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

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Project ID#: ST061

Overview

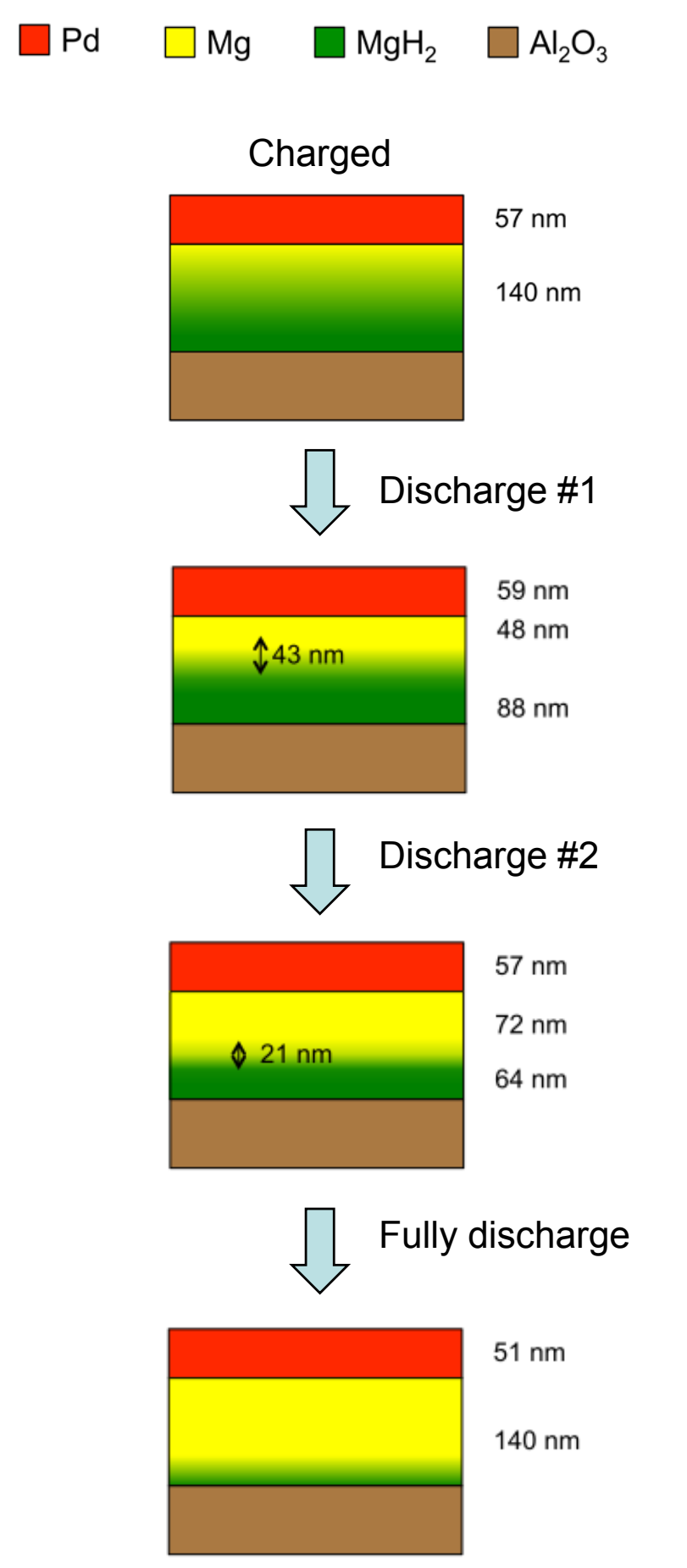
- **Timeline**
  - Project Start Date: January 2005
  - Project End Date: 2/28/2010
  - Percent Completion: 100%
- **Budget**
  - Total Project Funding: $997,921
    - DOE Share: $778,828
    - Contractor Share: $199,093
  - Funding Received FY07: $150,000/$37,500
  - Funding Received FY08: $150,000/$37,500
  - Funding Received FY09: $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 several material systems
  - 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 how metal hydride nanostructure and elastic strain energy will alter materials 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
  - Some experimental evidence shows the increase of equilibrium hydrogen pressure caused by the elastic strain energy
- **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

Neutron Reflectivity w/ NIST

- **Collaboration with NIST to exploit the sensitivity of neutrons to hydrogen in order to investigate the movement of the Mg/MgH_2 interface in epitaxial Mg films with a Pd capping layer**
  - Neutron reflectivity measurement can track the movement of the interface during charging and discharging. Hydrogen distribution in the sample can also be known
  - Analyze hydrogen depth profile through the sample and use model fitting to verify the metal regrowth mechanism
  - Epitaxial Mg films help understand the sample microstructure change during both charging and discharging
- **What we hope to learn**
  - Verify the metal regrowth mechanism of deeply charged samples during dehydrogenation.
  - How does the interface motion depend on the sample original state? (eg. A fully loaded film or a partially loaded film)
  - How does the nature of the interface roughness and sharpness change after discharging the films?
  - Is the metal regrowth by SPE mechanism, non-SPE mechanism or a mixed mechanism?



