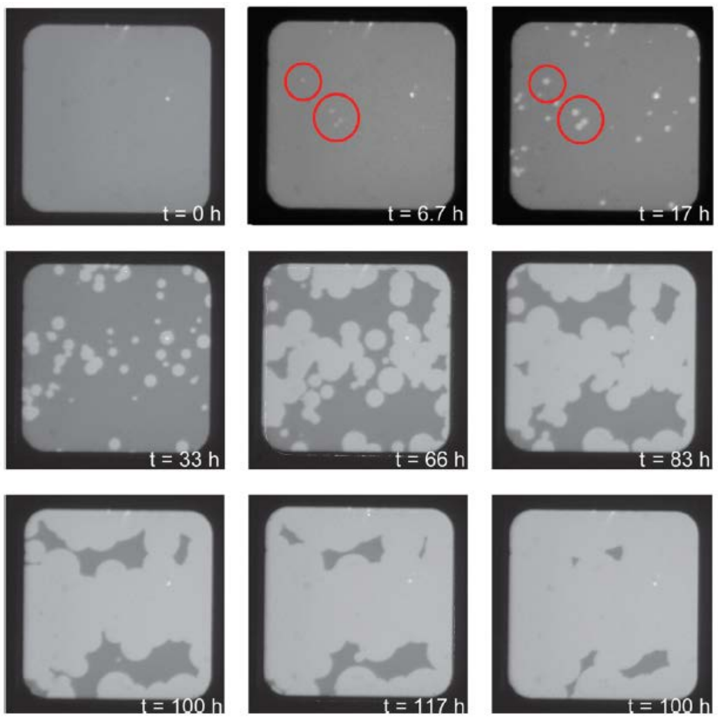
- better accessible for experimental methods
- better control of dimensions
- Pd: prevent oxidation
- Ti: prevent interdiffusion Pd - Ti

