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: ~60%

- **Budget**
  - Total Project Funding: $997,921
    - DOE Share: $778,828
    - Contractor Share: $199,093
  - Funding Received FY07: $150,000/$37,500
  - Funding Received FY08: $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
  - 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, Mg_2Si, 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

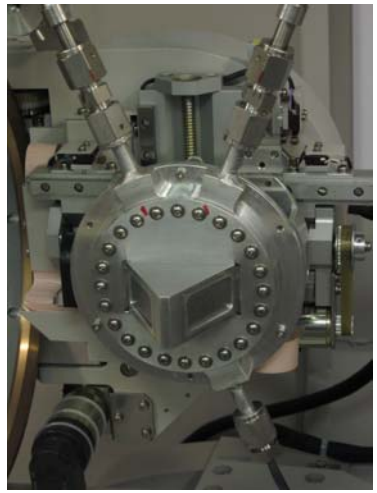
- **Develop understanding of metal hydride structures during phase change**
  - Material structure can play important role in reaction kinetics, especially during solid state phase transformations such as those in metal hydride reactions
  - Understanding the interplay between material structure and reaction kinetics may provide insight on how to successfully engineer new materials with improved kinetics and storage properties

Milestones

Date	Milestone or Go/No-Go Decision
03/2007	**Milestone:** Model kinetic transformation processes for thin film metal hydride material systems. **Status:** evidence seen for moving planar interface transformation kinetics.
06/2007	**Milestone:** Begin investigation of structural correlations in other material systems. **Status:** New material systems being introduced into all aspects of research. Nanostructured materials being investigated.
09/2007	**Milestone:** Investigate effects of cycling on material kinetics. **Status:** Textural degradation seen with cycling, leads to slower discharge kinetics.
09/2007	**Milestone:** Model kinetics of nanoparticle phase transformations and begin verification of model. **Status:** First steps towards verification made with quartz crystal microbalance (QCM) chamber development and initial implementation.

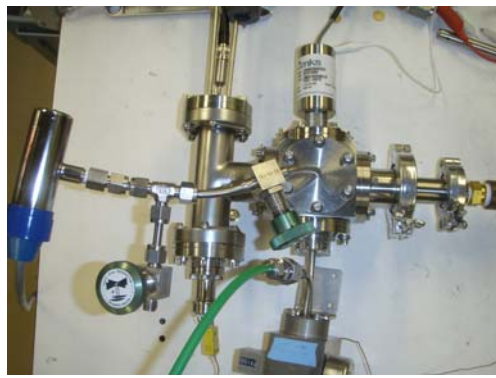
Approach

- **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
  - 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 with synchrotron radiation
  - Real time structural analysis to facilitate detailed kinetic mechanism determinations

- **Thin Film and Nanoparticle Uptake Monitoring**
  - Analysis chamber utilizing quartz crystal microbalance (QCM) to allow uptake measurements in thin film and nanoparticle samples



- **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

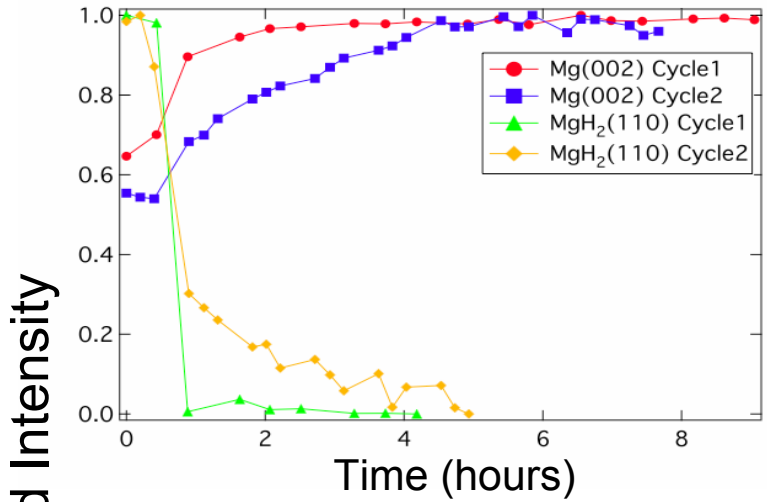
Thin Film Microstructural Evolution

- **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

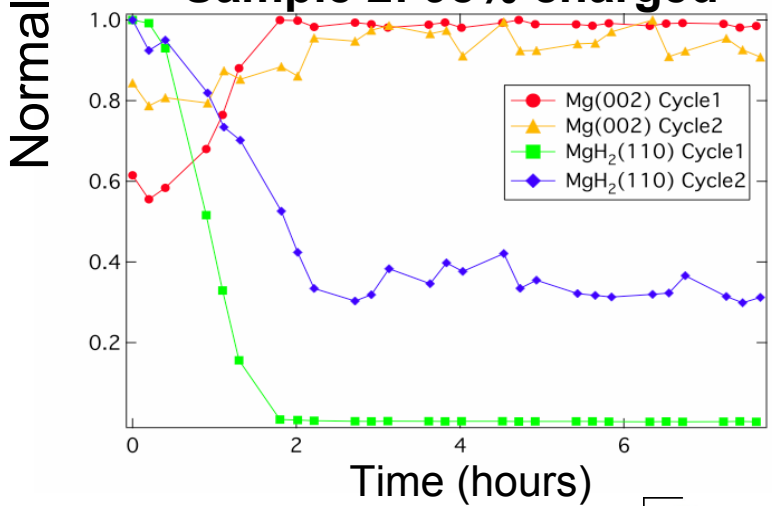
- **Previous work showed kinetic modification with loss of thin film texture**
  - Material texture degrades with cycling
  - Discharge kinetics slower with deeper cycling and less texture

- **New experiment to closely examine material texture with x-ray diffraction**
  - Compare films subjected to "shallow" and "deep" cycling
  - **"Shallow" Film** cycled at 85 psi and 100°C for 2.5 hrs
  - **"Deep" Film** cycled at 90 psi and 100°C for 13 hrs
  - Develop model for microstructural evolution with cycling

