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

Bruce Clemens
Stanford University
Project ID#: st_02_clemens
05/19/2009

This presentation does not contain any proprietary or confidential information

METAL HYDRIDE CENTER OF EXCELLENCE

STANFORD MATERIALS SCIENCE AND ENGINEERING

# Overview

- **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 $Mg/MgH_2$ interface
  - NIST Center for Neutron Research: collaboration to investigate reacting films using neutron reflectivity

# Relevance - Objectives

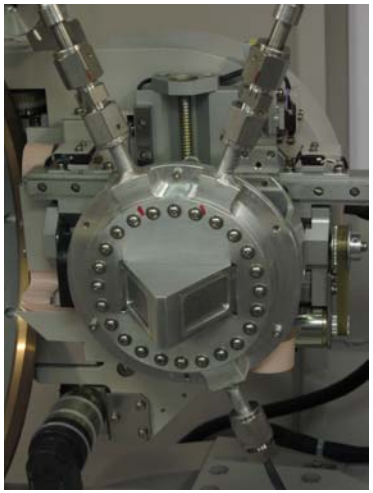
- **Develop fundamental understanding of metal hydride reaction kinetics**
  - Kinetics limit practicality and reversibility of many promising metal hydride material systems
    - Mg, $Mg_2Si$, $Mg(AlH_4)_2$, $Li_4Si$, $NaAlH_4$, $LiBH_4$+$MgH_2$, etc.
    - Initial work on $Mg_2Si$ showed that kinetic issues prevent system from achieving reversibility
  - Catalyst additions have shown some success in improving kinetics for some systems (ie. Ti in $NaAlH_4$), 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

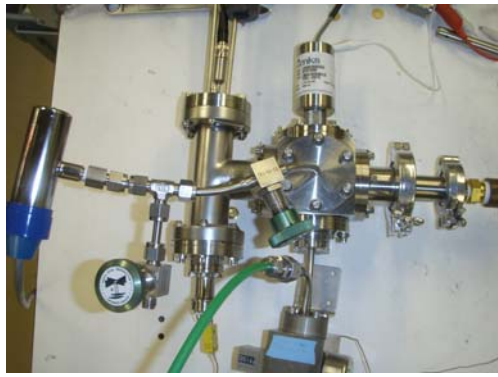
# Approach

- **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

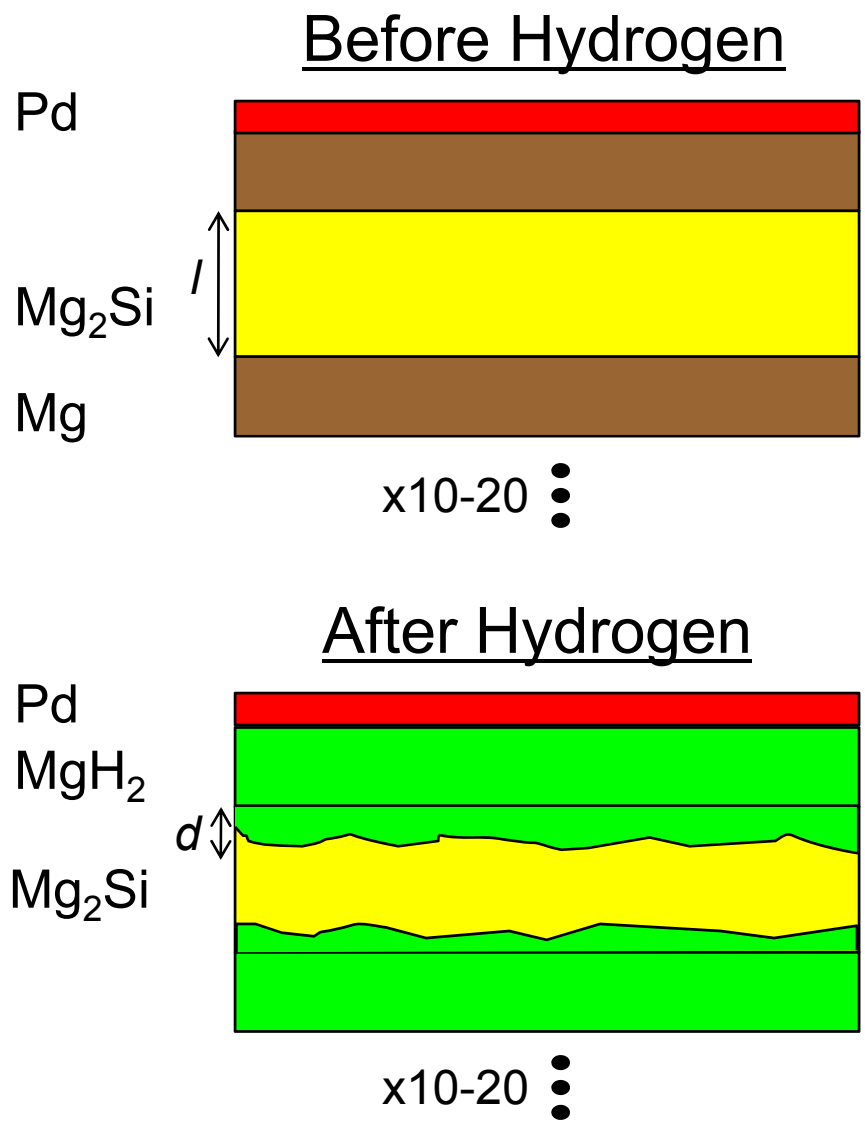
| Date | Milestone or Go/No-Go Decision |
|---|---|
| 07/2008 | **Milestone:** Model kinetic transformation processes for thin film metal hydride material systems.<br>**Status:** New model developed to describe moving planar interface kinetics in thin film samples |
| 05/2008 | **Milestone:** Investigate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

# Progress – $Mg_2Si$ 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 $Mg_2Si$ peak intensity reduction
  - Undertook *new* study with careful data analysis

