

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

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Overview

- **Timeline**

- Project Start Date: January 2005
- Project End Date: 2/28/2010
- Percent Completion: ~40%

- **Budget**

- Total Project Funding: \$997,921
 - DOE Share: \$778,828
 - Contractor Share: \$199,093
- Funding Received FY06: \$150,000/\$37,500
- Funding Received FY07: \$150,000/\$37,500

- **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

Objectives

- **Develop fundamental understanding of metal hydride reaction kinetics**
 - Kinetics limit practicality and reversibility of many promising metal hydride material systems
 - Mg, Mg₂Si, 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 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**

- Thin film growth methods such as sputtering allow for nearly atomic level compositional control
- Appropriate substrate choices allow for precise microstructural control
 - Epitaxial Mg films have provided valuable insight into the kinetic mechanisms for Mg not seen before such as the hydride orientation correlation, evidence for solid phase epitaxial regrowth of the metal and a layer-by-layer mechanism for hydride growth
- Initial experiments with Mg films have validated the approach as results concur with those seen for bulk Mg measurements where appropriate
 - Diffusion limited hydride growth, phase change crystallographic orientations

- ***In-Situ* Structural Characterization**

- Custom designed *in-situ* hydrogen pressure chamber for use during x-ray studies
- Utilize high brightness synchrotron facilities to expand x-ray capabilities
- Real time structural analysis to facilitate detailed kinetic mechanism determinations

- **Transition To More Complex Material Systems**

- After establishing techniques and approaches using simple model system, move on to two component system (Mg+Ti) and then more complex systems involving mass transport and phase segregation ($\text{LiBH}_4 + \text{MgH}_2$)

Focus Of Work

- **Develop understanding of Mg/MgH₂ phase change kinetics using well defined thin film model systems and *in-situ* structural characterization**
 - The Mg/MgH₂ metal hydride system, while very well studied, still lacks a fundamental understanding of some of the basic kinetic mechanisms present in the metal/metal hydride phase transformation
 - Textured and epitaxial thin films of Mg allow precise control of the microstructure and structural orientation for the system as opposed to traditional studies involving highly disordered powders that are often ball-milled
 - The simplicity of the MgH₂ system makes it easier to establish our techniques and refine our approach while learning a great deal about the kinetics of this well established material system
- **Transition to more complex systems involving more components and mass transport of the material constituents**
 - Once characterization of the relatively simple MgH₂ system is established, move on to the multi-component Mg/Ti system (ongoing) to examine the effects of additional elements without the additional complications of large scale mass transport
 - Next transition to look at the more complex LiBH₄+MgH₂ destabilized system (developed at HRL Laboratories) involving phase segregation and mass transport using designed thin film experiments

Epitaxial Film Cycling

Epitaxial Film Kinetics

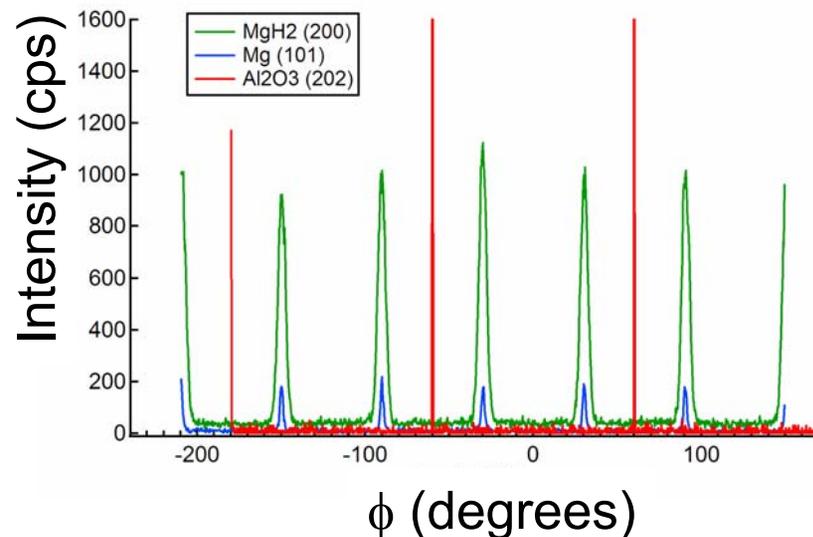
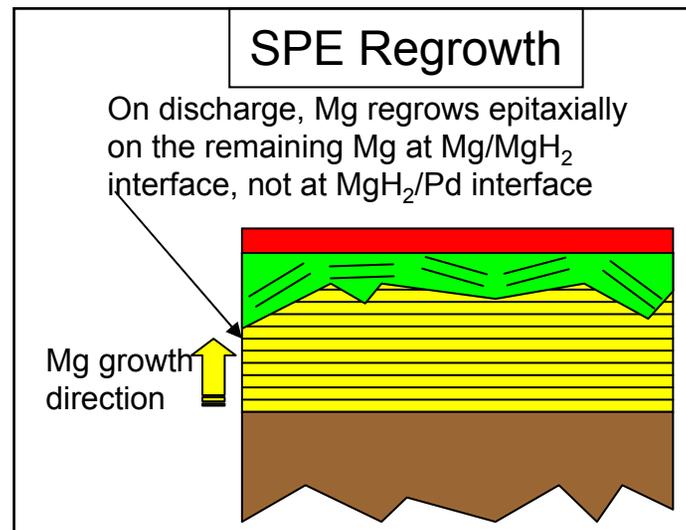
- Previous work showed interesting results regarding epitaxial film dehydrogenation kinetics
 - Evidence for solid phase epitaxial (SPE) regrowth mechanism seen
 - Epitaxial crystallographic relationship between Mg/MgH₂ for thin film samples

Cyclic Stability

- Material stability upon cycling is of great concern in the DOE long term goals
- An understanding of the kinetic mechanisms present during material cycling is essential in order to successfully engineer a material to withstand repeated cycling under normal operating conditions

Our Experiment

- Expose identical samples to different charging conditions and several charge/discharge cycles to examine the effect of cycling on material texture and related kinetic mechanisms