Sample 1: 87% charged



Sample 2: 98% charged



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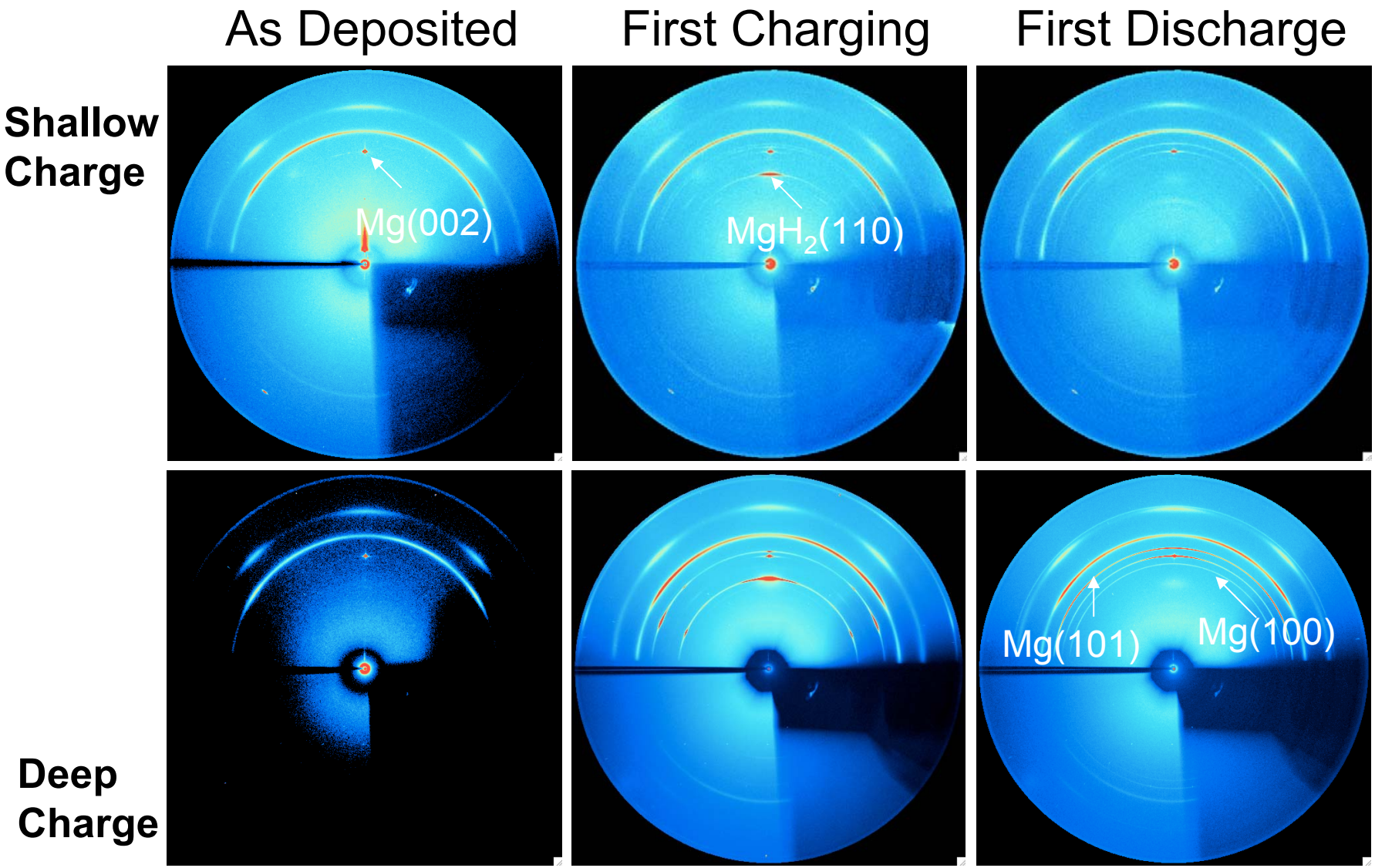
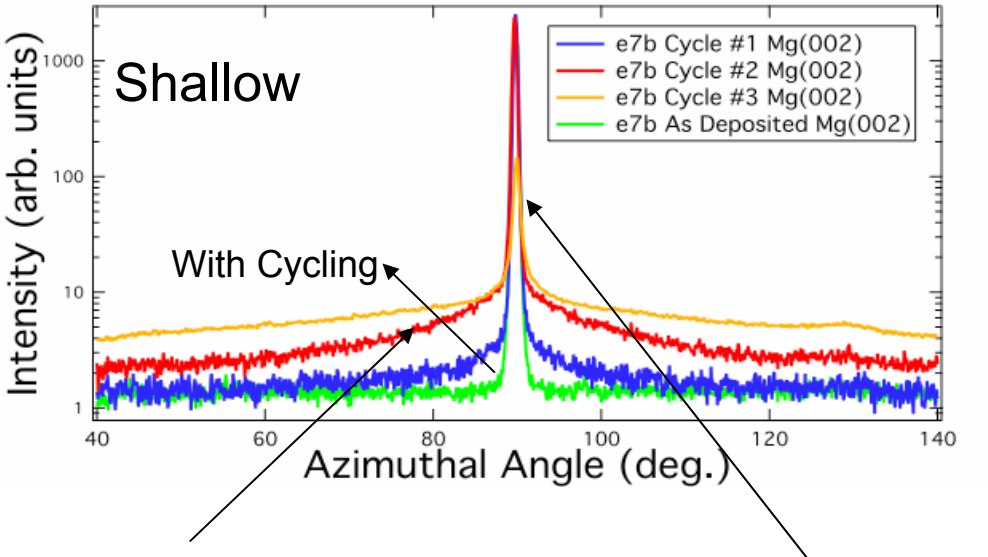
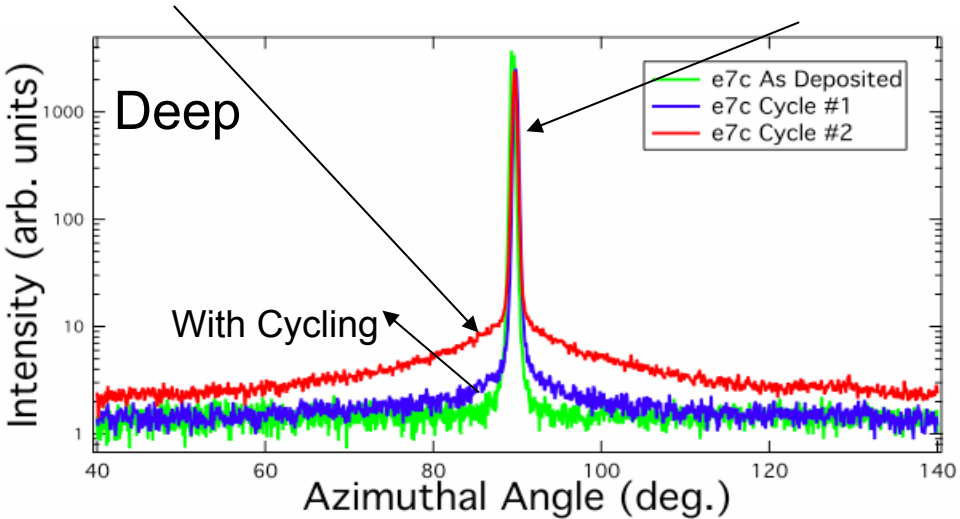
Thin Film Microstructural Evolution