Mooij and Dam, PCCP **15** (2013)2782

PREVIOUS STUDIES:
optical transmission experiments

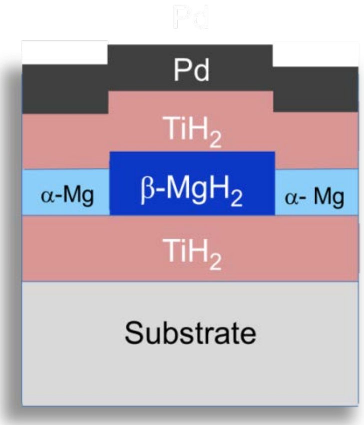


H loading kinetics



p_{H2} =70 Pa, T = 90 ^{o}C

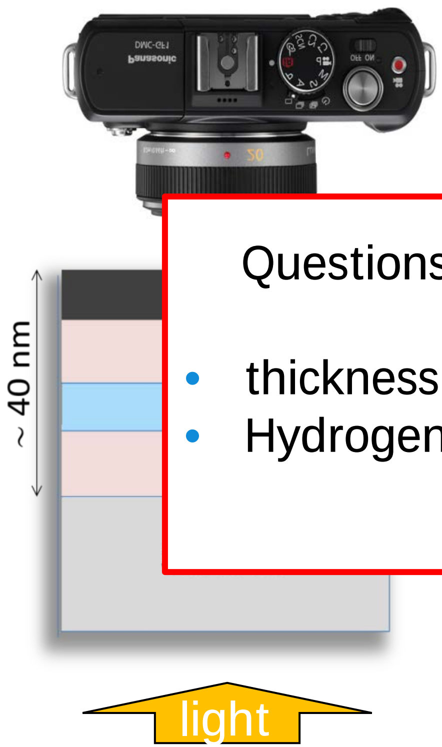
Interpretation



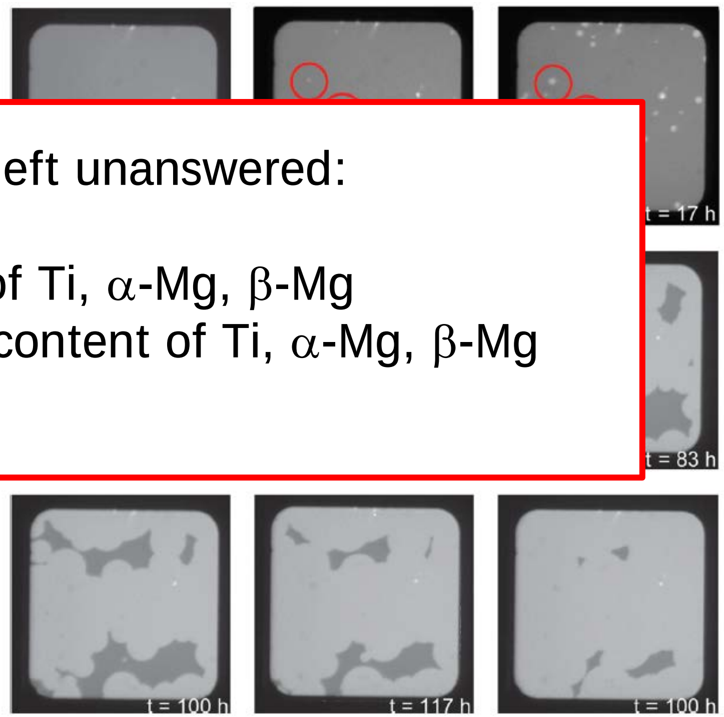
Coexistence of metallic α-Mg and insulating β-MgH_2 during hydrogenation

Mooij and Dam, PCCP **15** (2013) 2782

PREVIOUS STUDIES:
optical transmission experiments

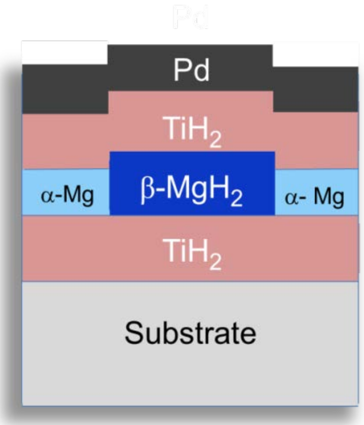


H loading kinetics



p_{H2} =70 Pa, T = 90 °C

Interpretation



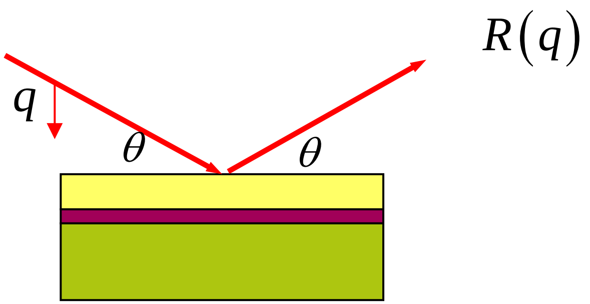
Coexistence of metallic α-Mg and insulating β-MgH_2 during hydrogenation

Questions left unanswered:

- thickness of Ti, α-Mg, β-Mg
- Hydrogen content of Ti, α-Mg, β-Mg

NEUTRON REFLECTOMETRY

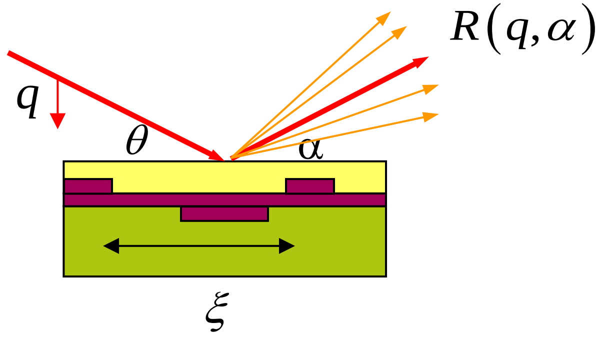
specular reflection



$R(q) \rightarrow$ depth profile

NEUTRON REFLECTOMETRY

off-specular reflection



$R(q,\alpha) \rightarrow$ in-plane structures
(if ξ < coherence length)

