IV.A.4I Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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Introduction

The mechanism and kinetics of the metal/metal hydride transformation in metal hydride hydrogen storage materials plays a crucial role in determining whether a material meets the DOE on-board storage targets for 2010 and 2015. A fundamental understanding of these issues provides valuable insight into the ways in which various material systems can be engineered in order to meet specific material targets. Additionally, as the ability to engineer materials on the nano-scale emerges, new routes to tailoring specific material properties become possible. Specifically, by reducing the dimensions of metal hydride storage materials you can alter properties such as the hydrogen vapor pressure and storage capacity.

We have extensively investigated reduced dimension metal hydride material systems and their hydrogen charging and discharging properties. We determined kinetic behavior and transformation mechanisms for magnesium-based thin film material systems. We also investigated the effects of reduced dimensionality on destabilized material systems such as Mg_2Si. Additionally, we modeled the effects of reducing dimensions of hydrogen storage materials to the nano-scale (i.e. nanoparticles), revealing the possibility of drastically altered hydrogen storage properties in metal hydride nanoparticles.

Approach

In order to determine ways to engineer material systems to meet the DOE on-board storage targets for 2010 and 2015 we use a combination of thermodynamic modeling efforts combined with nanoscale material synthesis and various characterization techniques to gain a better understanding of the underlying kinetic mechanisms present in the metal hydride phase transformations. We make extensive use of x-ray diffraction (XRD) techniques, using both in-house facilities and facilities at the Stanford Synchrotron Radiation Laboratory (SSRL), to characterize the structural changes of material systems as they undergo phase changes during hydrogen absorption and desorption. We can then correlate this structural information with kinetic data about the absorption and desorption rates to relate the structure of materials to their kinetic behavior. The modeling efforts provide insight on where future experiments should focus and help to explain behaviors seen in experimentally synthesized samples prepared using physical vapor deposition (PVD) techniques.

Results

We have developed a method for monitoring the kinetics of the magnesium hydride to magnesium phase transformation in thin film samples with high temperature XRD utilizing a hot stage attachment for our in-house XRD facilities. This method allows us to monitor both the kinetics of the phase transformation and the structural transformations that occur during the transformation. This ability allows us to correlate microstructural characteristics in hydrogen storage material samples with the kinetics and use this information to engineer material systems to meet the 2010 and 2015 DOE targets. We are currently designing a chamber that will allow us to examine samples with XRD while charging them with hydrogen *in situ*. This allows us to better correlate charging kinetics with microstructural changes in material systems.

Additionally, we investigated the destabilized Mg_2Si material system by PVD of various thin film structures. Building on efforts from the HRL Laboratories team, we first deposited monolithic thin films of Mg_2Si to investigate the possibility of hydriding the material directly from the dehydrogenated state. We deposited the 72 nm Mg_2Si films on silicon wafer substrates with the native oxide layer present and capped them with a 15 nm palladium layer to catalyze the hydrogen

absorption. However, we were unsuccessful in hydriding these films. In order to analyze the system further, we deposited several other thin film structures. The first of these was a "sensor layer" sample that contained a 200 nm magnesium layer underneath a 100 nm Mg_2Si layer as shown in Figure 1a. The magnesium layer acts as a sensor to indicate whether hydrogen diffuses through the Mg_2Si layer, or whether there is a diffusion problem with the material. After hydrogen charging, we saw no Mg signal in the XRD scans. All of the Mg sensor layer transformed into MgH_2, while the Mg_2Si signal remained unchanged. The next structure we deposited consisted of a "catalyst layer" designed to nucleate the transition from Mg_2Si into MgH_2 and Si. This sample consisted of a 25 nm Pd layer covering a 100 nm Mg layer over a 100 nm Mg_2Si layer as shown in Figure 1b. After charging the sample with hydrogen, all of the Mg layer converted to MgH_2 while the Mg_2Si layer remained according to the XRD scans. Next, we attempted to reduce the diffusion lengths required of the Mg and Si in the Mg_2Si layers by depositing multilayer structures of several (10-20) very thin (5-10 nm) Mg_2Si layers separated by thin (5-10 nm) Pd or Mg layers. The sample containing Pd layers attempts to deliver hydrogen directly to the Mg_2Si layers while the sample containing Mg layers attempts to nucleate the growth of MgH_2 from the Mg_2Si.