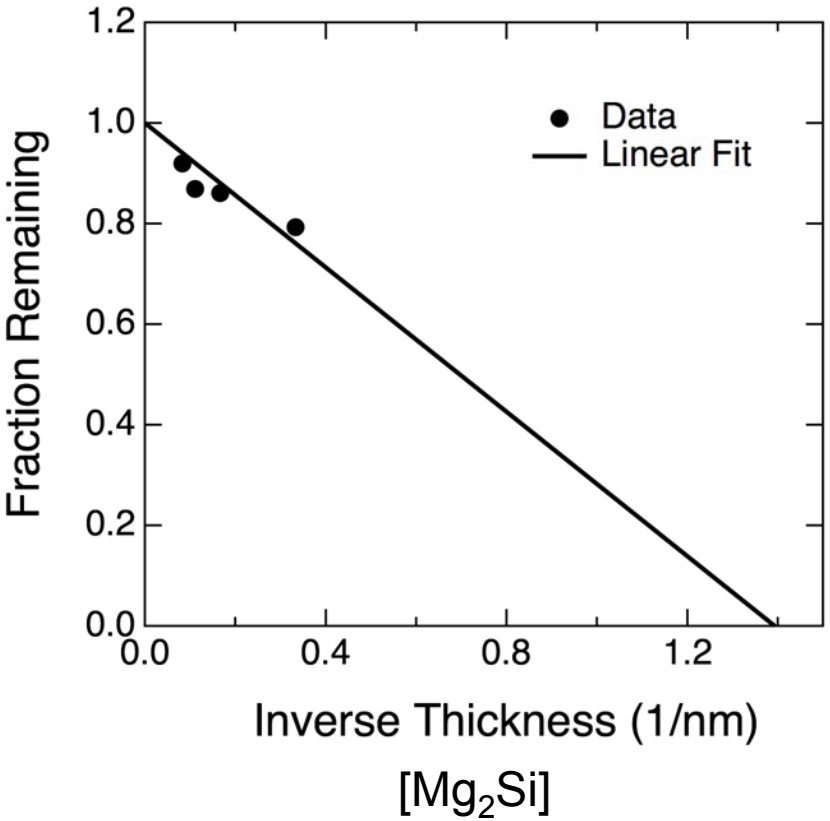
- **Multilayer samples allow analysis of very small reaction depths using XRD**

*Fraction remaining = 1 - 2d/l*



# Progress – $Mg_2Si$ 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 $H_2$
- **Particle sizes <1 nm needed to achieve complete hydrogenation from $Mg_2Si$ phase**
  - Phase transition **not** limited by hydrogen diffusion through $Mg_2Si$ or nucleation of $MgH_2$ phase (separate experiments)
  - Reverse reaction kinetics severely limited by transport of Mg and Si during phase segregation from $Mg_2Si$ into $MgH_2$ 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

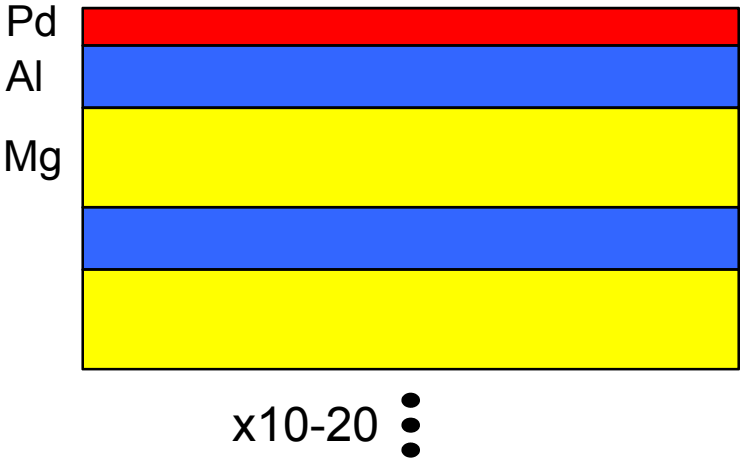


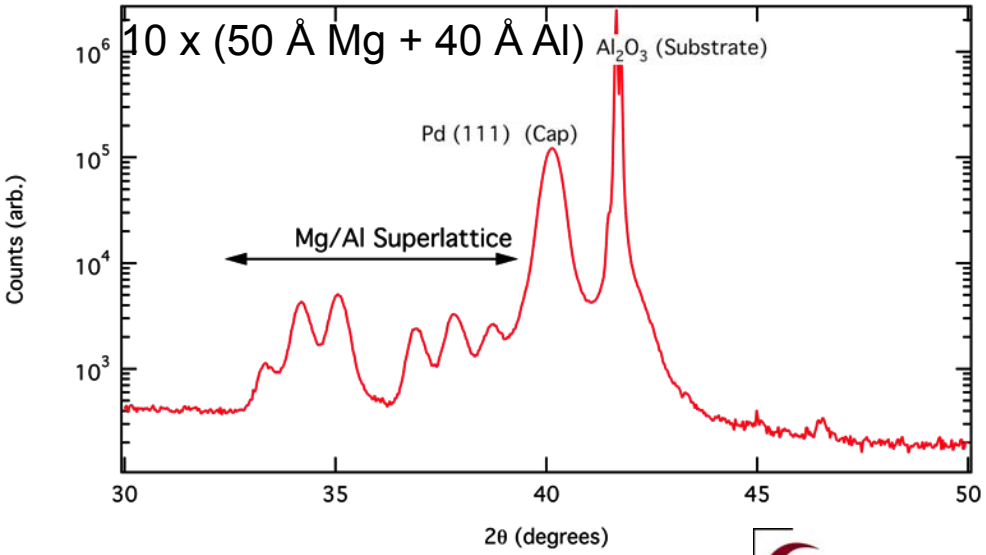

*Kelly, et al., Nanotechnology **20** (in press)*

Hydrogen diffusion >> host diffusion

# Progress – Mg/Al System

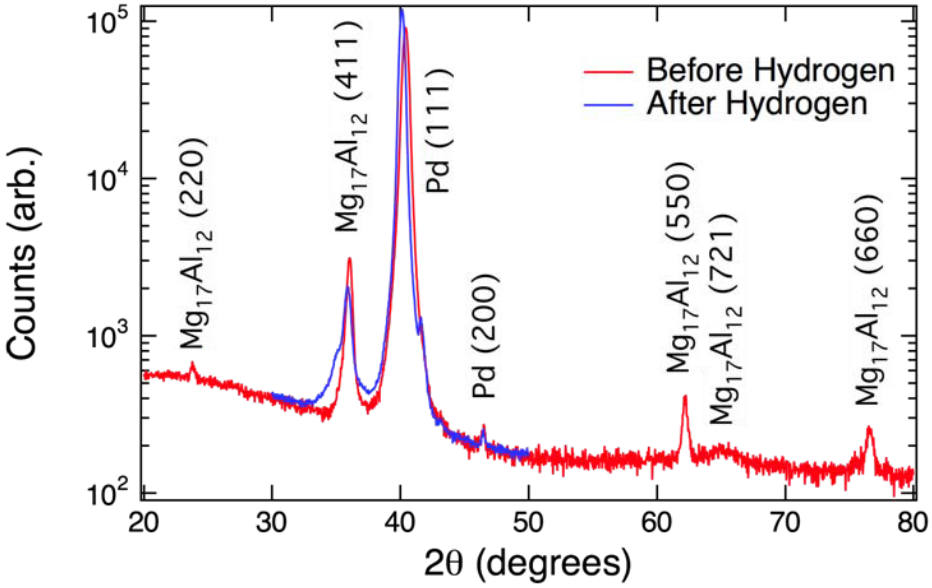
- **Apply thin film methods to new material system with kinetic problems (like $Mg_2Si$)**
  - $Mg(AlH_4)_2 \rightarrow MgH_2 + 2Al + 3H_2$
  - Reverse reaction very difficult
  - Varying reports of thermodynamic parameters in literature
- **Our approach:**
  - Mg/Al multilayer films with Pd capping 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 straighforward
  - Layers intermixing at room temperature over a few days
  - Hydrogen diffusion



