An Integrated Approach of Hydrogen Storage in Complex Hydrides of Transitional Elements

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STP 32

Overview

Timeline

- July 2006
- August 2009
- Percent complete 45%

Budget

- Total project funding $
  - DOE share $ 544,160
  - Contractor share $ 234,991
- Funding received in FY06 $ 544,160

Barriers

- *Barriers addressed*
  - Durability/Operability (3.3.4 D)
  - Charging/Discharging Rates (3.3.4 E)
  - Lack of understanding of Hydrogen Physisorption & chemisorption (3.3.4 P)

Partners

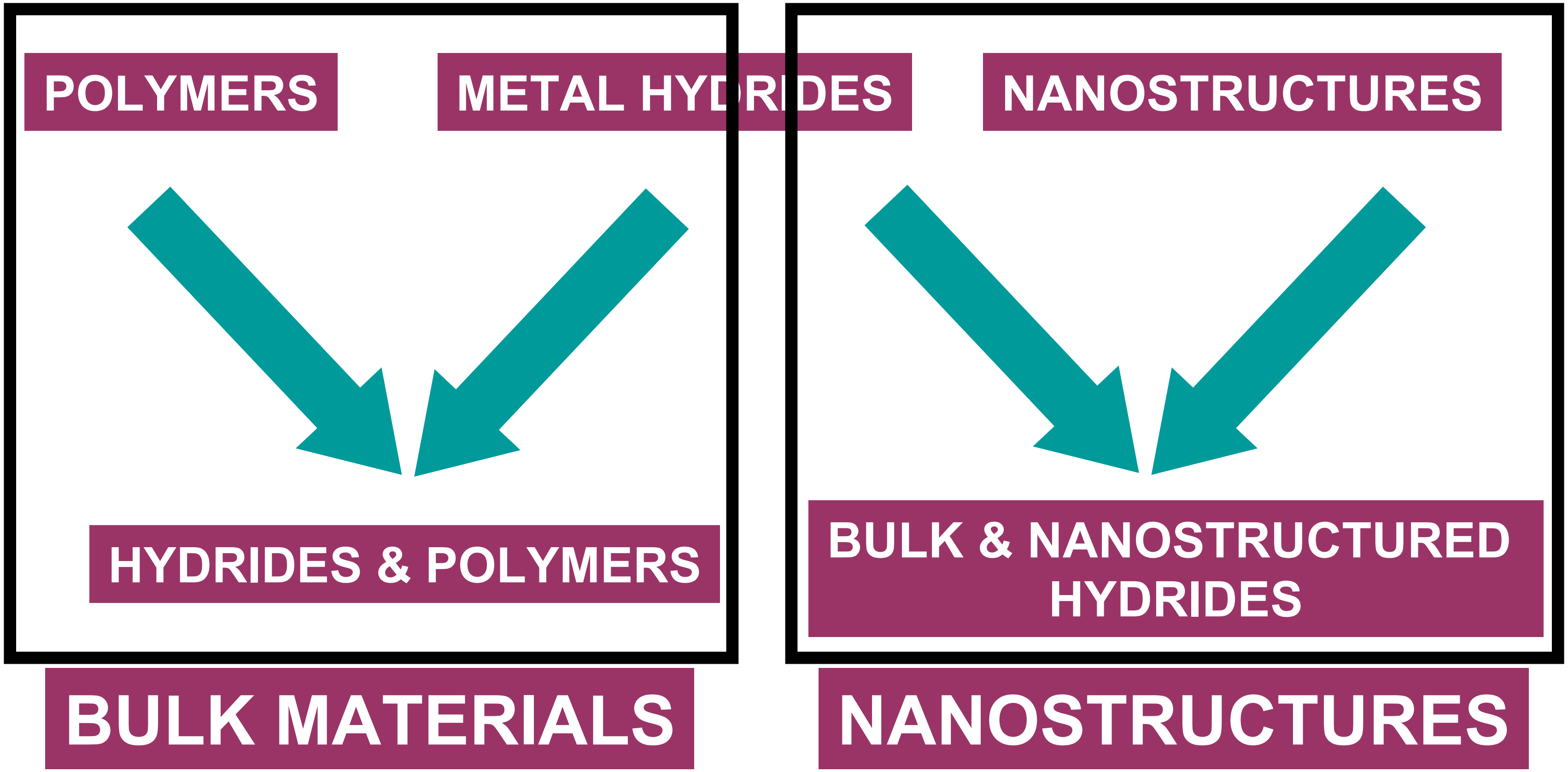
- University of Arkansas Nanotechnology Center, Little Rock
- National Institute for Isotopic & Molecular Technologies, Romania
- Los Alamos Neutron Diffraction Center

OBJECTIVES

PARAMETER	YEAR		
	2007	2010	2015
Weight (%)	4.5	6	9
Pressure (bar)	100	100	100
Kinetics (Min.)	10	3	2.5
Temp. (^{o} C)	-20/50	-30/50	-40/60

PROJECT TARGETS: 6 wt.% , 100 bar, 3 min , -30/50 deg C

OBJECTIVES


POLYMERS
METAL HYDRIDES
NANOSTRUCTURES
HYDRIDES & POLYMERS
BULK & NANOSTRUCTURED HYDRIDES
BULK MATERIALS
NANOSTRUCTURES

OBJECTIVES

BULK MATERIALS

- ***Hydrogen Storage Characterization***

  –**Design and fabrication of a Sievert Type high pressure high temperature gas titration / chemical reactor setup**.

- ***Develop materials for hydrogen storage based on DOE's system storage target for 2010***

  ➢ **Increase of reversible hydrogen storage capacity in complex metal hydrides by developing new systems including hydride phases**

  ➢ **Development of catalytic compounds to enhance the formation and decomposition of complex metal hydrides.**

  ➢ **Investigation of hydrogen storage capacity in metal (Ti and Li) decorated polymers.**

  ➢ **Investigation of enhancement of hydrogen storage capacity in metal hydrides dispersed in polymer matrix**.

MILESTONES

BULK MATERIALS

Month/Year	Milestone or Go/No-Go Decision
Jan 08	**Milestone**: Design, fabrication and testing of the Sievert Type high pressure and high temperature gas titration setup is completed and tested successfully.
Mar 08	**Milestone**: An inert atmosphere synthesis and compound treatment (moisture less than 5 ppm and oxygen less than 10 ppm) facility has been installed.
Apr 08	**Milestone**: Characterization of Hydrides initiated
Apr-08	**Milestone**: Synthesis and characterization of Ti-decorated polymers started; 1.3 wt % of hydrogen stored in Ti-decorated polyaniline at 80 bar and 25 deg C.

