

Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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This presentation does not contain any proprietary or confidential information

- **Timeline**

- Project Start Date: January 2005
- Project End Date: 2/28/2010
- Percent Completion: ~80%

- **Budget**

- Total Project Funding: \$997,921
 - DOE Share: \$778,828
 - Contractor Share: \$199,093
- Funding Received FY08: \$150,000/\$37,500
- Funding Received FY09: \$150,000/\$37,500 (Planned)

- **Barriers Addressed**

- **B:** Weight and Volume
- **M:** Hydrogen Capacity and Reversibility
- **N:** Lack of Understanding of Hydrogen Physisorption and Chemisorption.

- **Partners**

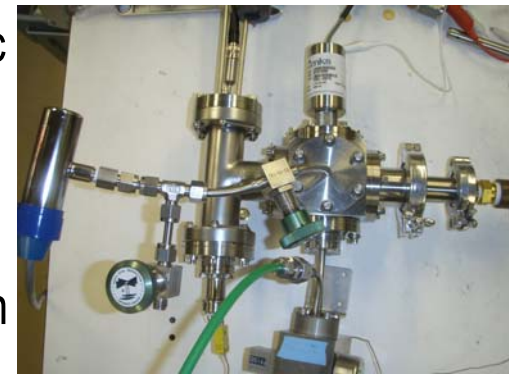
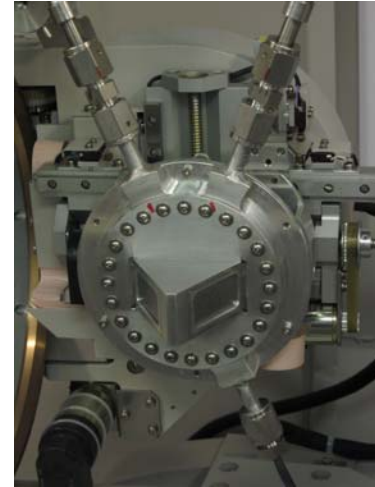
- HRL Laboratories: collaborations about new material systems and complex/destabilized hydride system development
- University of Pittsburgh: collaborated to obtain interfacial energies for Mg/MgH₂ interface
- NIST Center for Neutron Research: collaboration to investigate reacting films using neutron reflectivity

Relevance - Objectives

- **Develop fundamental understanding of metal hydride reaction kinetics**
 - Kinetics limit practicality and reversibility of many promising metal hydride material systems
 - Mg, Mg₂Si, Mg(AlH₄)₂, Li₄Si, NaAlH₄, LiBH₄+MgH₂, etc.
 - Initial work on Mg₂Si showed that kinetic issues prevent system from achieving reversibility
 - Catalyst additions have shown some success in improving kinetics for some systems (ie. Ti in NaAlH₄), but little is known about the nature of these effects
 - Little is known about the kinetic mechanisms present in these systems, and in order to improve the kinetics for any of these metal hydride systems a sound understanding must be developed
- **Develop understanding of metal hydride nanostructure thermodynamics**
 - Many systems suffer from inappropriate thermodynamics (equilibrium pressure)
 - Mg, Al
 - Continuum modeling suggests that reaction thermodynamics should be modified by reducing particle size to the nanometer regime
- **Develop understanding of metal hydride structures during phase change**
 - Material structure can play important role in reaction kinetics, especially during solid-state phase transformations such as those in metal hydride reactions
 - Understanding the interplay between material structure and reaction kinetics may provide insight on how to successfully engineer new materials with improved kinetics and storage properties

Approach

- **Thin Film Model Systems**
 - Physical vapor deposition allows nearly atomic level composition control
 - Appropriate substrate choices allow for microstructural control
 - Initial experiments with Mg films have validated the approach as results concur with bulk Mg measurements where appropriate
 - Diffusion limited hydride growth, crystallographic orientations
- ***In-Situ* Structural Characterization**
 - Custom designed hydrogen pressure chamber for x-ray studies
 - Real time structural analysis for kinetic studies (refueling time)
- **Thin Film and Nanoparticle Uptake Monitoring**
 - Quartz crystal microbalance (QCM) chamber for thermodynamic measurements (P_{eq}) in thin film and nanoparticle samples
- **Transition To More Complex Material Systems**
 - After establishing techniques and approaches using model system, move to two component system (Mg/Ti, Mg/Al) and then more complex systems involving mass transport and phase segregation



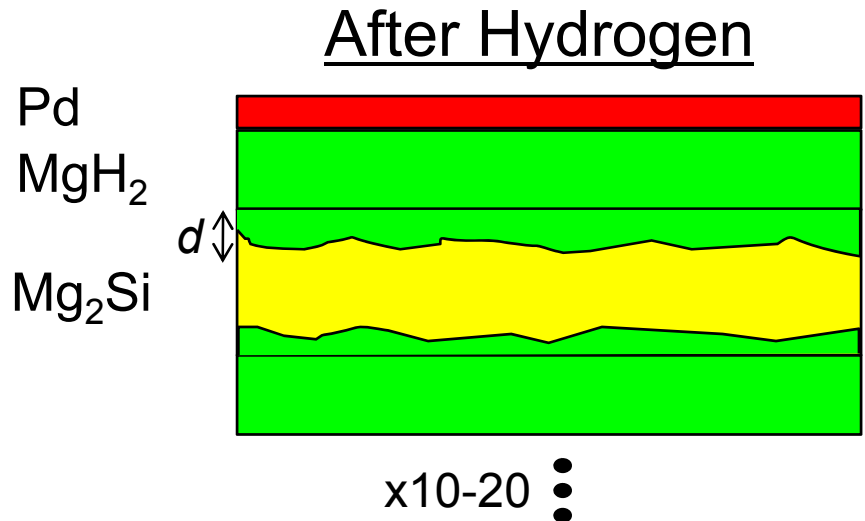
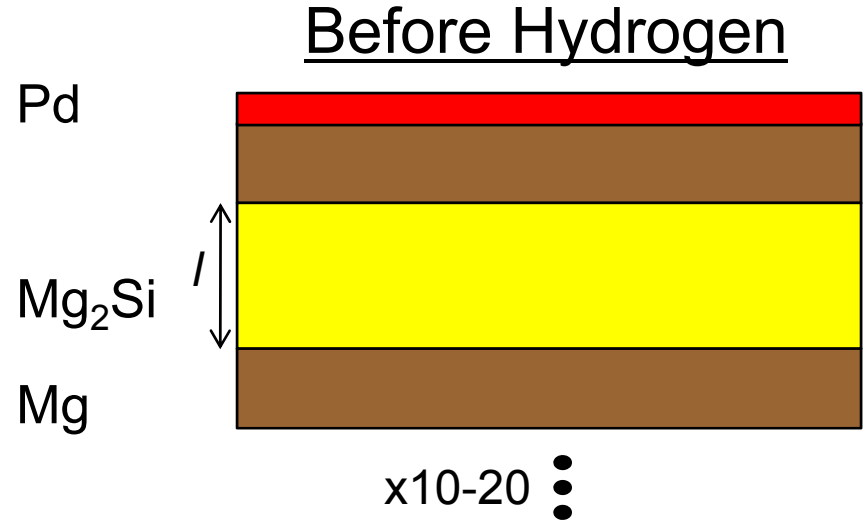
Approach - Milestones