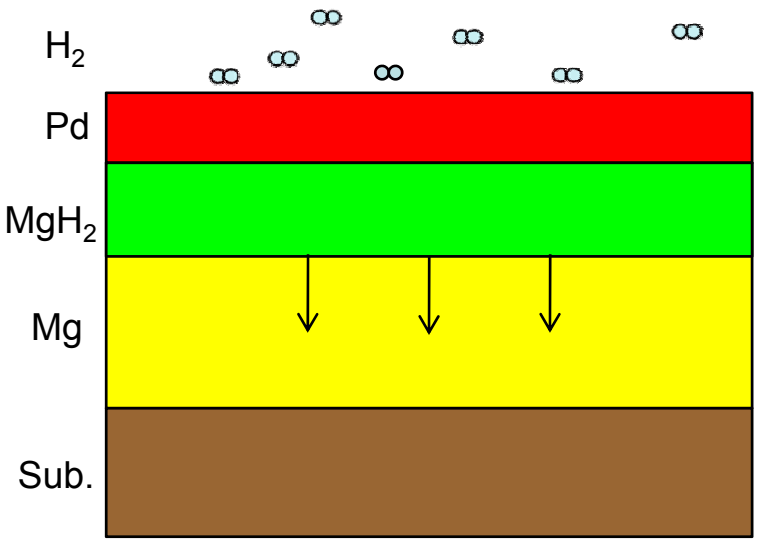
# Progress – Mg/Al System

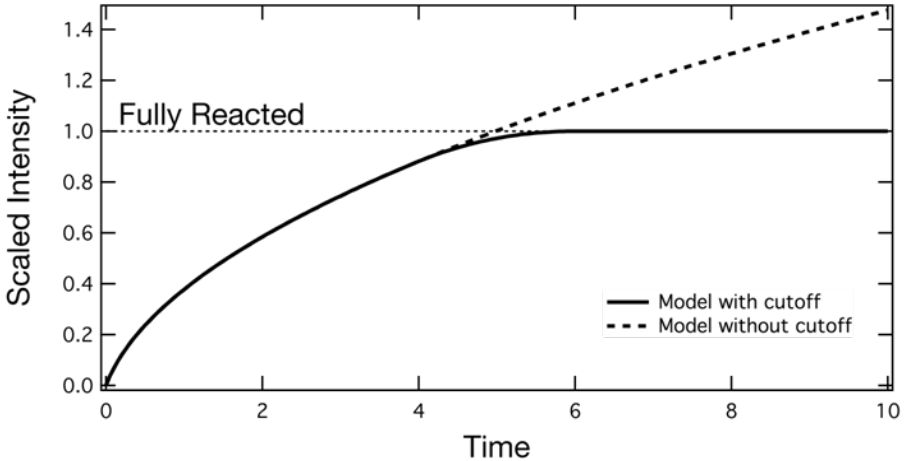
- **After hydrogen annealing under 1 bar $H_2$ at 110 °C for 10-20 hrs took new XRD spectra**
  - Some spectra identical to those taken before annealing
  - Others show intermetallic phases
- **Films do not seem to readily react with $H_2$**
  - No $MgH_2$ formation seen
  - Evidence for alloy formation 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 Grove[1] **(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




[1]B. E. Deal and A. S. Grove, J. App. Phys. **36** 3770 (1965)

# 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:**

$$\boldsymbol{J} = k_1(\mu_1 - \mu_2)$$

- **Fick's First Law across layers:**

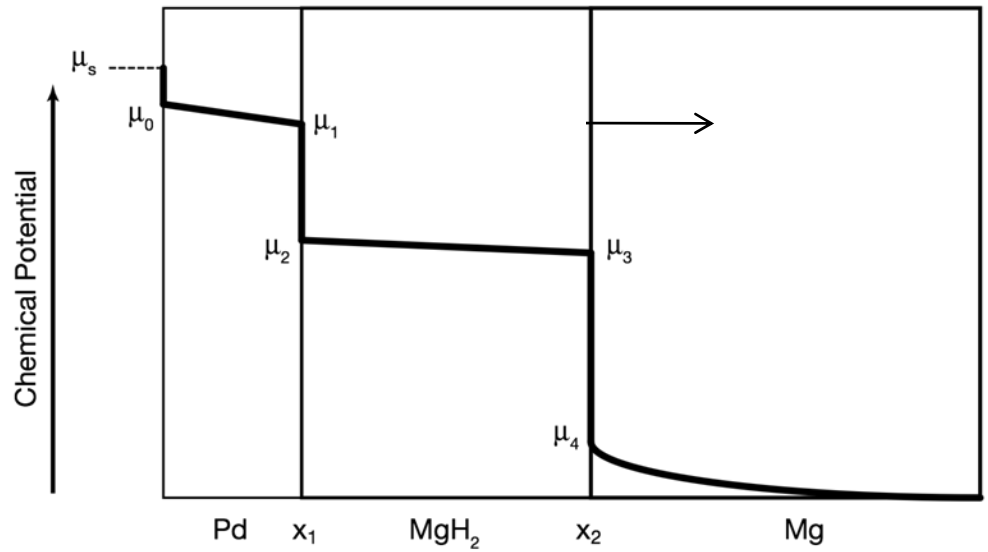
$$\boldsymbol{J} = -M\nabla\mu = -M\frac{\mathrm{d}\mu}{\mathrm{d}x}$$

