Integrated Nanoscale Metal Hydride – Catalyst Architectures for Hydrogen Storage

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Program Scope

By tailoring the structural properties of nanomaterials, the thermodynamics and kinetics of hydrogen adsorption can be designed to satisfy the future hydrogen storage requirements. A fundamental understanding of hydrogen-nanostructure interactions also depends largely on the ability to fabricate nanostructures with the desired structural properties.

Our program goal is to use a novel nanofabrication technique, glancing angle deposition (GLAD), to design and produce metal hydride nanorods and nanowires with different topography, structure, and composition, and to probe how hydrogen interact with different metal hydride nanostructures using in-situ Raman and IR spectroscopic techniques. We hope to investigate the following important issues for hydrogen storage applications: (1) How would different nanoscale structures change the hydrogen storage behavior? (2) Would nanoscale catalysts, incorporated into nanostructured hydrogen storage materials in different forms, greatly enhance the storage behavior? (3) Is there a cost-effective fabrication technique to integrate nanoscale hydrogen storage materials and catalysts?

Our specific aims are:

- Fabricating metal hydride nanostructures with different diameter, separation, alignment, and shape
- Fabricating metal hydride nanostructures with different catalysts and dopants
- Fabricating multilayer metal hydride nanostructures
- Characterizing hydrogen sorption thermodynamics, kinetics and hydrogen-nanostructure interactions

Recent Progress

Currently most of our efforts are focusing on the very initial stage of the project, especially on the further proof-of-concept stage.

(1) ***Designed a unique GLAD fabrication system with two e-beam sources and a glove box.*** Due to the reactive nature of the metal hydride materials, we have designed a very unique deposition system (Fig. 1) that integrates the vacuum chamber and a glovebox together so that the as-deposited nanostructure will not be exposed to any oxygen. This guarantees that we are probing the metal–hydrogen interaction rather than metal oxide-hydrogen interaction. The two e-beam sources will be used for in-situ catalyst and nanostructure fabrication, or multilayer structure fabrication. The system will be delivered to UGA in late May, 2006.

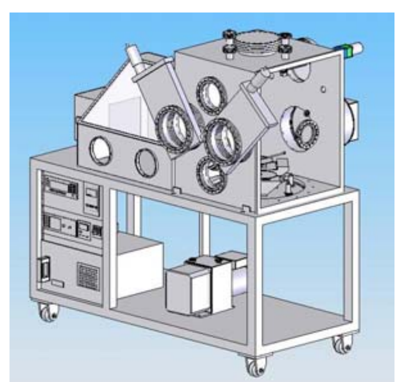

Fig. 1 The unique GLAD system designed for this project.

(2) ***Preparing multilayered nanospring and decorated nanorods (poster).*** To demonstrate the feasibility of

the GLAD technique, we have performed several experiments using the existing lab equipment to fabricate multilayered nano-spring structure, as well as decorated nanorod structures. Figure 2 shows the sketch of the Ni/Si nanospring structure and their SEM and TEM characterization. The magnetic property of this unique structure has been characterized using a vibrating sample magnetometer (VSM). The Au nanoparticle decorated Si nanorod array has also been fabricated.

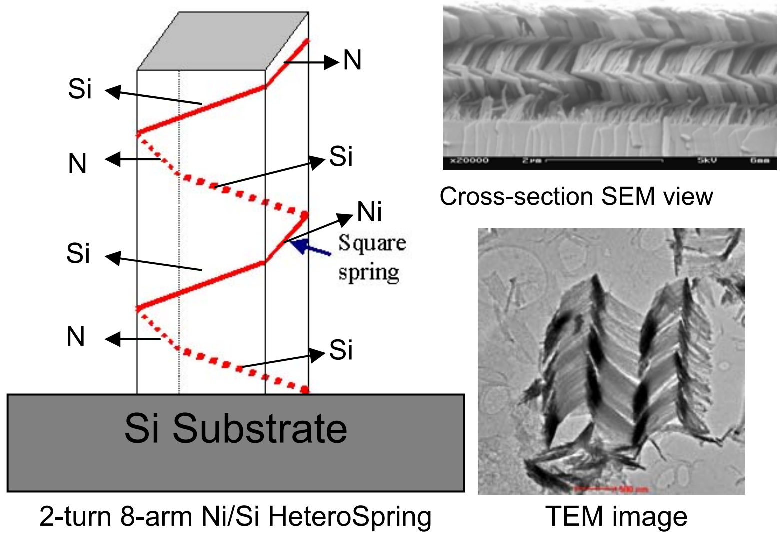

Fig. 2 The Si/Ni nanospring structure fabricated by GLAD.

(3) ***Investigating how the substrate rotation speed affects the growth of low melting point metallic materials.*** The surface diffusion rate of adatoms on a substrate is one of the dominate effects that determine the GLAD growth mechanism. Since Mg is a low melting point metallic material, the adatom surface diffusion is relatively fast. This may play a major role in nanostructure fabrication. With the current lab setup, we have investigated Ag (also a low-melting point metal) nanorod growth for rotation rate of 0 rev/s, 0.05 rev/s, 0.5 rev/s, and 5rev/s, and different morphologies have appeared when characterized by SEM and optical absorbance spectroscopy.

