

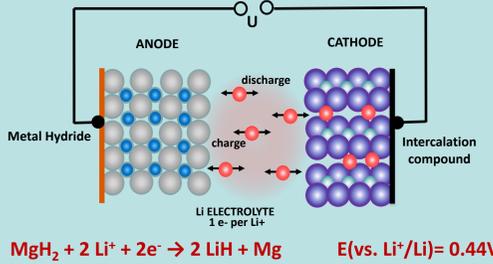
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## INTRODUCTION

Conversion reactions have emerged as an interesting alternative to the current intercalation mechanism of typical Li-ion batteries. Magnesium hydride (MgH<sub>2</sub>) specifically, is a noteworthy material because of its dual use as both a hydrogen storage material and as a battery electrode. The MgH<sub>2</sub> reversible conversion reaction (MgH<sub>2</sub> + 2Li ⇌ Mg + 2LiH) has good theoretical capacity (1480mAh/g) and takes place at ≈0.5V Li<sup>+</sup>/Li<sup>0</sup>, which makes it a great candidate for a negative electrode in Li-ion batteries. The following work is focused on characterizing MgH<sub>2</sub> thin films deposited with ion beam sputtering. Here we study Mg metal sputtered samples that are hydrogenated under 10bar pure hydrogen atmosphere and at 300°C. Electrochemical characterization with LiClO<sub>4</sub> as electrolyte will later be performed in conjunction with SEM, TEM and XRD measurements before and after cycling. Atom probe tomography measurements will also be investigated for information on phase transformation.

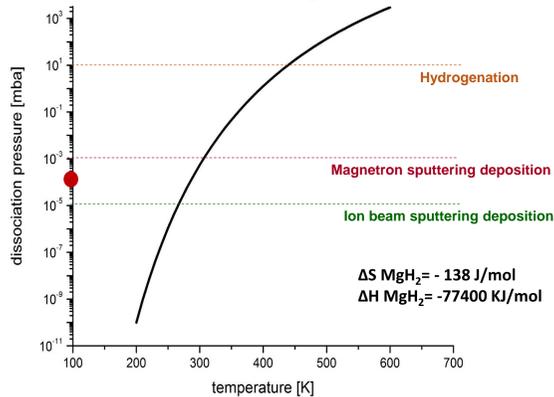


## MAIN OBJECTIVE

- Creation of MgH<sub>2</sub> layers with ion beam sputtering
- Pure Mg layers sputtered and hydrogenated under high pressure and temperature
- Study of the effect of hydrogenation time
- Investigation of Pd catalytic effect
- Field ion microscopy for studying the microstructure of the sputtered layers
- Preparation of samples for atom probe tomography measurements

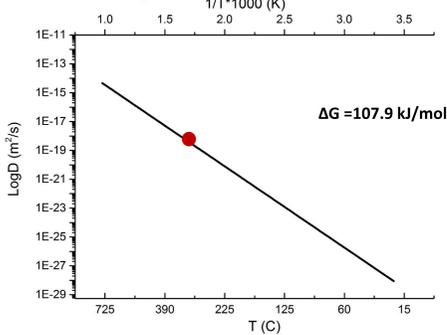
## Mg AND THERMODYNAMICS

### • Dissociation Pressure of MgH<sub>2</sub>

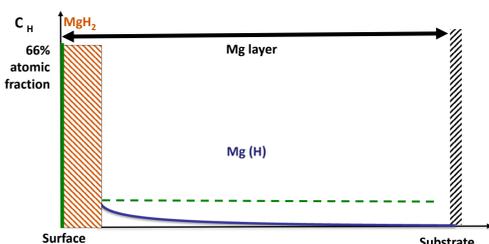


Partial pressure of H<sub>2</sub> at RT = 5\*10<sup>-4</sup> mbar

### • Diffusion of H<sub>2</sub>

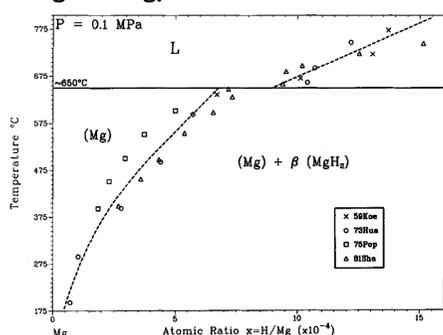


Diffusion of H<sub>2</sub> in Mg at 300°C is ≈ 10<sup>-18</sup> m<sup>2</sup>/s



Creation of MgH<sub>2</sub> on the surface of the layer

### • Phase diagram Mg/H<sup>(2)</sup>



## ION BEAM SPUTTERING

Ion beam sputtering is a physical vapor process that we use to deposit thin film materials.