Date	Milestone or Go/No-Go Decision
07/2008	<p>Milestone: Model kinetic transformation processes for thin film metal hydride material systems.</p> <p>Status: New model developed to describe moving planar interface kinetics in thin film samples</p>
05/2008	<p>Milestone: Investigate structural correlations in other material systems.</p> <p>Status: New material systems introduced into all aspects of research: Mg/Al, Mg/Ti. Nanostructured materials under investigation.</p>
03/2008	<p>Milestone: Investigate effects of cycling on new material kinetics.</p> <p>Status: Data collected for Mg/Ti system with cycling, data processing underway and results forthcoming.</p>
10/2008	<p>Milestone: Measure thermodynamics of nanoparticle phase transformations and begin verification of model.</p> <p>Status: First (mixed) results obtained for nano-Mg system. Verification of results underway.</p>

Progress – Mg₂Si System

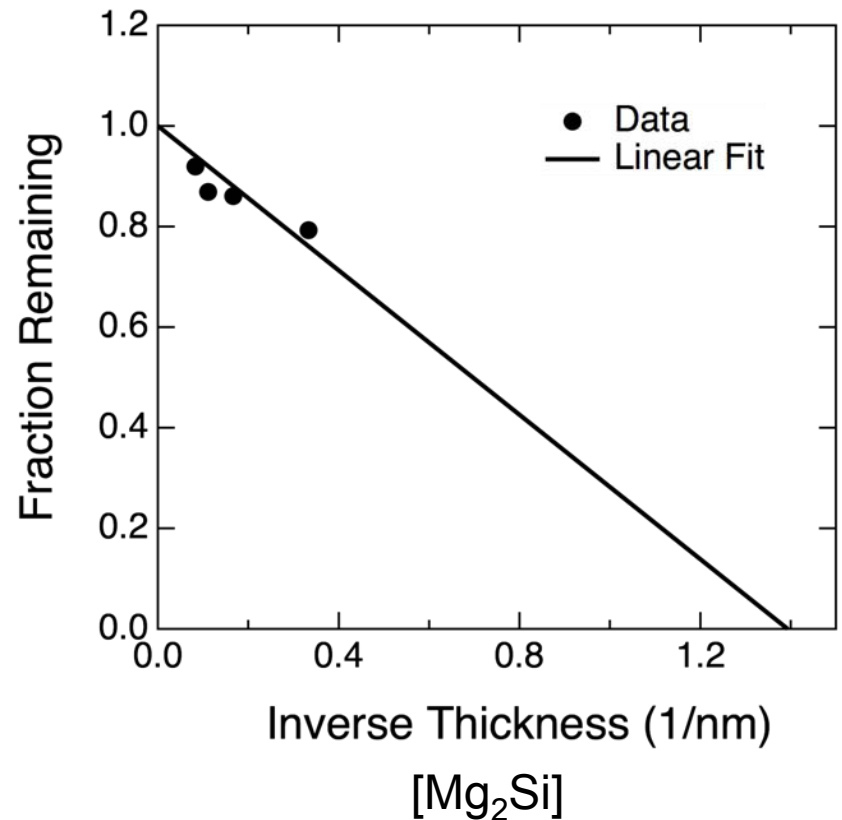
- System exhibits very poor kinetics for reverse reaction and previous work showed little evidence for reversibility at length scales down to 5 nm
 - Trend seen in data after processing between layer thickness and Mg₂Si peak intensity reduction
 - Undertook *new* study with careful data analysis
- Multilayer samples allow analysis of very small reaction depths using XRD

$$\text{Fraction remaining} = 1 - 2d/l$$



Progress – Mg₂Si System

- **New analysis shows reaction depth < 0.5 nm**
 - Attempted to charge samples by cooling them from 240 to 70 °C at 12 °C h⁻¹ in 200 bar H₂
- **Particle sizes <1 nm needed to achieve complete hydrogenation from Mg₂Si phase**
 - Phase transition **not** limited by hydrogen diffusion through Mg₂Si or nucleation of MgH₂ phase (separate experiments)
 - Reverse reaction kinetics severely limited by transport of Mg and Si during phase segregation from Mg₂Si into MgH₂ and Si
- **Very small reaction depth makes the system impractical for reversible hydrogen storage – downselected**
 - Thin film + XRD approach very powerful way to examine kinetic limitations



Kelly, et al., Nanotechnology 20 (in press)

Hydrogen diffusion >> host diffusion

Progress – Mg/Al System

- **Apply thin film methods to new material system with kinetic problems (like Mg_2Si)**

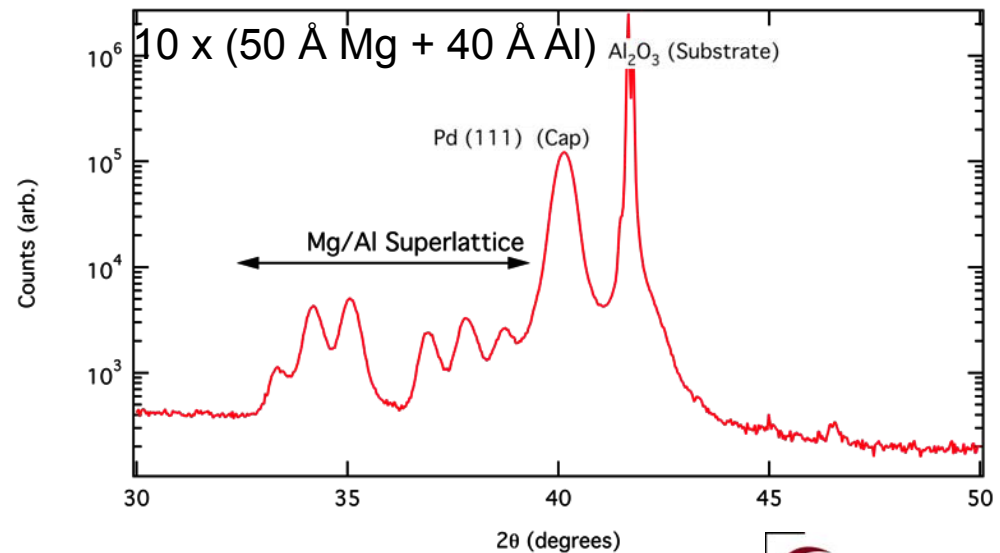
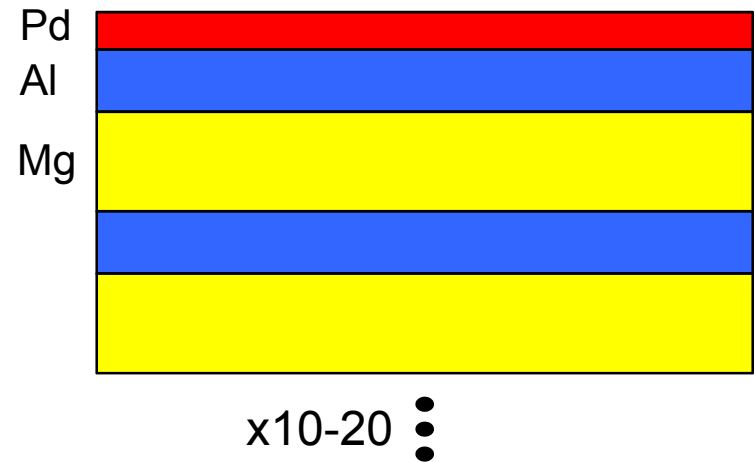
- $\text{Mg}(\text{AlH}_4)_2 \rightarrow \text{MgH}_2 + 2\text{Al} + 3\text{H}_2$
- Reverse reaction very difficult
- Varying reports of thermodynamic parameters in literature

- **Our approach:**

- Mg/Al multilayer films with Pd capping layer
- Vary relative amount of Al in each film
- Examine amount of Al before/after hydrogen exposure to deduce reaction extent (if any)