Experimental Data

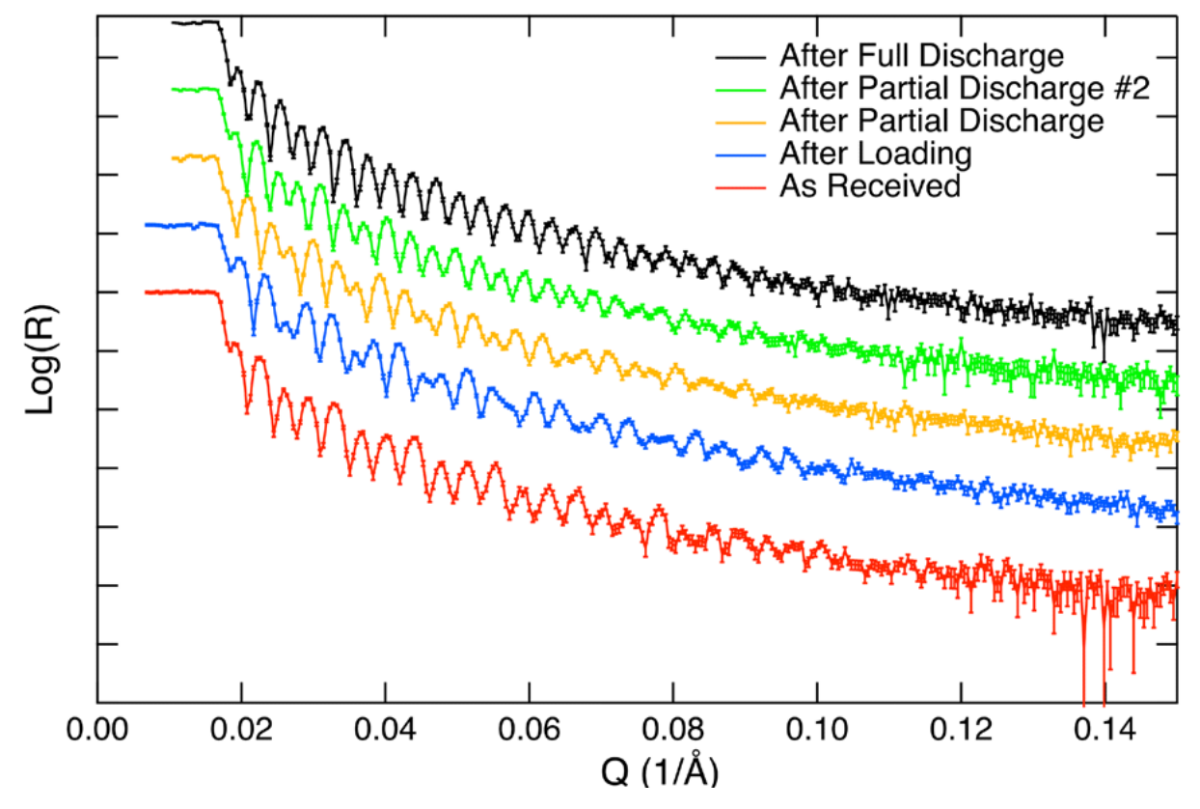
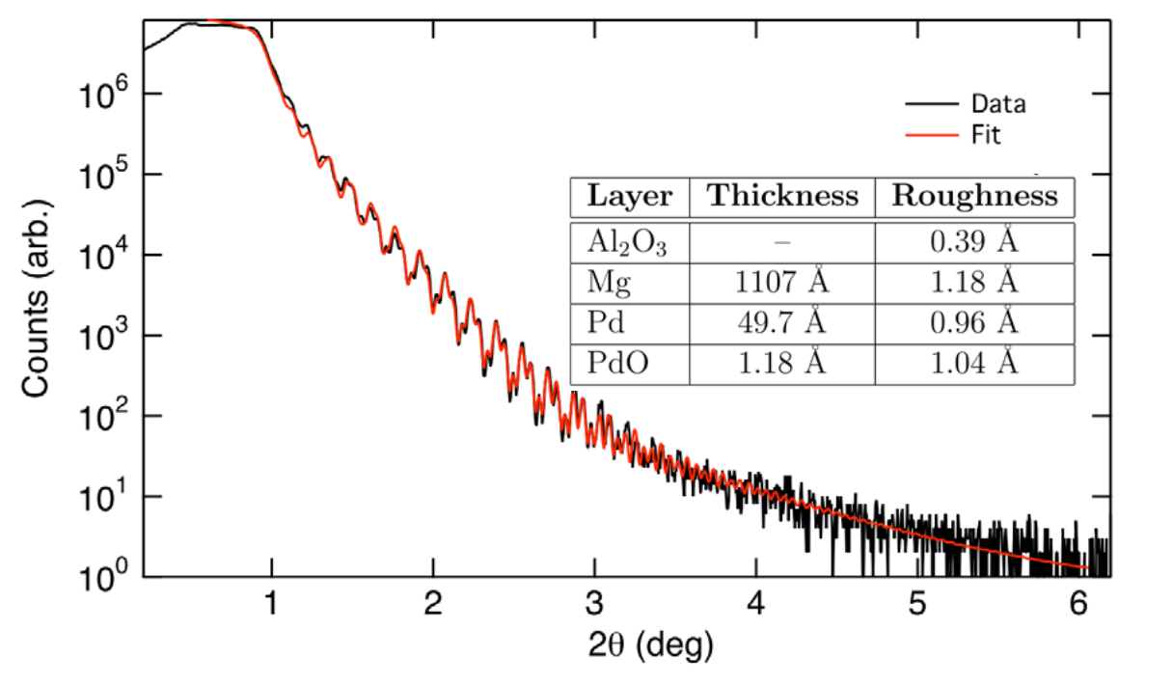


Fig: Neutron reflectivity patterns for the epitaxial sample at the various points along the annealing path outlined below.