APPROACH

BULK MATERIALS

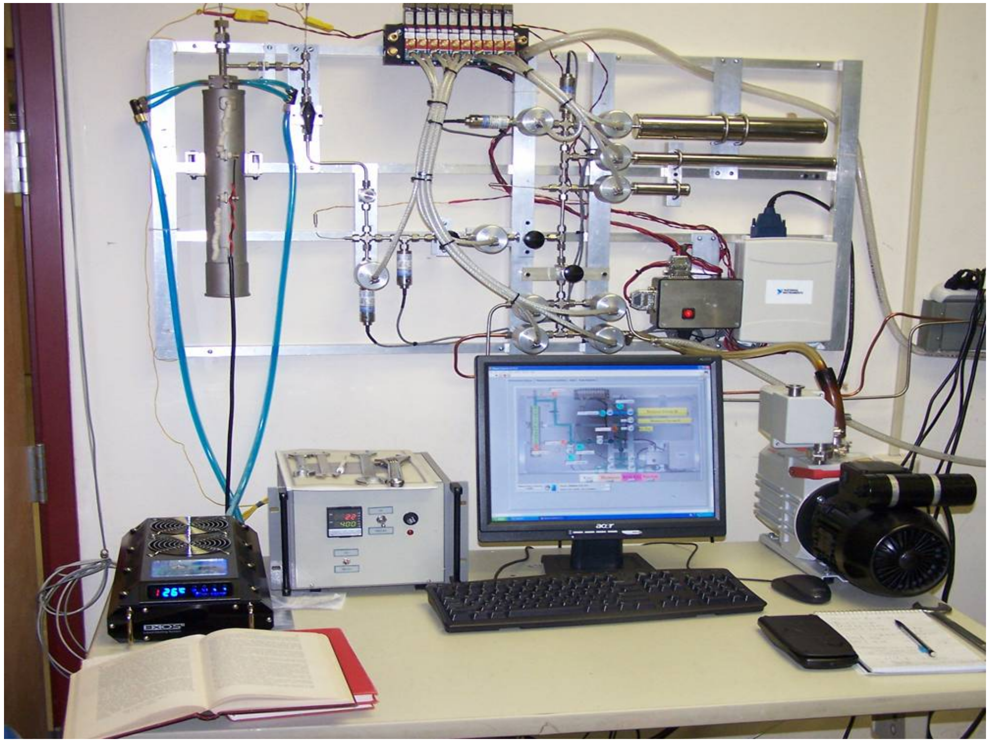
- **H_2 absorption/desorption measurement setup**
  1. Scalable sensitivity
  2. Wide range of operating temperature and pressure conditions
  3. Increase the degree of automation

- **Metal hydrides**
  4. Decrease reaction temperature
  5. Increase reaction rates
  6. Decrease reaction pressure

- **Polymer based materials**
  7. Synthesis of metal (Ti, Li, Sc)-decorated stable polyaniline/polyacetylene
  8. Use of metal nanoparticles in synthesis
  9. Reducing cluster formation of nanoparticles
  10. Increase surface area
  11. Dispersing polymers in metal hydrides

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS



Specifications

1. Pressure: Vacuum to 200 bar
2. Temperature: Ambient to 500 deg C
3. Sample volume: 10 mL
4. Computer controlled & automated

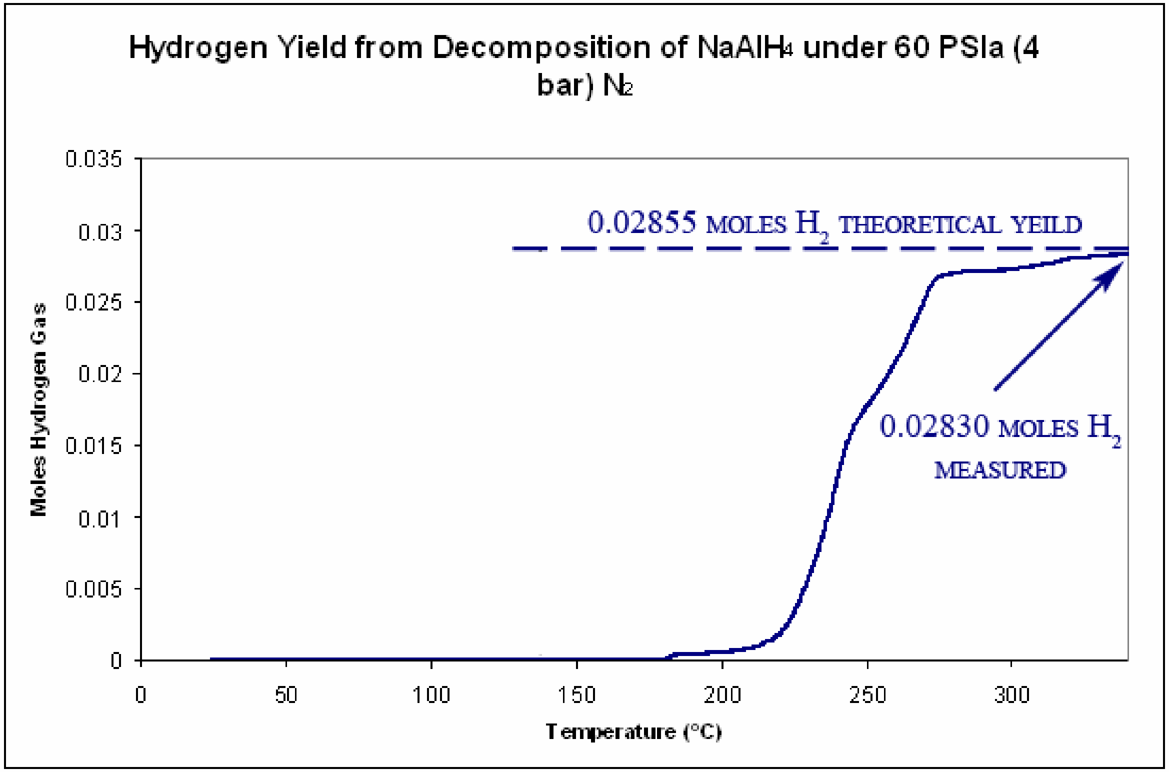
DOE funded

COST OF COMMERCIAL DEVICE: ~ $ 130,000
OUR DEVELOPMENTAL COST: ~ $ 20,000

SIEVERT APPARATUS DEVELOPED IN-HOUSE

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

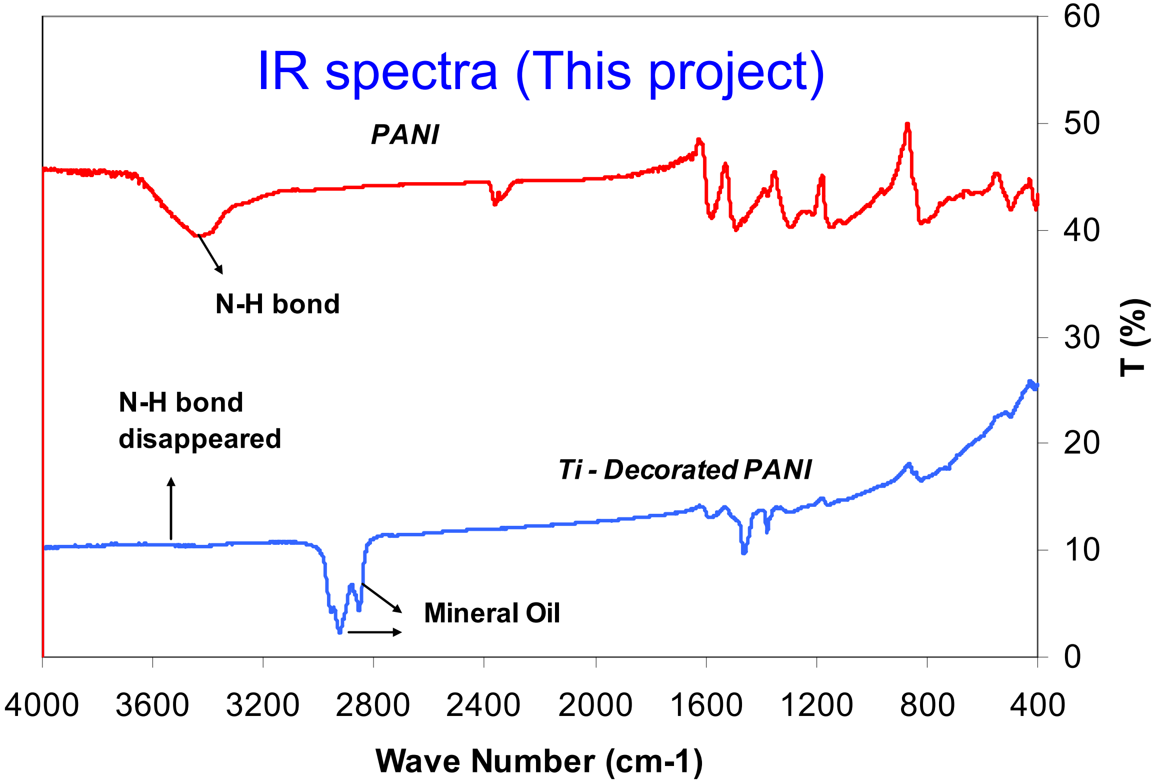


The measured hydrogen yield from a sample of batch certified NaAlH4 during thermal decomposition