Epitaxial Film Cycling

- Investigate effect of charging extent on film texture over multiple cycles

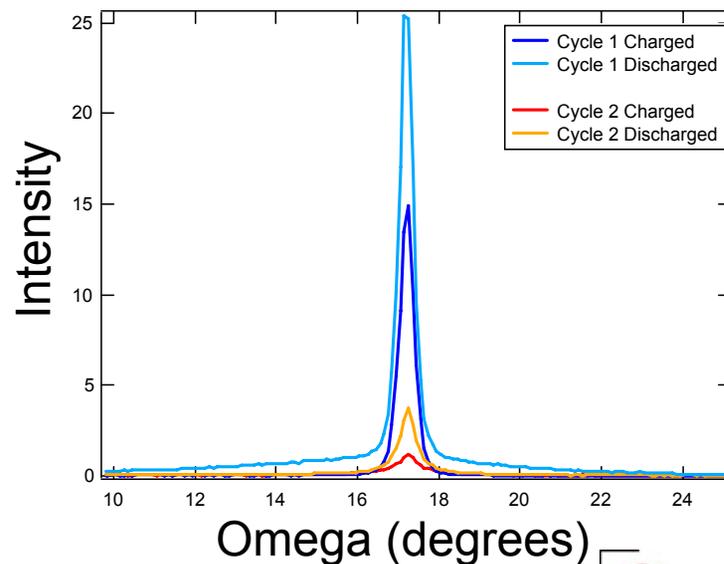
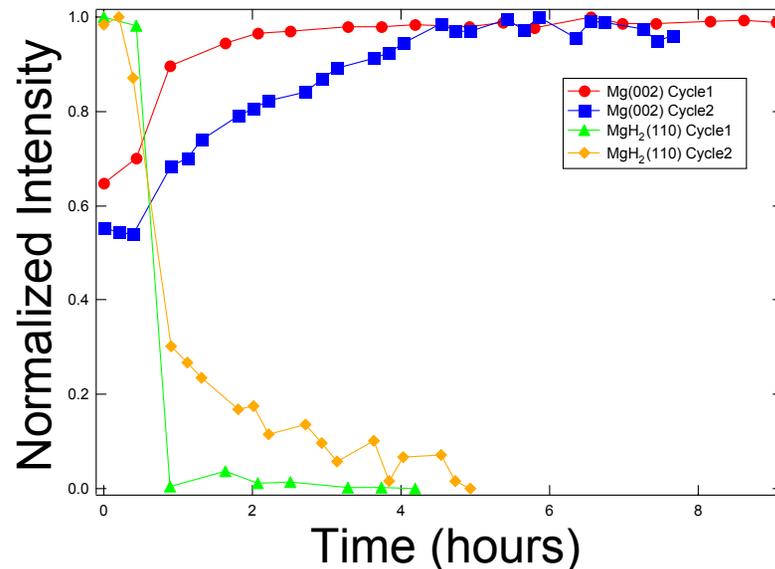
- Observe growth/regrowth mechanism in films
- All films 4000 Å Mg on (001) Al₂O₃ substrates with 250 Å Pd capping layer

- We cycled two identical films twice each, but with different charging conditions

- Film #1: shown at right

- Charged at 90 psi H₂ and 100 °C for 5 hrs
- Resulting film ~87% charged
- Discharged at 82 °C in air

Analysis of rocking curves shows that (002) textured Mg regrew almost completely in the highly textured orientation



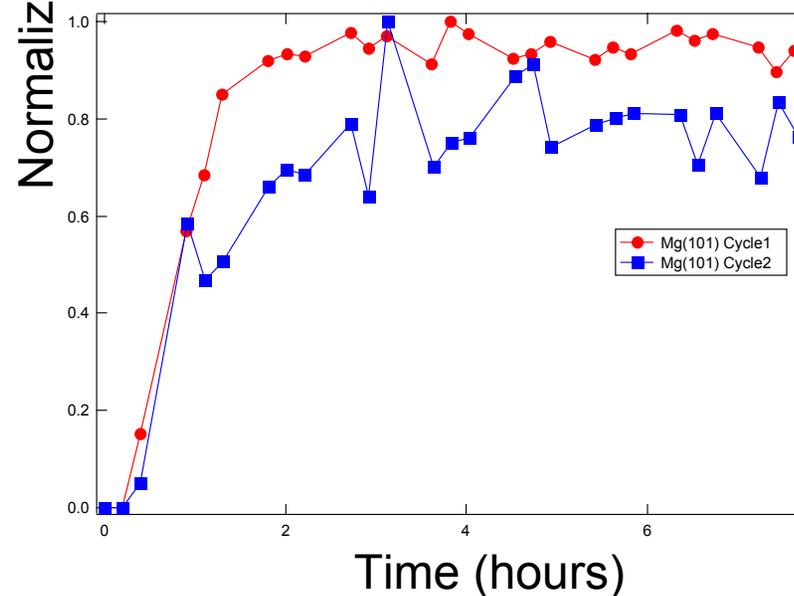
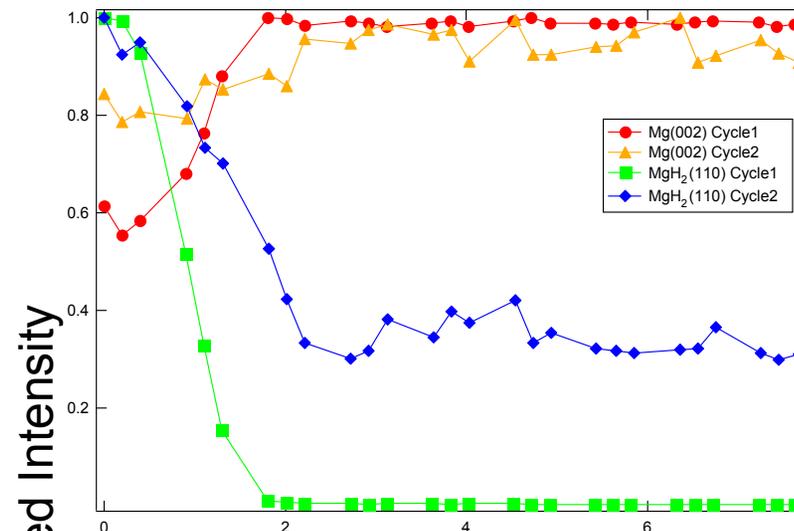
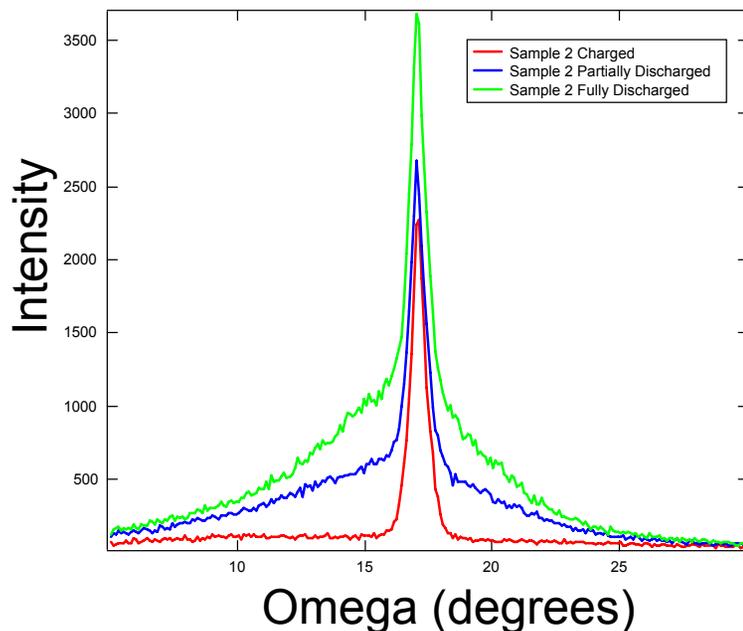
Epitaxial Film Cycling