Layer	Thickness	Roughness
Al_2O_3	–	0.39 Å
Mg	1107 Å	1.18 Å
Pd	49.7 Å	0.96 Å
PdO	1.18 Å	1.04 Å

Fig: Sample layer parameters extracted from fitting the x-ray reflectivity data for the sample studied

- **Data obtained for a bilayer Mg/Pd sample under various loading conditions**
  - (100 nm Mg capped with 50 nm Pd sputtered onto Al_2O_3 substrate
  - Data taken in as-received (AR) state, after 1.5 hrs loading under ~2 atm D_2 at 100 ℃ (After Loading) , after partially discharge under vacuum at 70 ℃ for 1.5 hrs(After Partial discharge), after secondary discharge under vacuum at 70 ℃ for 2 hrs to discharge more(After Partial discharge #2) and after heating at 80~150 ℃ in slowly increasing temperature steps to fully discharge the sample (After Full Discharge)

Models for different conditions constructed and compared to data

- The analysis indicates that the layers are distinct with sharp interfaces in the as-deposited state. Changes to this structure due to the introduction of hydrogen result in noticeable changes to the reflectivity pattern.
- The pattern changes noticeably at each point, indicating changes to the microstructure of the sample.
- After fitting the model calculations to the measured neutron reflectivity patterns, the best fits for sample architectures are illustrated in the figure below.
- The as received state indicates a 110 nm thick Mg layer capped by a 54 nm thick Pd layer with a 4.1 nm thick interfacial region between the two from the data fitting.

Conclusions

- Neutron reflectivity patterns show significant changes with incorporation of D(H)
- After exposure to hydrogen gas, the neutron reflectivity patterns can be explained by these two scenarios:
  - A layer of magnesium hydride with less hydrogen covering a layer of magnesium hydride with more hydrogen and an interface of roughly the entire hydride film thickness represents a single film with a gradient of hydrogen concentration through it. More hydrogen resides near the substrate, with less near the surface of the film.
  - A 111 nm thick layer of magnesium hydride with less hydrogen covers a 28 nm thick layer of magnesium hydride with more hydrogen with a 11 nm thick interfacial region separating the two.
  - In both scenarios the layer with "less hydrogen" could also merely be less dense than the other layer since this would have the same effect on the neutron scattering length density in t he sample.
- After first partial desorption, the pattern indicates that a 48 nm thick layer of Mg lies above a 88 nm thick layer of MgH_2 with a 44 nm thick transitional layer.
- After the second partial desorption, the pattern indicates the sample of a 73 nm thick layer of Mg located above a 63 nm thick layer of MgH_2 with a narrower 21 nm wide interfacial region between the two layers.
- The models for the sample in the first and second desorption conditions support the existence of a metal regrowth mechanism in fully charged thin film samples where the newly formed metal regrows from the top of the film downward, which is speculated to occur via the non-SPE mechanism in the mixed regrowth mode.
- After fully discharge, the film consists of an 81 nm thick layer of Mg located above a 60 nm thick layer of less dense Mg. The total thickness of the film remains in the expanded state after the final desorption, where voids or cracks in the film structure accounts for the extra volume of the film.