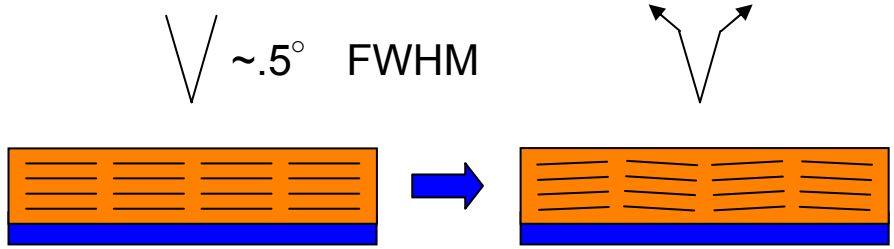


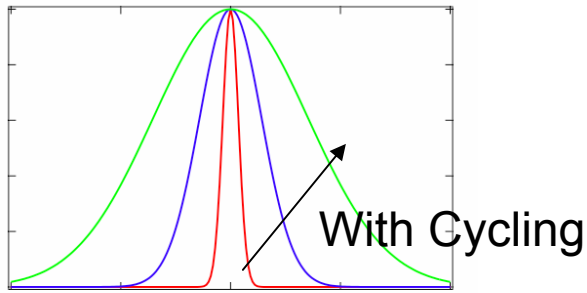
XRD patterns from 2D image plate detectors

Thin Film Microstructural Evolution



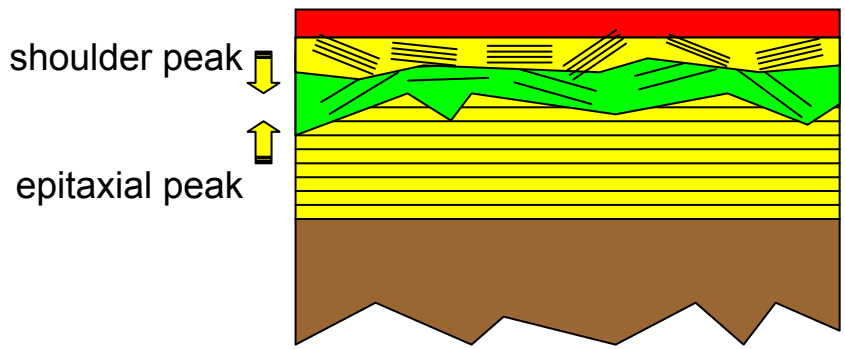






Mg (002) Rocking Curve

Mixed Regrowth



Percentage of well aligned material decreases with cycling.

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Thin Film Microstructural Evolution

- **Data shows successive peak broadening in Mg(002) rocking curves**
  - Mg(002) rocking curve becomes broader as sample is cycled between metal and hydride states
  - Less textured MgH_2 phase creates less textured Mg that regrows from it
  - Broadening mechanism repeats each time sample is cycled
  - Deeper cycling promotes further (faster) degradation of texture

- **Compilation of data shows evidence for mixed regrowth modes**
  - Characteristics of both solid phase epitaxial (SPE) and non-SPE modes seen in x-ray rocking curve progressions
  - Both broad shoulder and sharp epitaxial peak shapes seen
  - Mechanism depicted in cartoon on previous slide

