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

Bruce Clemens
Stanford University
Project ID#: STP 5
04/21/06

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: ~25%
- **Budget**
  - Total Project Funding: $997,921
    - DOE Share: $778,828
    - Contractor Share: $199,093
  - Funding Received FY05: $150,000/$37,500
  - Funding Received FY06: $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/MgH_2 interface

Objectives

- **Perform In-Situ Structural Studies of Hydrogen Storage Materials**
  - Utilize high brightness x-ray source at Stanford Synchrotron Radiation Laboratory
  - Construct Sieverts apparatus for in-situ control of hydrogen content
  - Demonstrate feasibility of in-situ synchrotron studies

- **Investigate Light Metal Hydride Model Material Systems**
  - Use designed thin film model systems to investigate phase change and catalytic processes associated with hydrogen cycling

- **Develop Kinetic Model of Nanoparticle Phase Transformations**
  - Build continuum models of nanoparticle kinetics to illuminate mechanisms of hydride formation in nanoscale materials

Approach

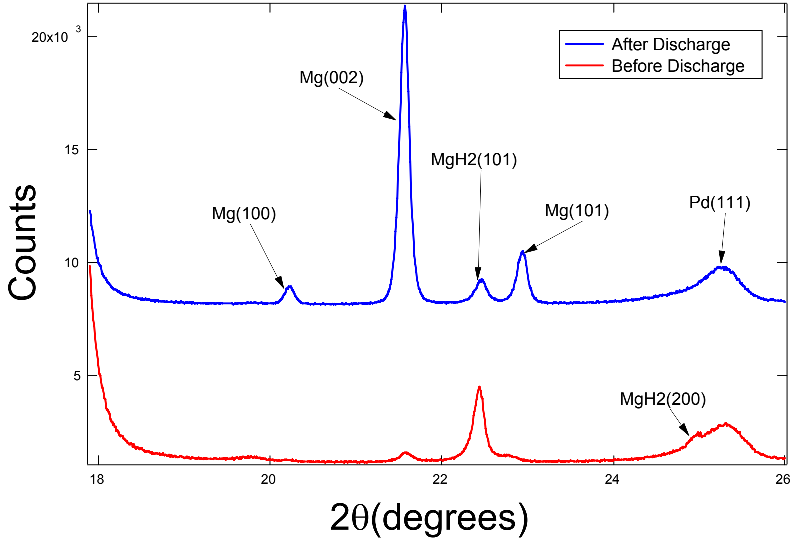
- **In-Situ Structural Studies**
  - Real time structural analysis using high brightness synchrotron radiation
  - in-situ hydrogen charging of candidate materials
  - Correlate structural changes with hydrogen charging characteristics

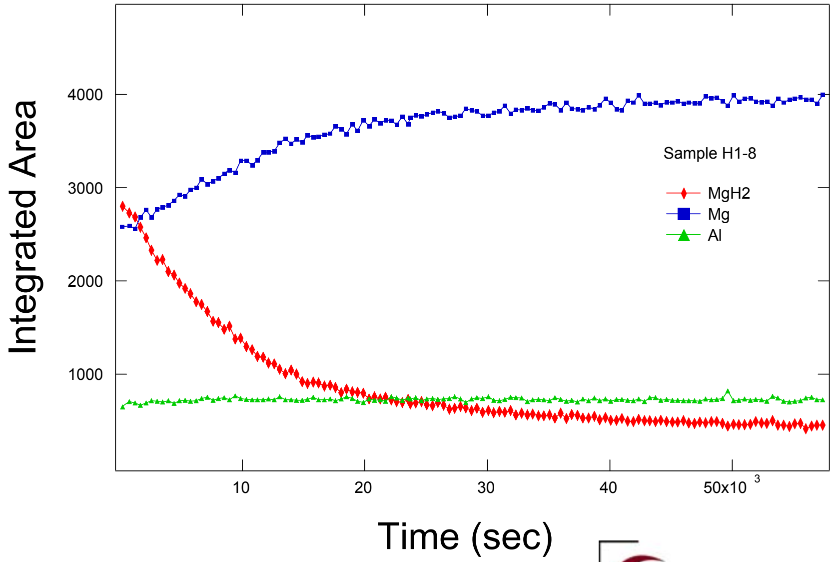
- **Model Material System Design and Synthesis**
  - Design and grow model material systems using physical vapor deposition techniques such as sputtering

- **Kinetic Modeling of Nanoparticle Transformations**
  - Model kinetic processes of phase transformations in nanoparticles to guide future material selection and design

Kinetic Studies Using XRD

- **Hot stage attachment on diffractometer allows hydride content to be monitored during sample discharge**
  - Comparison of integrated intensities for Mg and MgH_2 yields fraction of film reacted
- **Initial studies at Stanford Synchrotron Radiation Laboratory (SSRL) showed promise of XRD technique**
  - Mg peaks intensify while MgH_2 peaks disappear as sample is discharged
- **Further applications using in-house XRD equipment brought more quantitative kinetic data**
- **Utilizing hotstage on in-house XRD we obtained detailed kinetic information for several thin film samples**
  - Plot integrated intensity for Mg(002) and MgH2(110) peaks vs. time





Mg_2Si System

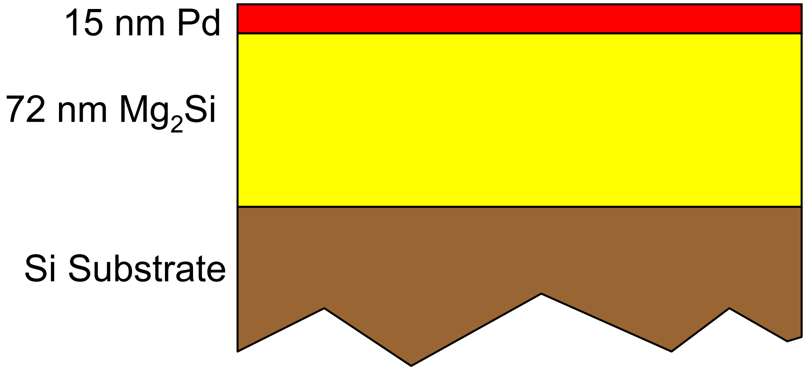
- **Initial attempts at hydriding monolithic Mg_2Si films were unsuccessful**
  - Even at high (~200 bar) pressures and long (~48 hr) times using HRL's facilities
  - No MgH_2 phase seen in XRD data