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

Ti-decorated polyaniline



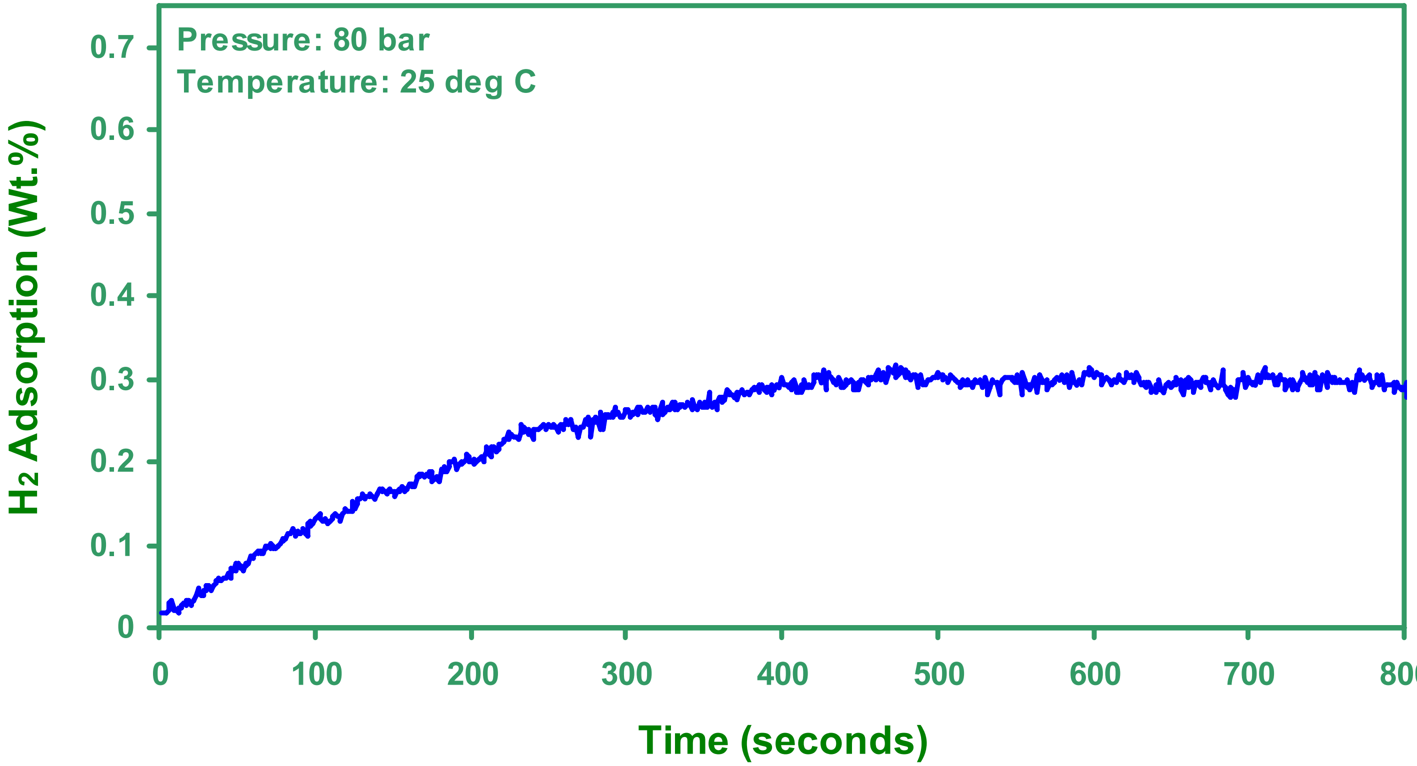
Theory (1) predicts replacement of N-H bond by Ti in polyaniline. The IR spectra confirms that N-H bond in Ti-decorated polyaniline has disappeared. Experiments are needed to confirm that N-H has been replaced by Ti.

1. Lee et al., Physical Review Letters, 97 (2006) 056104

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

Ti-decorated polyaniline



Incremental Adsorption curve of Ti decorated polyaniline

following a two-step adsorption of 0.7 % at 35 bar, and an additional 0.3% at 50 bar, both at 25 deg C

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

Ti-decorated polyaniline

Pressure (bar)	Weight (%)	Kinetics (min)	Temp (° C)
35	0.7	40	25
50	0.7+0.3	25	25
80	0.7+0.3+0.3= 1.6	5	25

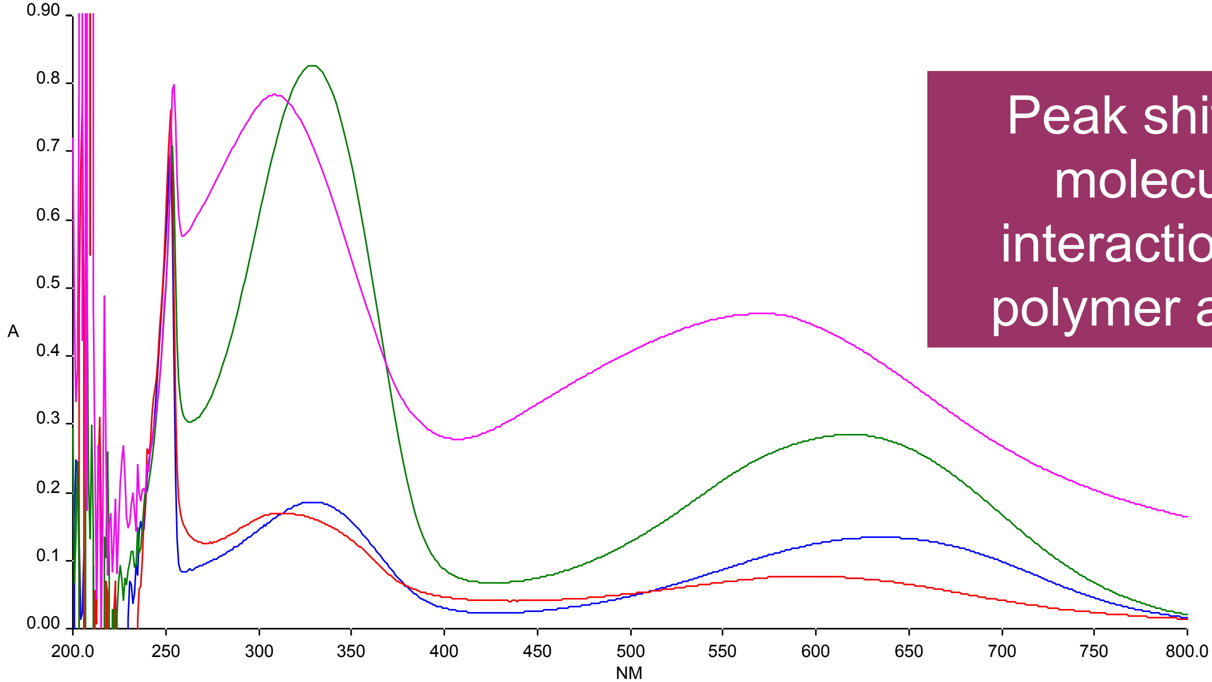
Possible Ti clustering (1)

(1) Li and Jena, Physical Review Letters, 97 (2006), 209601.