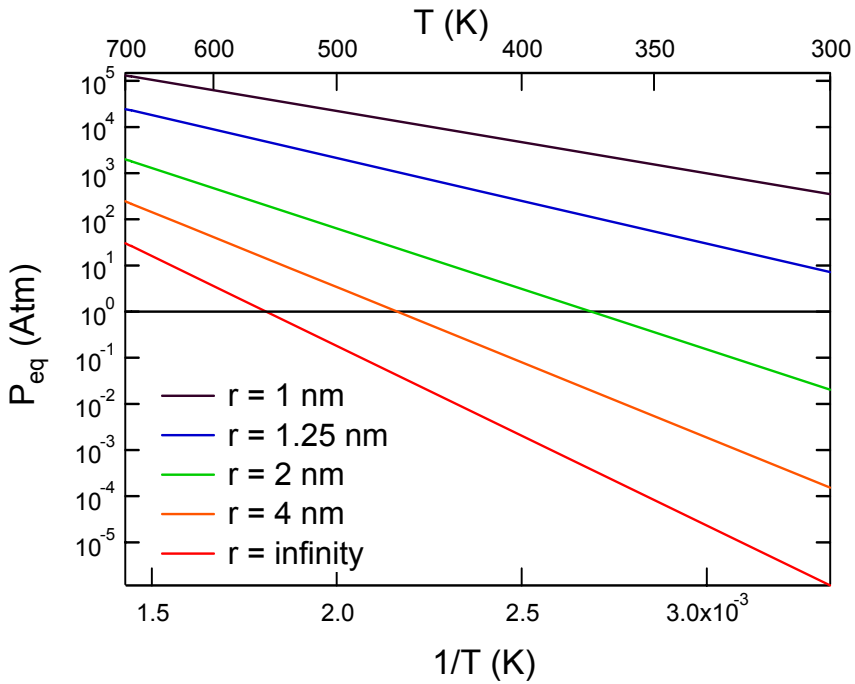
Thin Film Microstructural Evolution

- **Conclusions**
  - Deeper cycling promotes faster degradation of thin film texture, leading to slower discharge rates
    - New XRD measurements provide further evidence and more insight into the nature of the degradation
  - Successively broadening rocking curves indicate gradual degradation of texture as material is cycled
  - In combination with previous observation of solid phase epitaxial (SPE) regrowth in epitaxial Mg films, new observations suggest a “mixed” regrowth mode with characteristics of both SPE and non-SPE mechanisms
  - Stabilizing material texture and microstructure should lead to improved hydrogen discharge kinetics and better stability with cycling
  - New data (yet to be processed) showing effect of cycling on <u>charging</u> kinetics should provide insight into mechanisms responsible for this effect
  - Efforts should be made to stabilize material microstructure through alloy additions, nanostructuring, etc. and models should be developed to explain correlation between charging extent, charging rate, textural degradation and charging/discharging kinetics

QCM Studies: Can Size Change Thermodynamics?

- **Continuum modeling indicates that reaction kinetics and thermodynamics should change as particle size is reduced**
  - Large effects should show up when particles reach few nanometers in size
- **QCM analysis provides a method for measuring hydrogen uptake in very small sample sizes to verify predictions of models**
  - Capability to measure sub-monolayer amounts of hydrogen uptake
- **Nanoscale samples can be prepared directly on QCM crystal:**
  - Solution deposited nanoparticles
  - Islanded thin films

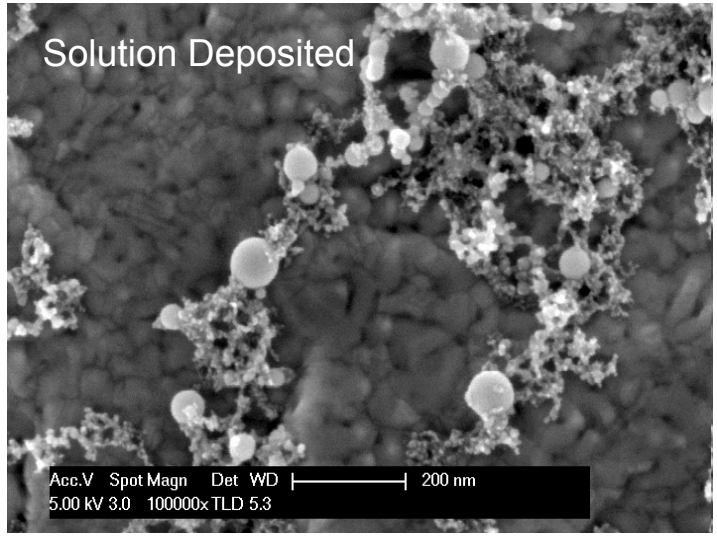
Calculated P_{eq} for Mg/MgH_2 particles

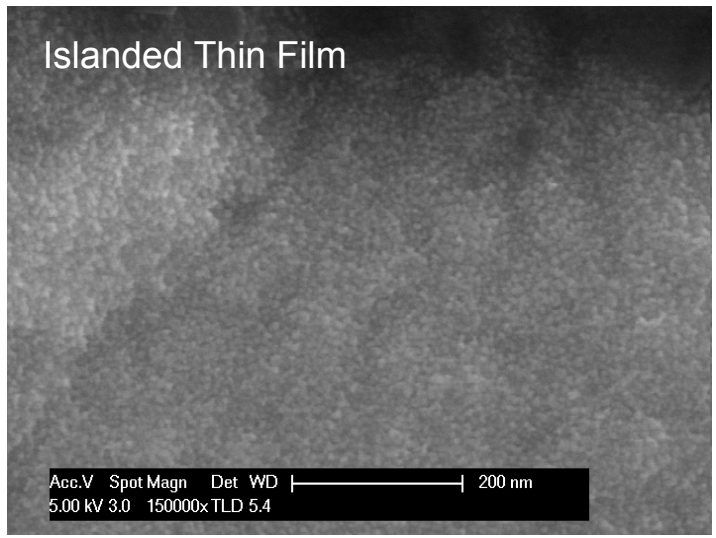


*Based on preliminary calculations by Karl Johnson's team

QCM Studies: Can Size Change Thermodynamics?