Film #2

- Charged at 100 psi H₂ and 150 °C for 5 hrs
- Resulting film ~98% charged
- Discharged at 82 °C in air

Examination of rocking curves indicates that (002) Mg regrows with less texture than initial film

Mg regrowth occurs slower in cycle #2



Epitaxial Film Cycling

• Conclusions

- Faster charging and more extensive material conversion results in more textural disorder on discharging
- Repeated cycling to high conversion fractions of initially highly textured films results in significant loss of film texture
 - Mg(002) peak rocking curve significantly broadened
 - New Mg orientations seen, especially (101), after only one cycle to high conversion fraction at the elevated temperature and pressure of Film #2
- Loss of texture in films leads to slower discharge rates as seen in the discharge kinetics of Films #1 and #2
- Presence of residual highly textured metal leads to solid phase epitaxial regrowth where the newly forming metal grows on the existing metal with the same degree of textural perfection
- Attempts should be made to stabilize material texture during transformations (ie. Nanostructuring, alloy additions, etc) as discharging rates decrease with loss of material texture
- Modeling efforts to explain increased textural degradation with faster charging rates and higher conversion fractions could provide insight into ways to avoid degradation effects

In-Situ Film Hydriding

In-Situ Film Dehydriding

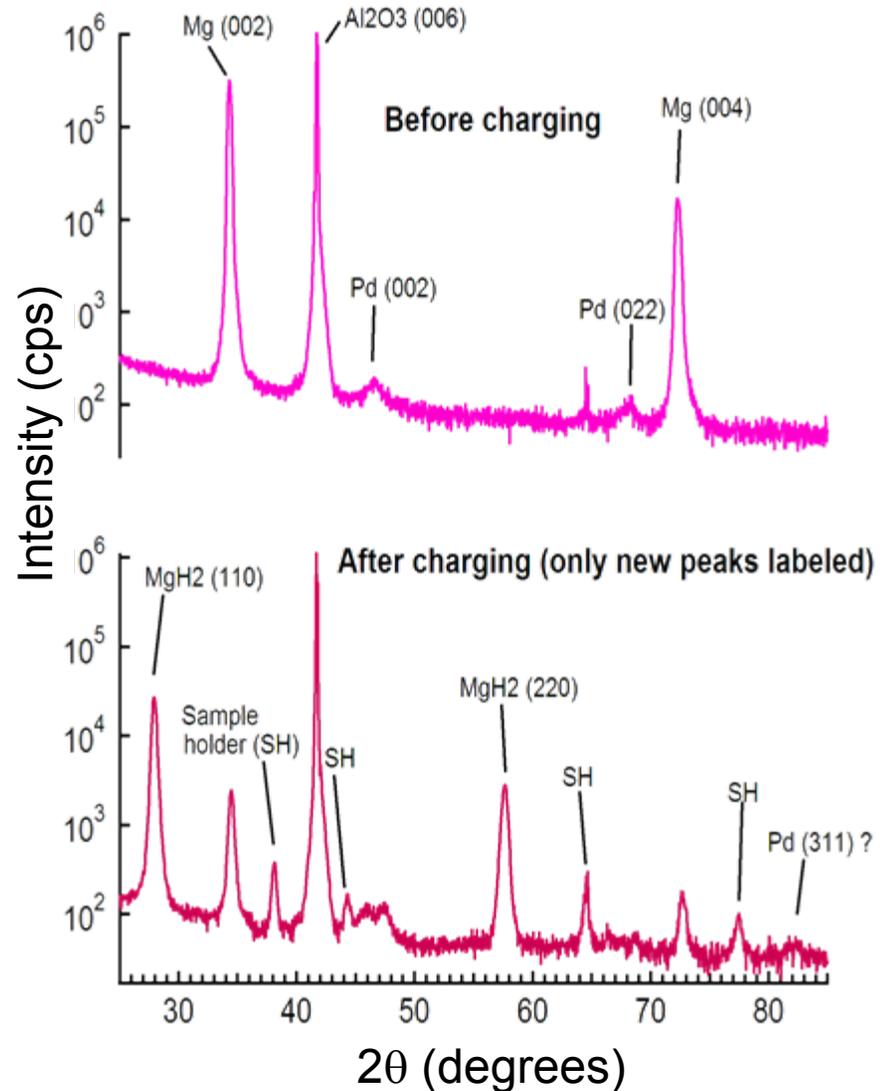
- Studies involving x-ray diffraction of samples while dehydriding showed interesting results
 - SPE regrowth, no nucleation period, structural information as phase change progressed
- These results made the case for pursuing *in-situ* hydriding capabilities

In-Situ Film Hydriding

- Monitoring peak intensities and analyzing peak shape during phase change allows analysis of reaction kinetics
- Examine similar samples as for dehydriding studies and look for new effects