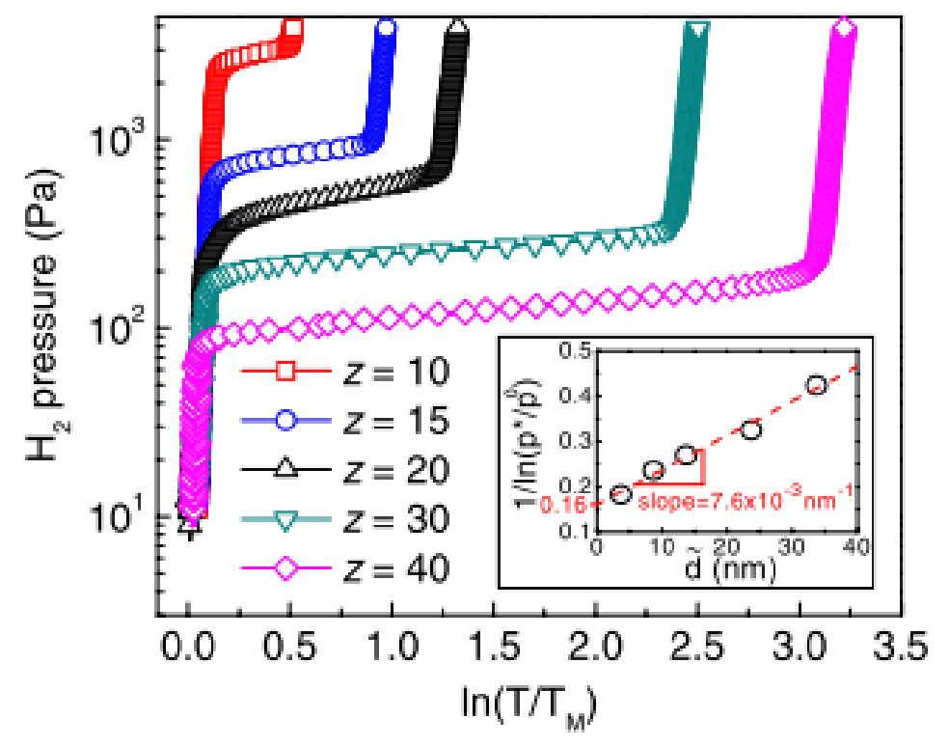
Milestone Chart

Date	Milestone or Go/No-Go Decision
04/2009	**Milestone:** Investigate the movement of Mg/MgH_2 interface in epitaxial Mg films with a Pd capping layer by in-situ neutron reflectivity in collaboration with NIST. **Status:** The Mg film remains in the expanded state of the hydride film after fully dehydrogenation.
07/2009	**Milestone:** Start curvature measurement of Mg thin films during hydrogenation/dehydrogenation and investigate how thermodynamics can be changed by elastic strain energy associated with hydrogenation of Mg. **Status:** The stress we measured during hydrogenation is from the volume expansion of Pd capping layer and the result is consistent with X-ray diffraction.
09/2009	**Milestone:** Begin to utilize quartz crystal microbalance chamber to monitor hydrogen absorption in samples in order to compare with the result of the curvature measurement. **Status:** Experiments are undergoing and expect to see the equilibrium pressure change from strained films.

In-Situ Curvature Measurement: Elastic Strain Energy and Thermodynamics of Hydride Formation in Mg-Based Thin Films

Effect of elastic energy on phase stability & equilibrium hydrogen pressure

Motivation

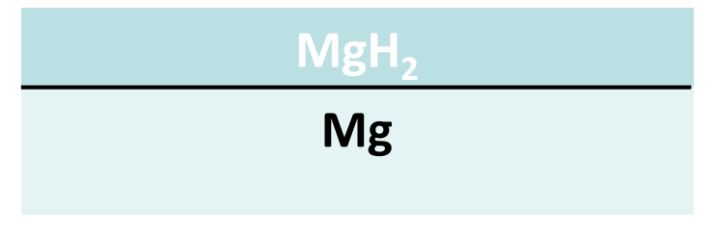


A. Baldi, et al., *Phys. Rev. Lett.*, **102**, 226102 (2009)

- The observed equilibrium hydrogen pressure in a 20 nm thick Mg film is 200 times higher than that of bulk Mg
- This is attributed to stress in the hydride
- This motivated our work to understand stress in thin film metal hydrides

Bulk, stress free

$$Mg_{(s)} + H_{2(g)} \leftrightarrow MgH_{2(s)}$$

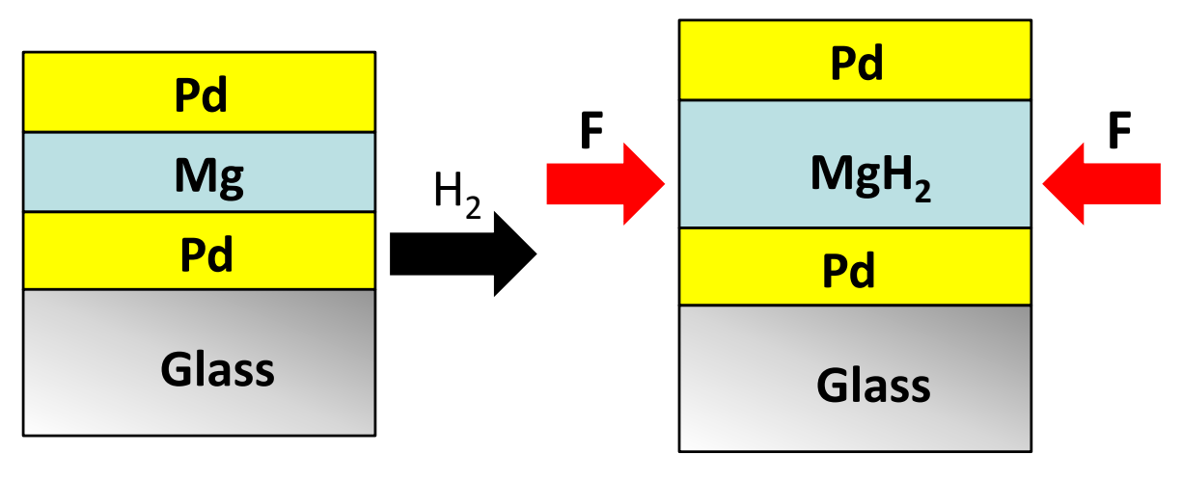


$$\Delta G_{rxn} = \Delta G^0 + RT\ln Q, Q = \frac{a_{MgH_2}}{a_{H_2} \cdot a_{Mg}}$$