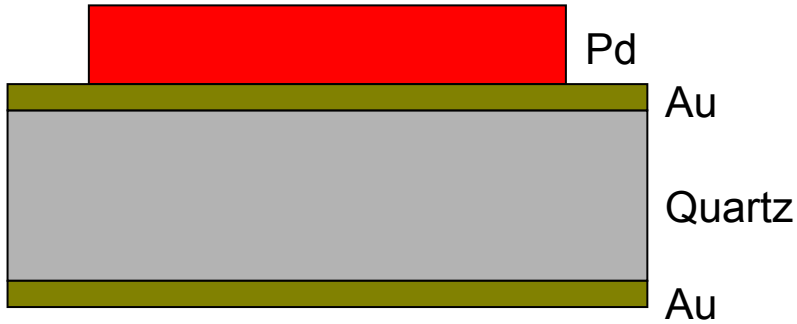
- **Palladium as a model system:**
  - Stores appreciable amount of hydrogen
  - Good kinetics
  - Preliminary calculations by Karl Johnson indicate that there should be an effect with reduced particle size
    - Equilibrium pressure should *decrease*
- **Thin film samples to verify technique**
  - Grow Pd film on QCM crystal as substrate
  - Compare P_{eq} to reported values for bulk Pd
- **Nanoscale Pd samples to test the size dependence**
  - Solution deposited nanoparticles
  - Islanded thin films formed by a thin layer of Pd deposited onto MgO layer

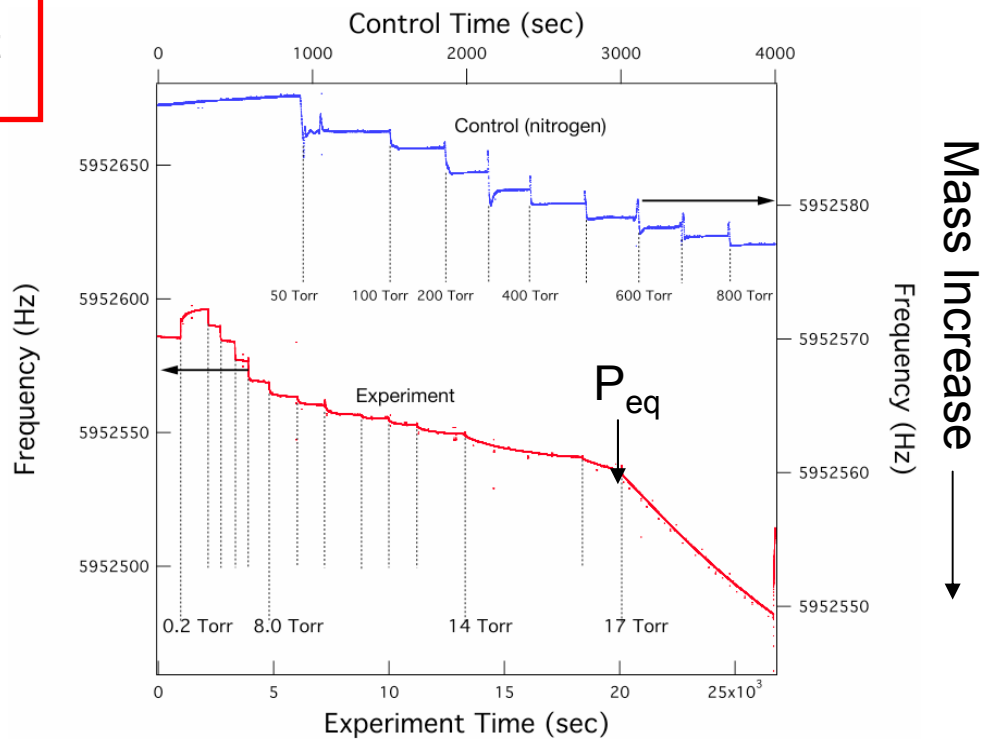




QCM Studies: Can Size Change Thermodynamics?

- **Measurements made on Pd thin film**
  - 400 nm Pd sputtered onto QCM crystal
  - Exposed to 2 % H_2 gas mixture (balance N_2) at room temperature (22°C)
  - Pressure adjusted until uptake observed in film
- **Uptake seen to set in at ~17 Torr H_2 partial pressure and 22°C**
  - Different from bulk value reported as ~17 Torr at 30°C, but fairly close
- **Confirmation of data needed to verify observation**
  - Repeat experiment
- **Performing experiment at different temperatures allows reconstruction of Van't Hoff plot and extraction of thermodynamic parameters**



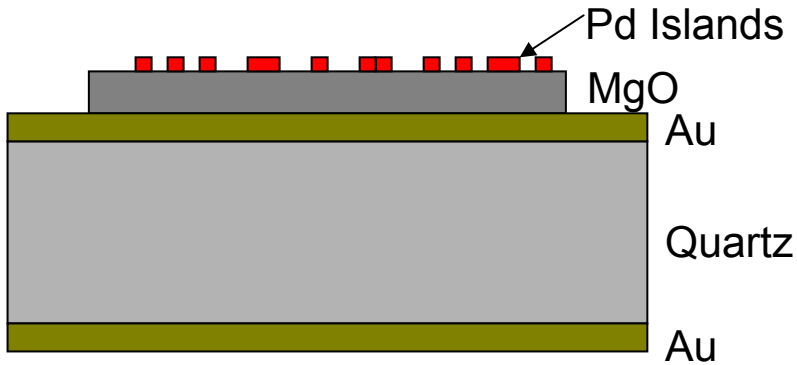


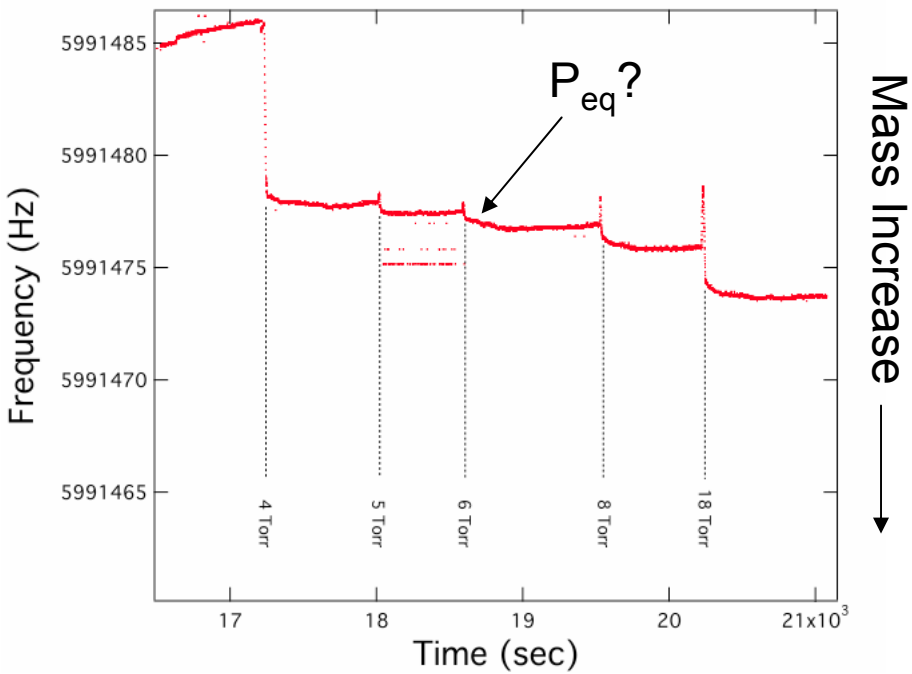
QCM Studies: Can Size Change Thermodynamics?