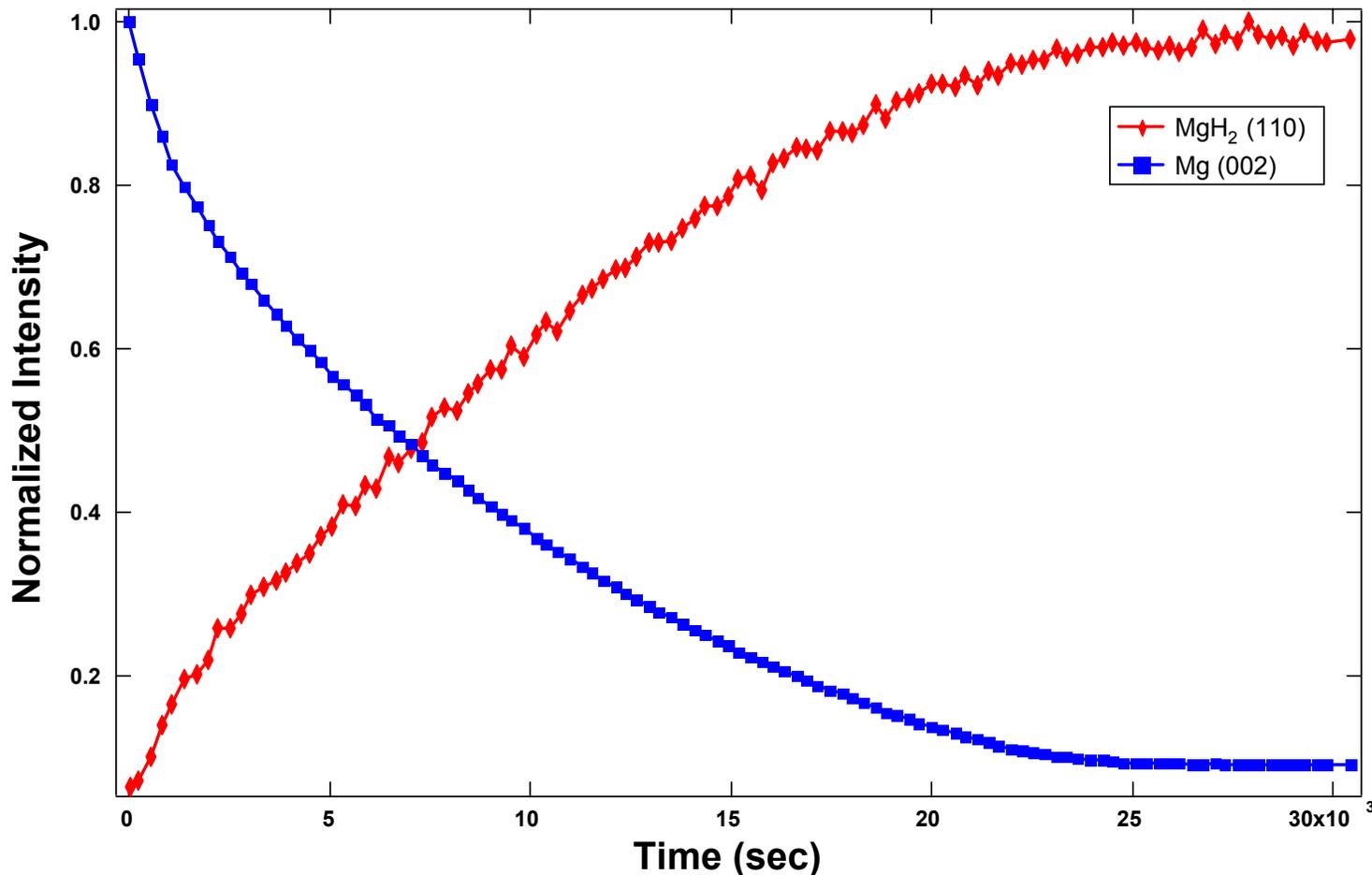
Controlled Systems

- Using thin film systems provides precise control of material parameters--composition, microstructure, etc.
- Previous kinetic studies carried out highly on random bulk ingots, powders and ball milled samples



In-Situ Film Hydriding

- Relative intensities of the Mg and MgH₂ peaks during in-situ sample hydriding illustrating the growth kinetics of the phase transition in thin epitaxial films



In-Situ Film Hydridding

- **Film Hydridding Kinetics**

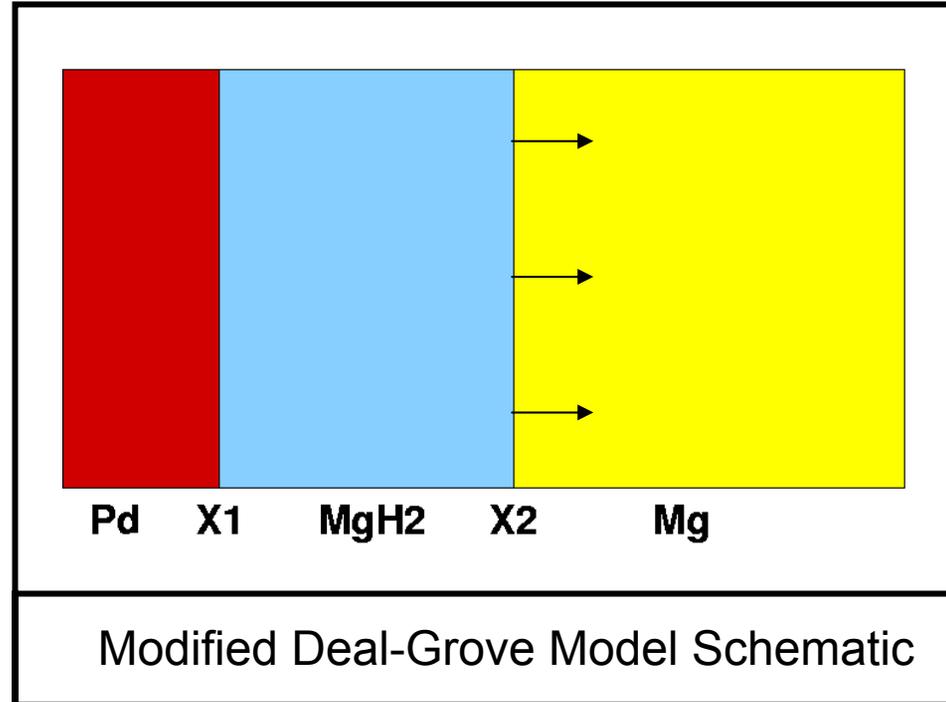
- In order to draw conclusions about the nature of the hydridding kinetics, we compare the data obtained to that expected for a simple model

- **Model Development**

- Modified Deal-Grove model:
 - Moving interface in a film
 - Oxidation of Si \Rightarrow Hydridding Mg
- Interface position / film thickness = fraction transformed

- **Compare Model To Data**

- Fit functional form of model to data and examine similarities



$$x_2(t) = x_1 - A + \sqrt{Bt + A^2}$$

In-Situ Film Hydridding

- **Magnesium data:**

- Good agreement between data and fit
- Fit constants:
 - $A=0.029$; $B=0.000041$