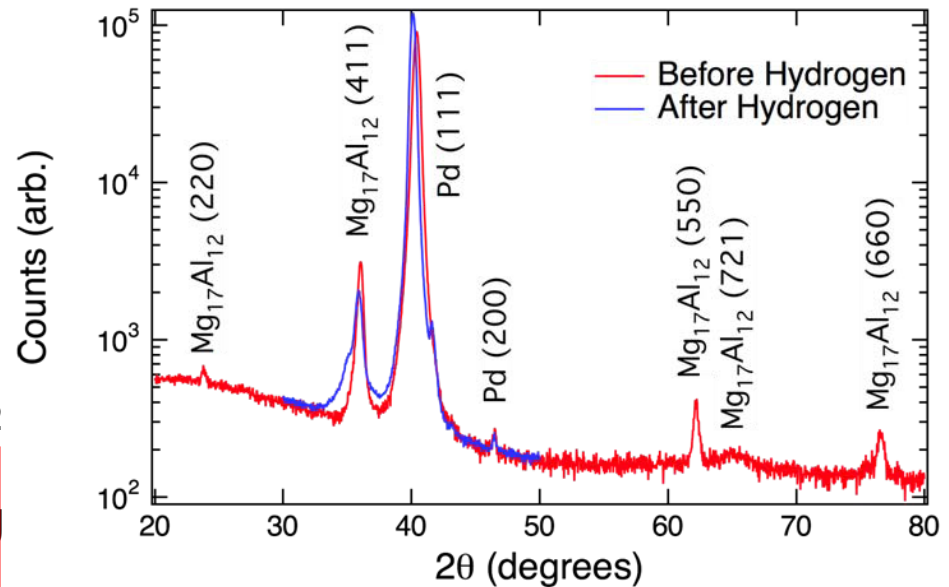
- **Issues:**

- Layers deposited as superlattices due to lattice parameter similarities
 - XRD analysis not straightforward
- Layers intermixing at room temperature over a few days
- Hydrogen diffusion



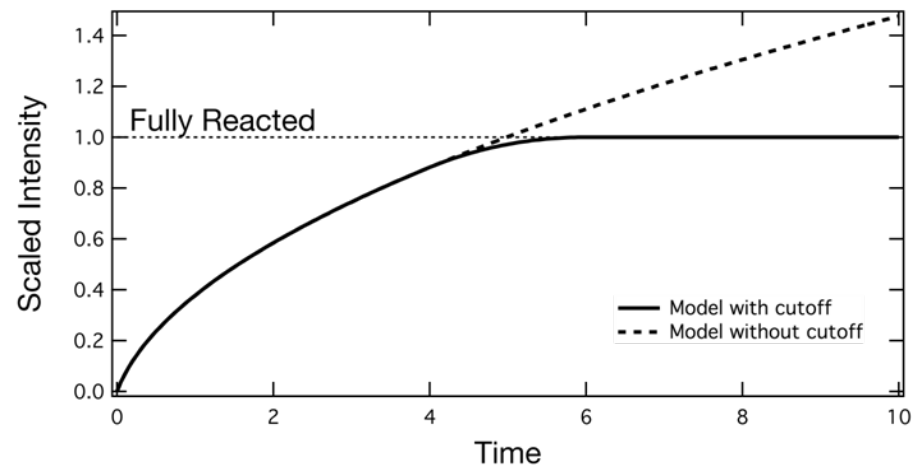
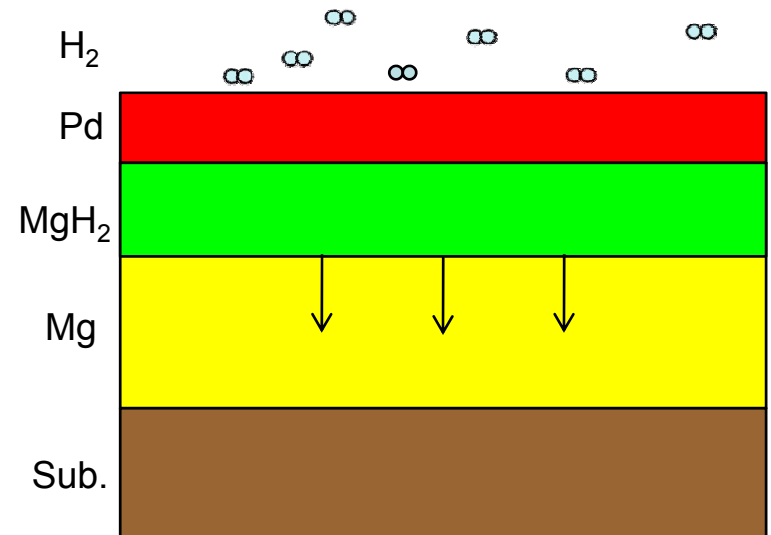
Progress – Mg/Al System

- **After hydrogen annealing under 1 bar H_2 at 110 °C for 10-20 hrs took new XRD spectra**
 - Some spectra identical to those taken before annealing
 - Others show intermetallic phases
- **Films do not seem to readily react with H_2**
 - No MgH_2 formation seen
 - Evidence for alloy formation after annealing
 - Al or Mg/Al alloy seems to block hydrogen diffusion or doesn't form hydride phase
- **New samples needed to probe kinetics further**
 - Single Mg film with Al (varying thickness) between it and Pd layer to probe hydrogen diffusion through thin Al layers



Progress – Hydride Growth Kinetics

- Previous *in-situ* XRD data showed evidence for moving planar interface hydride growth kinetics
 - Described with kinetic model based on silicon oxidation described by Deal and Grove¹ (previous results)
 - Model predictions diverged from data for long times
- This year developed model further to account for thin film nature of samples
 - Include cutoff where growing hydride layer reaches substrate
 - Better describes geometry of our samples



Progress – Hydride Growth Kinetics

- Build model by considering concentration profile across sample
- Sieverts' Law for gas to Pd transport:

$$c_s = K_s \sqrt{p}$$

- Flux proportional to chemical potential drop across interfaces:

$$J = k_1(\mu_1 - \mu_2)$$

- Fick's First Law across layers:

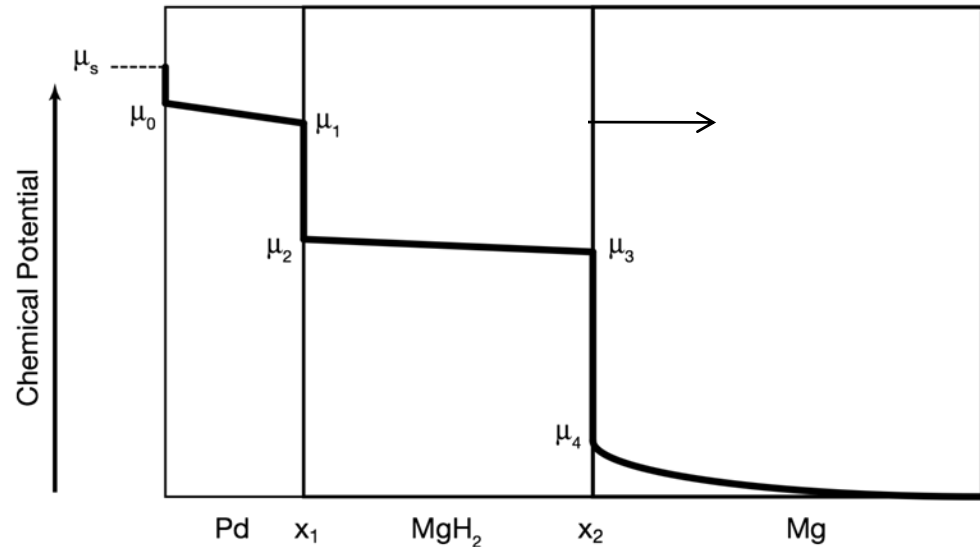
$$J = -M \nabla \mu = -M \frac{d\mu}{dx}$$