- **Assume concentration in Mg is zero:**

$$c_{Mg} = 0$$

- **All flux into Mg creates $MgH_2$:**

$$\boldsymbol{J} = N_1\frac{\mathrm{d}x_2}{\mathrm{d}t}$$




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

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

# Progress – Hydride Growth Kinetics

- **To account for finite film thickness, introduce cutoff function to model**
  - Multiply derivative by linear cutoff

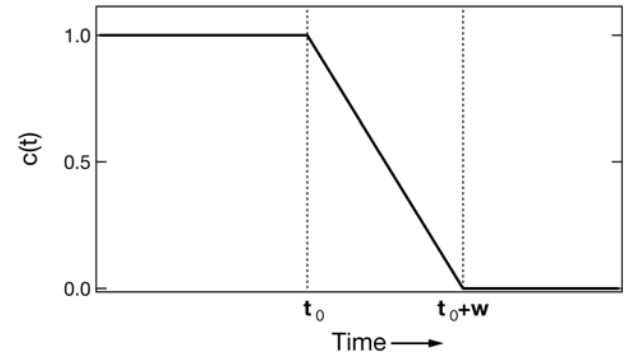
$$c(t) = \begin{cases} 1 & t < t_0 \\ 1 - \frac{t-t_0}{w} & t_0 \le t \le t_0 + w \\ 0 & t_0 + w < t \end{cases}$$

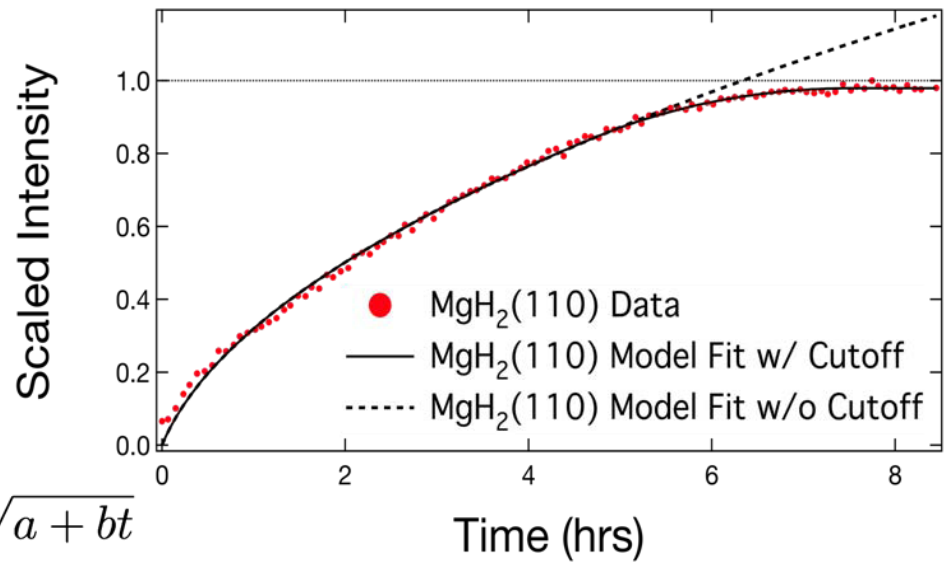
$$\frac{\partial y(t)}{\partial t} = \left(\frac{b}{2\sqrt{a+bt}}\right)\left(1 - \frac{t-t_0}{w}\right)$$

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

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

Cutoff function:

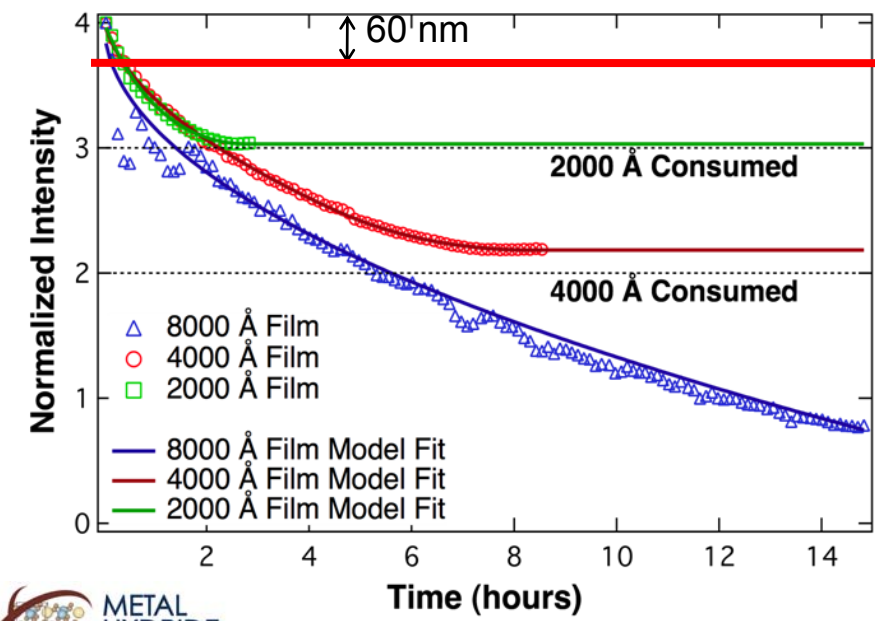


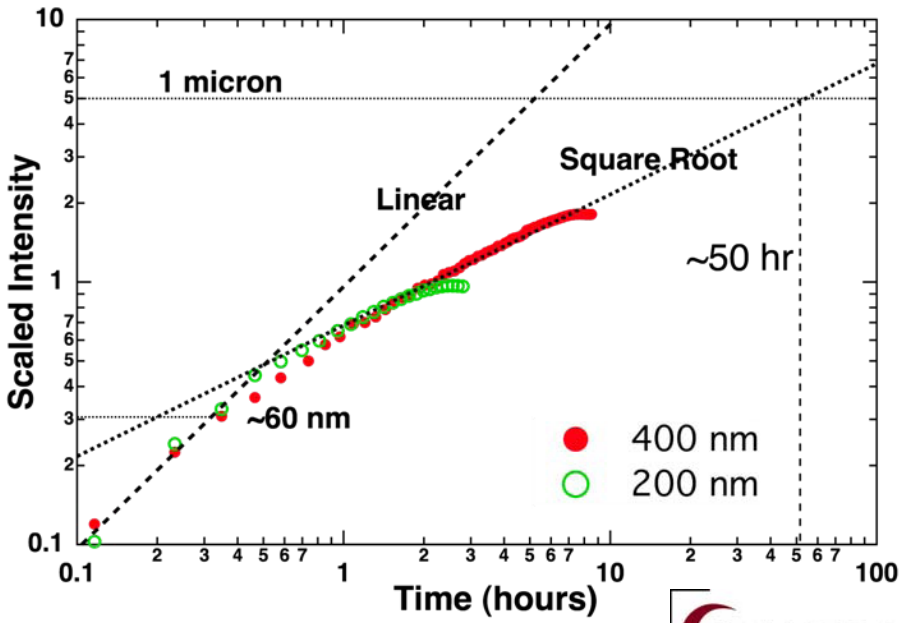




$$z(t) = \begin{cases} \frac{x_2(t)}{y(t_0+w)} & t < t_0 \\ \frac{y(t)}{y(t_0+w)} & t_0 \le t \le t_0 + w \\ 1 & t_0 + w < t \end{cases}$$