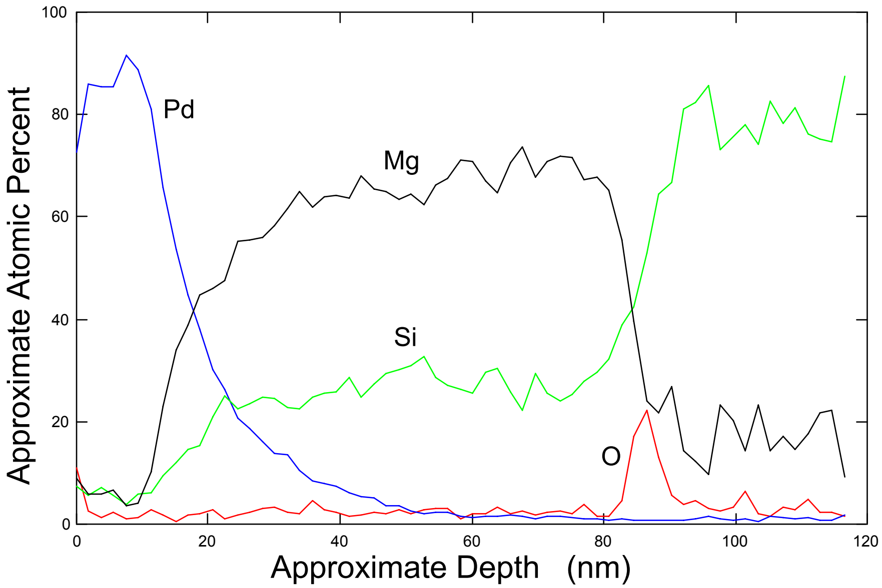
- **Questions:**
  - Is the hydrogen diffusing through the Mg_2Si?
  - Is there a problem with nucleation of the hydride phase in the Mg_2Si?
  - Are the distances for the Si or Mg to diffuse in the structure to form the MgH_2 phase to large?
  - Is the Mg_2Si compound too stable for the reaction to proceed at an appreciable rate?

- **Designed and deposited wide variety of multilayered structures to examine problems being encountered**
  - Structures contained layers of Mg, Mg_2Si, and Pd in various configurations

Mg_2Si System: Samples

- **Monolithic Mg_2Si films with Pd capping layer**
  - Demonstrate ability to deposit alloy samples and attempt to hydride from dehydrided state
  - Unable to hydride samples (200 bar H_2 for 48 hr)
- **Non-stoichiometric monolithic Mg_2Si film with Pd capping layer**
  - Deposited with excess Mg at ~$Mg_{2.8}Si$
  - Attempt to nucleate hydride formation with excess Mg
- **Attempted same geometry with Ge additions**
  - No silicide decomposition
- **After hydriding at 200 bar H_2 for 48 hr**
  - Complete transformation of Mg_2Si into MgH_2 and Si not observed

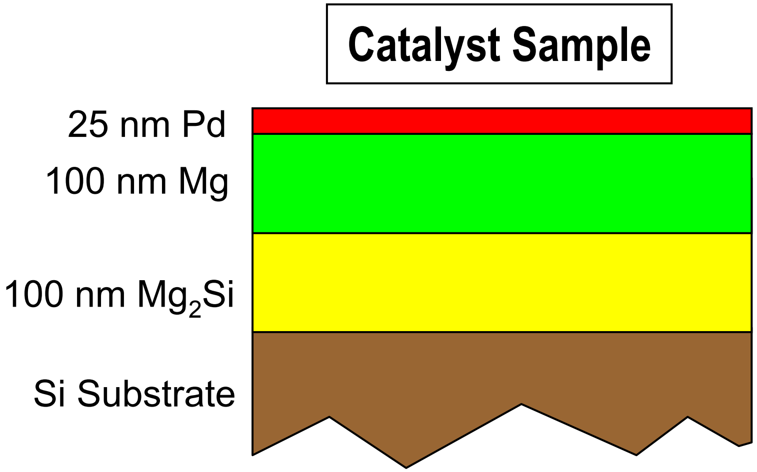




Depth Resolved AES

Mg_2Si System: Samples

- **Catalyst layer sample**
  - Attempt to catalyze formation of MgH_2 with layer of Mg on top of Mg_2Si layer
  - Mg completely hydrided
  - Mg_2Si did not decompose into MgH_2 + Si
- **Sensor layer sample**
  - See if H_2 is diffusing through the Mg_2Si layer
  - Mg layer beneath Mg_2Si completely hydrided - H_2 diffused through Mg_2Si layer
  - Mg_2Si did not decompose into MgH_2 + Si
- **Other multilayer samples**
  - Thin Mg_2Si/Mg and Mg_2Si/Pd multilayers deposited to investigate effect of reducing diffusion length for Si in samples
  - Mg_2Si did not decompose into MgH_2 + Si