In addition to the work on the Mg_2Si system, we grew epitaxial Mg films on Al_2O_3 and MgO for the first time. Samples were prepared using sputter deposition at room temperature and up to 100°C. Upon exposure to hydrogen at 100°C and 72 psi the Mg transformed into singly oriented MgH_2. Using detailed XRD scans we determined from these samples that the crystallographic orientation between Mg and MgH_2 is MgH_2 (110) [001] // Mg (001)[100]. In addition, through examination of the rocking curve and phi scans of both the Mg and MgH_2 after charging and after discharging we observed strong evidence for a

solid phase epitaxial (SPE) regrowth mechanism for the Mg. In this mechanism, the regrowing Mg forms on the leftover, untransformed Mg and regains the original crystal quality of the as-deposited Mg film as shown in a. This is indicated by the fact that the rocking curve scans of the regrown Mg retain the width of the as-deposited Mg, and not the width of the lesser quality MgH_2 as would be the case for non-SPE regrowth such as that shown in Figure 2b.

In a new effort, we aim to investigate the effect of catalyst material placement on the kinetics of metal hydride hydrogen storage systems. To accomplish this we deposited samples with a surface catalyst layer where a thin (8 nm) layer of titanium sits between a 400 nm magnesium film and a 25 nm palladium capping layer as shown in Figure 3a. We deposited another sample where the same amount of titanium found in the first sample was dispersed throughout the magnesium layer as a codeposited alloy as in Figure 3b. The 8 nm of Ti corresponds to ~5 wt% for the sample, similar to amounts used when doping $NaAlH_4$ samples. Both of these samples are compared against a 400 nm thick pure magnesium film with a 25 nm palladium cap as a control sample. Understanding the differences in kinetic behavior between these samples will further the understanding of the role of catalyst materials for hydrogen absorption in metal hydride hydrogen storage materials.

In our thermodynamic modeling efforts we have revealed several promising consequences of reducing the dimensions of metal hydride systems into the nano-scale regime. When the increasingly dominant surface energy effects are taken into account, the thermodynamics and hydrogen storage properties of materials are significantly altered. For example, taking the surface energy difference between Mg and MgH_2 into account, the equilibrium pressure of nanometer sized particles of MgH_2 shows a dramatic dependence on particle size. As shown in Figure 4, a 2 nm radius particle would
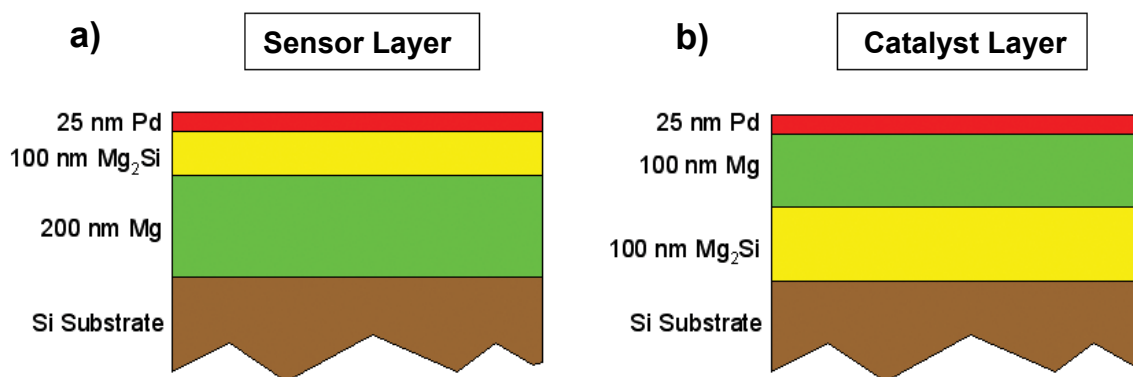

a) **Sensor Layer**

25 nm Pd
100 nm Mg_2Si
200 nm Mg
Si Substrate

b) **Catalyst Layer**

25 nm Pd
100 nm Mg
100 nm Mg_2Si
Si Substrate

FIGURE 1. Schematic Showing Sensor and Catalyst Layer Samples used to Study Mg_2Si System

a)