# Progress – Hydride Growth Kinetics

- **New model better describes the data**
  - Hydride formation kinetics limited by diffusion (~$t^{1/2}$) 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 °C)
  - Reaction limited (~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



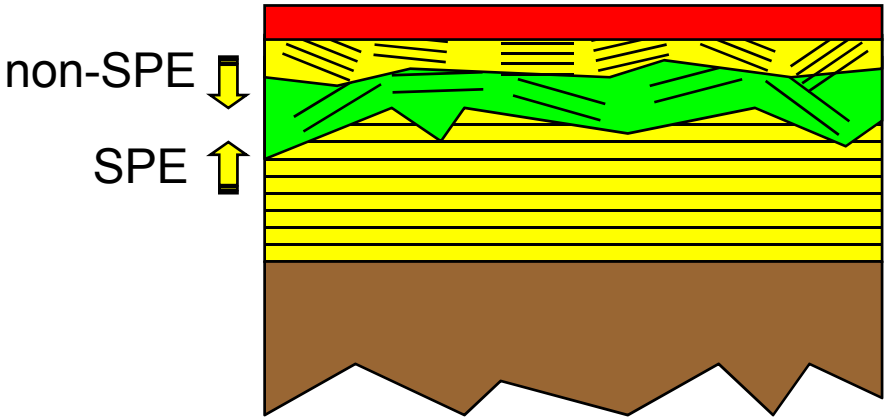

METAL HYDRIDE CENTER OF EXCELLENCE

STANFORD MATERIALS SCIENCE AND ENGINEERING

# Progress – Hydride Growth Kinetics

- **Previously observed solid phase epitaxial (SPE) regrowth of $Mg/MgH_2$ 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?

**Mixed Regrowth**

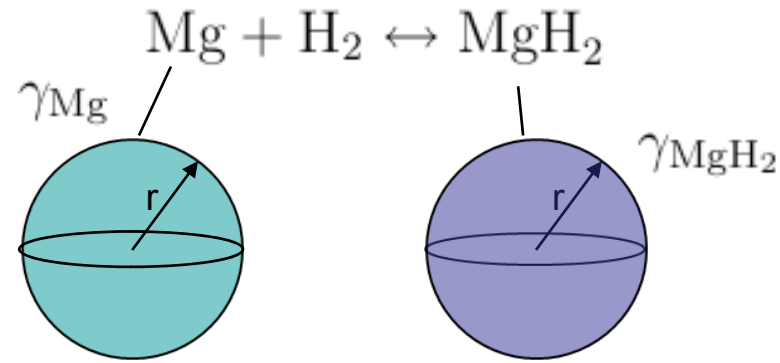


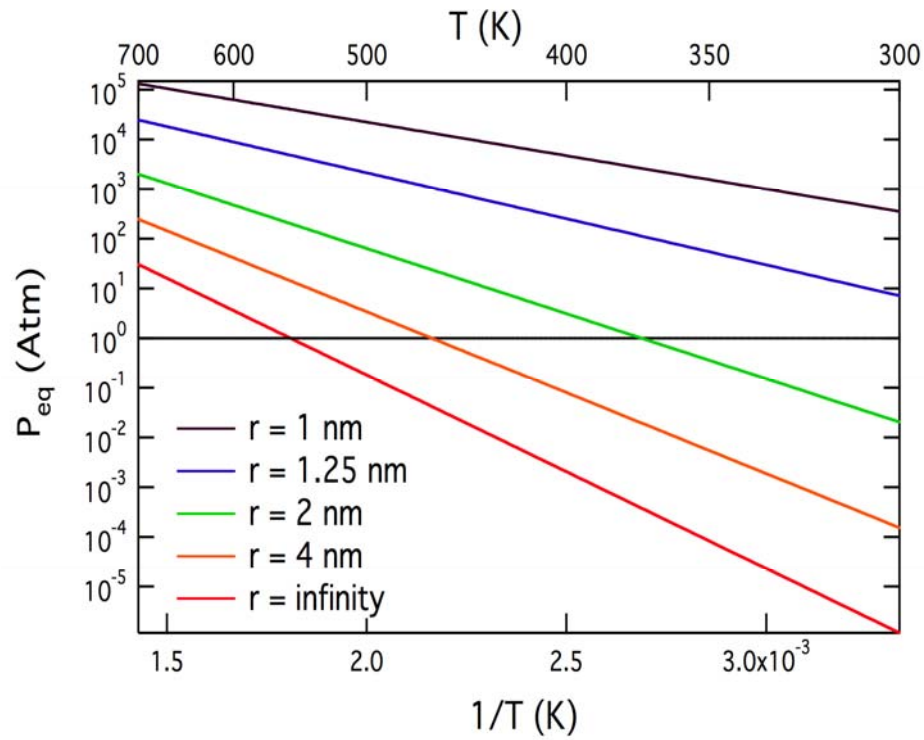
# Progress – Nanoscale Mg

- **Continuum modeling (previous work) predicts enhanced equilibrium pressure in $MgH_2$ with reduced particle size**
  - Particles with r = 2 nm should have $P_{eq}$ = 1 atm at T~100 °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

$$P^{r}_{\mathrm{H_2(eq)}} = \exp\left[\frac{\Delta G^{\circ}}{RT} + \frac{2\Delta\gamma V_M^{\mathrm{Mg}}}{r_{\mathrm{Mg}} RT}\right]$$