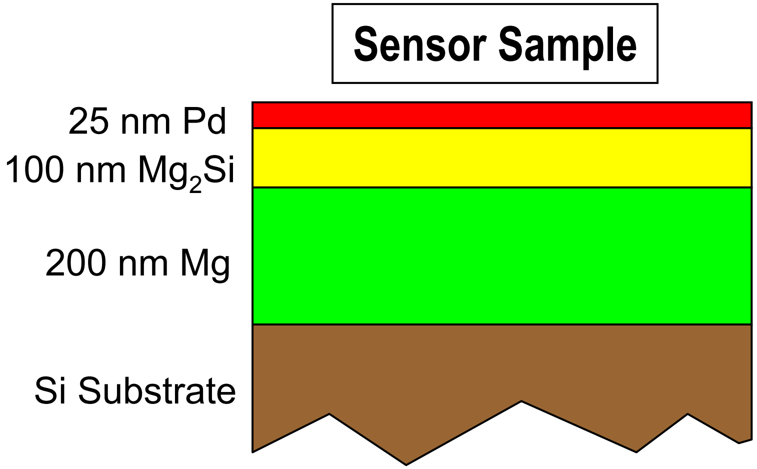
Catalyst Sample

25 nm Pd

100 nm Mg

100 nm Mg_2Si

Si Substrate



Sensor Sample

25 nm Pd

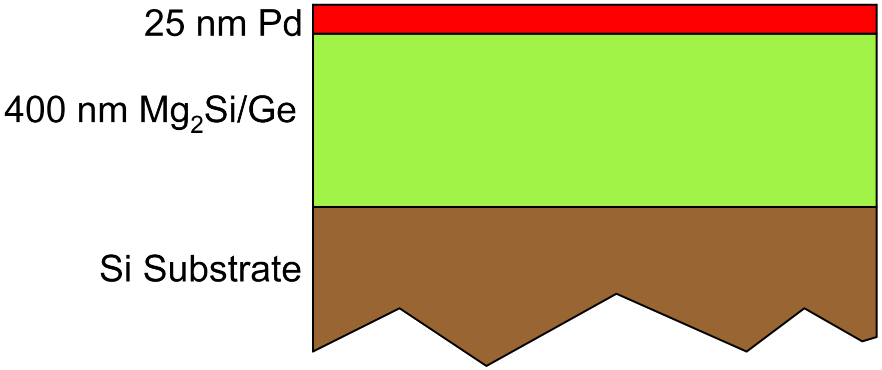
100 nm Mg_2Si

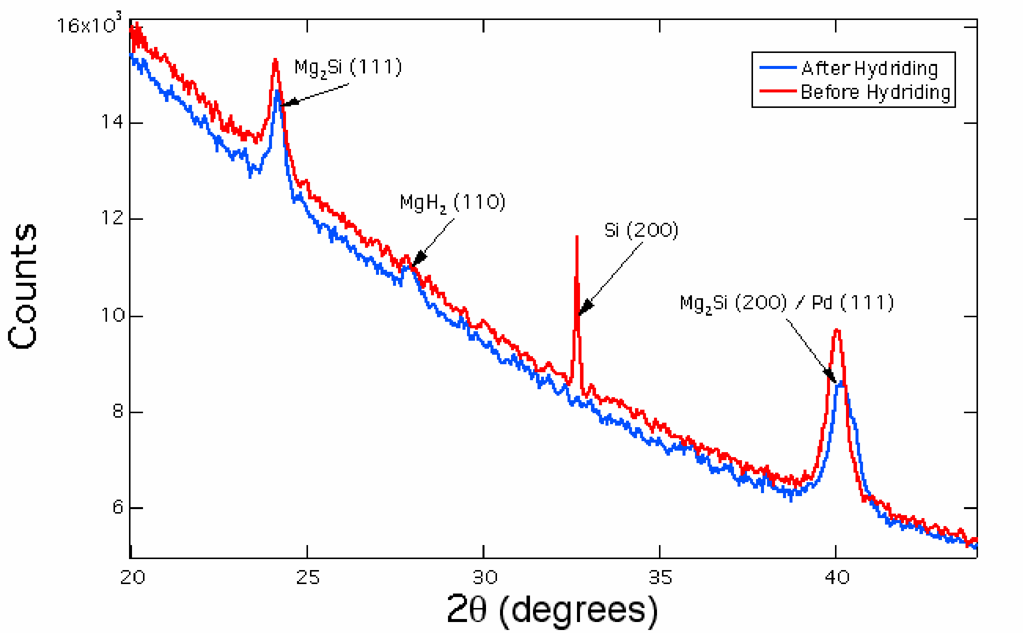
200 nm Mg

Si Substrate

Mg_2Ge/Si Structures

- **With little success of Mg_2Si system, we looked at alloying with Ge**
  - Samples with Ge additions have shown increased kinetics over pure MgH_2*
    - *Gennari, et al. *J. Alloys Comp.,* vol. 334, p. 277-284
- **Using co-deposition, we deposited alloy samples of Mg2Si/Ge**
  - 400 nm Mg2Si.75Ge.25 + 25 nm Pd
  - Mg2Si.5Ge.5 + 25 nm Pd
- **After hydriding at 200 bar H_2 for 48 hr, Mg_2Si/Ge remained**
  - Small amount of MgH_2 seen
  - System still kinetically limited