The apparatus consists of:

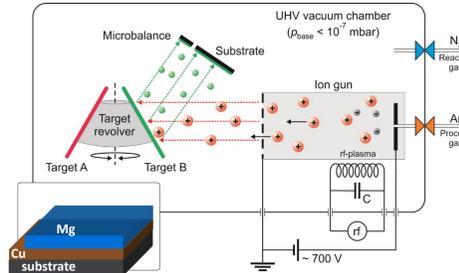
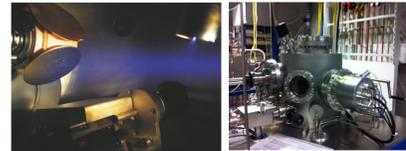
- an ion source (Ar or O<sub>2</sub> gas),
- a target revolver which can hold up to four different materials
- a sample holder with the substrates that can be heated up to 700°C

Ionization of the gas is attained by a cathodic source. The ions are then accelerated, deflected and focused using high voltage. Finally, they are neutralized in a plasma before they hit the target. A major advantage of this technique is a completely field-free space around targets and substrates. It is possible to deposit layers from a monolayer to few μm in thickness, and it's suitable for a broad range of materials. Reactive sputtering under oxygen, nitrogen or hydrogen atmosphere is easily performed.

Metal targets (ø 80mm) were used

**Sputtering conditions:**  
Base pressure: 10<sup>-7</sup> mbar  
Working Pressure: 2\*10<sup>-4</sup> mbar  
Acceleration voltage: 900V

Ion Beam Sputtering was used to produce thin films. Si (111) wafers served as substrates for films to be analyzed by XRD. Glass substrates will be used for samples dedicated to electrochemical measurements.

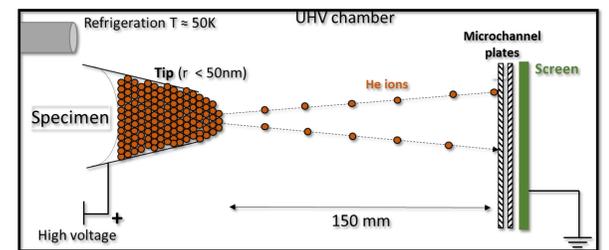


## FIELD ION MICROSCOPY (FIM)

FIM techniques use the physical effect of high surface fields. Applying moderate voltages, enormous field strengths in the range of some 10 V/nm are easily obtained at the apex of nanometer sized tips. Fields of such magnitude could never be obtained in macroscopic scale geometries. In order to produce a field ion micrograph an imaging gas (He) is necessary. Gas atoms are polarized and drawn toward the surface by inhomogeneous field around the tip.

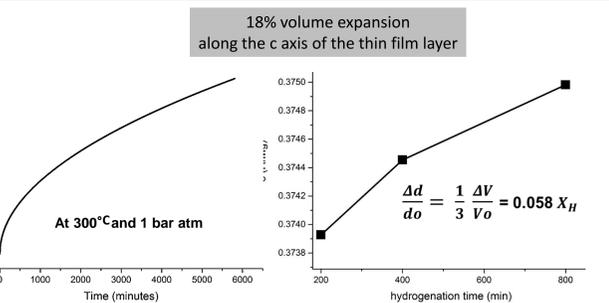
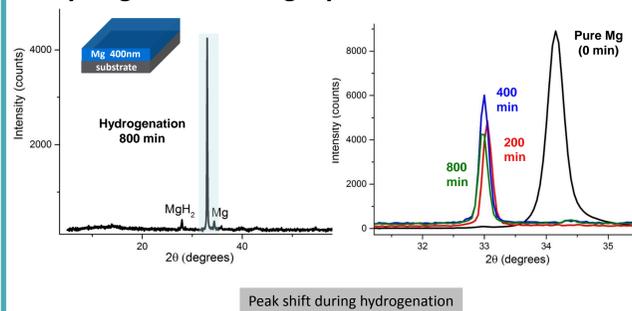
A typical field ion microscope consists of:

- an ultra-high vacuum chamber
- a specimen stage holding the tip
- a viewing screen with the capability of imaging the ion impacts
- a cryostat is to cool the tip down to 50 K in order to reduce the effect of thermal energies
- high positive voltage is applied between the metallic tip and the microchannel plates
- He gas atmosphere as imaging gas



## RESULTS AND DISCUSSION

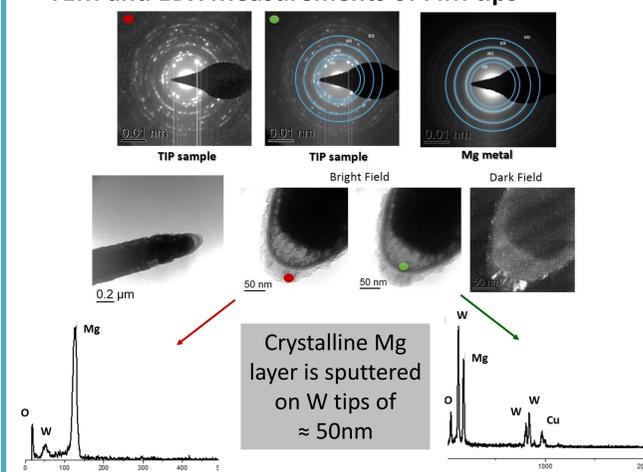
### • Hydrogenation of Mg layers



Mg layer 200nm needs about 10hours to hydrogenate

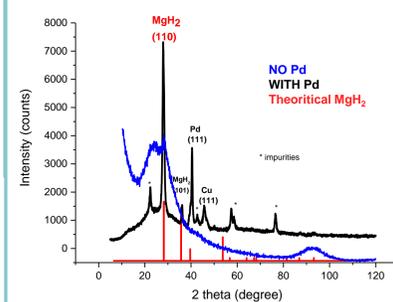
Increasing hydrogenation time increases content of H<sub>2</sub> in the layer

### • TEM and EDX Measurements of FIM tips



Hydrogenation time (min)	α = β	c
0	3.209	5.210
200	3.126	5.414
400	3.130	5.422
800	3.135	5.430

H<sub>2</sub> pressure: 10 bar  
Time: 5 hours  
Temperature: 300°C



H<sub>2</sub> pressure: 100 bar  
Time: 5 hours  
Temperature: 300°C  
Samples where kept at same pressure while cooling down

## CONCLUSIONS

- ✓ Partial pressure of H<sub>2</sub> at room temperature is 5\*10<sup>-4</sup> mbar. It is necessary to reach this pressure for hydrogenation of Mg thin film layers
- ✓ Hydrogenation of Mg layers at 10 bar and 300°C shows promising results. Longer time under H<sub>2</sub> atmosphere shifts the characteristic peak in XRD analysis, showing an increase of c lattice parameter
- ✓ Hydrogenation of Mg layers with Pd accelerates kinetics significantly and shows clear presence of MgH<sub>2</sub>
- ✓ TEM images of field ion microscopy tips show the presence of crystalline Mg metal layer deposited, and W oxide of the tip

## FUTURE WORK

- Hydrogenation of Mg at different times in order to see where saturation is reached
- Study further the effect of Pd as catalyst on Mg thin films
- Cycle electrochemical cells with hydrogenated Mg samples as electrodes and LiClO<sub>4</sub> electrolyte
- Atom probe tomography tests of hydrogenated samples

## REFERENCES

1. Hydrogen diffusion and effect of grain size on hydrogenation kinetics in magnesium hydrides. X.Yao, 2008, J.Mater. Res Vol 23, No2,
2. A. San-Martin and F.D. Manchester, 1987
3. The Metal-Hydrogen system, Basic Bulk Properties, Y.Jukai
4. Diffusion in Solids, Fundamentals, Methods, Materials, Diffusion-Controlled Processes, Helmut Mehrer.

## ACKNOWLEDGMENTS

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