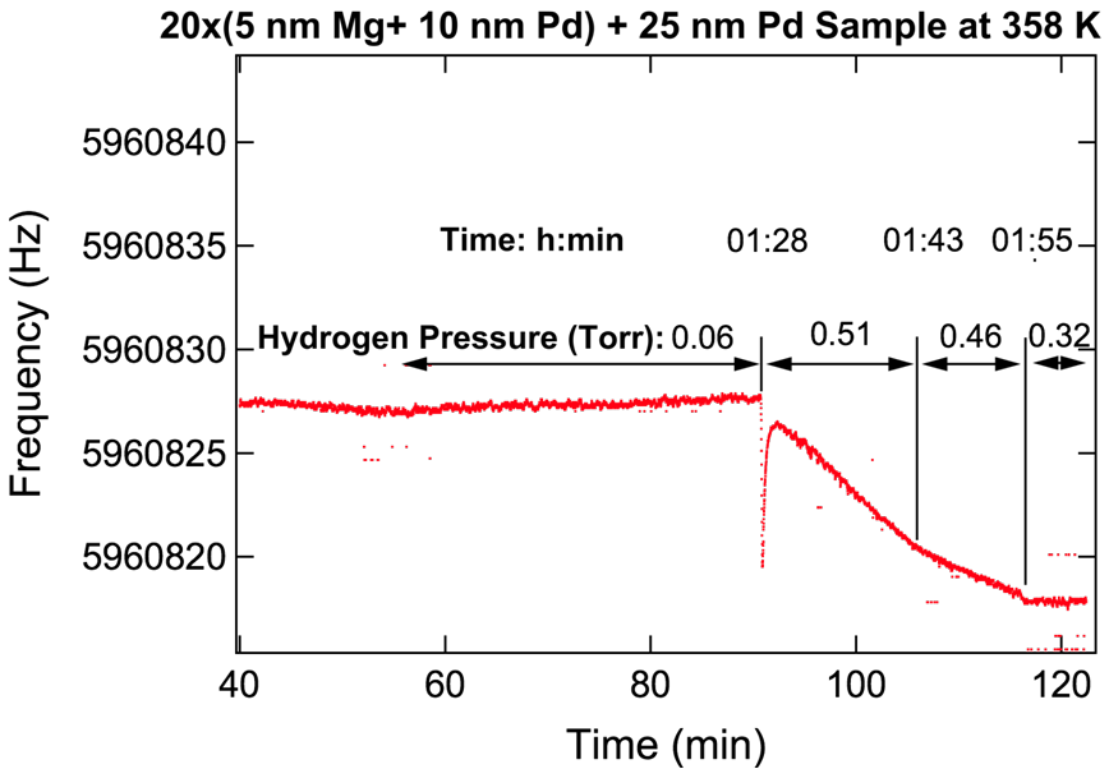
$$\Delta\gamma = 1.74\ \mathrm{J/m^2}$$



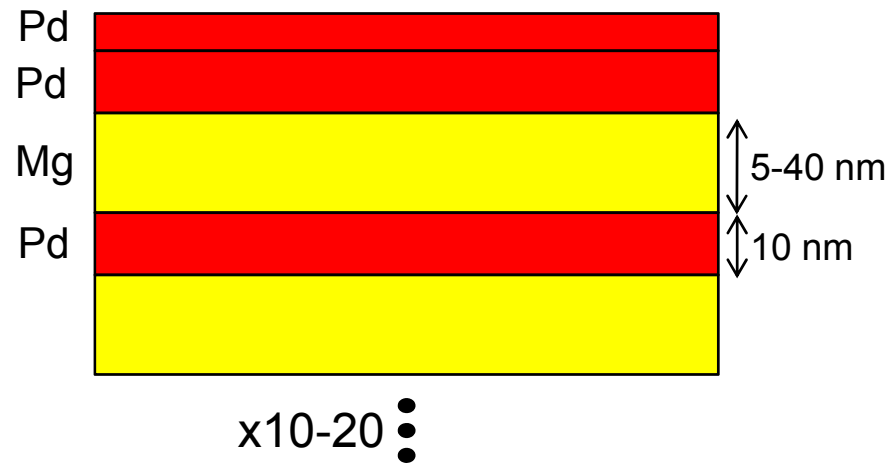
# Progress – Nanoscale Mg

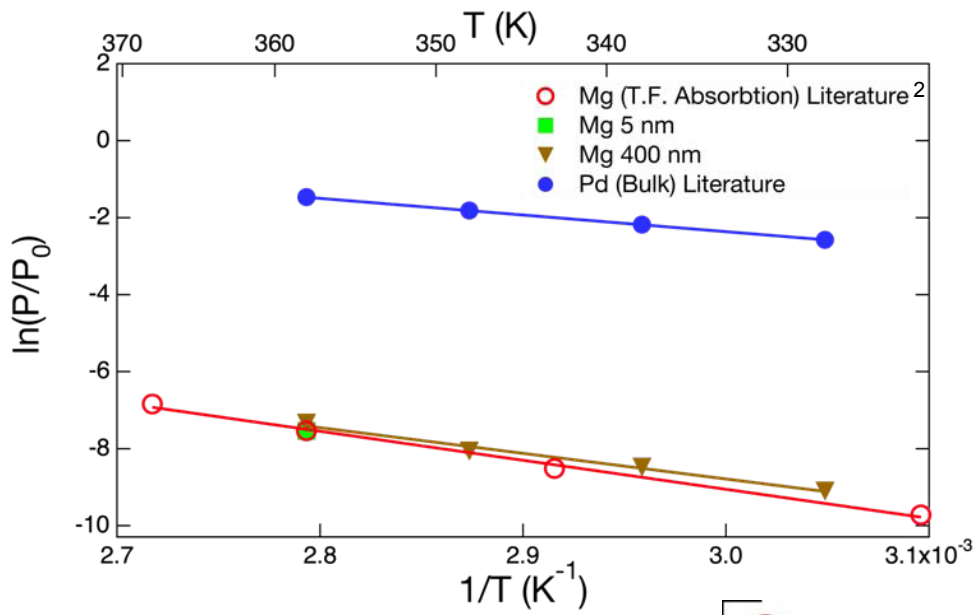
- **QCM data collection procedure:**
  - Sample and chamber controlled at fixed temperature
  - Process gas (pure $H_2$ or mixture) bled in via leak valve
  - Crystal frequency constantly monitored
    - Frequency down = mass uptake
  - Pressure stepped up until uptake seen
  - Pressure reduced until 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 mn) 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**