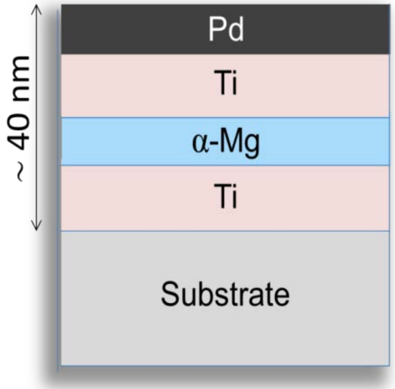
$$q = \frac{2\pi\theta}{\lambda}$$

time-of-flight:
constant angle θ,
broad wavelength band

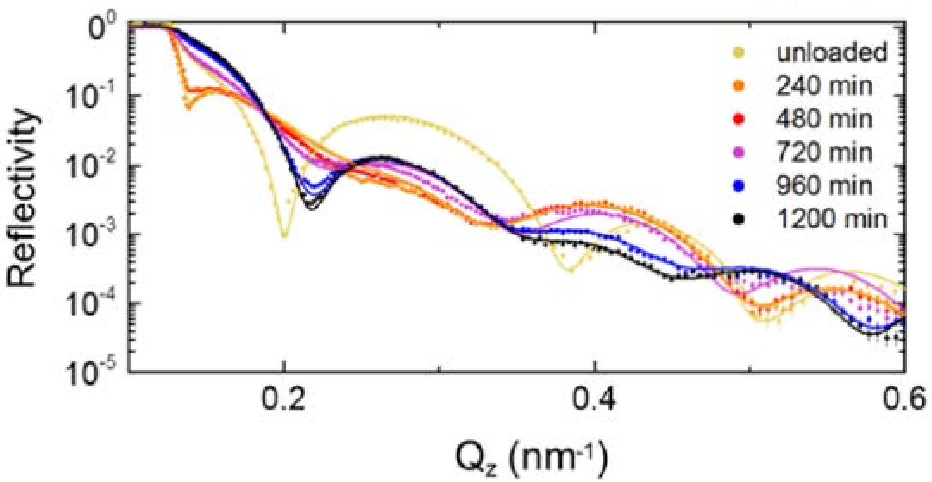
OffSpec, ISIS, UK

EXPERIMENTS

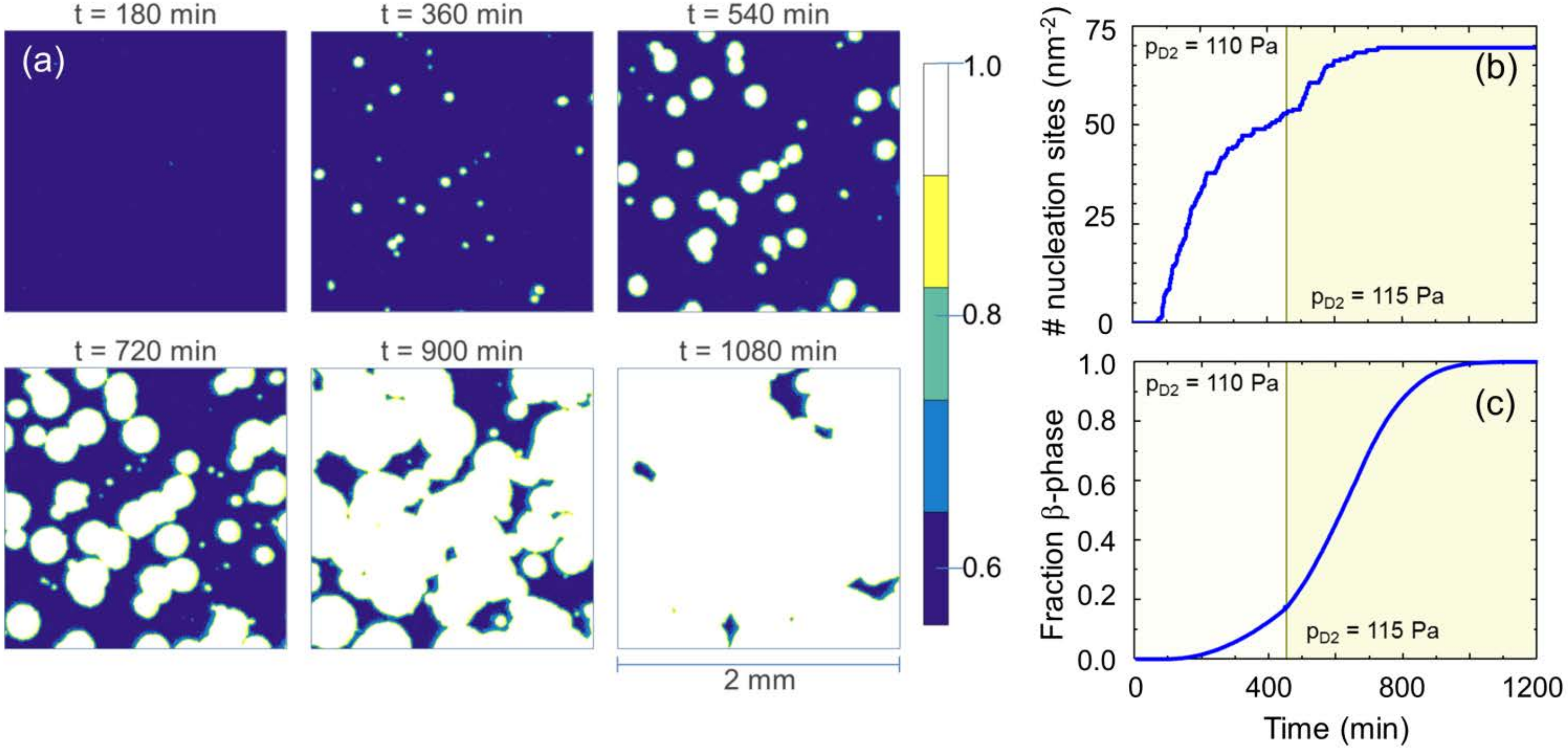