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

Hydride-dispersed polyaniline



Peak shift confirms molecular level interaction between polymer and $NaAlH_4$

Variation of optical absorption peaks as function of concentration of NaAlH4 in polyaniline

	PANI	PANI/NaAlH4 2:1	PANI/NaAlH4 1:1	PANI/NaOH
$\lambda 1$ (nm)	330	308	312	329
$\lambda 2$ (nm)	618	571	597	636

FUTURE WORK

BULK MATERIALS

Synthesis, H_2 storage & Kinetics

- Ti-decorated polyaniline

  4.1 wt.% , 30 bar, 25 deg C (1)

- Ti-decorated cis-polyacetylene ,

  7.6 wt.% , 30 bar, 25 deg C (1)

- Ti-decorated trans-polyacetylene ,

  12 wt.% (2)

- Sc-decorated trans-polyacetylene

  14 wt.% (2)

All are theoretical predictions

Promising

(1) Lee et al., Physical Review Letters, 97 (2006) 056104 ,

(2) Lee et al., Journal of Alloys of Compounds, 446-447 (2007) 373-375.

FUTURE WORK

BULK MATERIALS

Synthesis, dissociation studies

- Magnesium Borohydride ($Mg(BH_4)_2$) and Magnesium Alanate ($Mg(AlH_4)_2$),
- $Mg(BH_4)_{2-n}$ $(AlH_4)_n$
- Sodium Aluminium Hydride ($Na(AlH_4)$) and Ti-Na(AlH4)) as model systems

SUMMARY

BULK MATERIALS

- **A state-of-the-art hydrogen storage material synthesis and characterization facility has been established at University of Arkansas at Little Rock.**
- **A highly automated Sievert type gas titration setup to measure the hydrogen sorption has been developed and fabricated in-house.**
- **Titanium nanoparticle decorated polyaniline shows promising preliminary results (1.3 wt.%, 80 bar, 25 deg C) for validating the theoretically predicted hydrogen storage capacity.**

OBJECTIVES

NANOSTRUCTURES

- Investigation of **maximum hydrogen storage capacity and adsorption/desorption kinetics of thin films and nanostructures of magnesium alanate and magnesium borohydride** for hydrogen storage.
- Utilization of **glancing angle deposition** (**GLAD**, also known as oblique angle deposition) technique for the growth of **nanorod arrays of magnesium (Mg) as a model system, magnesium alanate ($Mg(AlH_4)_2$), and magnesium borohydride ($Mg(BH_4)_2$).**
- Construction and utilization of new **quartz crystal microbalance (QCM)** gas chamber system for the dynamic investigation of **maximum hydrogen storage capacity and adsorption/desorption kinetics of the nanostructures produced with nanograms measurement sensitivity.**
- Investigation of **effect of catalyst** on hydrogen adsorption/desorption properties of Mg, magnesium alanate, and magnesium borohydride. Possible **catalyst materials that we plan to incorporate are Pt, Ti, Ni, Pd, and V.**

MILESTONES

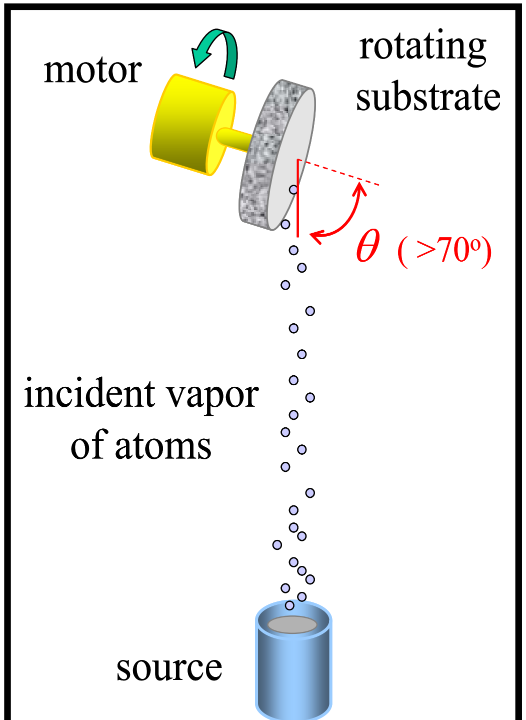
NANOSTRUCTURES

Month/Year	Milestone or Go/No-Go Decision
Jun-07	**Milestone:** Fabrication of nanostructures in the shapes of vertical nanorods using GLAD approach. Material: Mg as model system.
Dec-07	**Milestone:** Started design and set-up of a QCM gas chamber for the dynamic measurement of hydrogen adsorption/desorption kinetics, thermal stability, and oxidation properties of nanostructured coatings.
May-08	**Milestone:** Finished investigation of thermal stability and oxidation properties of thin films and nanostructures produced by GLAD. Material: Mg as model system.
May-08	**Milestone:** Started investigation of hydrogen adsorption/desorption properties of thin films and nanostructures produced by GLAD. Material: Mg as model system
Sep-08	**Milestone:** Will start the fabrication and investigation of hydrogen adsorption/desorption properties of magnesium borohydride and alanate thin films and nanostructures produced by GLAD. Materials: $Mg(AlH_4)_2$ and $Mg(BH_4)_2$

APPROACH

NANOSTRUCTURES

Glancing Angle Deposition (GLAD)



- Large surface-to-volume ratio ,
- Control of crystal orientation,
- Lower oxidation rate,
- Porosity allows for volumetric changes

- **Quartz Crystal Microbalance (QCM) method for the investigation of hydrogen storage, thermal stability, and oxidation properties of nanostructures and thin films produced**

APPROACH

NANOSTRUCTURES

Nanostructured Materials to be Studied

Nanostructured Material	Hydrogen Storage (wt %)	Decomposition T (°C)
$Mg(AlH_4)_2$ Magnesium Alanate [1]	**9.3**	**200**
$Mg(BH_4)_2$ Magnesium Borohydride [2]	**14.9**	**320**
Mg Magnesium [3]	**7.6**	**300**

Model System ←

+

Catalyst Incorporation

Pt
Ti
Ni
Pd
V

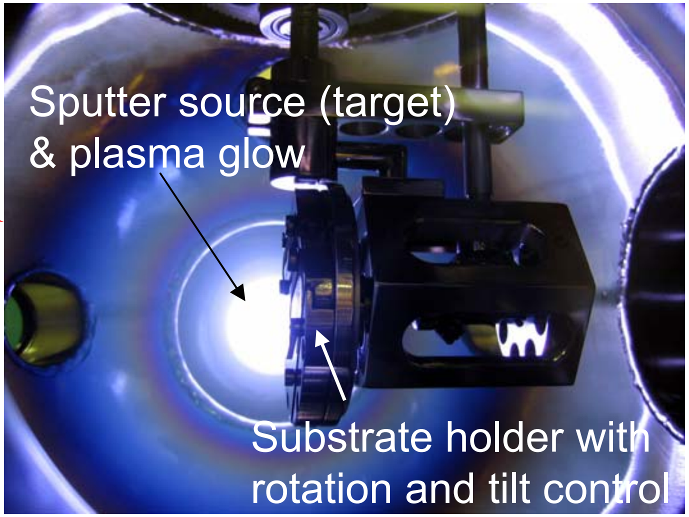
[1] Fichtner etal. Journal of Alloys and Compounds 356-357: 418-422, 2003.
[2] Zuttel *et al.* Renewable Energy 33(2): 193-196, 2007; Zuttel *et al*. Journal of Alloys and Compounds 446-447: 315-318, 2007.
[3] Sakintuna et al. Int. J. of Hydrogen Energy 32: 1121-1140, 2007; Li *et al.* J. Am.. Chem. Soc. 129: 6710-6711, 2007; Wagemans *et al.* J. Am.. Chem. Soc. 127: 16675-16680, 2005.