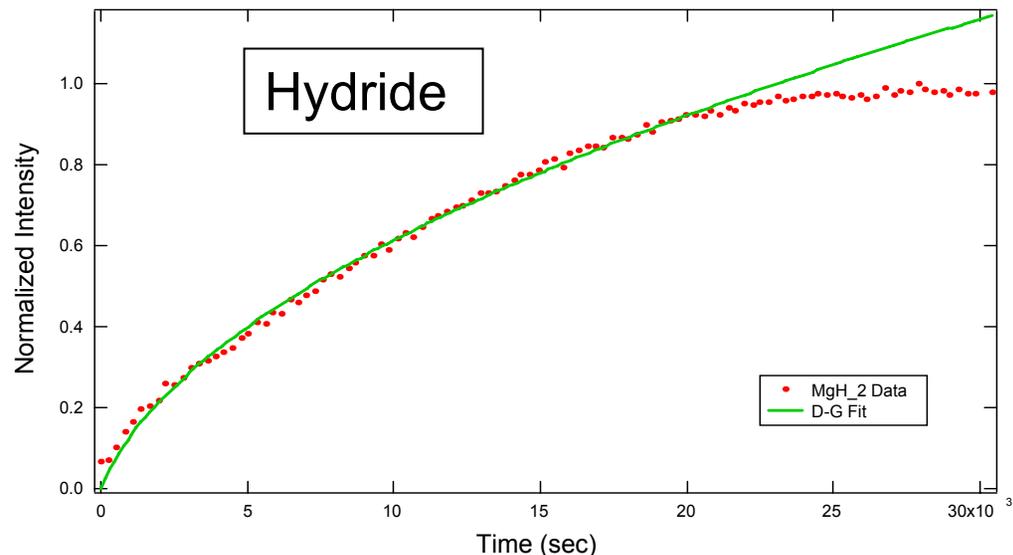
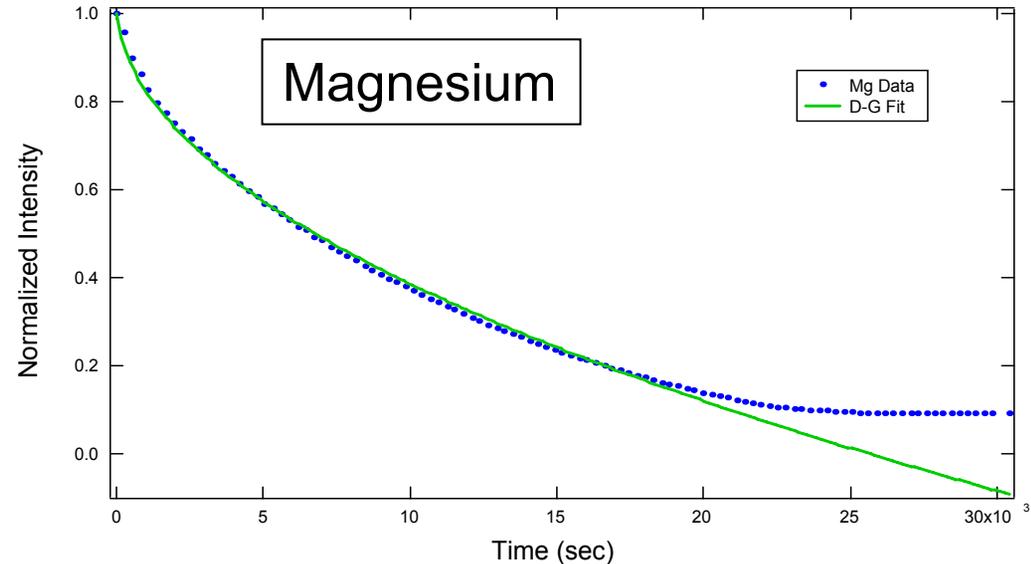
- **Hydride Data:**

- Fit constants:
 - $A=.158$; $B=0.000057$
- Difference between fits most likely due to normalization effects

- **As transformation nears completion model becomes unphysical**

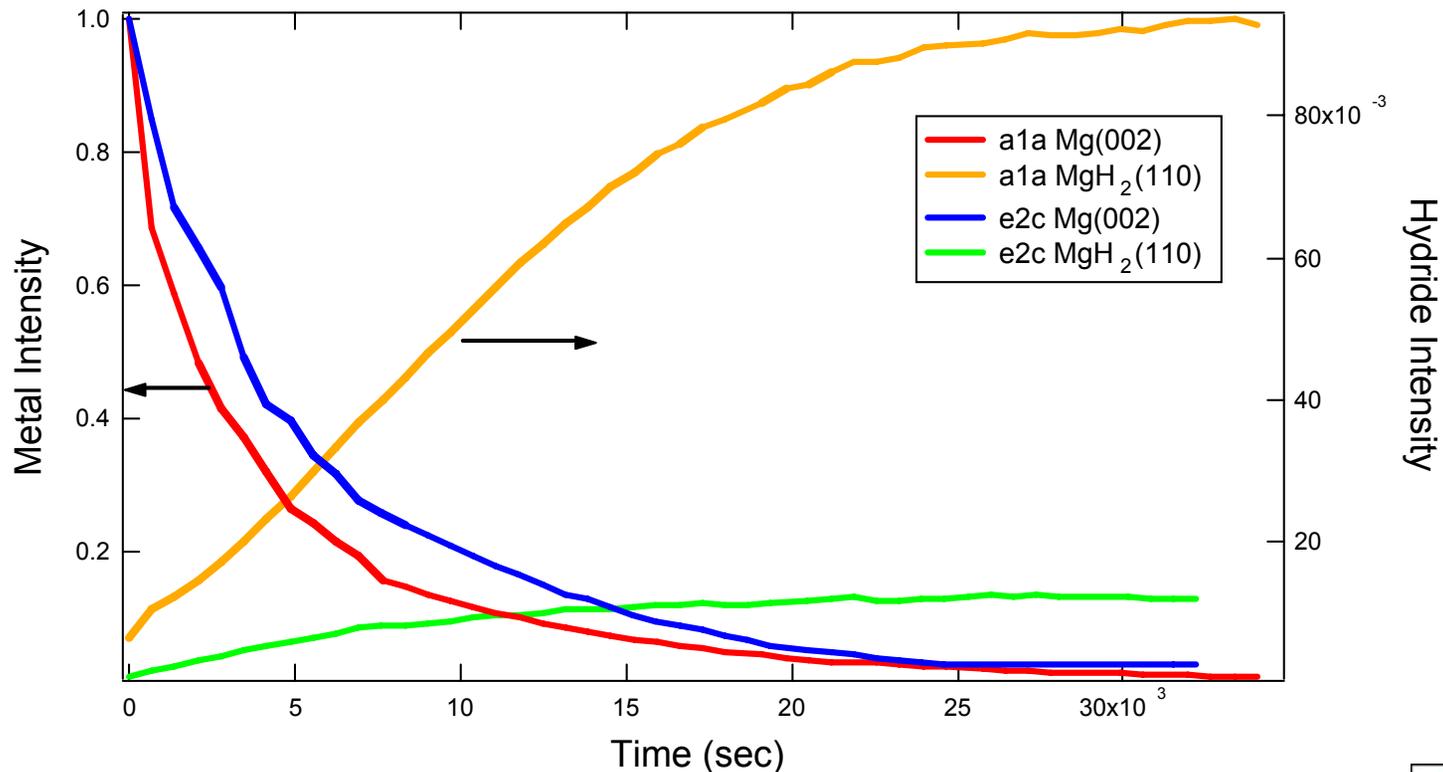
- **Agreement between model and data shows strong evidence for planar interface motion growth mechanism in capped thin film systems**