- Simultaneous optical transmission and NR
- D instead of H for enhancing contrast
- Kinetic measurements (event mode)



Example specular reflection:



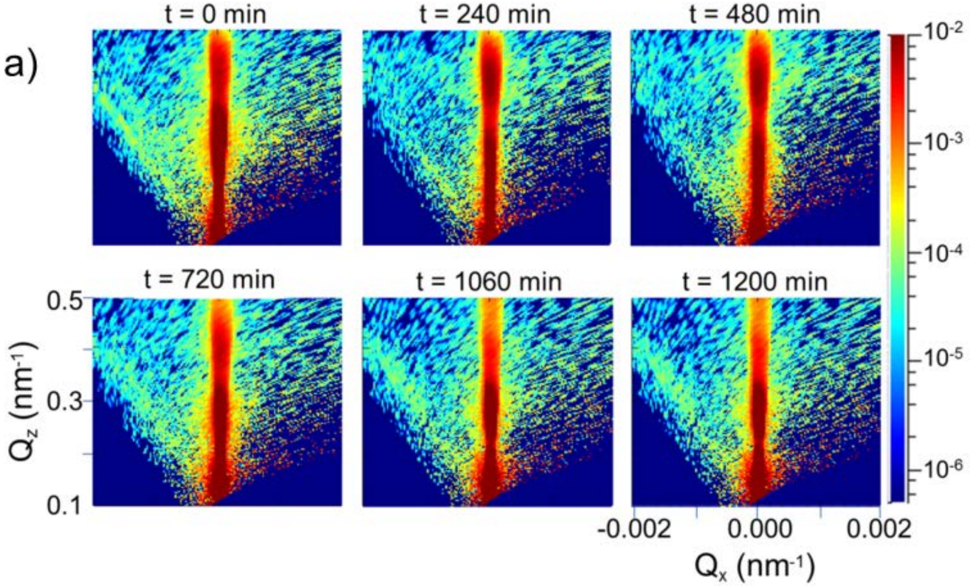
RESULTS HYDROGEN LOADING
Optical transmission