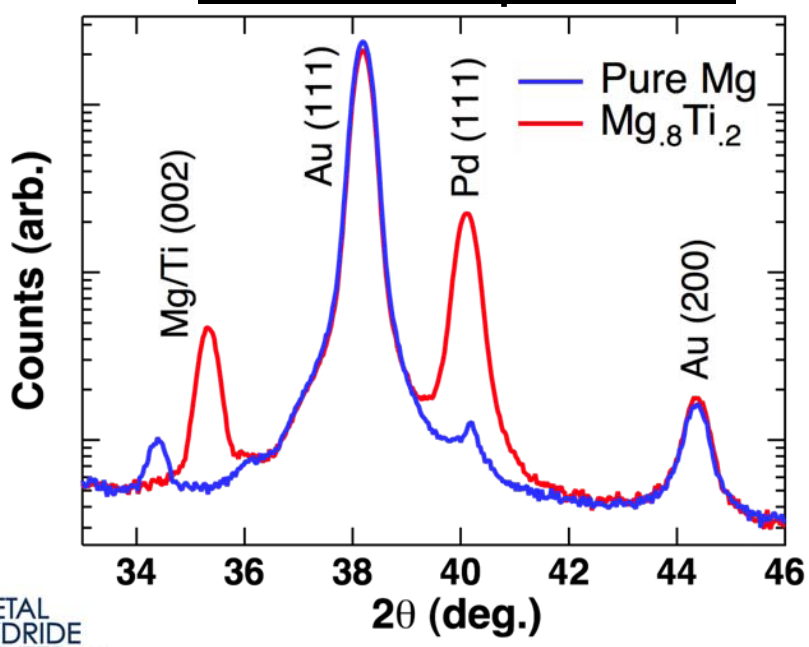



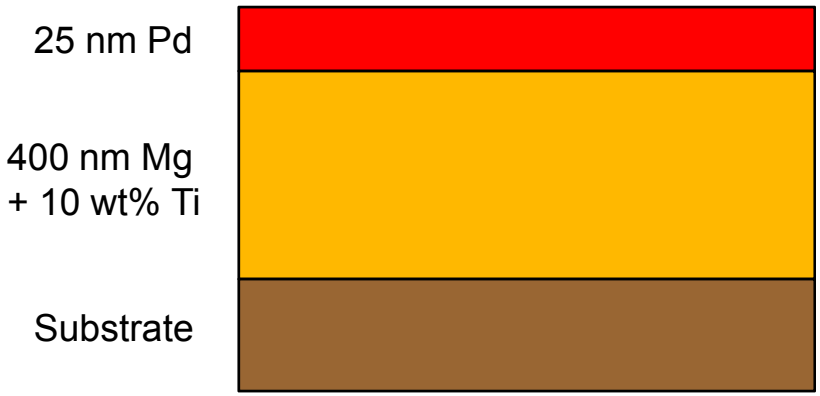

[2]Krozer, *et al*, *J. Less-Common Metals*, **160** 323 (1990)

# 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

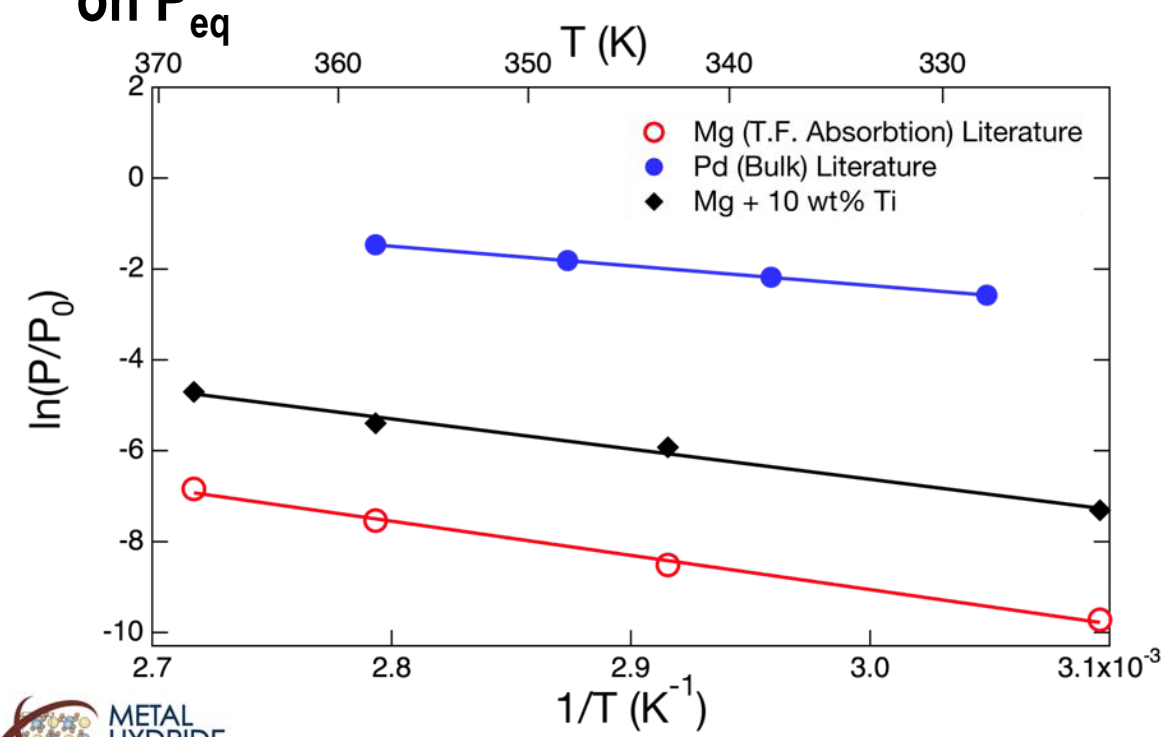
## QCM Sample XRD



# Progress – Mg/Ti System

- **Addition of 10 wt % Ti results in ~10x increase in $P_{eq}$ compared to pure Mg**
  - ΔH comparable to literature calculations[3] (-55 kJ/mol (this work) vs -51.6 kJ/mol (literature) for $Mg_{.8}Ti_{.2}H_2$)
  - $P_{eq}$ values comparable to other literature reports for this system[4,5]
- **Further work needed to verify and examine effects of Ti concentration on $P_{eq}$**