$$\Delta G^0 = -RT\ln K_{eq} = RT\ln\left(\frac{P_{H_2(eq)}}{P^0}\right)$$

$$\Rightarrow \quad P_{H_2(eq)} = \exp\left(\frac{\Delta G^0}{RT}\right)$$

Elastic constrained



$$\Delta G_{rxn} = \Delta G^0 + RT\ln Q + E^{el}$$

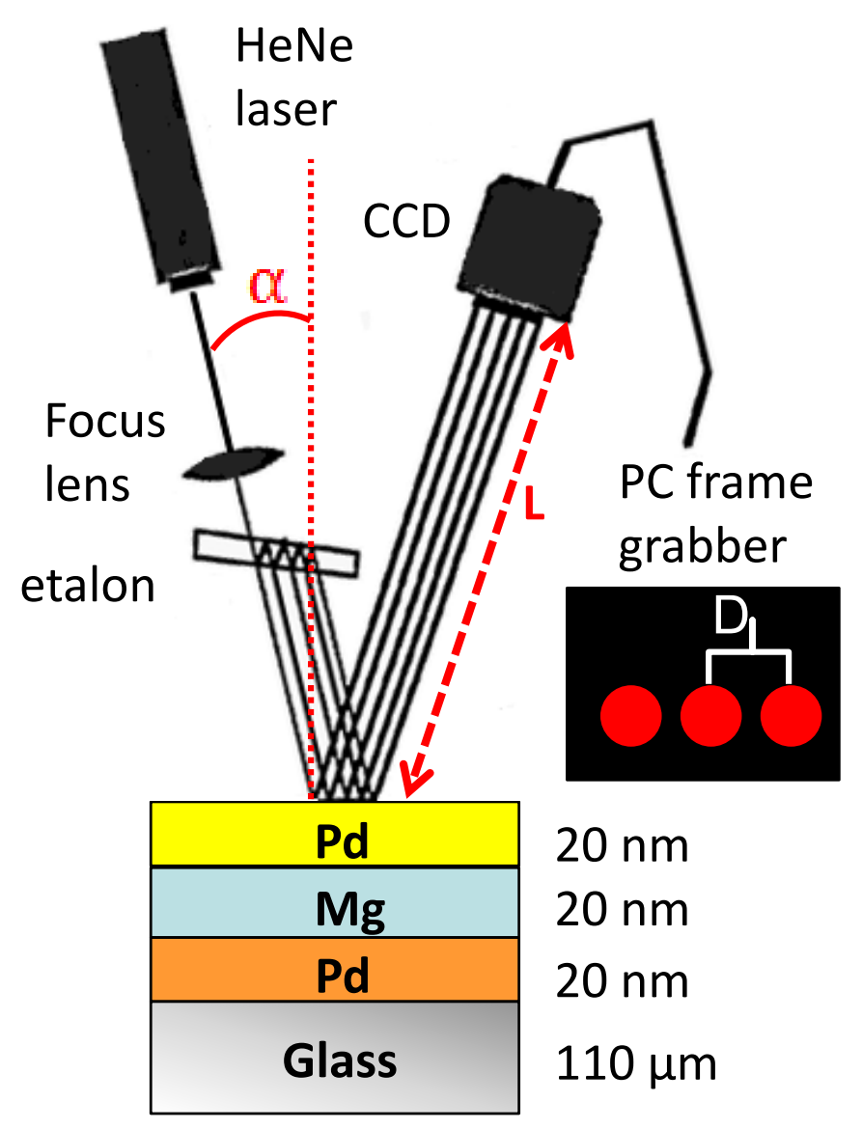
$$\Delta G^0 + E^{el} = -RT\ln K_{eq} = RT\ln\left(\frac{P^{el}_{H_2(eq)}}{P^0}\right)$$

$$\Rightarrow \quad \boxed{\frac{P^{el}_{H_2(eq)}}{P_{H_2(eq)}} = \exp\left(\frac{E^{el}}{RT}\right)}$$

- **Effect of elastic energy**
  - Equilibrium hydrogen pressure may be modified by the elastic energy associated with hydride formation in which the thin films are constrained elastically by the substrate.
  - An extreme case would be a strong film clamped to a substrate, where the entire expansion associated with hydride formation might be accommodated with elastic (rather than plastic) deformation. Take Mg for example, where the elastic energy associated with the ~30% volume expansion on hydride formation could increase the enthalpy of the strained hydride by about 10 kJ/mol. We also assume that all the elastic strains are accommodated in magnesium hydride. The corresponding equilibrium hydrogen pressure at RT will be 25 times higher than that of bulk sample at the same temperature. However we should notice that the assumption which uses 10% linear strain is not realistic for most of materials.

In-Situ Curvature Measurement

Curvature measurement setup



Curvature:

$$\kappa = \frac{\cos\alpha}{2L}\frac{D_0 - D}{D_0}$$

D_0: spot spacing reflected from flat mirror
D : spot spacing reflected from sample
α: the angle between incident laser beam and sample normal
L : the distance from sample to CCD

Stoney Equation:

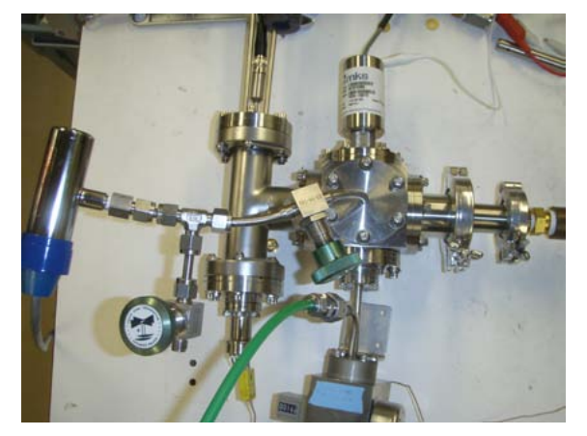
$$\Delta\kappa = \frac{1}{R} = \frac{6F/W}{M_s t_s^2} = \frac{6\sigma_f t_f}{M_s t_s^2}$$

σ_f : stress in the film
t_f : thickness of the film
M_s : biaxial modulus of substrate
t_s : thickness of the substrate
F/w : force in the film per unit width

- **What we want to know:**
  - How large the stress will be associated with hydride formation in our study system?
  - How does stress change with different the Mg film thickness or the Pd film thickness?
  - Does the stress come from the formation of magnesium hydride?
  - What is the relationship between the sample geometry, stress caused by hydride formation and the equilibrium hydrogen pressure?

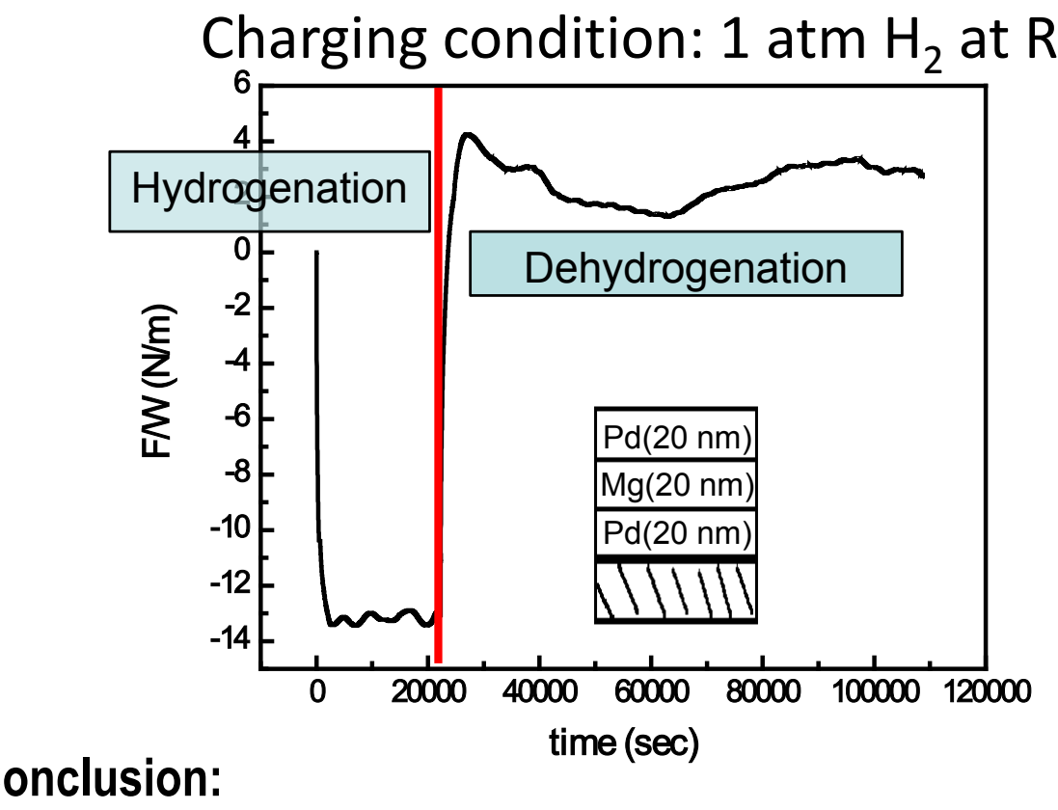
Approach

- **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* Curvature Measurement**
  - In order to know how the elastic strain energy will change the hydride thermodynamics
  - Experiments are done by using in-situ curvature measurement technique to monitor the stress change in the film during hydrogenation
  - Stress in the film can be calculated from the curvature, hence the elastic strain energy
- **Thin Film Uptake Monitoring**
  - Analysis chamber utilizing quartz crystal microbalance (QCM) to allow uptake measurements in thin film samples. The equilibrium pressure of the sample can be acquired and compared with stress measurement result.