- Assume concentration in Mg is zero:

$$c_{Mg} = 0$$

- All flux into Mg creates MgH₂:

$$J = N_1 \frac{dx_2}{dt}$$



$$x_2(t)^2 + \frac{2\psi}{\phi} x_2(t) = \frac{2\alpha}{\phi N_1} t + \frac{2\psi}{\phi} x_1 + x_1^2$$

$$x_2(t) = \chi \pm \sqrt{a + bt}$$

Progress – Hydride Growth Kinetics

- To account for finite film thickness, introduce cutoff function to model

- Multiply derivative by linear cutoff

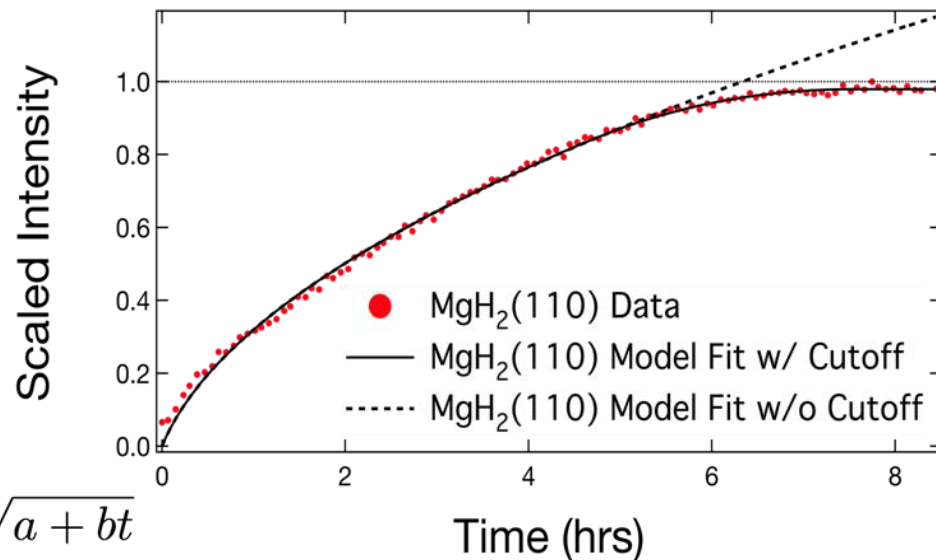
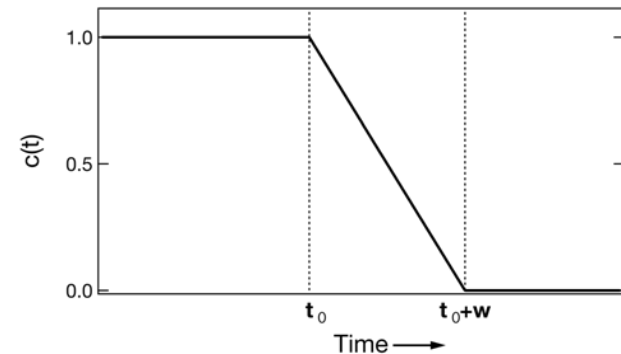
$$c(t) = \begin{cases} 1 & t < t_0 \\ 1 - \frac{t-t_0}{w} & t_0 \leq t \leq t_0 + w \\ 0 & t_0 + w < t \end{cases}$$

$$\frac{\partial y(t)}{\partial t} = \left(\frac{b}{2\sqrt{a+bt}} \right) \left(1 - \frac{t-t_0}{w} \right)$$

- Then integrate and solve for boundary conditions to get new function

$$\begin{aligned} y(t) &= \int \frac{\partial y(t)}{\partial t} dt \\ &= \gamma + \left(1 + \frac{t_0}{w} + \frac{b}{w} \cdot \frac{2a-bt}{3b^2} \right) \cdot \sqrt{a+bt} \end{aligned}$$

Cutoff function:

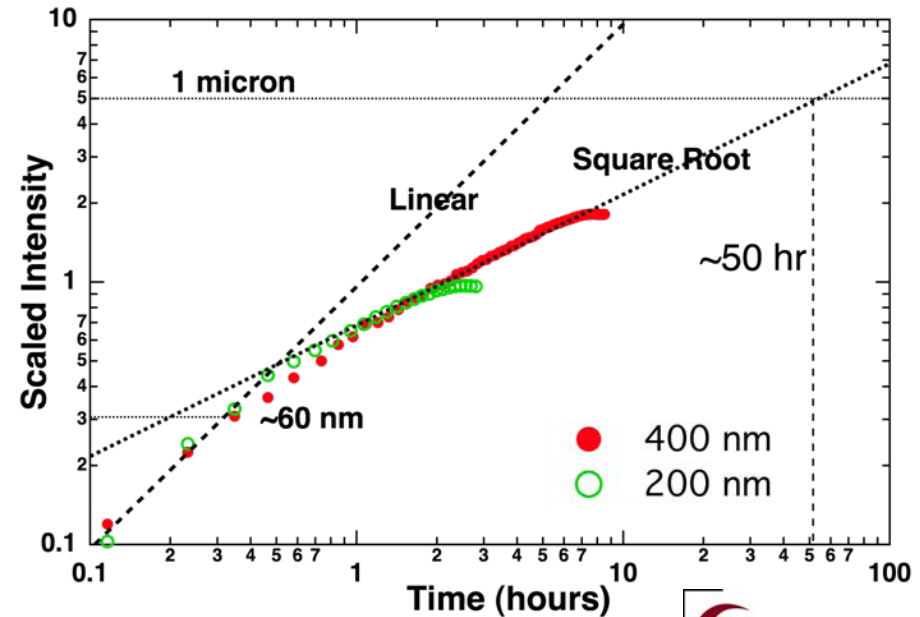
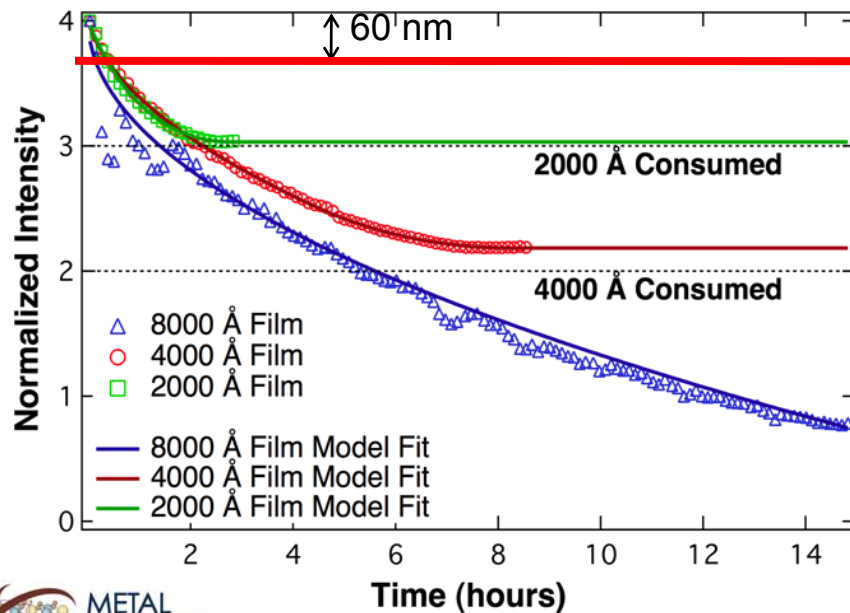


$$z(t) = \begin{cases} \frac{x_2(t)}{y(t_0+w)} & t < t_0 \\ \frac{y(t)}{y(t_0+w)} & t_0 \leq t \leq t_0 + w \\ 1 & t_0 + w < t \end{cases}$$