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

GLAD SPUTTER/EVAPORATION DEPOSITION SYSTEM

DOE funded (in part)



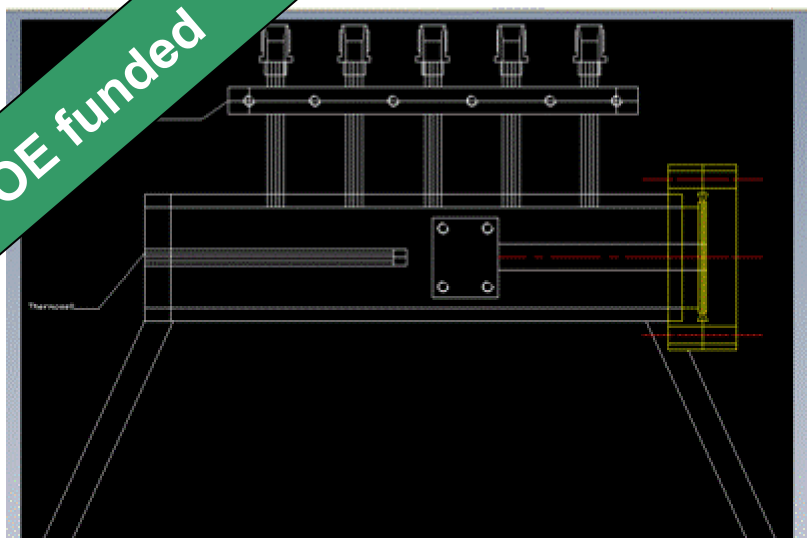
COST OF COMMERCIAL DEVICE: ~ $ 160,000
OUR DEVELOPMENTAL COST: ~ $ 80,000

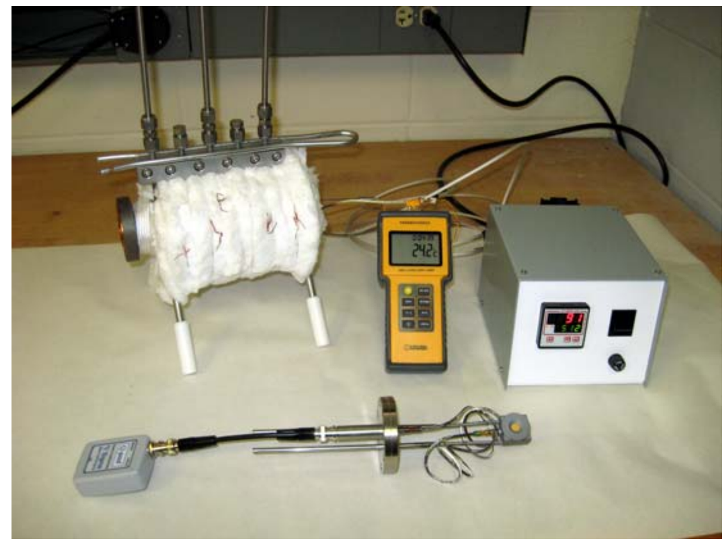
TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

QUARTZ CRYSTAL MICRO-BALANCE (QCM) SYSTEM DEVELOPED IN-HOUSE

DOE funded





SPECIFICATIONS

- Operating Pressure Range: 10^{-3} – 30 bars
- Gasses available: Hydrogen, argon, oxygen
- Stable Temperature Range: room temperature – 500 deg C
- Nanostructure/thin film coating surface area: ~ 1 cm^2
- Mass Sensitivity: down to 0.001 ng/cm^2

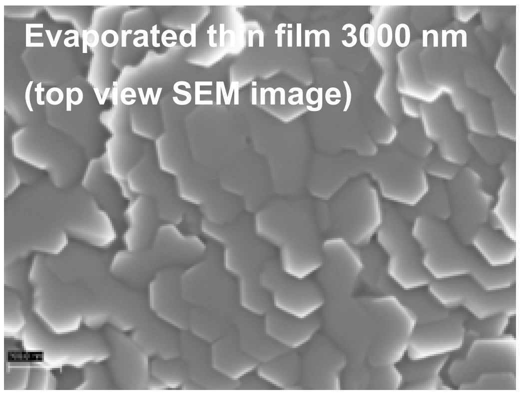
COMMERCIAL DEVICE: Not Available

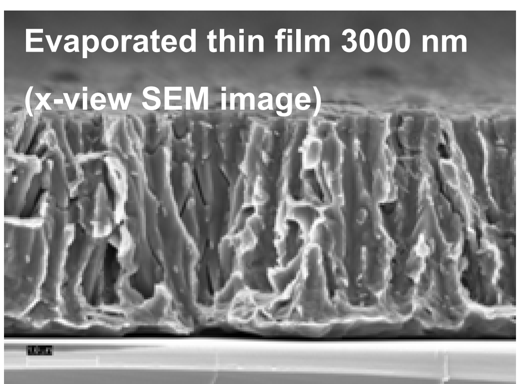
OUR COST: ~ $ 6,000

TECHNICAL ACCOMPLISHMENTS

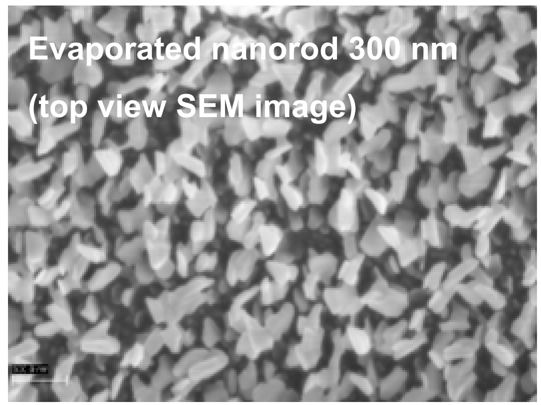
NANOSTRUCTURES

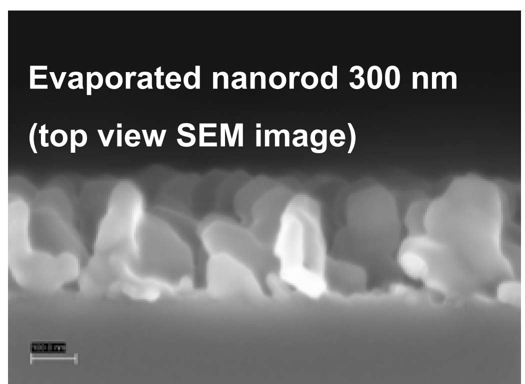
Thin film





Nanoblades





Deposition conditions:

Tilt angle :