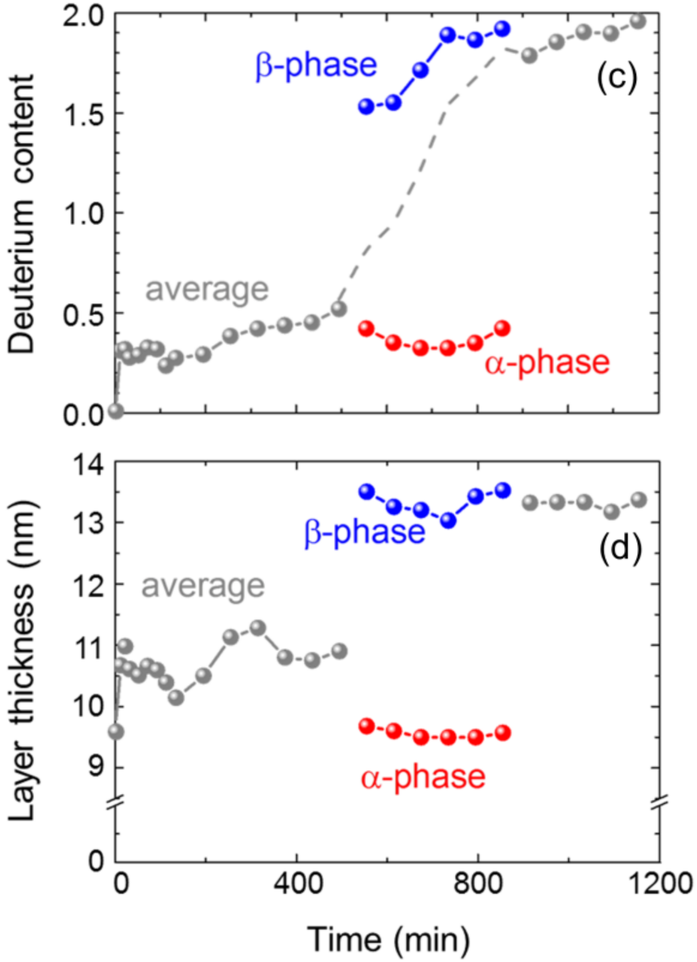


- A Nucleation-and-Growth process governs the transition from metallic α-Mg and insulting β-MgH_2.