SPE Regrowth

On discharge, Mg regrows epitaxially on the remaining Mg at Mg/MgH$_2$ interface, not at MgH$_2$/Pd interface

Mg growth direction

b)

Non-SPE Regrowth

Non-epitaxial (less highly oriented) Mg regrows from MgH$_2$/Pd interface

Mg growth direction
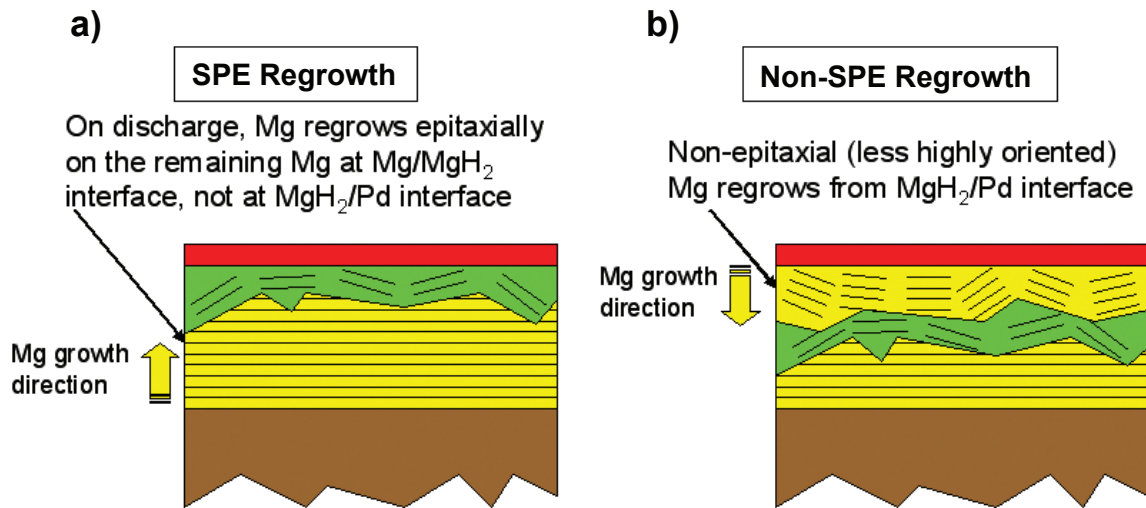
FIGURE 2. SPE and Non-SPE Regrowth Schematics

a)

Surface Sample

25 nm Pd
8 nm Ti
400 nm Mg
Si Substrate

b)