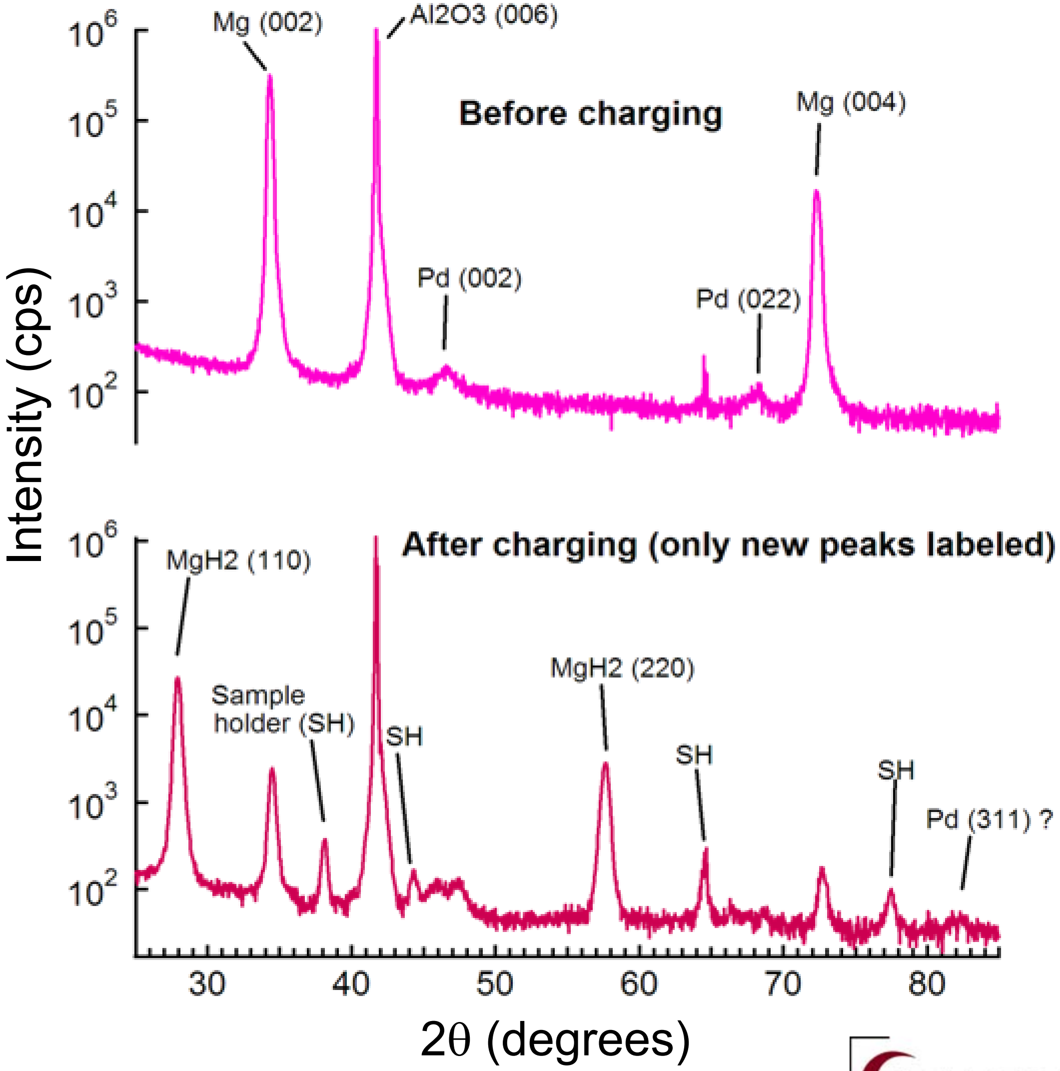




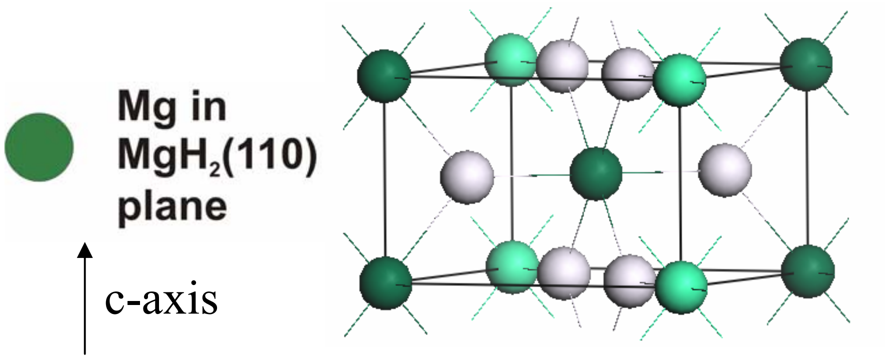
XRD

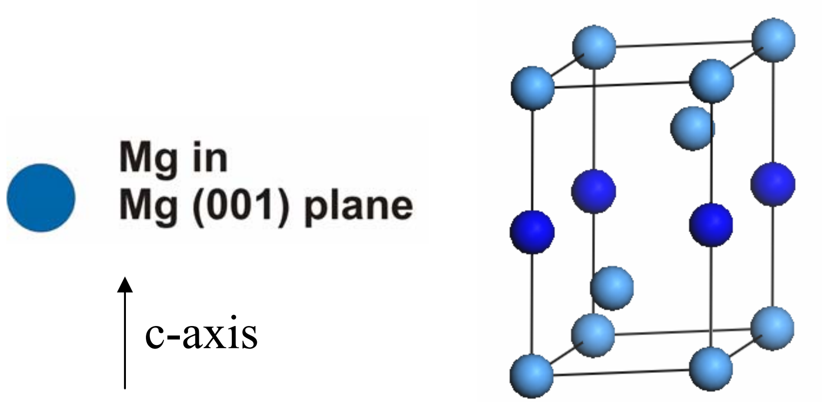
Epitaxial Mg Films

- **We grew Mg epitaxially on Al_2O_3 (001) and MgO (111) for the first time; done at RT and up to 100° C.**
  - High-angle x-ray diffraction of as deposited samples indicates Mg grows singly oriented in the (001) orientation, with the c-axis out of plane
  - High-angle x-ray diffraction after charging indicates MgH2 forms singly oriented in the (110) orientation
- **From this information we are able to determine the crystallographic orientation between Mg and MgH_2 in the films**