Progress – Hydride Growth Kinetics

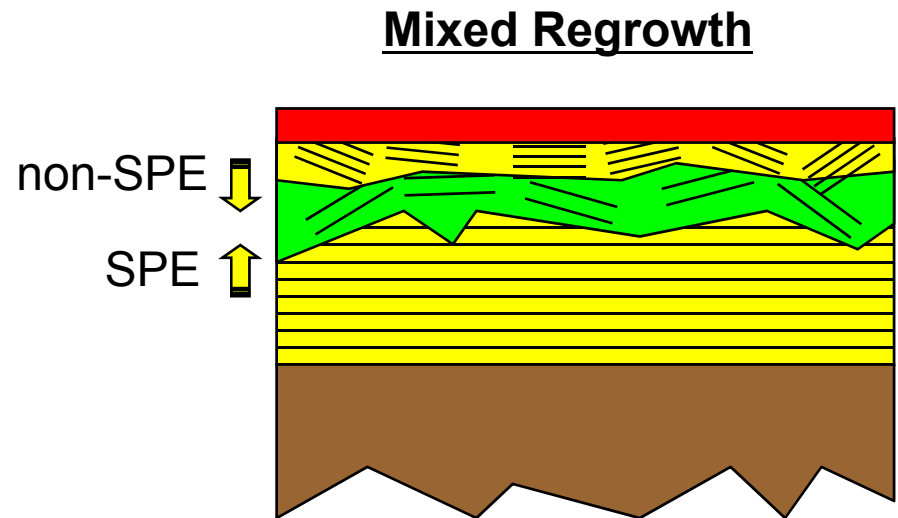
New model better describes the data

- Hydride formation kinetics limited by diffusion ($\sim t^{1/2}$) of H through the growing MgH_2 layer for long times
 - ~ 50 hr to hydrogenate 1 μm thick film under our conditions (5.7 bar, 125 $^\circ\text{C}$)
- Reaction limited ($\sim t$) regime confined to thicknesses < 60 nm from examination of data
- Structures should have critical dimensions < 120 nm to improve kinetics (avoid diffusive control)
- Comparison of different thickness samples shows agreement with moving interface growth



Progress – Hydride Growth Kinetics

- **Previously observed solid phase epitaxial (SPE) regrowth of Mg/MgH₂ films motivates kinetic study**
 - Observed in x-ray diffraction rocking curve development during hydrogen discharge
- **Provides motivation for future development of comprehensive model to describe material cycling**
 - Where does new Mg grow/nucleate from?
 - What kinetic mechanisms operate in composite materials/thin films during hydrogen charging/discharging?
 - How can kinetics for different material architectures be improved?
 - Under what cycling conditions is regrowth of existing metal template (SPE) faster than nucleation of new metal phase?

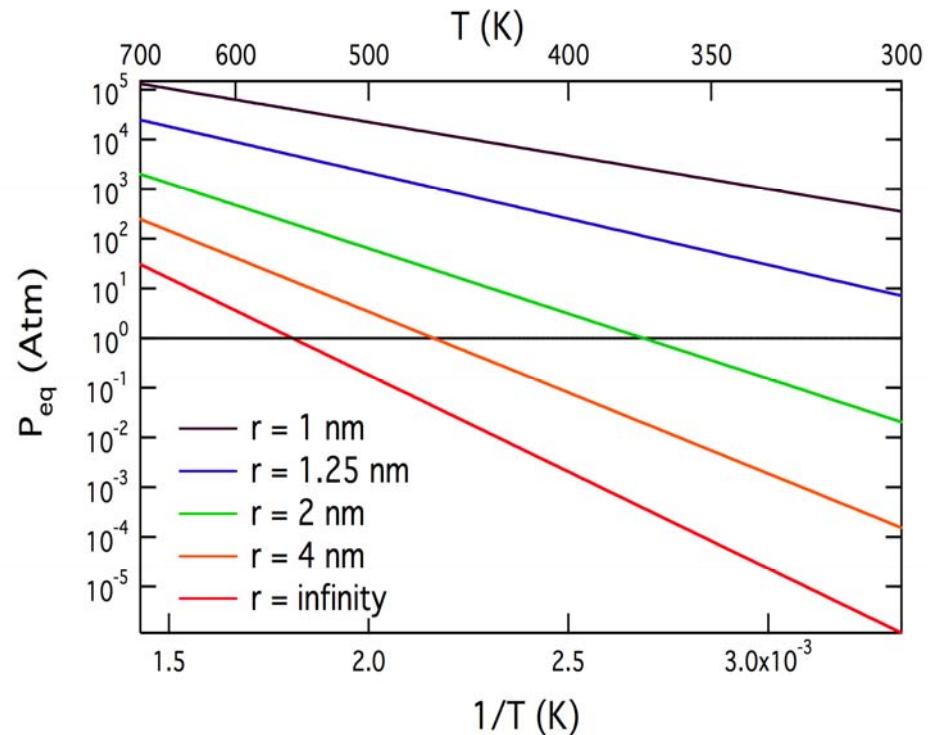
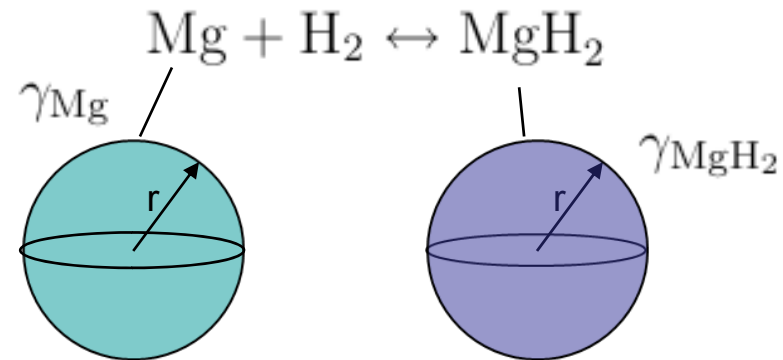


Progress – Nanoscale Mg

- Continuum modeling (previous work) predicts enhanced equilibrium pressure in MgH_2 with reduced particle size
 - Particles with $r = 2 \text{ nm}$ should have $P_{\text{eq}} = 1 \text{ atm}$ at $T \sim 100 \text{ }^\circ\text{C}$
- Mg nanoparticles hard to handle
 - Oxidation, agglomeration, etc.
- Same effect should happen in very thin Mg films
 - Deposit multilayer films (separated by Pd layers) with varying Mg thicknesses onto quartz crystal microbalance (QCM) crystal for P_{eq} vs T analysis

$$P_{\text{H}_2(\text{eq})}^r = \exp \left[\frac{\Delta G^\circ}{RT} + \frac{2\Delta\gamma V_M^{\text{Mg}}}{r_{\text{Mg}} RT} \right]$$