Thin films :0°

Nanorods :83.7°

Pressure: 6.9 $*10^{-6}$ mbar

Rotation: 1 RPM

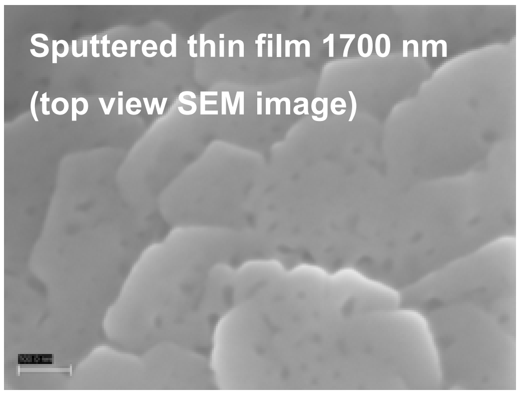
Substrate : Si (100)

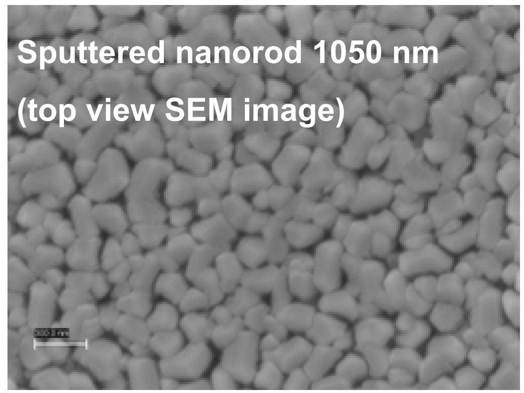
Thermally Evaporated Mg Nanoblades and Thin Films

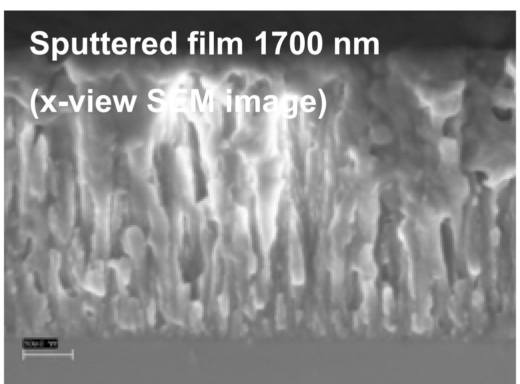
TECHNICAL ACCOMPLISHMENTS

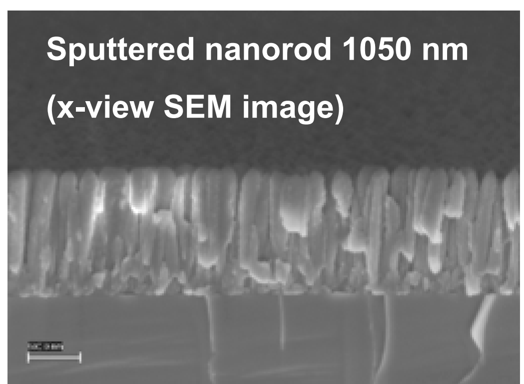
NANOSTRUCTURES

Thin film | **Nanorods**









Deposition conditions:

Tilt angle :
- Thin films :0°
- Nanorods :83.7°

Power: 80 watts

Pressure: 2.7 $*10^{-3}$ mbar

Rotation: 1 RPM

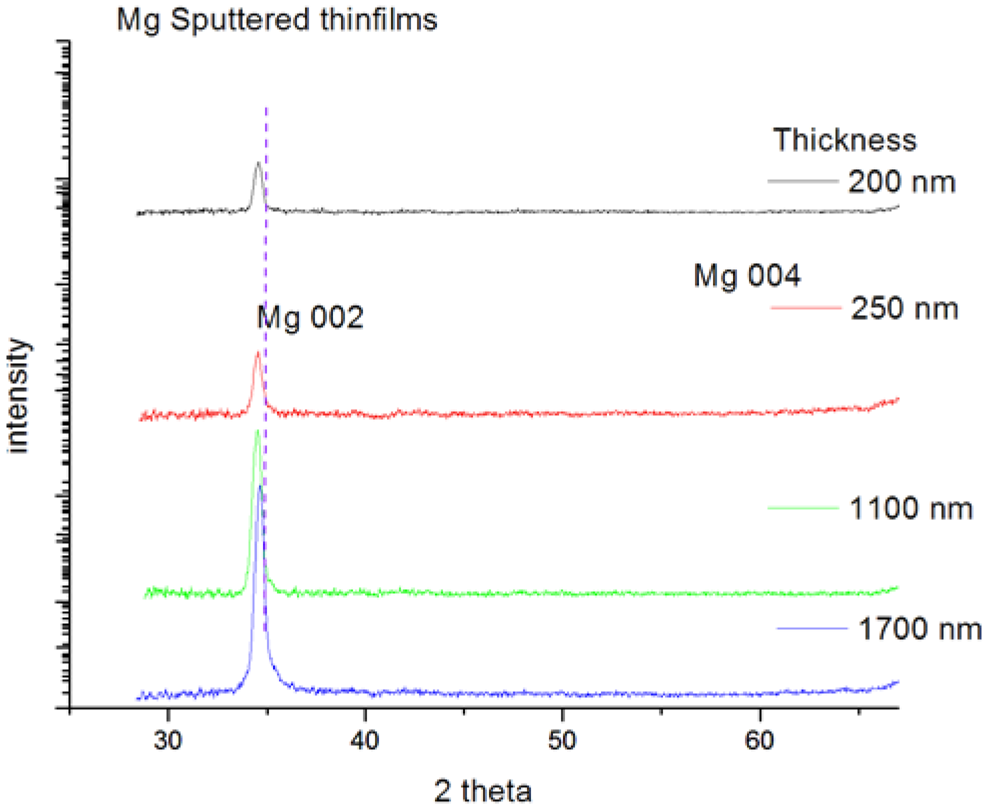
Substrate : Si (100)

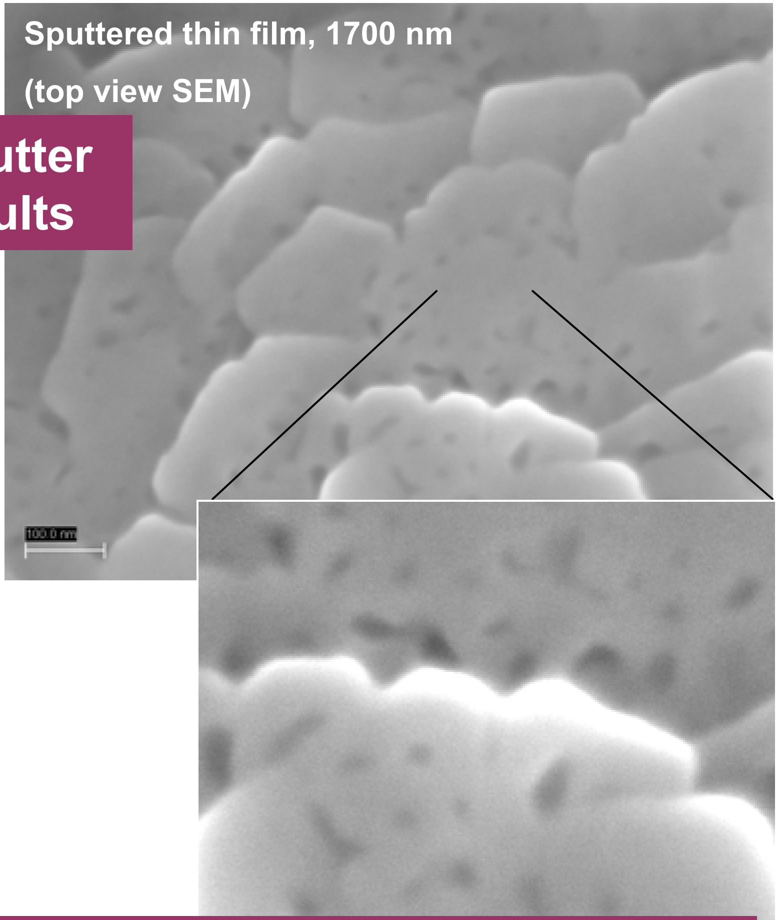
Sputter Deposited Mg Nanorods and Thin Films