- Does not follow nucleation and growth rate law



In-Situ Film Hydridding

- **Addition of Ti into films shows improved hydrogen uptake kinetics**
 - Films still epitaxial on (001) Al_2O_3 substrates w/ Mg (002) peak out of the sample plane
- **Film with 10 wt.% Ti shows substantially enhanced uptake kinetics**
 - 42% faster ($t_{1/2}$) w/ inclusion of 10 wt.% Ti in the films



In-Situ Film Hydriding

• Conclusions

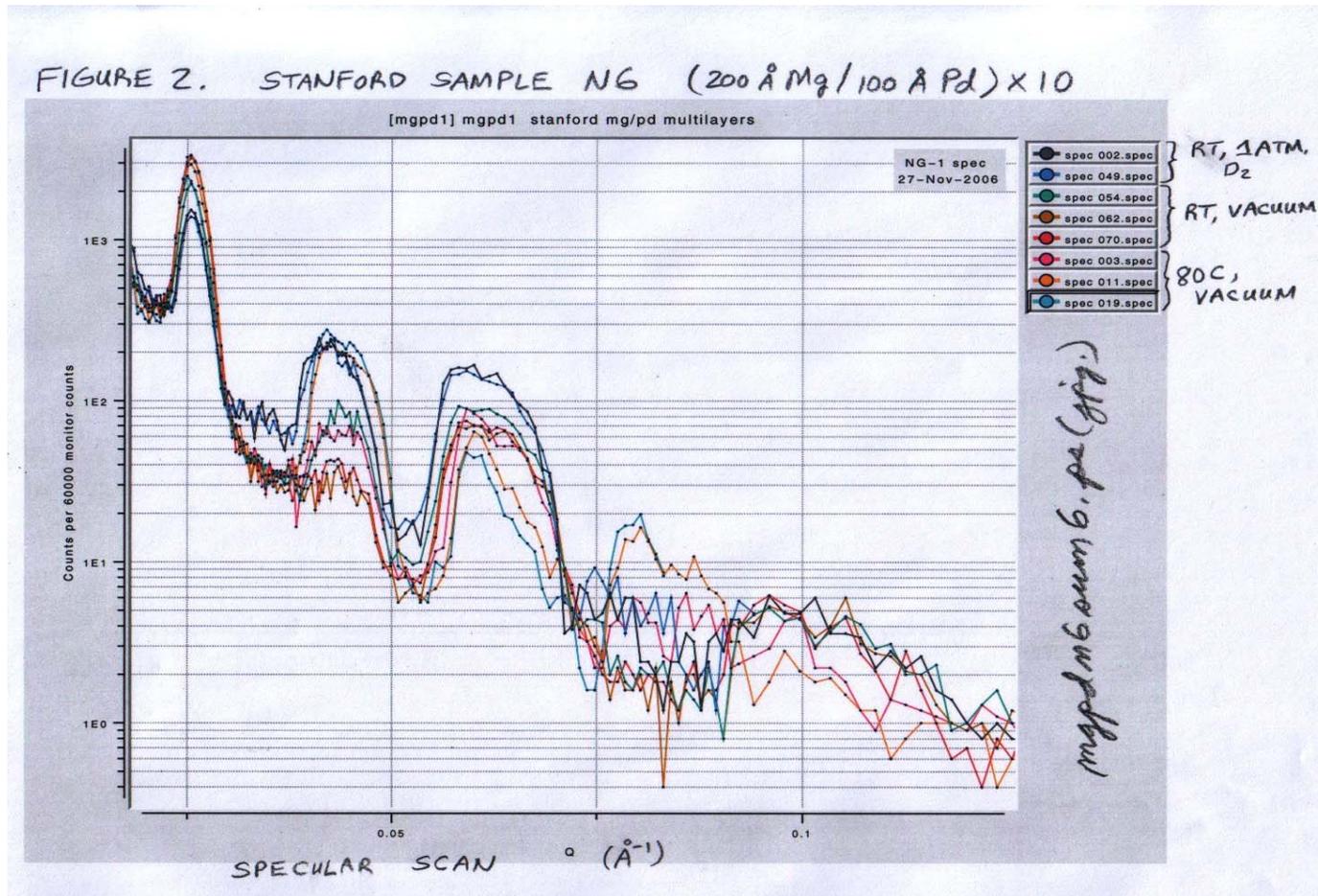
- Completed development of custom *in-situ* hydrogen charging chamber for XRD studies and began experiments using chamber with synchrotron radiation facilities
 - Can monitor film structure successfully during charging
- Examination of epitaxial film charging shows good agreement with a modified Deal-Grove type model for hydride growth kinetics
 - Strong evidence for a moving planar interface mechanism for hydride growth in thin films instead of a nucleation and growth mechanism
 - Diffusion limited growth behavior seen for longer times, just as in bulk sample studies
- Addition of 10 wt.% (5.35 at.%) Ti to epitaxial Mg films dramatically enhances uptake kinetics compared to pure Mg film
 - Film deposited as epitaxial solid solution of Ti in Mg grown on Al_2O_3
 - Time to reach 1/2 of initial metal peak intensity reduced by 42% with addition of small amount of Ti into the film
- Theory groups should investigate how addition of catalyst elements such as Ti affect hydride formation transformation kinetics and structure
- Mg containing systems should be nanostructured to enhance kinetics as growth model indicates diffusion limited growth