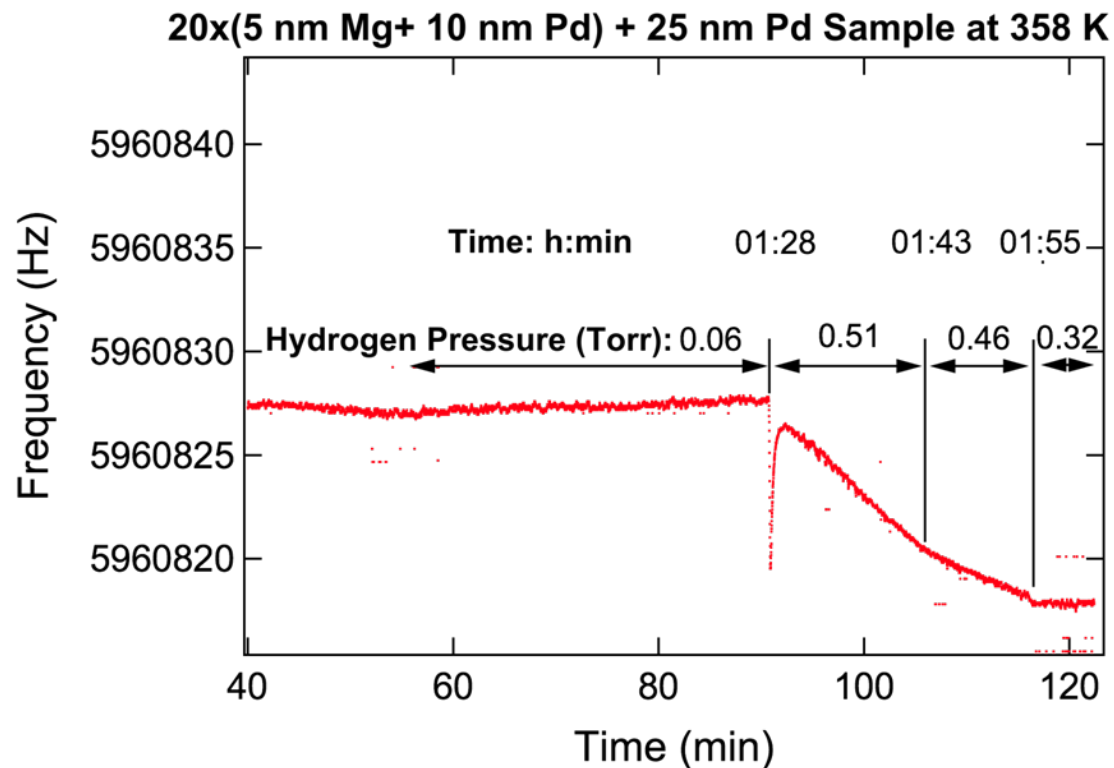
$$\Delta\gamma = 1.74 \text{ J/m}^2$$



Progress – Nanoscale Mg

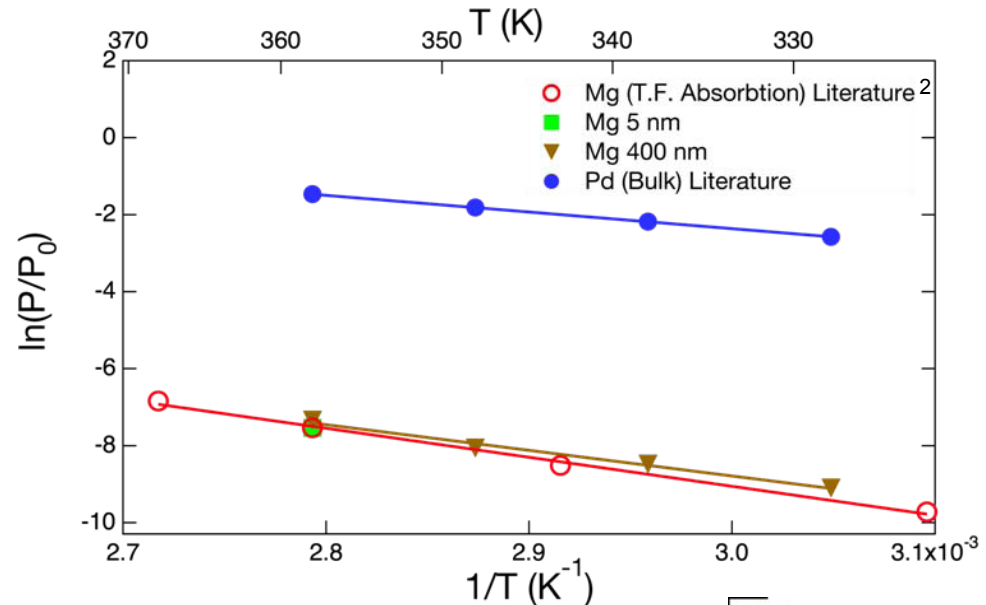
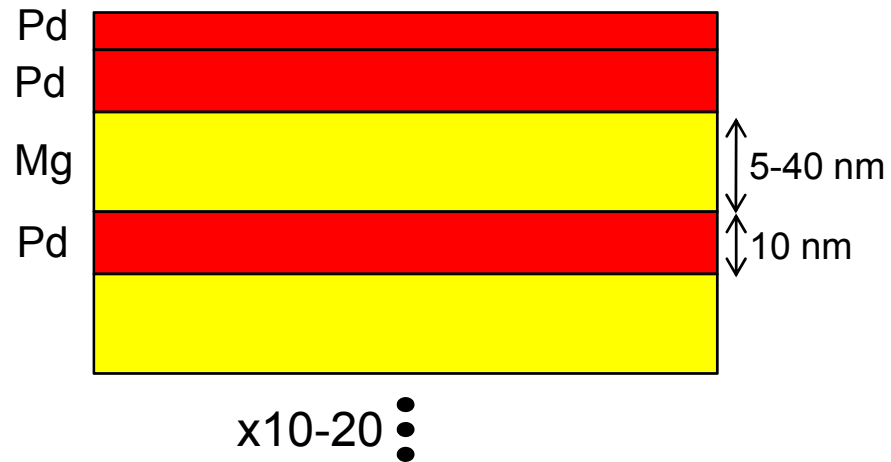
• QCM data collection procedure:

- Sample and chamber controlled at fixed temperature
- Process gas (pure H₂ or mixture) bled in via leak valve
- Crystal frequency constantly monitored
 - Frequency down = mass uptake
- Pressure stepped up until uptake seen
- Pressure reduced until uptake halts
- P_{eq} then taken as average of last point where uptake seen and point where uptake ceases



Progress – Nanoscale Mg

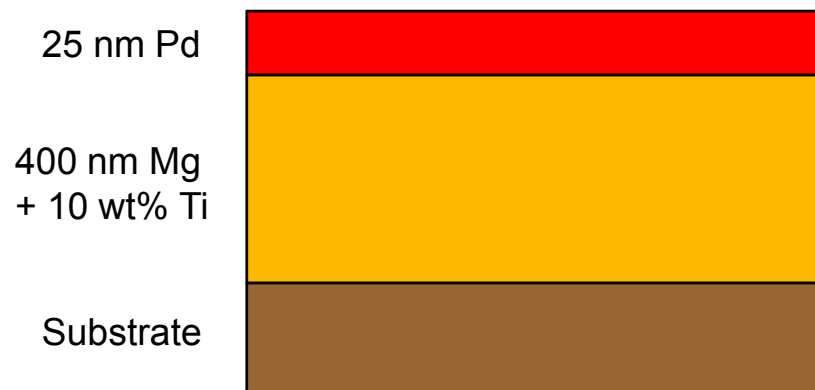
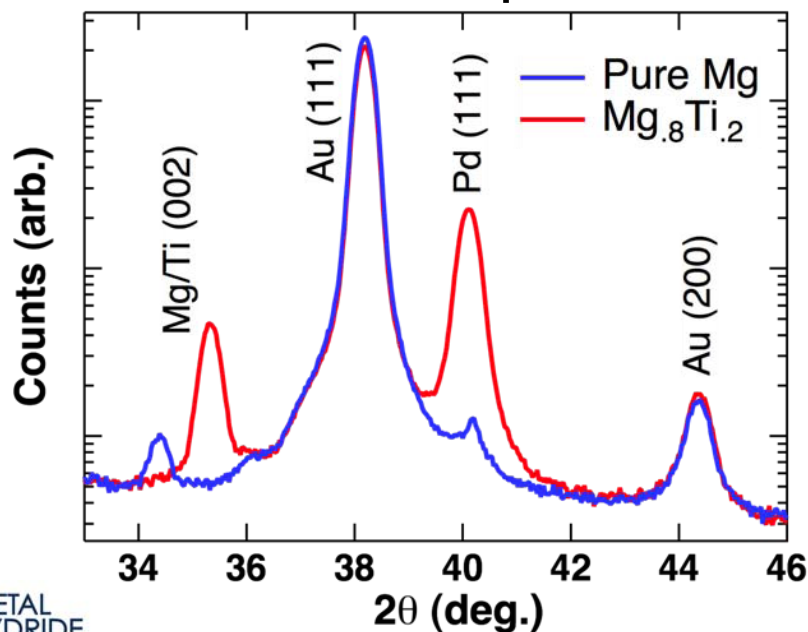
- Thick film (400 nm) agrees well with literature values for film/bulk absorption
- Thinnest film sample (5 nm) shows preliminary P_{eq} consistent with bulk measurements
 - Modeling predicts effect for this size, but very sensitive to surface energy differences
- QCM able to measure P_{eq} in very small samples: early results show little to no effect for very thin films, but results need verification