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Microstructure and Crystal Orientation of Sputter Deposited Mg Thin Films: XRD and SEM results



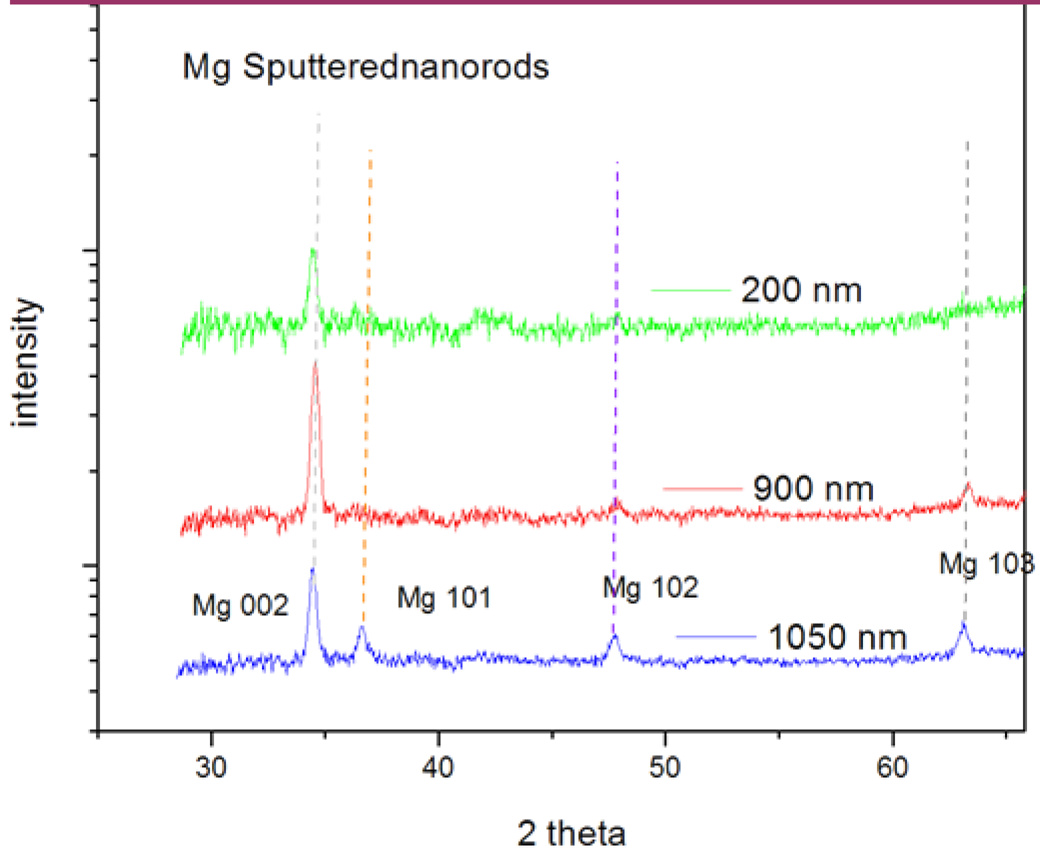


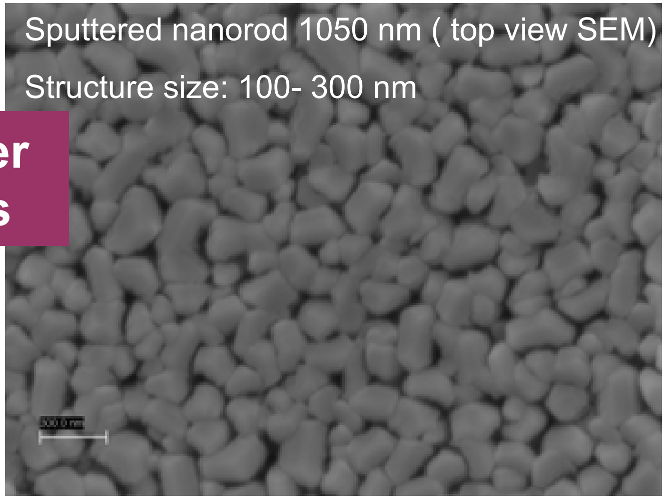
- Growth in (002) direction
- Surface porosity

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Microstructure and Crystal Orientation of Sputter Deposited Mg Thin Films: XRD and SEM results