RESULTS HYDROGEN LOADING

Neutron reflectometry

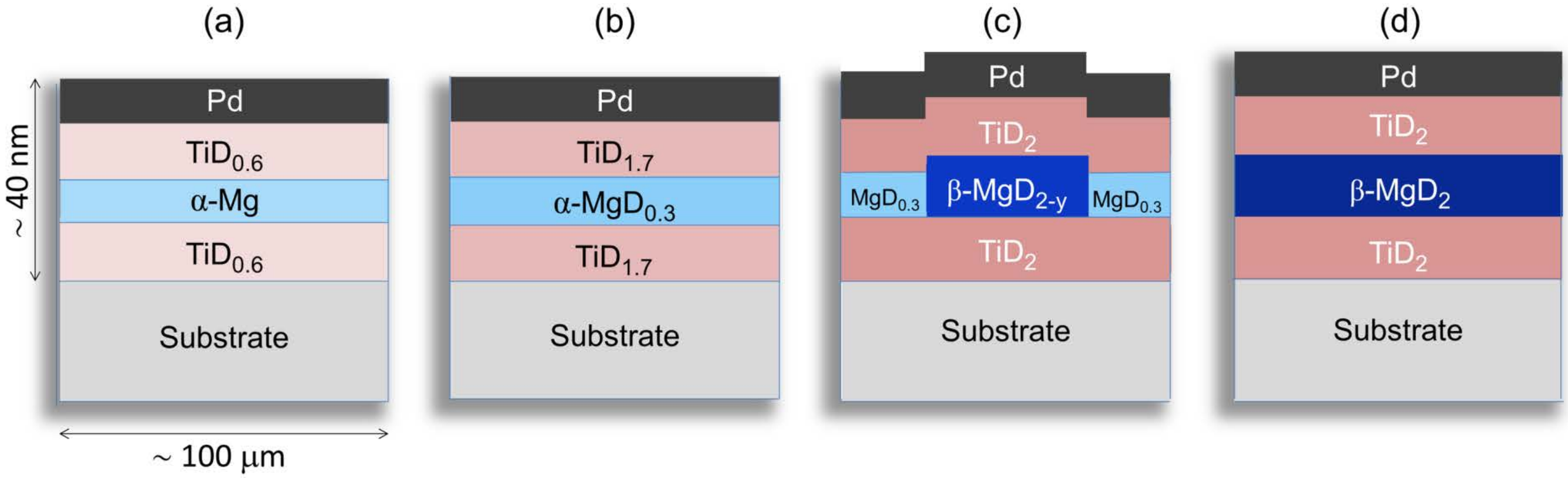




- We can discriminate between α-MgD_x and β-MgD_{2-y} when the domains are larger than coherence length
- Nanostructuring causes nonstoichiometric phases and increases solubility limits