Progress – Mg/Ti System

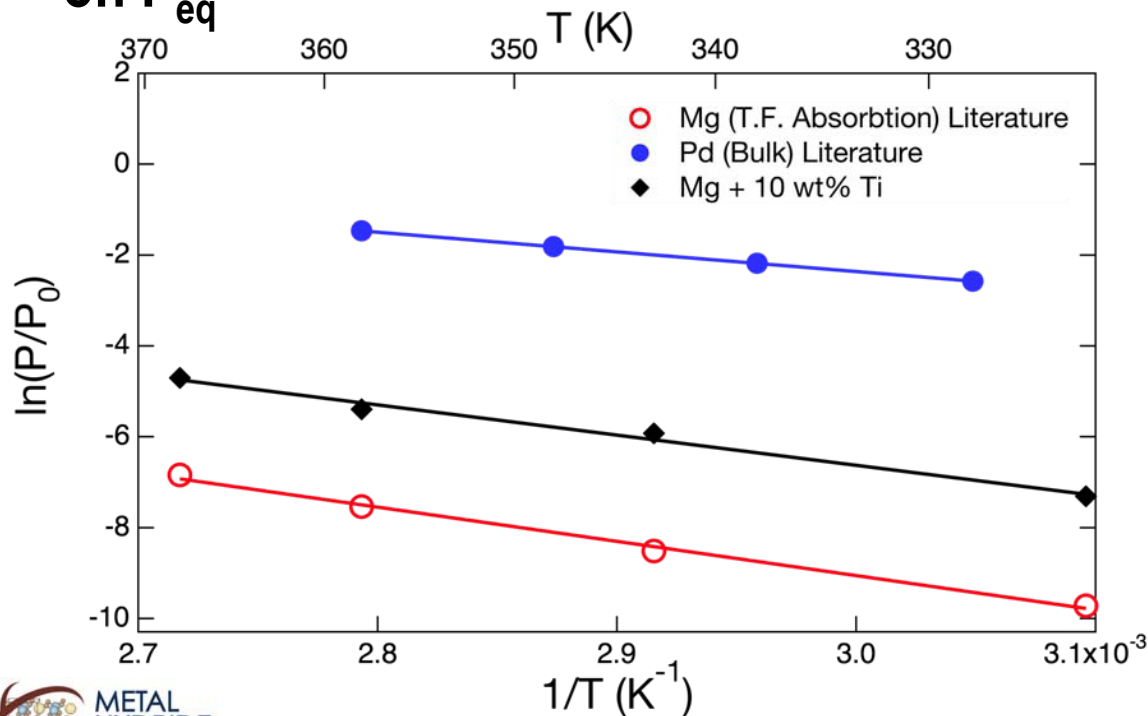
- Previous work showed 42% faster uptake kinetics in epitaxial Mg films with 10 wt. % Ti addition
 - Does the addition of Ti in Mg alter the *thermodynamics* as well?
- Examine Mg + Ti films using QCM to monitor P_{eq} vs T to determine thermodynamic properties
 - 10 wt % Ti in Mg + Pd capping layer
 - Samples deposit as *single phase* hcp Mg with Ti in solid solution for all compositions attempted

QCM Sample XRD



Progress – Mg/Ti System

- Addition of 10 wt % Ti results in $\sim 10x$ increase in P_{eq} compared to pure Mg
 - ΔH comparable to literature calculations³ (-55 kJ/mol (this work) vs -51.6 kJ/mol (literature) for $Mg_8Ti_2H_2$)
 - P_{eq} values comparable to other literature reports for this system^{4,5}
- Further work needed to verify and examine effects of Ti concentration on P_{eq}



³Song, et al., *Mat. Sci. Eng. A*, **365** 73 (2004)

⁴Gremaud, et al., *Adv. Mater.*, **19** 2813 (2007)

⁵Vermeulen, et al., *J. Mat. Chem.*, **18** 3680 (2008)

Progress – Neutron Reflectivity with NIST

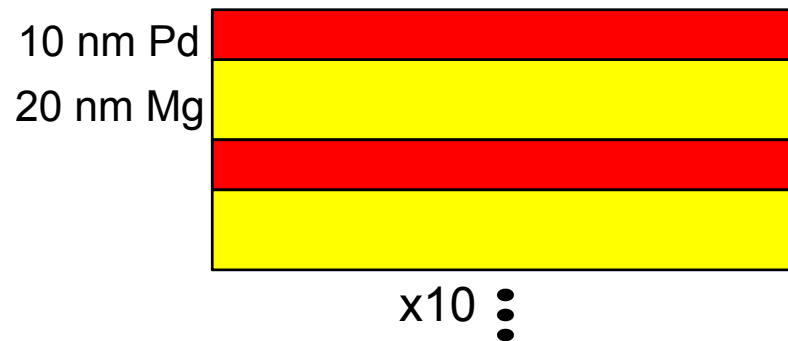
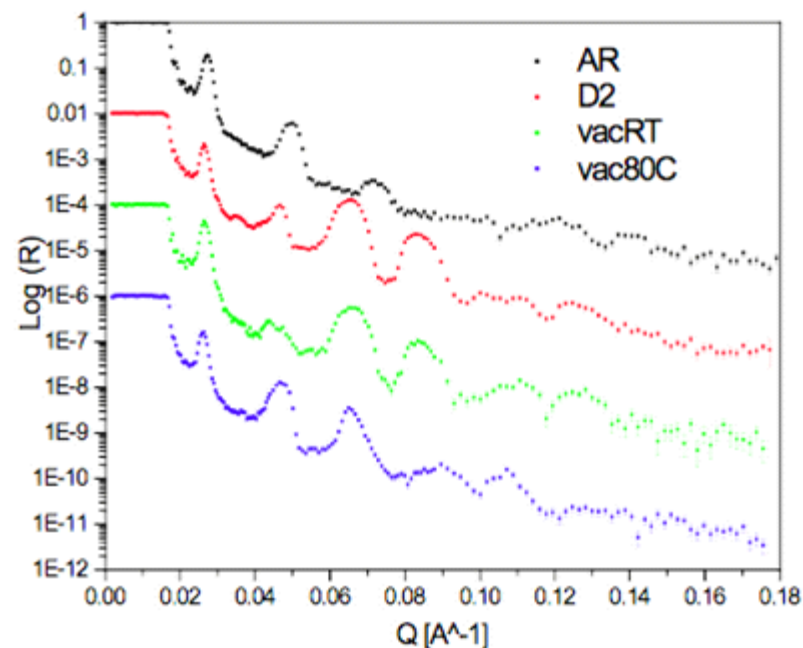
- **Previous results showed large changes to neutron reflectivity spectra in Mg/Pd multilayers with hydrogen (deuterium) introduction**

- Modeling the spectra resulted in some success – hydrogen profile through structure
- Want to look at single layer films to verify and reveal details about hydrogenation model (interface roughness, motion, sharpness, etc.)