- **Measurements made on islanded Pd film grown on QCM crystal**
  - 50 nm MgO evaporated onto QCM crystal at room temperature
  - 1 nm (nominal) Pd evaporated onto MgO at 300°C

- **Evidence seen for P_{eq} ~6 Torr H_2 partial pressure**
  - Signal small compared to much larger film of Pd

- **More measurements needed to verify observation**
  - Observed P_{eq} difference compared to bulk and thin film matches direction predicted by calculations
    - P_{eq} *decreases* with reduced particle size



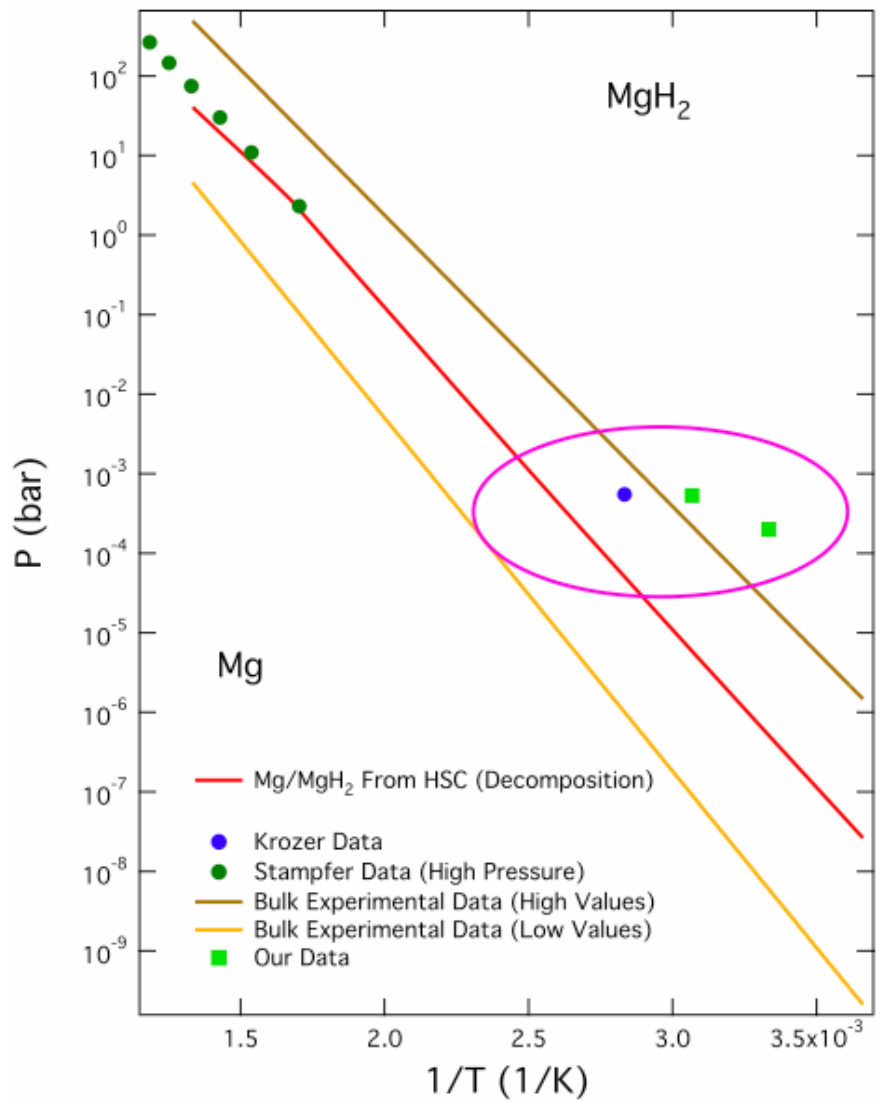


QCM Studies: Can Size Change Thermodynamics?

- **Measure Mg film P_{eq} to verify technique capabilities**

- **Measurements made on Mg thin films with Pd capping layer**
  - 400 nm Mg + 25 nm Pd sputter deposited onto QCM crystal
  - P_{eq} measurements made at RT and 50°C
  - Data shown at right compared to other literature values for thin films and bulk systems
- **Our data does not match reported values exactly, more work needed**
- **QCM allows measurements to be made at much lower temperatures than other techniques**

- **Data taken before temperature control system improvements**
  - Our measured Peq values are higher than others
  - Additional measurements needed to verify initial measurements



QCM Studies: Can Size Change Thermodynamics?