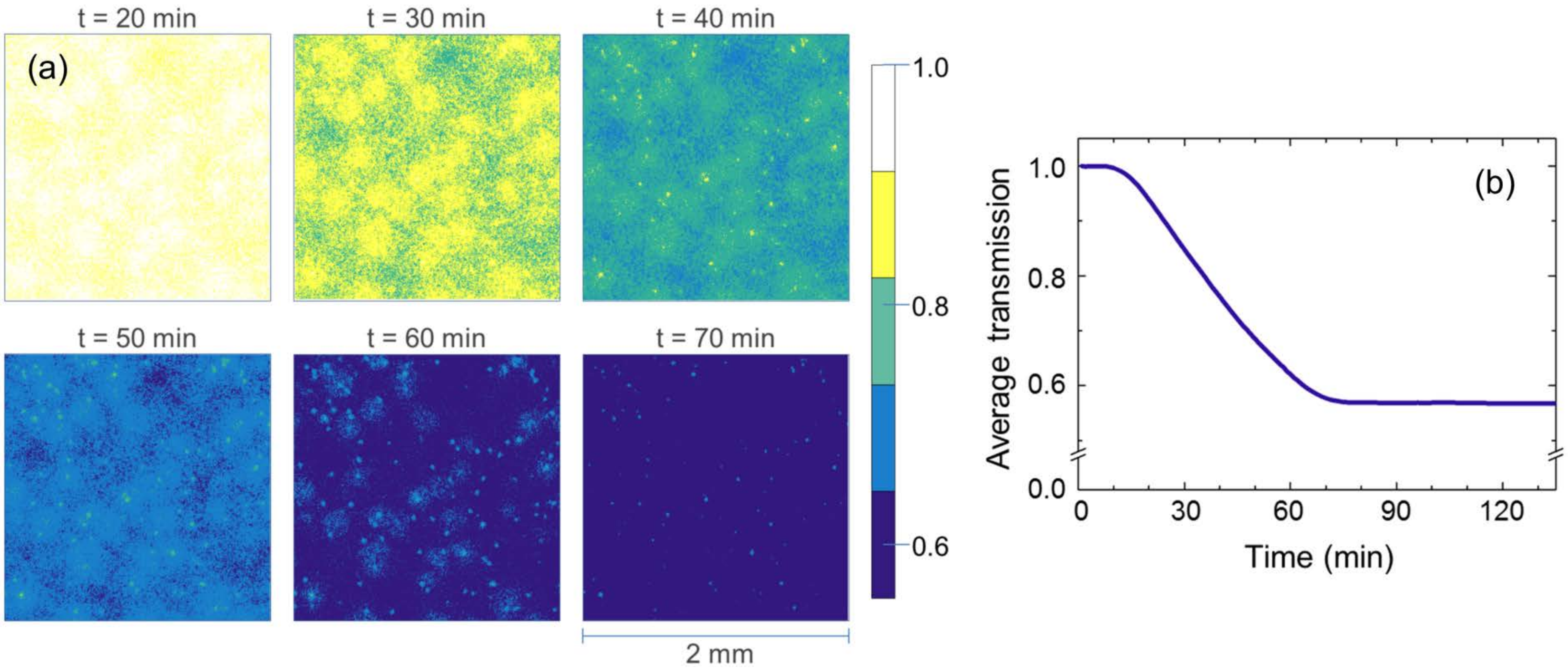
NEW HYDROGEN LOADING MODEL

- We present a new model based on the optical transmission and neutron reflectometry results
- The model is an extended version of the previous model by Mooij and Dam (2013)