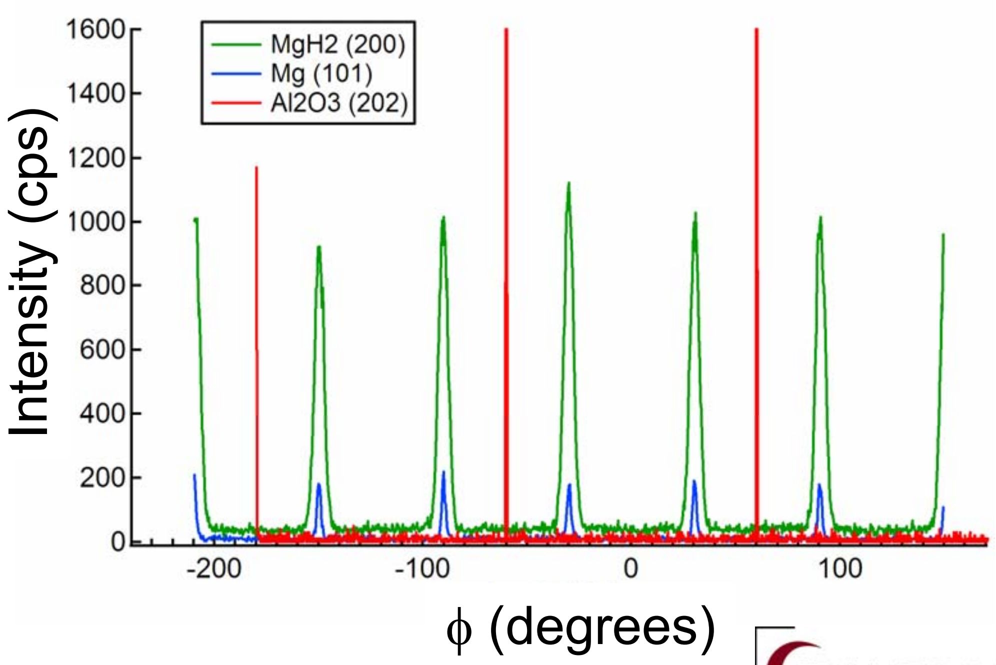


Epitaxial Mg Films



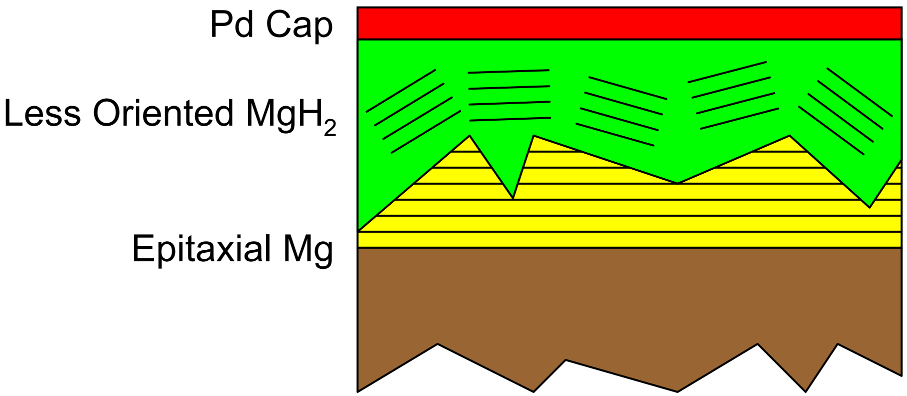


- **Phi scans indicate how MgH2 (110) plane lies on the Mg (001) plane**
- **With the high angle scans, they show MgH2 (110) [001] // Mg (001)[100]**
- **Observed solid phase epitaxial (SPE) re-growth of Mg during dehydriding process**
  - Mg grew back in original orientation
  - Evidenced by comparing scans (a)-before hydriding vs. (c)-after dehydriding



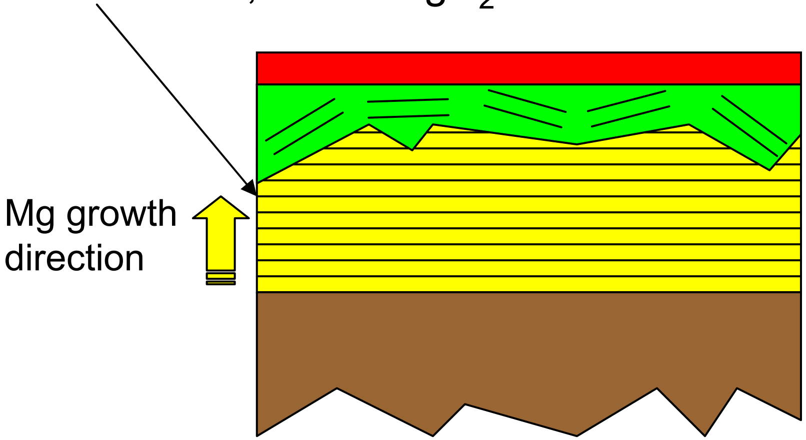
Epitaxial Mg Films

- **Solid Phase Epitaxial (SPE) regrowth**
  - Growth of solid phase occurs at interface between original material and transformed material, not in transformed material or at another interface
  - Crystal quality of regrown material will match that of original material, not that of transformed material
    - XRD rocking curves will match



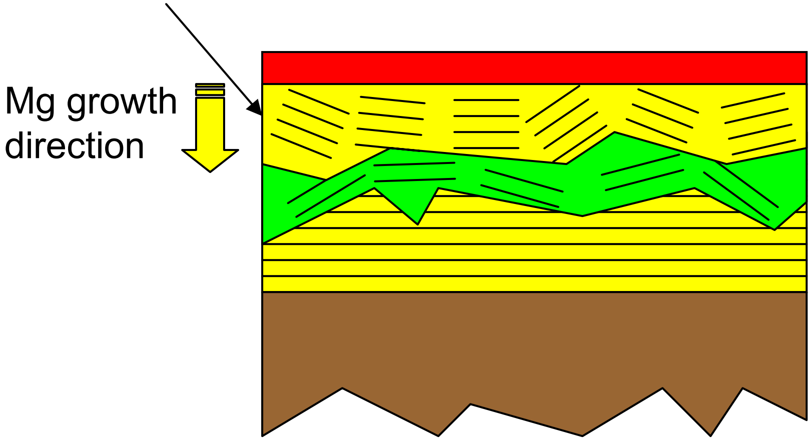
SPE Regrowth

On discharge, Mg regrows epitaxially on the remaining Mg at Mg/MgH_2 interface, not at MgH_2/Pd interface



Non-SPE Regrowth

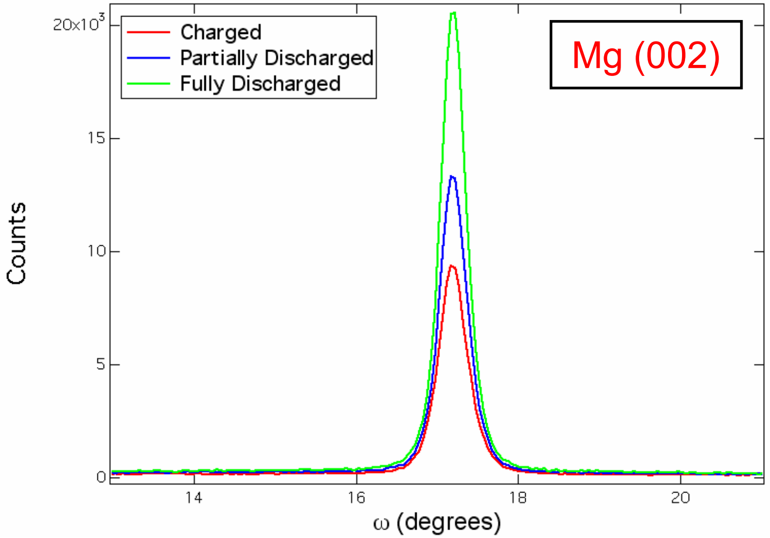
Non-epitaxial (less highly oriented) Mg regrows from MgH_2/Pd interface