In-Situ Stress Measurement

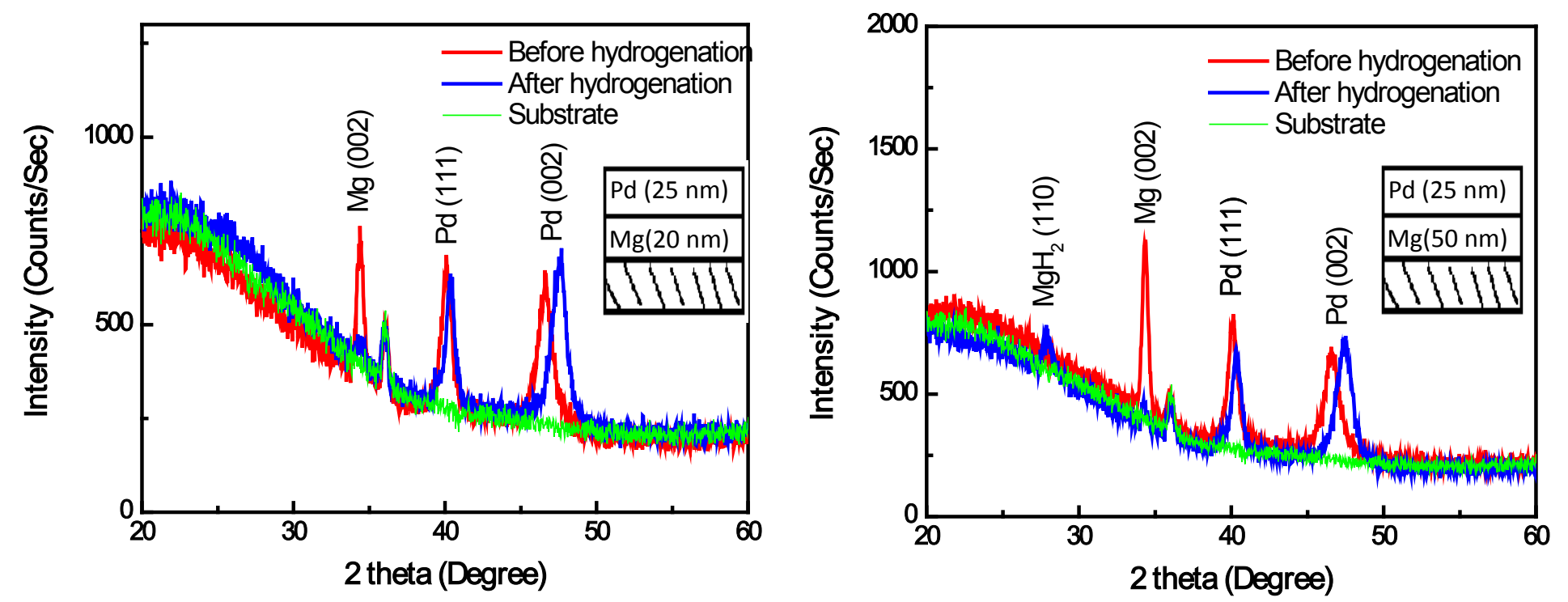
Charging condition: 1 atm H_2 at RT



- **Conclusion:**
  - Stress change occurs more quickly than MgH2 formation. Therefore the change may be associated with hydrogen swelling of Pd.
  - The residual stress during dehydrogenation may be caused by the volume change of Pd films, where plastic deformation occurs.
  - If we assume the stress associated with hydrogenation is caused by formation of MgH_2, the magnitude of stress is about 700 MPa, which corresponds to 2 times increase in equilibrium pressure. However, from the recent literature the similar structure will have equilibrium pressure 200 times higher than that of bulk Mg.
  - Therefore, the large change of equilibrium pressure change observed can not be due to the stress.