Neutron Reflectivity w/ NIST

- **Collaboration with NIST to exploit the sensitivity of neutrons to hydrogen in order to further characterize the kinetics of the Mg/MgH₂ phase change in thin film systems**
 - Reflectivity measurements to track the motion of the Mg/MgH₂ interface
 - Hydrogen depth profiling through appropriate system modeling and data analysis
- **What we hope to learn**
 - How does the interface motion depend on the charging and discharging conditions (temperature and hydrogen pressure)?
 - How does the nature of the interface itself change with these same conditions (roughness, sharpness, etc.)?
 - How does the nature and motion of the interface affect the phase change kinetics for hydride growth and subsequent metal regrowth?
- **Initial measurements show promising results**
 - Significant change in reflectivity pattern due to incorporation of hydrogen into the film
 - Substrate quality and cleanliness issues being addressed for future experiments
 - Seeking flatter substrates and improved cleaning procedures

Neutron Reflectivity w/ NIST

- Preliminary data showing changing reflectivity for multilayer samples of Mg and Pd with and without hydrogen incorporation



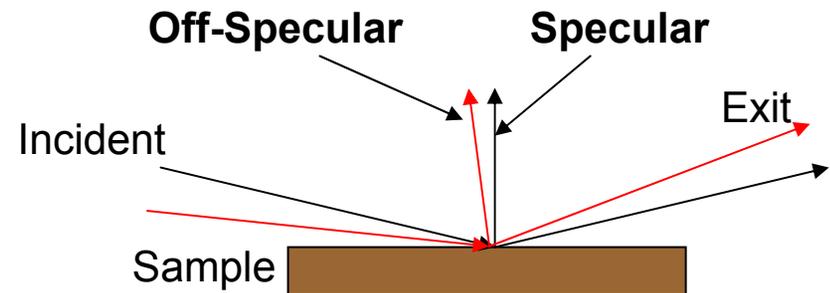
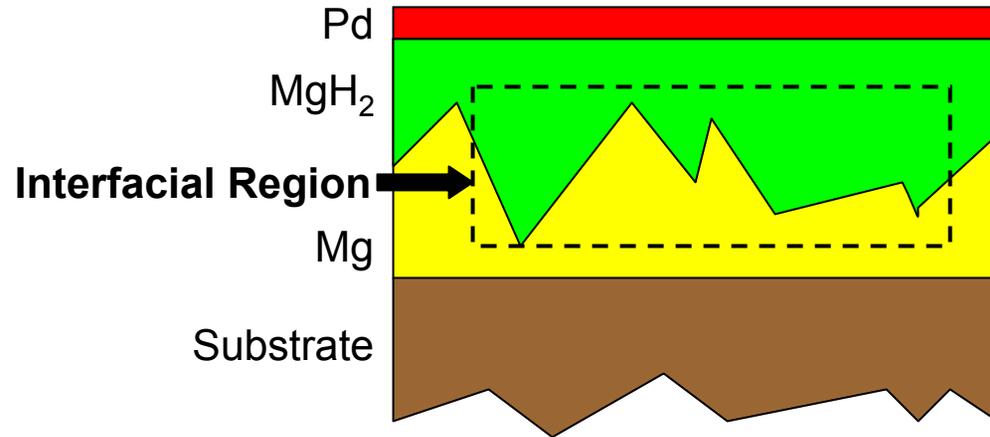
Neutron Reflectivity w/ NIST

- **More detailed studies will enable hydrogen depth profiling of samples**

- Verify layer-by-layer growth mechanism and refine model
- Show the actual hydrogen content of the samples as a function of depth

- **Can also characterize the interface separating the metal and hydride phases with additional studies**

- Off-specular scans allow more detailed interface characterization
- How rough is the interface?
- Does the interface change character with different charging conditions?
- How does the addition of other elements (like Ti) affect the interface character and development?



Neutron Reflectivity w/ NIST

• Conclusions

- Collaboration undertaken with NIST to leverage neutron capabilities and examine hydrogen distribution in thin film model metal hydride samples
- Learn more about interfacial region between the hydride and metal phases
 - Characterizing the interfacial region is crucial to understanding the kinetic processes involved in the metal hydride phase transition
- With continued experiments will gain further insight into how the interface moves and changes character with hydrogen charging and how charging conditions affect these behaviors
- Ultimately learn more about the kinetic mechanisms present in metal hydride reactions and in future use same techniques to investigate more complex systems such as Mg/Ti and $\text{LiBH}_4 + \text{MgH}_2$
- Communicate findings to other groups within MHCoe and elsewhere in order to advise on suggested approaches for improving kinetics in candidate material systems