- **Sent single layer sample to NIST**

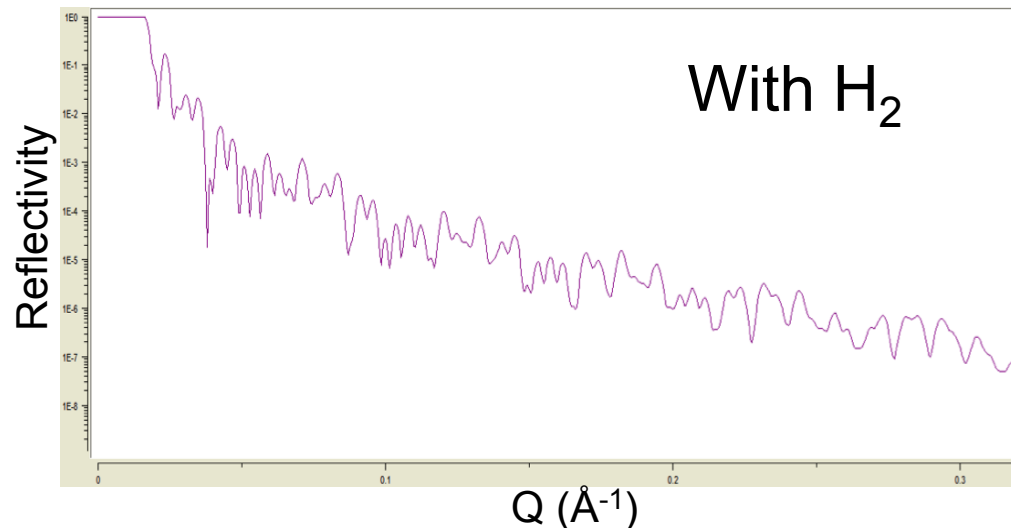
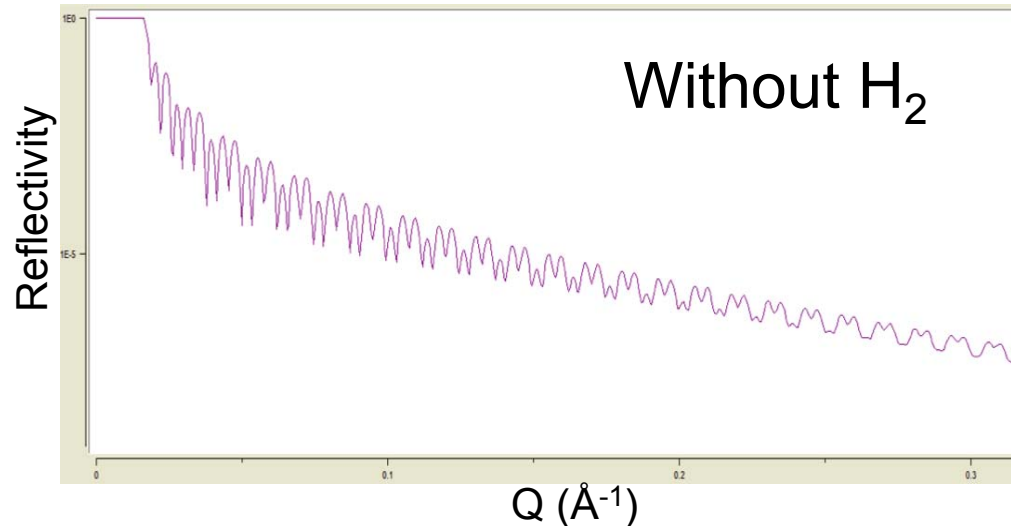
- No changes in NR seen before/after hydrogen loading
- Sample suffered from surface oxidation
- Significant MgO formation detected

Previous Results



Progress – Neutron Reflectivity with NIST

- **New samples to include thicker Pd capping layer over 100 nm Mg**
- **Modeling shows that hydride formation should still be detected with new layer thicknesses**
 - Neutron reflectivity spectra show distinct differences with and without hydrogen
- **With better samples and procedures neutron reflectivity should reveal important details of metal/hydride interface characteristics**



Collaborations

- **Collaborated with HRL team on the new Mg_2Si experiment**
 - Samples fabricated and initial XRD at Stanford, sent to HRL for hydrogenation and additional XRD
- **Ongoing collaboration with NIST team to investigate Mg/MgH₂ interfacial motion in thin film samples using neutron reflectivity**

Future Work

- **Continue data collection and analysis with QCM chamber**
 - Find and exploit the limits of hydrogen uptake sensitivity for the instrument
 - Attempt to confirm theoretical predictions about the change in equilibrium pressure as particle size is reduced
 - Examine kinetics and thermodynamics for thin film and nanoparticle samples
- **Finish Mg/Al study**
 - New film architectures
 - Higher pressure H₂ anneals
 - Faster turnaround to prevent intermixing
- **Finalize nanoscale Mg study**
 - Thinner Mg layers on QCM
 - Careful measurements on existing samples
- **Further develop MgH₂ kinetic model**
 - Develop general model to describe reverse reaction and phase growth with cycling
- **Continue/finalize Mg/Ti study**
 - Examine different Ti concentrations to look for P_{eq} differences and trends
 - Examine cycling behavior of Ti-doped Mg films compared to pure Mg
- **Continue with neutron reflectivity study on Mg/MgH₂ thin films with NIST**
 - Determine more specifics of reaction kinetics
 - Interface motion/roughness/sharpness/etc.
 - Utilize new *in-situ* hydrogen loading chamber at NIST
 - Develop new models to describe data and incorporate findings into MgH₂ growth model

Summary

- **Relevance:**
 - Reveal fundamental reaction mechanisms in metal hydride phase transformations to address kinetic limitations that plague nearly all candidate metal hydride material systems
- **Approach:**
 - Utilize well controlled thin film model systems and *in-situ* characterization to investigate kinetic mechanisms in metal hydride material systems
- **Technical Accomplishments:**
 - Reaction depth into Mg_2Si < 1 nm, making system impractical for reversible storage
 - Hydride growth kinetic experiments support moving planar interface model, < 60 nm of reaction controlled growth from data – anything thicker suffers from diffusion limited growth (slower)
 - QCM chamber able to detect P_{eq} in very thin Mg layers, no size vs P_{eq} dependence seen yet
 - Addition of 5 % Ti in Mg gives $\sim 10\text{x}$ increase in P_{eq} , verification needed with further study
 - Mg/Al kinetic study underway using multilayer film/XRD approach successfully used with Mg_2Si
 - Neutron reflectivity with NIST should provide details about thin film hydride growth model
- **Collaborations:**
 - Collaboration with NIST to utilize neutron capabilities to complement x-ray work
 - Collaboration with HRL to examine reaction depth in Mg_2Si system
- **Future Work:**
 - Finalize QCM studies of nanoscale Mg system – does size change MgH_2 thermodynamics?
 - Continue Mg/Ti study to examine P_{eq} and cycling behavior dependence on Ti alloying content
 - Finish Mg/Al study using thin film approach to study reaction depth and limiting kinetic mechanisms
 - Finalize neutron reflectivity study of thin film metal hydride reactions to reveal reaction details