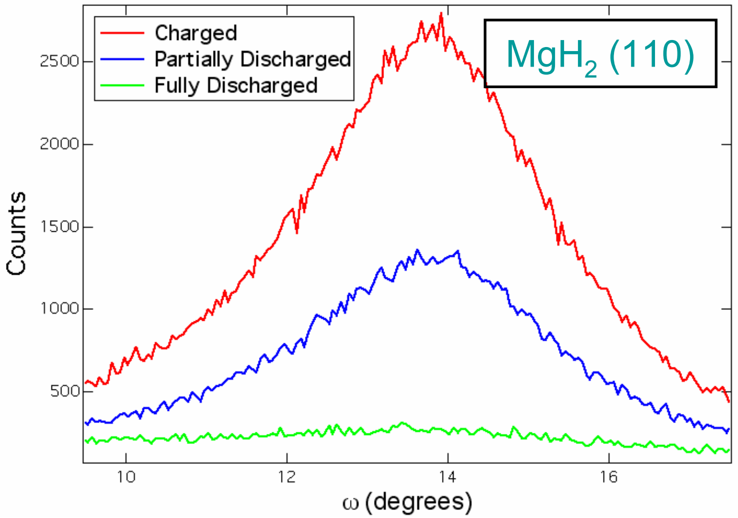


Epitaxial Mg Films

- **Films regrew in original Mg orientation upon discharging**
  - Verified with XRD Phi scans

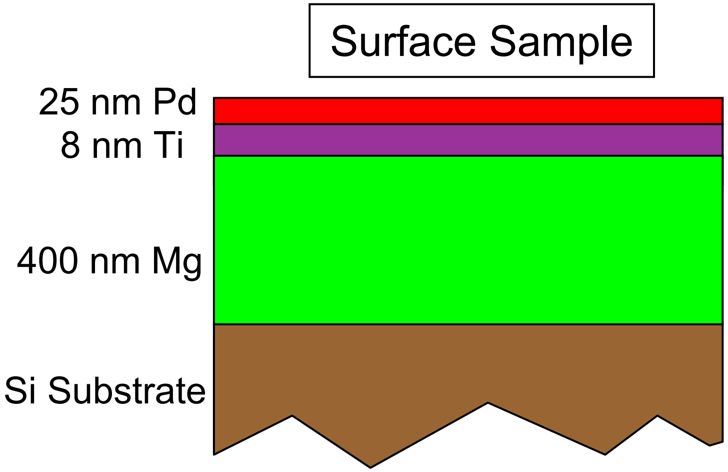
- **XRD rocking curves show that Mg regrew on existing (untransformed) Mg**
  - Strong evidence for SPE regrowth
  - Mg rocking curves returns to original shape after discharging
  - Did not nucleate at MgH_2/Pd interface due to broad rocking curves for MgH_2
    - Much wider than Mg rocking curves

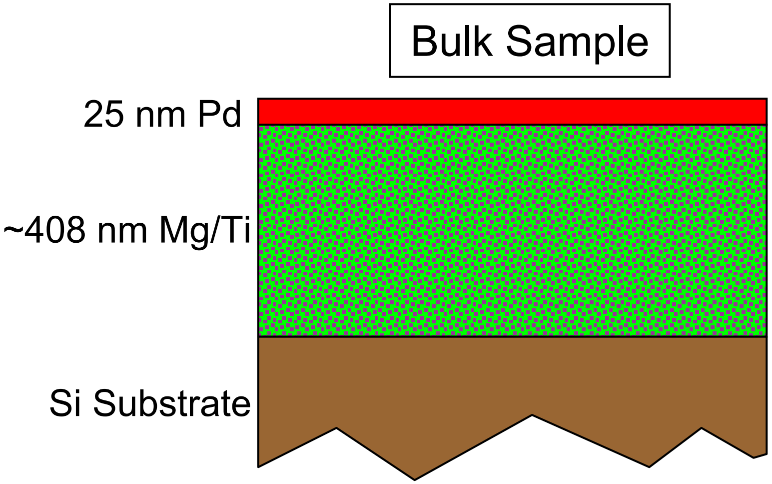




Catalyst Placement

- **Investigate effect of bulk vs. surface catalyst placement**
  - Ti catalyst has shown good results with NaAlH4, try with Mg as initial system
  - Compare kinetics to Mg films without Ti catalyst
- **Reference sample**
  - 400 nm Mg film with 25 nm Pd capping layer on Si wafer substrate
  - Discharged over ~12 hrs at 82°C on XRD hotstage
  - Kinetics similar to samples used to establish technique
- **Surface catalyst:**
  - Thin layer of Ti (corresponds to ~5 wt. % Ti in Mg) deposited between Mg and Pd
- **Bulk catalyst:**
  - Same mass of Ti from above co-deposited with Mg
  - Deposited as solid solution mostly

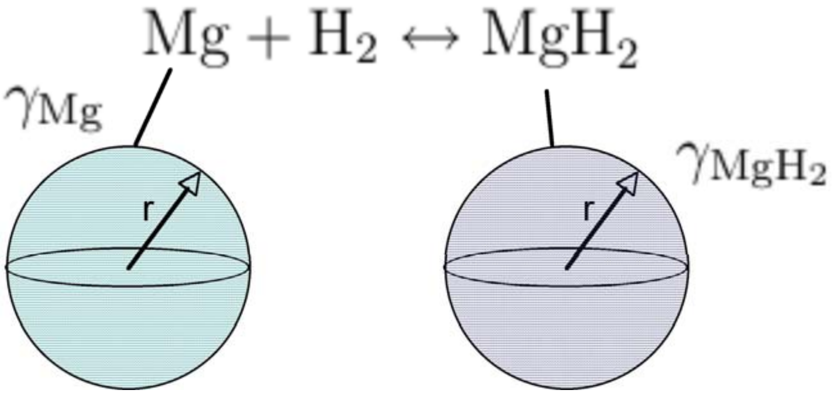




Thermodynamic Modeling

- **Hydrogenation of Mg nanoparticles**
  - Equilibrium pressure altered by interface terms:

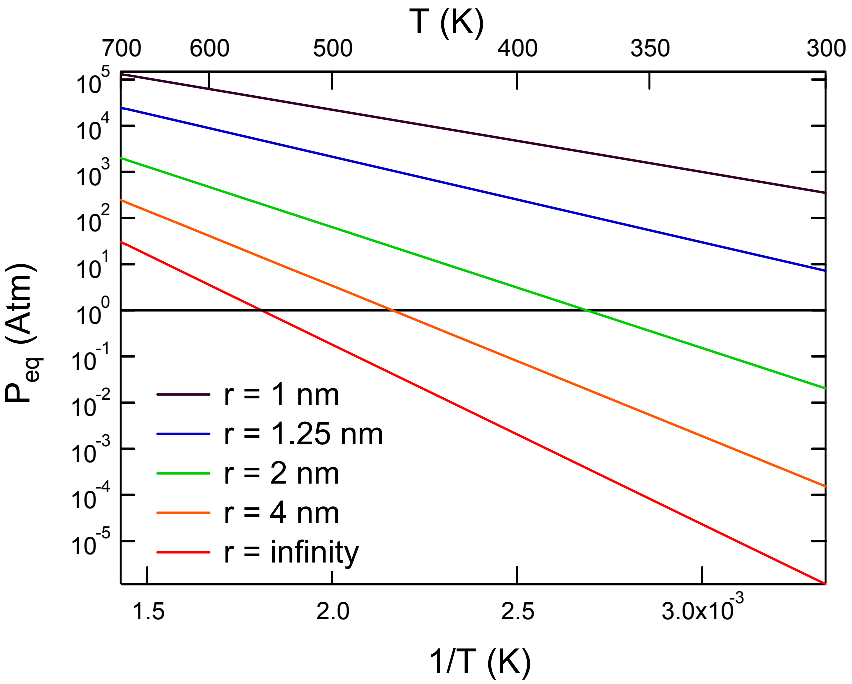
$$P^r_{H_2(eq)} = \exp\left[\frac{\Delta G^\circ}{RT} + \frac{2\Delta\gamma V_M^{Mg}}{r_{Mg}RT}\right]$$



  - Bond counting estimate for surface energy difference:

$$\Delta\gamma = 1.74\ J/m^2$$

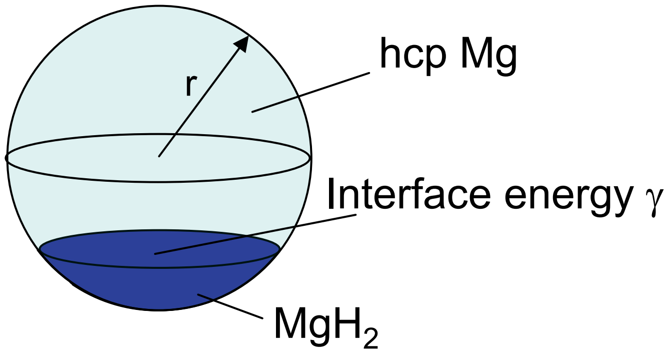
  - First principles calculation gives 1.86 J/m2, Karl Johnson and Bing Dai, private communication 2005.
  - Particles with d~4 nm have attractive Peq

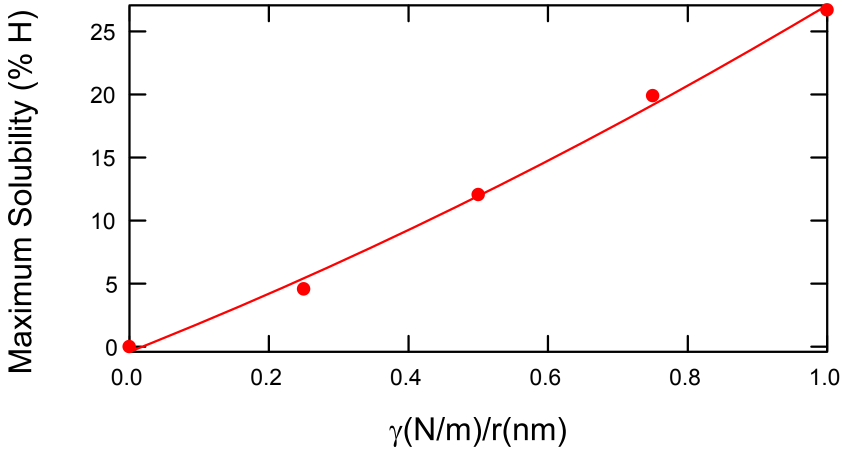


Thermodynamic Modeling

- **Extended solid solubility of H in Mg Nanoparticles**
  - Interface cost drives up the energy of two-phase configuration

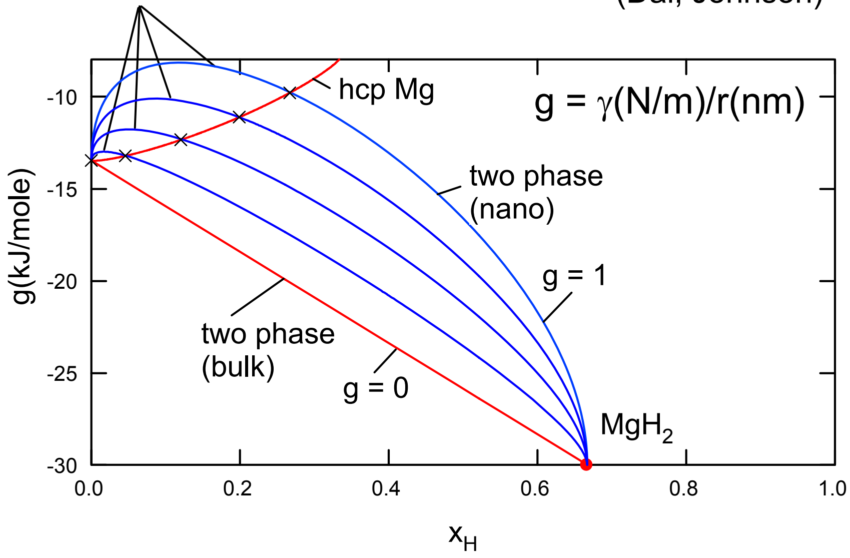
Two phase nanoparticle





Energy of two-phase system above that of supersaturated solution!