- **Conclusions**
  - Continuum modeling suggests that nanostructured materials display altered P_{eq} compared to bulk systems
  - QCM analysis provides a method for measuring hydrogen uptake in very small sample sizes to verify predictions of models
  - Nanoscale samples can be prepared directly on QCM crystal: solution deposited, islanded films
  - Thin film Pd sample shows P_{eq}=17 Torr compared to 11.5 Torr in bulk systems
    - Looking into reason for difference
  - Islanded thin film nanoparticle sample shows evidence for P_{eq} at 6 Torr
    - More measurements needed to verify observation, but follows trend predicted by calculations and theory
  - QCM measurements show promise for measuring dependence of P_{eq} on particle size

Neutron Reflectivity w/ NIST

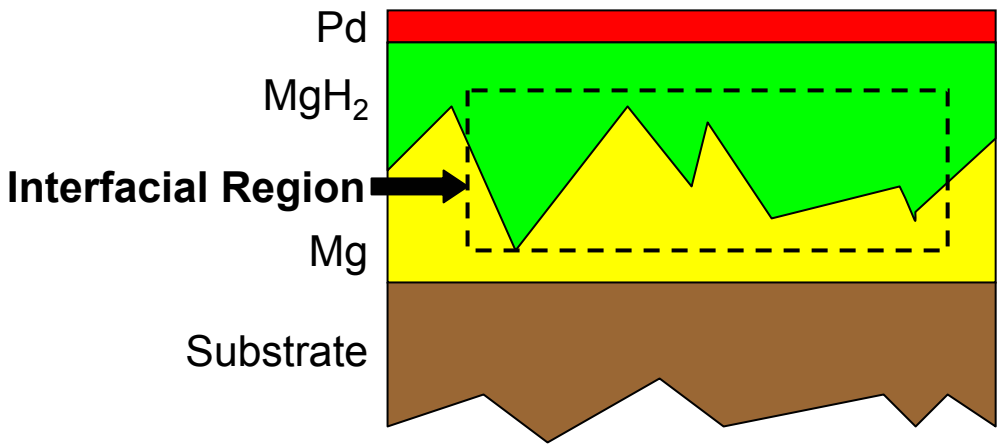
- **Collaboration with NIST to exploit the sensitivity of neutrons to hydrogen in order to further characterize the kinetics of the Mg/MgH_2 phase change in thin film systems**
  - Reflectivity measurements to track the motion of the Mg/MgH_2 interface
  - Hydrogen depth profiling through appropriate system modeling and data analysis

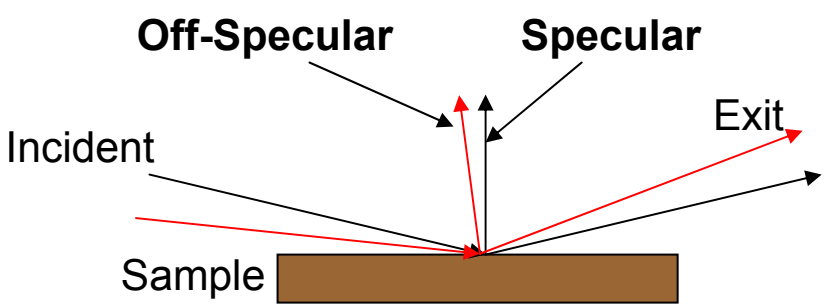
- **What we hope to learn**
  - How does the interface motion depend on the charging and discharging conditions (temperature and hydrogen pressure)?
  - How does the nature of the interface itself change with these same conditions (roughness, sharpness, etc.)?
  - How does the nature and motion of the 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
  - Sample modeling reveals potential of technique with initial semi-quantitative results

Neutron Reflectivity w/ NIST

- **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 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?

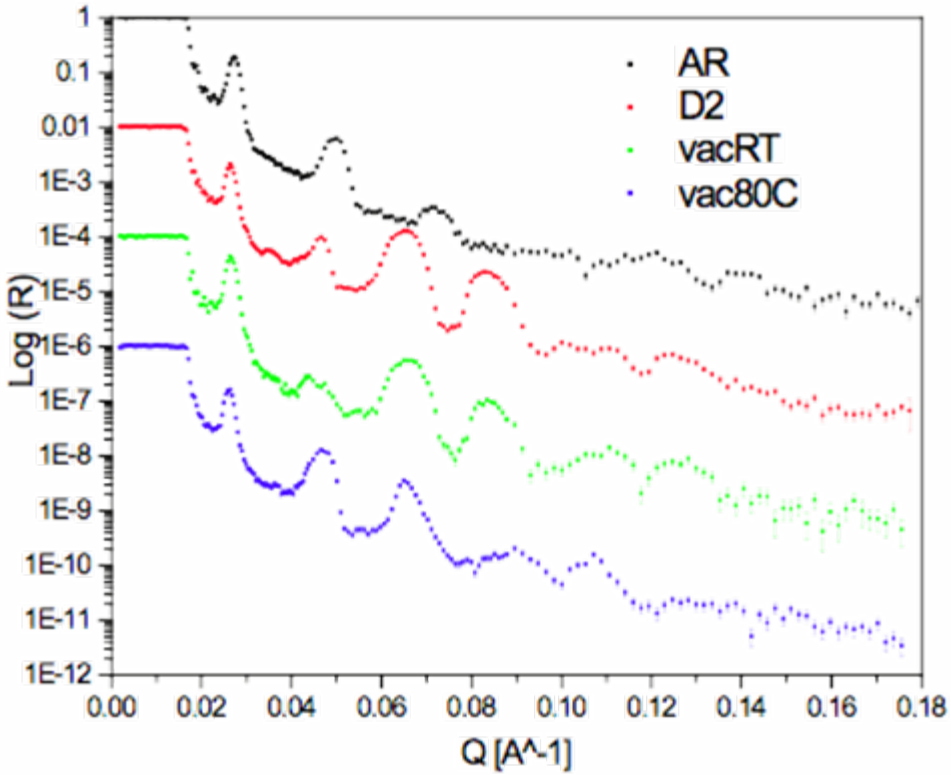




Neutron Reflectivity w/ NIST

- **Data obtained for multilayer Mg/Pd sample under various loading conditions**
  - (20 nm Mg + 5 nm Pd) x 10 sputtered onto Al_2O_3 substrate
  - Data taken in as-received (AR) state, after 17 hrs loading under ~7.5 atm D_2 at 100°C (D2) (scan at RT under 1 atm D_2), at RT under vacuum (vacRT), and at 80°C under vacuum (vac80C)