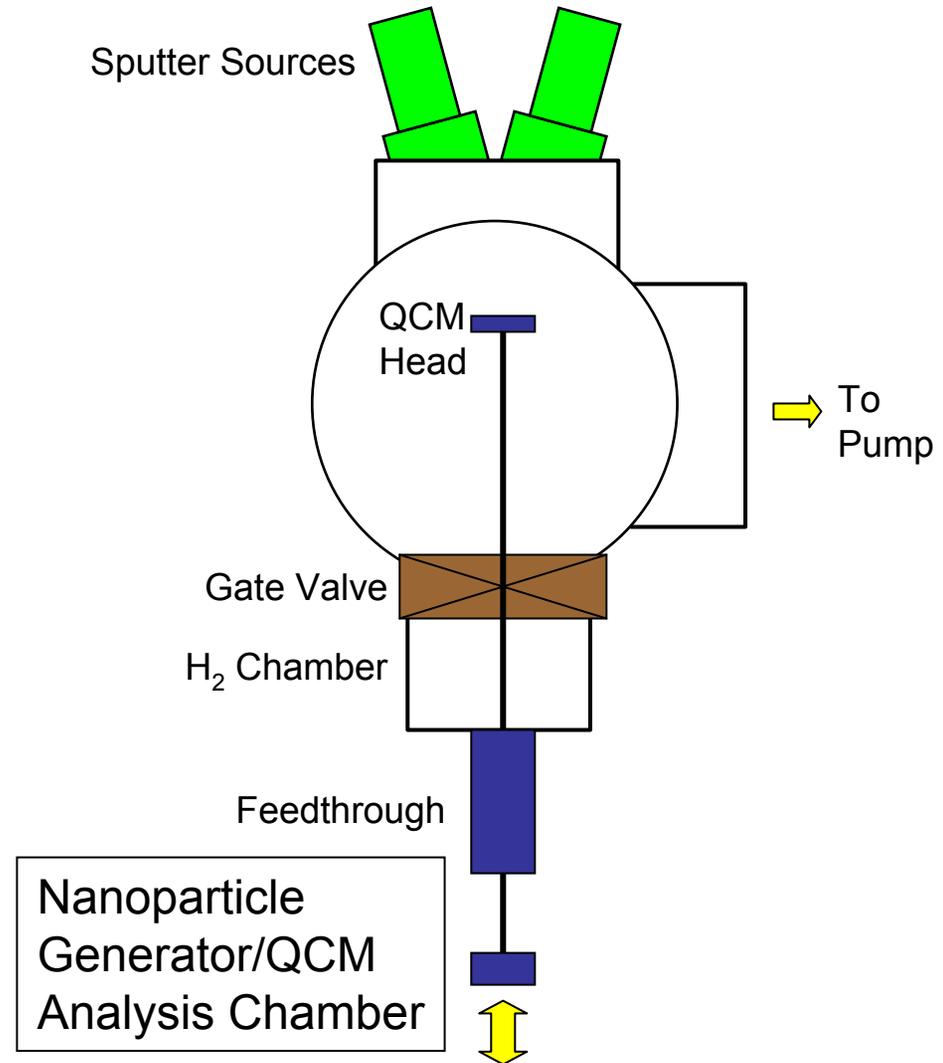
Future Work

- **Develop capability to synthesize nanoparticle samples as well as thin films**

- Attempt to verify predictions of thermodynamic modeling of size dependent equilibrium hydrogen vapor pressure for metal hydride materials

- **Develop quartz crystal microbalance (QCM) apparatus to measure hydrogen uptake in samples directly**

- Ability to measure ng/cm^2 mass change in materials
- Use to characterize hydrogen absorption in thin film and nanoparticle samples
- Ability to study nanoparticle samples and hydrogen uptake therein *without* exposure to oxygen



Future Work

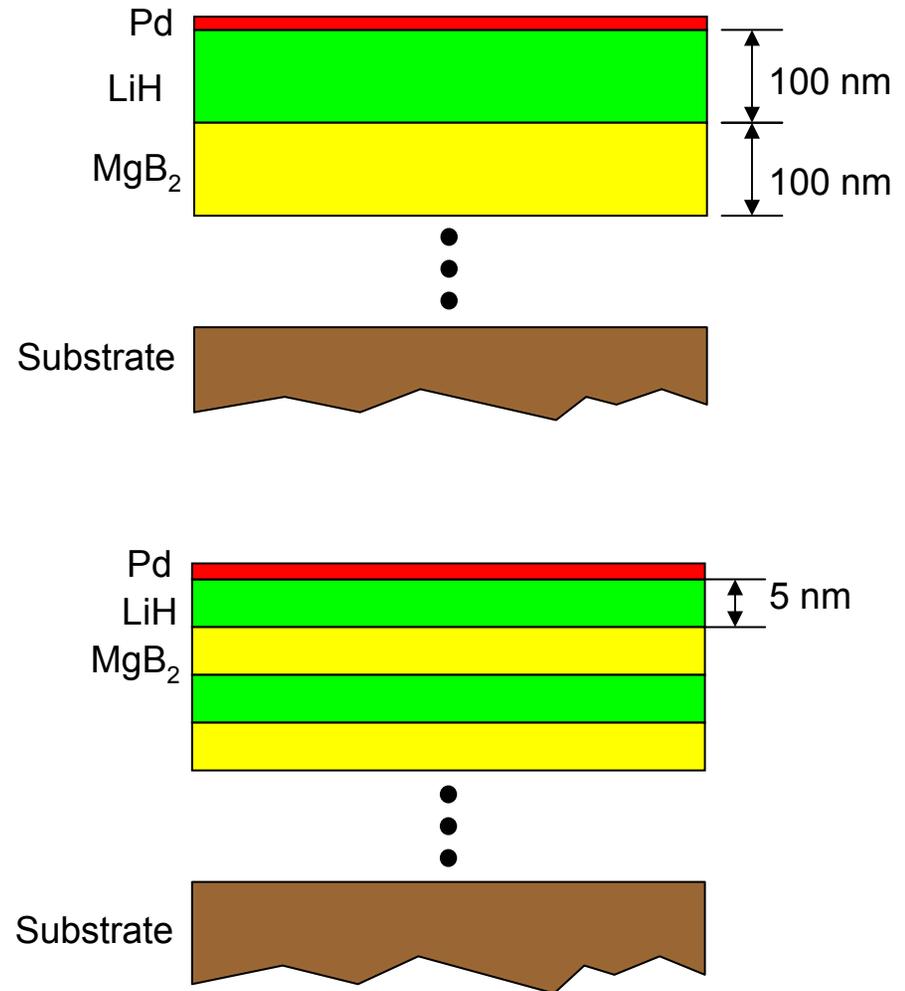
- **Examine additional material systems**

- Further investigation into Mg/Ti system
- $\text{LiBH}_4 + \text{MgH}_2$ system (experiment shown)
 - Vary length scale of materials and examine mass transport in system using *in-situ* XRD experiments to monitor presence of constituent phases
- Al containing systems

- **Expand capabilities related to *in-situ* structural characterization**

- Modify x-ray chamber to allow additional characterization techniques
- Continue collaboration with NIST to use *in-situ* neutron reflectivity

$\text{LiBH}_4 + \text{MgH}_2$ System Experiment



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:**
 - Slower discharge rates seen with loss of texture in epitaxial Mg films
 - Strong evidence for moving planar interface growth and diffusion limited kinetics for epitaxial Mg films, with 42% faster uptake kinetics seen for films containing 10 wt.% Ti
 - Collaboration begun with NIST to leverage neutron reflectivity to gain further insight into kinetic mechanisms in thin film systems, particularly information regarding the interfacial region separating the metal and hydride regions of the films
- **Collaborations and Tech. Transfer:**
 - Last year's Mg₂Si work motivating move to nanoscale materials design (HRL aerogel work, etc.)
 - Collaboration with NIST to utilize neutron capabilities to complement x-ray work
 - Working with HRL to design new LiBH₄+MgH₂ thin film experiment
- **Future Work:**
 - Develop nanoparticle synthesis and characterization equipment using QCM techniques to measure hydrogen uptake *in-situ*
 - New LiBH₄+MgH₂ thin film experiment to look at phase segregation during reaction
 - Extend *in-situ* characterization capabilities for x-rays and neutrons