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

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

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


METAL HYDRIDE CENTER OF EXCELLENCE

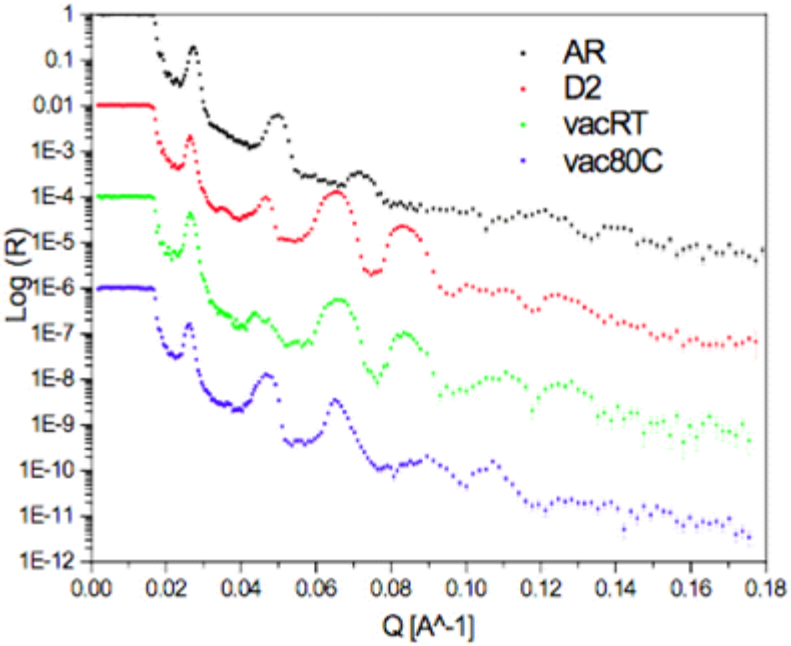
STANFORD MATERIALS SCIENCE AND ENGINEERING

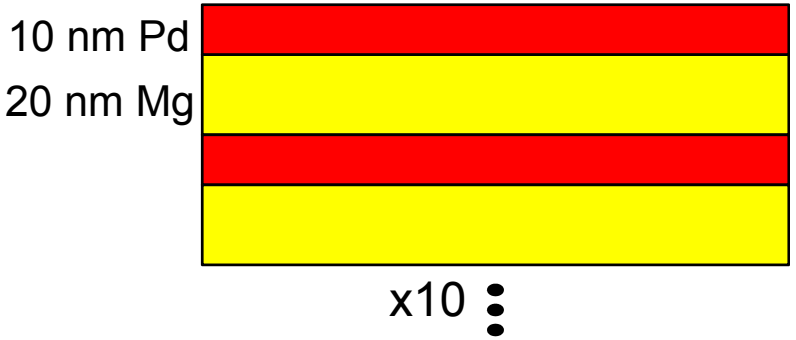
# Progress – Neutron Reflectivity with NIST

- **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

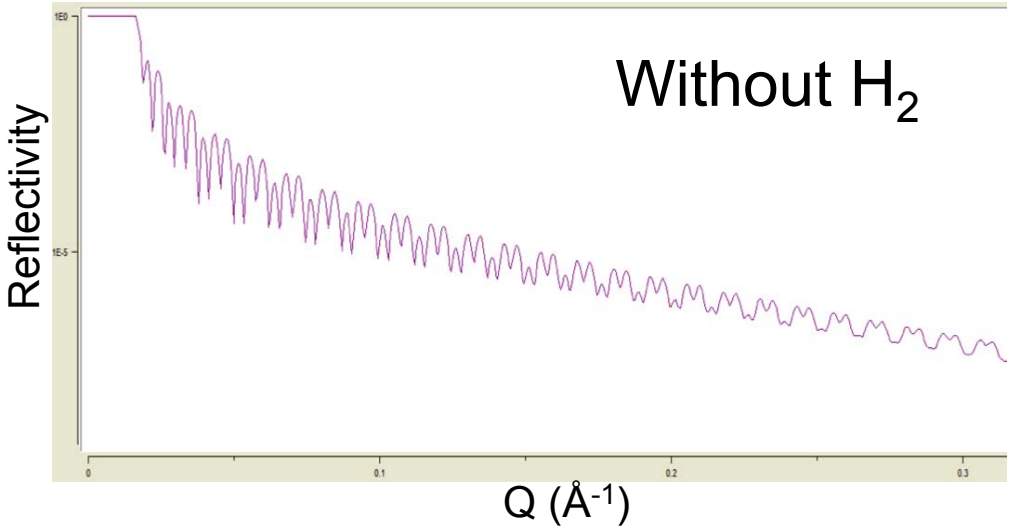
## Previous Results

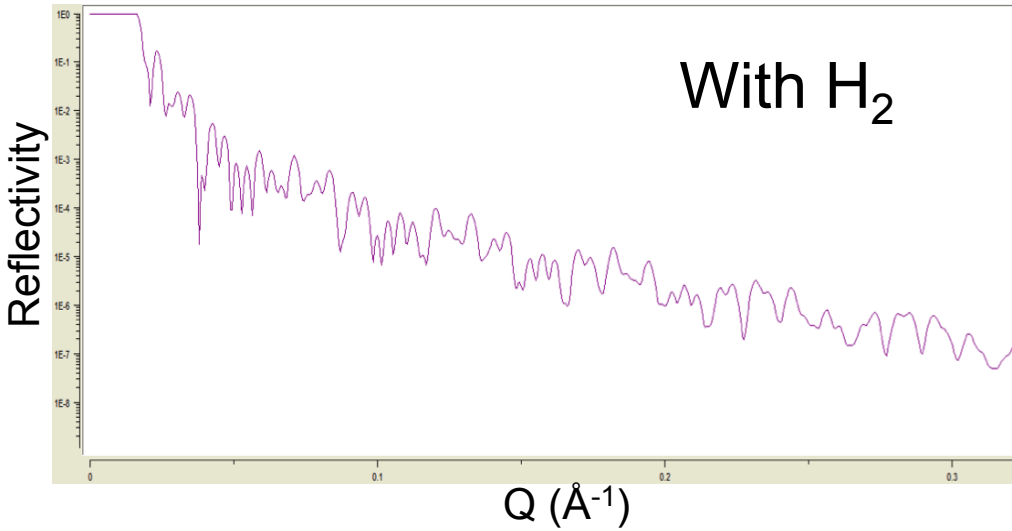


# Progress – Neutron Reflectivity with NIST

- **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 $Mg/MgH_2$ 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 $H_2$ anneals
  - Faster turnaround to prevent intermixing
- **Finalize nanoscale Mg study**
  - Thinner Mg layers on QCM
  - Careful measurements on existing samples
- **Further develop $MgH_2$ 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/$MgH_2$ 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 $MgH_2$ 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 ~10x increse 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