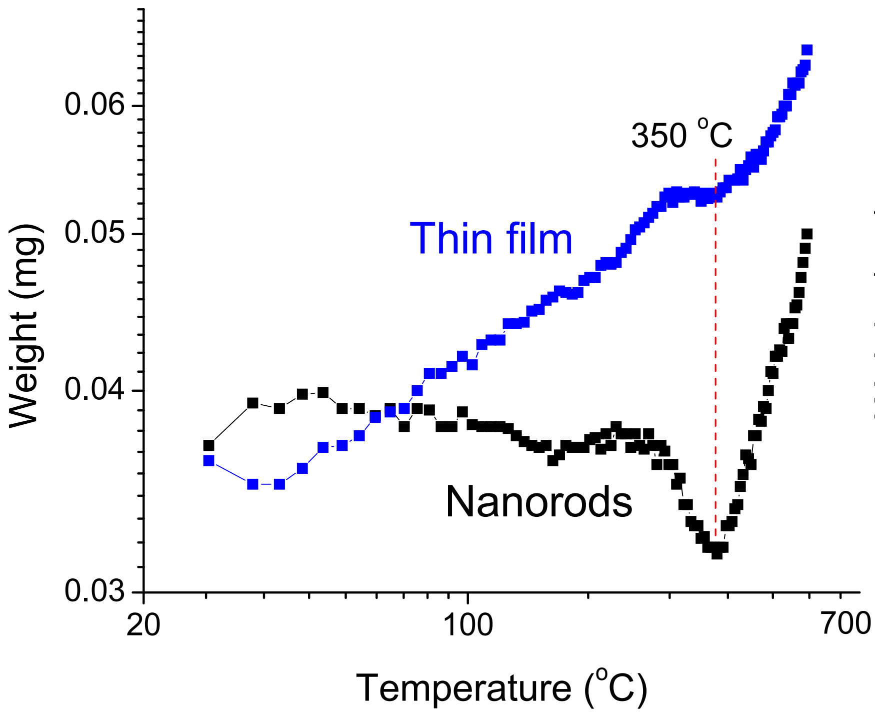


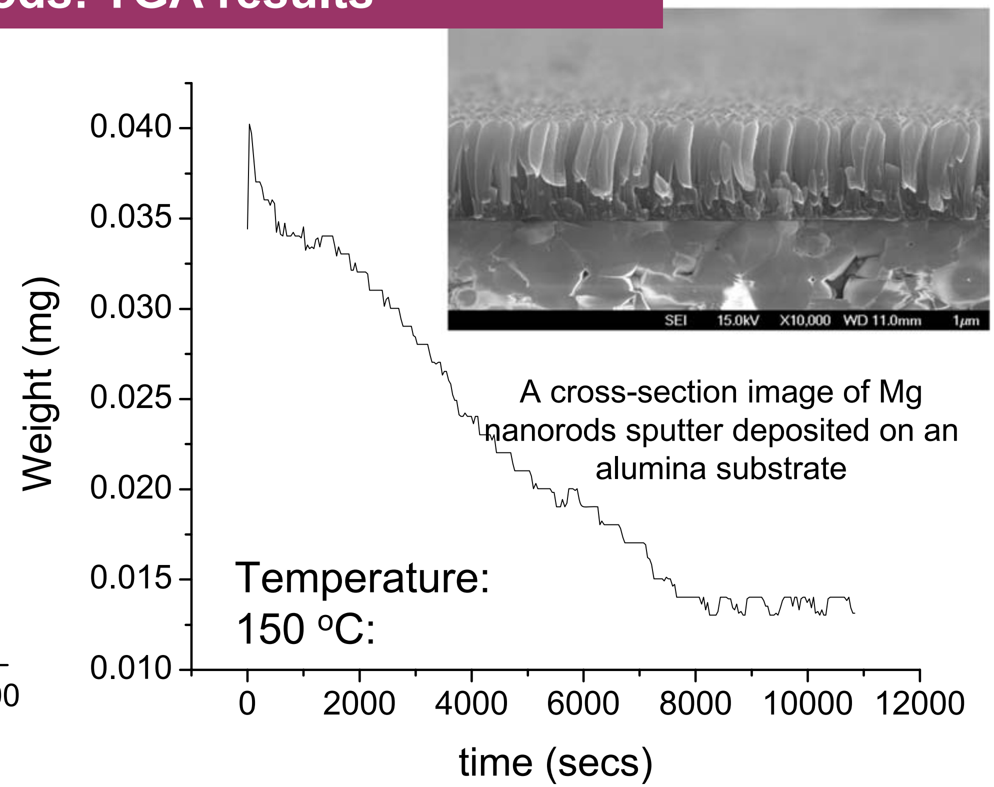
- **Growth in (002), (101), (102), and (103) directions, unlike 002 Mg thin films**
- **Highly columnar microstructure**

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Thermal Stability and Oxidation of Mg Thin Film and Nanorods: TGA results





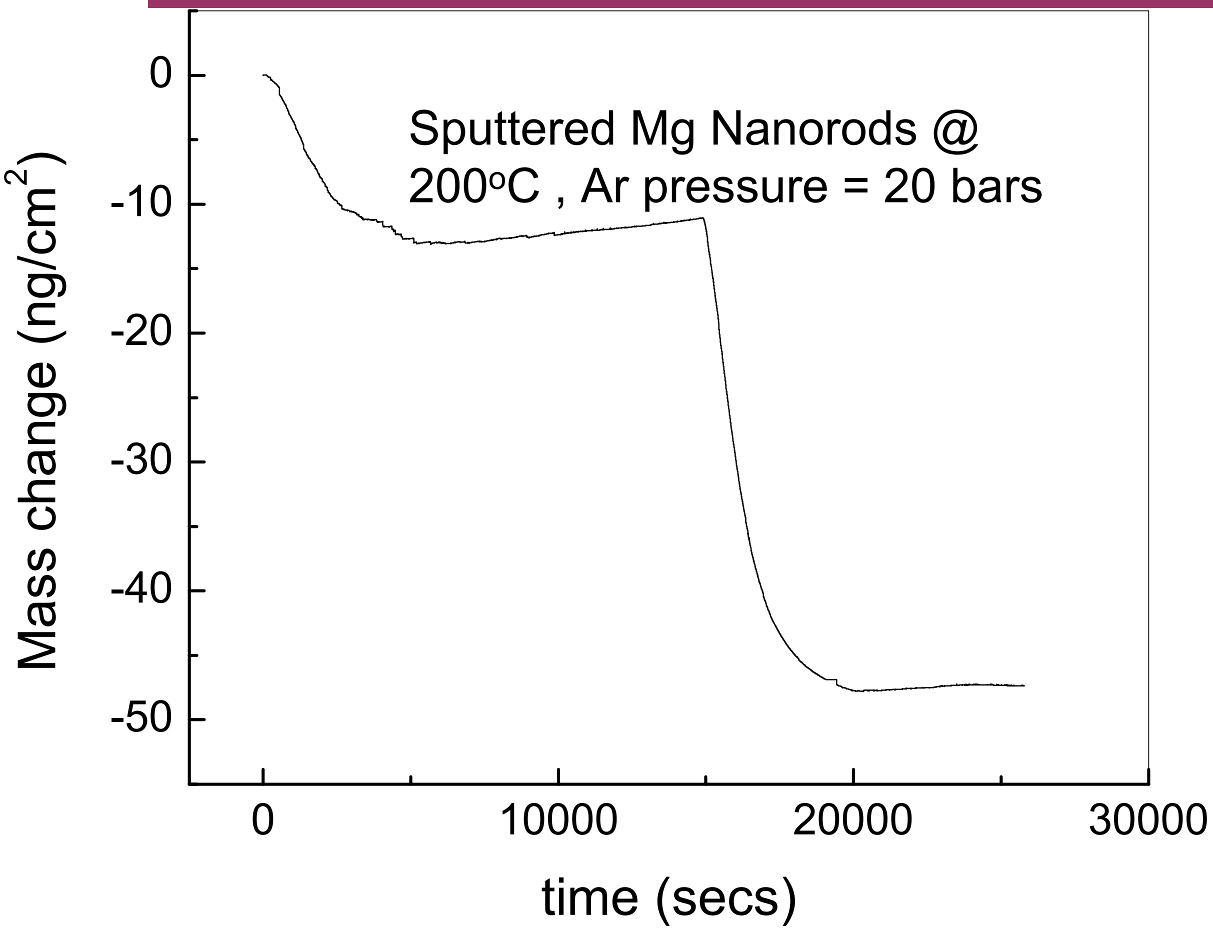
A cross-section image of Mg nanorods sputter deposited on an alumina substrate

Reduced oxidation and enhanced evaporation in Mg nanorods; needs to be accounted for during hydrogen adsorption studies

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Thermal Stability of Mg Nanorods: QCM results



Enhanced evaporation in Mg nanorods at low temperatures; needs to be accounted for during hydrogen adsorption experiments

SUMMARY

NANOSTRUCTURES

- **Identified magnesium borohydride and alanate as materials of choice for nanofabrication and hydrogen storage studies.**
- **Mg nanostructures as model material system: Hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, crystal orientation, and oxidation properties.**
- **Glancing angle deposition (GLAD) technique is utilized for the growth of nanostructured arrays in the shapes of vertical nanorods and nanoblades.**
- **A new quartz crystal microbalance (QCM) system is developed for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings.**

FUTURE WORK

NANOSTRUCTURES

Study of hydrogen storage capacity & kinetics

- Thin films and nanostructures of magnesium alanate and borohydride,
- Effect of catalysis,
- Effect of nanostructure size, shape & separation,
- Nanorod arrays of Mg as a model system.

SUMMARY (OVERALL PROJECT)

POLYMERS	METAL HYDRIDES	NANOSTRUCTURES
FOCUS		
Polyaniline Polyacetylene	Magnesium Borohydrides & Alanates	Magnesium Borohydrides & Alanates

HYDRIDES+POLYMERS

BULK & NANOSTRUCTURED HYDRIDES