Bulk Sample

25 nm Pd
~408 nm Mg/Ti
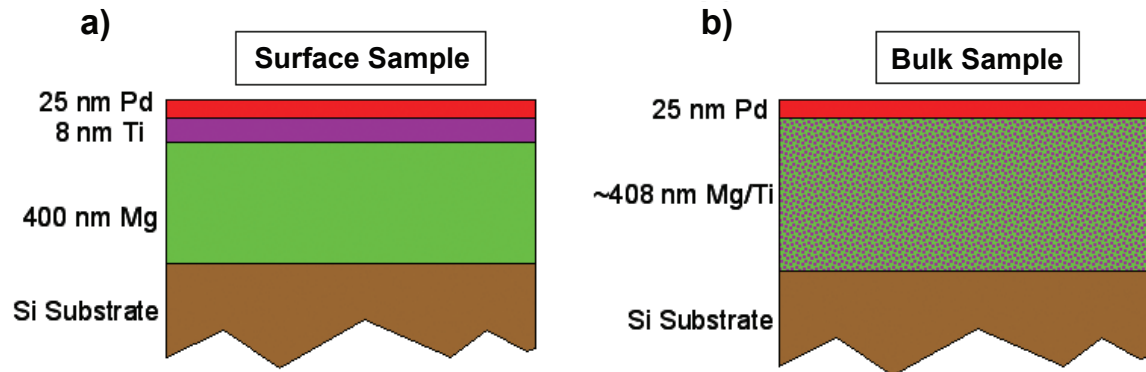Si Substrate

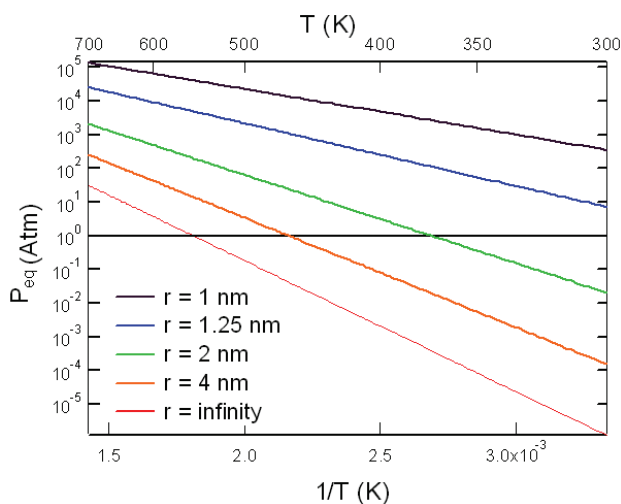**FIGURE 3.** Schematics Showing Samples Deposited for Catalysis Placement Study

FIGURE 4. Equilibrium Hydrogen Pressure vs. Reciprocal Temperature for Different Sized Magnesium Nanoparticles

display an equilibrium pressure of 1 bar at a temperature of around 325 K according to our calculations. Our thermodynamic modeling also indicates an increased solid solubility of hydrogen in nanoparticles of materials. Using a value for the surface free energy of 1.46 J/m^2 [1] our analysis shows that the solubility of hydrogen in Mg nanoparticles exceeds that of bulk Mg by up to three orders of magnitude. In addition to altering thermodynamic properties of hydrogen storage materials, reducing dimensions to the nanoscale can have dramatic effects on the nucleation barrier to the hydride phase transition. Our analysis indicates that, if we assume the new phase forms with a planar interface dividing the two phases of the nanoparticle, then for particle radii smaller than three times the critical nucleus size the nucleation of the new phase is easier than in the bulk material. Easier nucleation translates into faster kinetics for the transformation reaction.

Conclusions and Future Directions

Conclusions

1. Developed method to measure extent of hydride decomposition and structural changes during desorption using XRD:
   – Allows measurement of system kinetics during desorption.

2. Attempted to hydride Mg2Si directly using variety of thin film systems and configurations:
   – Unable to obtain segregated hydride system after H_2 exposure.

3. 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.

4. Began study of effect of catalyst placement (surface vs. bulk) on hydride formation and decomposition kinetics.

5. Continued efforts modeling the thermodynamics of nanoscale metal hydride material systems.

6. Predicted extended solubility of H in Mg and possibility of altered phase transformation kinetics.

Future Directions

1. 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.

2. Continue investigation of additional material systems:
   – MgB and MgAl systems.
   – Li-based systems.
   – Go/no-go decision point on Mg_2Si system.

3. Continue investigation into kinetics of thin film phase transitions and role of catalyst placement in those transitions:
   – Mg system and others.

4. Investigate nanoparticle systems as well as thin films using established techniques.

FY 2006 Publications/Presentations

1. "Nanostructures for Hydrogen Storage," Materials Research Society, Boston, MA, November 2005.

2. "Structure and Kinetics of Nanoparticle and Model Hydrogen Storage Materials", Bruce Clemens, Stephen Kelly, Hermione Giffard, Next Generation Neutron Source Workshop, June 7-8, 2005.

3. "The Formation and Dissociation of MgH2 in Thin Films Studied With X-ray Diffraction", Stephen Kelly, Hermione Giffard, Raj Kelekar, Bruce Clemens, Stanford Nanocharchterization Laboratory Inauguration, Sept. 2005.

References

1. Karl Johnson and Bing Dai, private communication, 2005.