$\gamma = 1.46\ \mathrm{J/m^2}$
(Dai, Johnson)



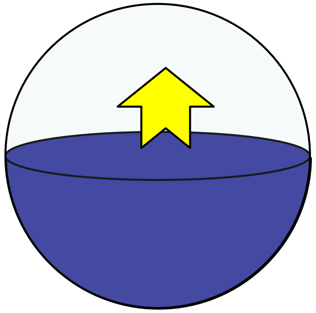
Thermodynamic parameters from: Zeng, Klassen, Oelerich, Bormann, Int. J. Hydrogen Eng. 24, 989 (1999)

- **Size changes the phase diagram!**
  - Predicated supersaturation is 3 orders of magnitude above bulk

Thermodynamic Modeling

- **Nanoparticle Nucleation**
  - Nucleation of second phase has interface energy cost

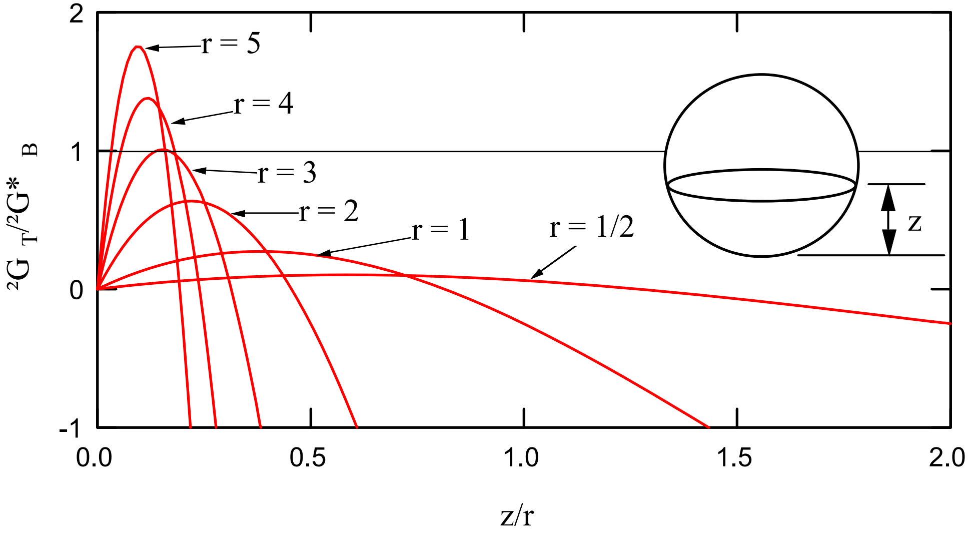
Transformation occurs as interface sweeps through particle



  - For r<3r* nucleation is easier than in bulk!

- **Easier nucleation means lower driving forces needed for phase transitions**

Energy as a function of interface position



- **Nanoparticles have:**
  - Dramatically different thermodynamics and phase stability
  - Faster reaction kinetics
  - Easier nucleation
  - No “growth” phase

Future Work

- **Construct pressure vessel for use with XRD facilities to enable *in-situ* sample charging**
  - Extract kinetic data for sample charging
  - Observe structural changes related to hydriding and correlate with kinetics of samples

- **Continue investigation of additional material systems**
  - MgB and MgAl systems
  - Li-based systems
  - Go/No-Go decision point on Mg_2Si system

- **Continue investigation into kinetics of thin film phase transitions and role of catalyst placement in those transitions**
  - Mg system and others

- **Investigate nanoparticle systems as well as thin films using established techniques**

Responses to Previous Year Reviewers’ Comments

- **Not applicable as we did not have a “Review” last year since it was our first year on the project**

Publications and Presentations

- **Presentations:**
  - "Nanostructures for Hydrogen Storage," Materials Research Society, Boston, MA, November 2005.
  - “Structure and Kinetics of Nanoparticle and Model Hydrogen Storage Materials”, Bruce Clemens, Stephen Kelly, Hermione Giffard, Next Generation Neutron Source Workshop, 7-8 June 2005.
  - “The Formation and Dissociation of MgH2 in Thin Films Studied With X-ray Diffraction”, Stephen Kelly, Hermione Giffard, Raj Kelekar, Bruce Clemens, Stanford Nanocharachterization Laboratory Inauguration, Sept. 2005.

Critical Assumptions and Issues

- **Unable to observe hydriding directly with XRD using current equipment**
  - Developing new *in-situ* hydrogen charging chamber for use on XRD equipment

- **Assuming thin film materials absorbing at optimal storage capacity**
  - May be absorbing more/less hydrogen than bulk systems
  - Verify hydrogen content using quantitative methods
    - Sieverts, TGA, etc.

- **Have not directly observed phase transformation kinetics inferred from XRD studies**
  - Working on directly observing hydride distribution in thin film samples using other methods (SEM, TEM, SIMS, etc.)

Summary

- **Developed method to measure extent of hydride decomposition and structural changes during desorption using XRD**
  - Allows measurement of system kinetics during desorption
- **Attempted to hydride Mg_2Si directly using variety of thin film systems and configurations**
  - Unable to obtain segregated hydride system after H_2 exposure
- **Grew epitaxial Mg films on Al_2O_3(001) and MgO(111) for the first time**
  - Determined crystal orientation relationship between Mg and MgH_2 to be MgH_2 (110) [001] // Mg (001)[100]
  - See strong evidence for solid phase epitaxial (SPE) regrowth of Mg during desorption of films not completely hydrided
- **Began study of effect of catalyst placement (surface vs. bulk) on hydride formation and decomposition kinetics**
- **Continued efforts modeling the thermodynamics of nanoscale metal hydride material systems**
  - Predicted extended solubility of H in Mg and possibility of altered phase transformation kinetics