- **Models for different conditions constructed and compared to data**
  - Models indicate that layers contain more D near surface and less near substrate
  - Layers also thicker near surface than at substrate
  - Heating sample acts to redistribute the D in the layers, flattening out the gradient
  - After heating under vacuum, the sample did not return to the as-deposited state
    - D remained in the Mg and Pd layers
  - Interesting feature in off-specular scattering
    - Possible in-plane structure

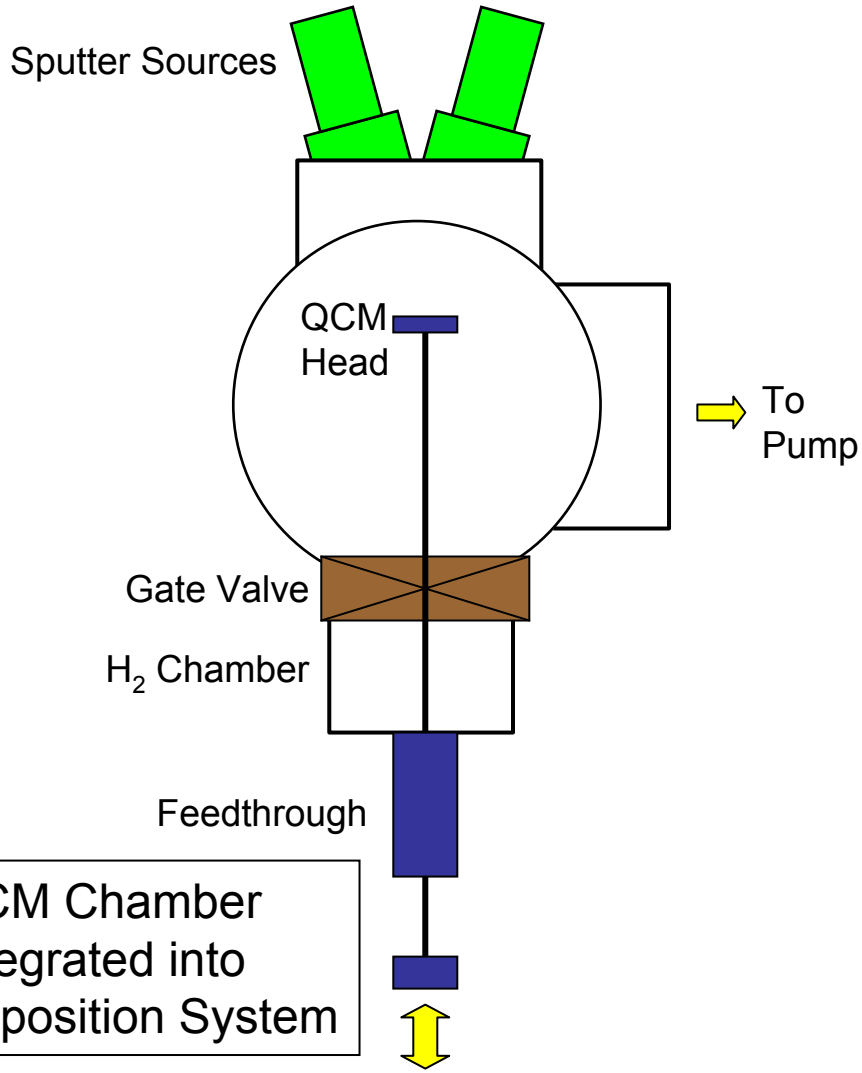


Neutron Reflectivity w/ NIST

- **Conclusions**
  - Neutron reflectivity patterns show significant changes with incorporation of D(H)
  - Sample modeling and data analysis reveal D(H)-content and layer thickness gradient in multilayer sample
    - Heating sample in vacuum acts to redistribute D(H), flattening out the gradient
    - Sample does not return to as-deposited state after annealing in vacuum at 80°C
    - More experiments and modeling needed to determine implications of these observations
  - 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/Al
  - 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

- **Integrate QCM chamber into existing deposition chambers**
  - Develop capability to deposit thin film and nanoparticle samples onto substrate and analyze without removing from chamber
  - Enables studies of Mg and other light metal hydride nanoparticles that may otherwise oxidize upon removal from chamber
- **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



QCM Chamber Integrated into Deposition System

Future Work

- **Expand and continue collaboration with NIST team using neutron reflectivity**
  - Investigate new single layer sample to examine MgH_2 growth kinetics
  - Use new *in-situ* sample chamber to better control exposure to D_2 during analysis
  - Develop new models to describe hydrogen incorporation kinetics
  - Investigate off-specular scattering to examine the nature of the metal/hydride interface and the possibility of in-plane structure

- **Finalize thin film microstructural evolution work**
  - Finish examination of *in-situ* hydrogenation data
  - Explain observations and develop model to describe hydride growth in the thin films

- **New materials**
  - Introduce new materials into all aspects of our work; NIST collaboration, QCM analysis
    - Mg/Al/Ti alloys, borohydrides possibly, nanoparticles, etc.
  - Examine effects of nanostructuring materials on thermodynamics and kinetics

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:**
  - X-ray investigations showed that deeper cycling leads to faster loss of material texture and slower discharge rates, evidence for mixed SPE/non-SPE regrowth mode
  - QCM chamber constructed and initial measurements made of P_{eq} in Mg and Pd systems
  - Neutron reflectivity experiments show a hydrogen(deuterium) distribution gradient through multilayer samples as well as evidence for in-plane structure
- **Collaborations and Tech. Transfer:**
  - Collaboration with NIST to utilize neutron capabilities to complement x-ray work
  - Calculations from U. Pittsburgh team have given valuable insight into directions for nanoparticle storage research
- **Future Work:**
  - Integrate QCM chamber to existing deposition systems to allow *in-situ* experiments
  - Continue measurements with QCM chamber on thin film and nanoparticle samples
  - Introduce new materials into all aspects of our investigation
  - Continue with NIST neutron reflectivity experiments