X-ray Diffraction & Strain In Pd Films

Charging condition: 1.6 atm H_2 at 90 ℃

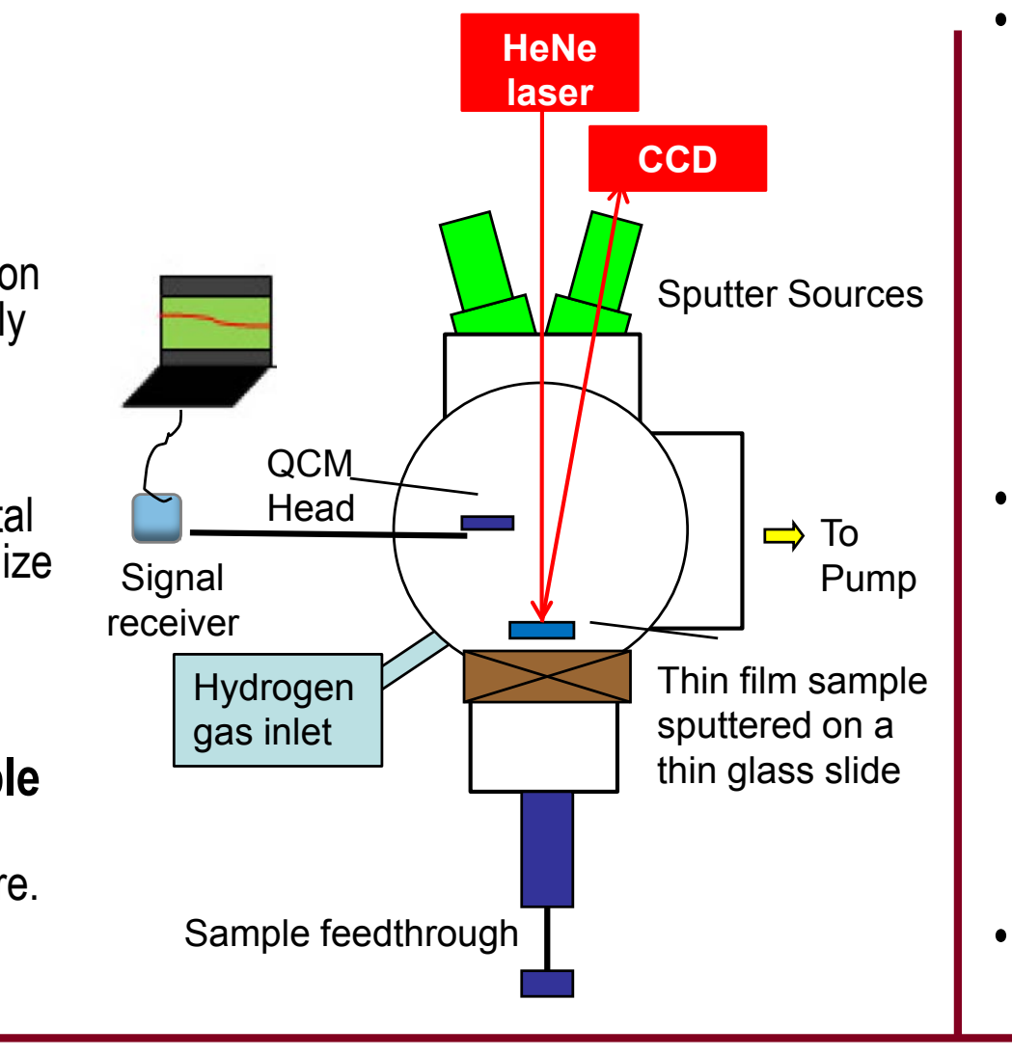


After hydrogenation	2 theta(°)	d (Å)	a(Å)	strain (%)
Pd (111)	40.3363	2.234	3.869	-0.530
Pd (200)	47.4339	1.915	3.830	-1.542
Mg (002)	34.2476	2.616	5.232	0.403
MgH_2 (110)	27.8959	3.19564	4.519	0.000

No strain in MgH_2

Future Work

- **Integrate QCM mass uptake measurement and in-situ stress measurement in the in-situ sputtering chamber**
  - Develop the ability to study mass uptake and curvature change during hydrogenation in in-situ chamber. Deposit films separately on QCM substrate and glass and then charge samples simultaneously at room temperature.
  - Enables studies of Mg and other light metal hydride materials that may otherwise oxidize upon removal from chamber
- **Continue data collection and analysis with QCM chamber of Mg/Ti alloy sample**
  - Preliminary result showed one order of magnitude increase in equilibrium pressure. Further experiments are undergoing to confirm the result.



- **Continue collaboration with NIST team using neutron reflectivity**
  - The result showed the evolution of the metal/hydride interface as material cycles between the metallic and hydride state. Finalize the hydrogen composition profile in the sample during hydride formation.
  - Complete our models to describe hydrogen formation dynamics of charging/discharging cycles.
  - Correlate textural degradation with kinetic differences seen with material cycling.
- **Investigate the possible reasons causing the increase in equilibrium hydrogen pressure**
  - The possible origins of change in equilibrium pressure can be interfacial energy or alloy effect.
  - Use QCM technique to monitor the equilibrium pressure change and develop a way to investigate the real reason for pressure change.
  - Start to write up our papers based on the our results.
- **Nanoparticle system**
  - Investigate hydride formation in nanoparticles .

Critical Assumptions and Issues

- **Assuming thin film materials absorbing at optimal storage capacity**
  - May be absorbing more/less hydrogen than bulk systems
  - Verify hydrogen content using quantitative methods such as QCM, 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.)
  - Initiating collaboration with NIST to examine hydrogen profile using neutron reflectivity
- **Assuming that thin film systems are representative of other systems**
  - Comparison to literature regarding bulk behavior can be found for early systems, compare with results from other groups in center for more advanced systems
  - Much of nanoscale work must be validated on suitable nanostructured systems, bulk measurements most likely are not applicable
- **Assuming that the films are biaxially strained by the substrate in our study system**
  - Specially designed sample holder fixture for curvature measurement allows no constraint in the bending of the sample
  - The elastic strain energy calculation in our model considers that the strain associated with hydride formation is accommodated elastically

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:**
  - Neutron reflectivity experiments showed the sequence of metal regrowth from a deeply charged epitaxial Mg thin film. The regrowth mechanism is determined to be non-SPE mechanism which is consistent with the previous experiments on kinetic and microstructural evolution during cycles.
  - In-situ curvature measurements are done successfully in in-situ chamber and the stresses in the films are analyzed to be ~ MPa.
  - QCM chamber has been setup and measurements are done to analyzed the equilibrium pressure of nanosized thin film samples.
  - X-ray diffraction showed the strain-stress state in the film after one hydrogenation/dehydrogenation cycle: there is no stress associated with magnesium hydride formation; the residual strain in Pd films after discharging is from the yielding during dehydrogenation.
- **Collaborations and Tech. Transfer:**
  - Collaboration with NIST to utilize neutron capabilities to complement x-ray work
- **Future Work:**
  - Integrate QCM and in-situ stress measurements to record the mass uptake and the stress change during charging cycles simultaneously. Help us understand the possible relations between these effects.
  - Continue measurements with QCM technique on Mg-based thin film samples incorporated with different materials.
  - Introduce new materials into all aspects of our investigation
  - Continue with NIST neutron reflectivity experiments and finalize our model for hydride formation dynamics as well as microstructure evolution during hydrogenation/dehydrogenation.
  - Start to investigate hydride formation in nanoparticles.
  - Write up our papers on what we have done