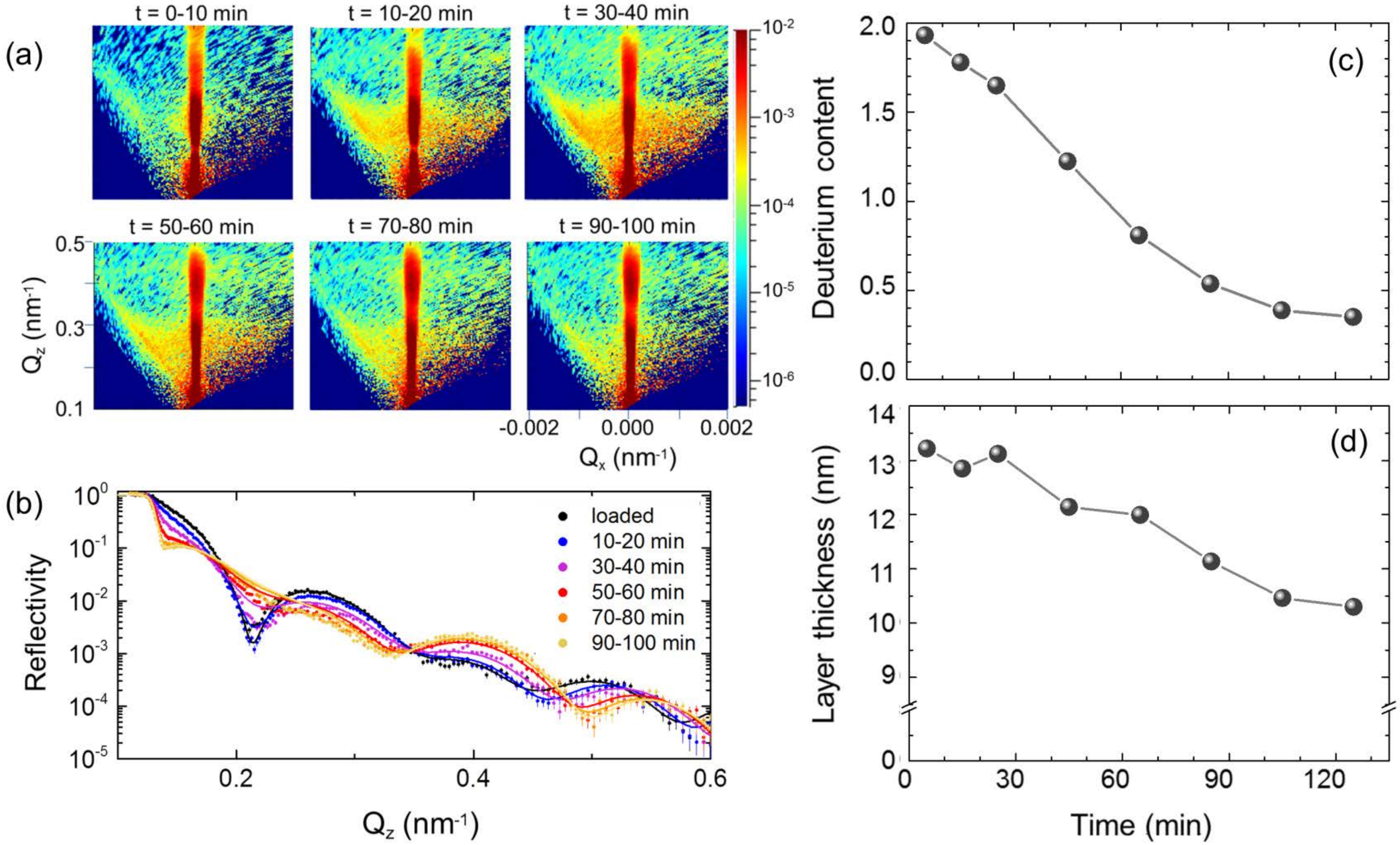
RESULTS HYDROGEN UNLOADING

Optical transmission



- Many nucleation sites (much more than during loading)
- Small domains (smaller than camera resolution, ~ 2 μm)

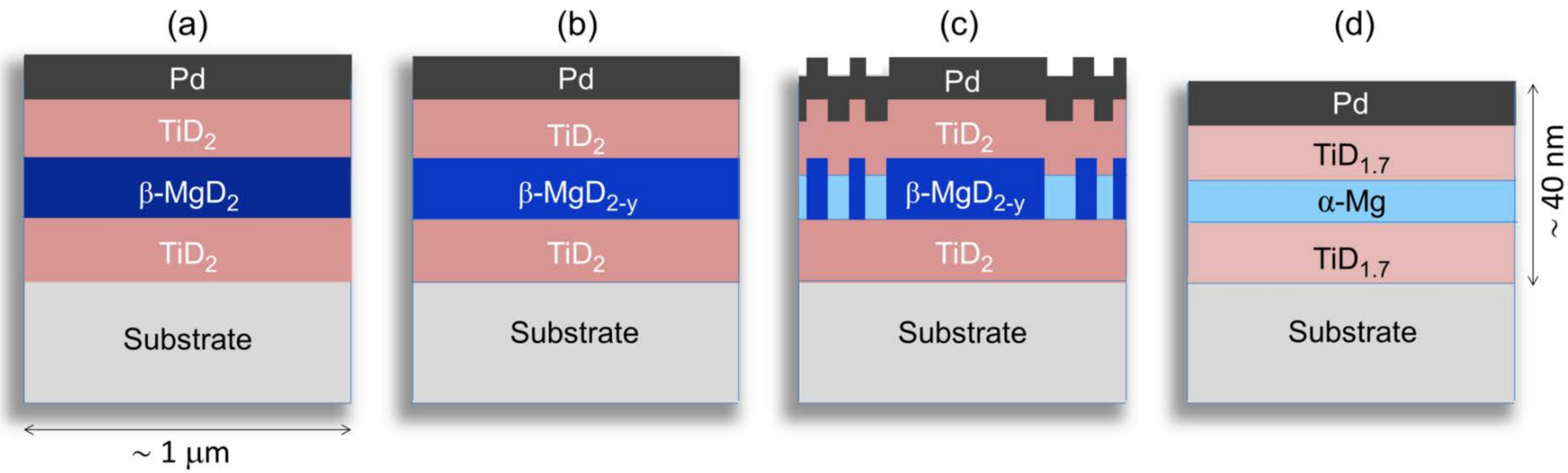
RESULTS HYDROGEN UNLOADING
Neutron reflectometry



- Domains smaller than coherence length: only average values can be determine

RESULTS HYDROGEN UNLOADING

New model



CONCLUSIONS

- Combination of optical transmission and neutron reflectometry measurements give detailed information about the deuterium loading and unloading kinetics
- The deuterium content of both Mg-phases deviate from the stoichiometric values in the bulk system during hydrogenation
- This has the important implication that kinetics are not only enhanced by shortened diffusion limits, but also by increased solubility limits