(4) ***Developing vibrational spectroscopic experiments to characterize how the hydrogen is stored in these materials.*** An understanding of the microscopic structure, hydrogen complex concentration, and its interaction with the host material will aid in improving the development of these materials. These will be elucidated using spectroscopic techniques of infrared (IR) and Raman spectroscopy over a range of temperatures and pressures. Currently, the PI Zhang group at UCSC has been conducting hydrogen detection experiments on a model metal hydride of $NaBH_4$. As seen in Fig. 3, we are able to detect hydrogen metal vibrations using a normal Raman scattering technique under standard conditions.

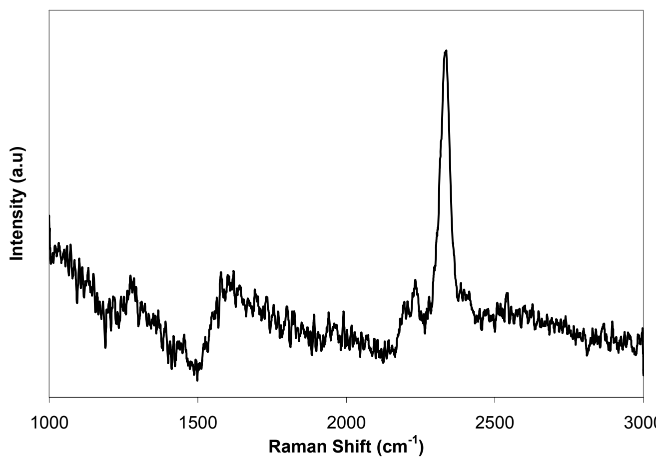

Fig. 3 Raman spectrum of $NaBH_4$ excited with 532 nm laser. The peak at 2230 cm^{-1} and 2340 cm^{-1} represents the asymmetric bending and symmetric stretching vibrations of the molecule, respectively.

The PI McCluskey group is investigating the interaction of hydrogen with ZnO nanoparticles. We synthesized ZnO nanoparticles using wet-chemistry techniques. A transmission electron microscopy (TEM) image (Fig. 4) shows that the average diameter of the nanoparticles is ~15 nm. XRD measurements indicate a wurtzite crystal structure. The nano-powder was pressed into thin pellets (~0.2 mm) for analysis. We found that annealing pellets in hydrogen at a moderate temperature (350°C) results in a dramatic increase in electrical conductivity and free-carrier absorption (Fig. 4). Bulk ZnO, annealed under similar conditions, does not result in these changes. The difference is likely due to the high surface-to-volume ratio of the nanoparticles. These new results will be submitted to Journal of Applied Physics.

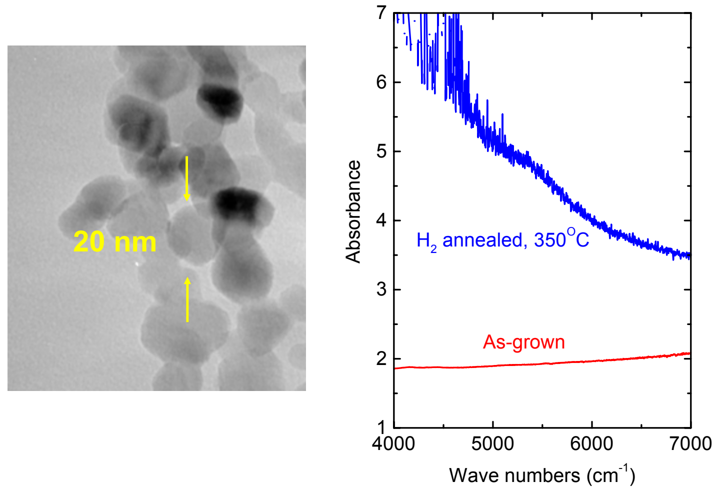

Fig. 4 TEM image of ZnO nanoparticles and Free-carrier absorption of as-grown and hydrogen-annealed ZnO nanoparticles.

Future Plans

With the completion of the unique GLAD deposition system, we will concentrate on the metal hydride nanostructure fabrication and characterization. We will fabricate metal hydride nanostructures with different diameter, separation, alignment, and shape, and with different catalysts and dopants, and multilayers, and perform vibrational spectroscopy characterization during the hydration process. The thermal dynamic behavior of the metal hydride nanostructures will be characterized at Savannah River National Laboratory, and the further characterization of hydrogen-metal hydride nanostructure interaction will be performed by neutron scattering at NIST.

Publications since the beginning of the project

1. Y.-P. He, J.-X. Fu, Y. Zhang, and Y.-P. Zhao, "Multilayered Si/Ni Nanosprings and Their Magnetic Properties", in preparation.
2. W.M. Hlaing Oo, M.D. McCluskey, and L. Bergman, "Hydrogen in ZnO Nanoparticles," in preparation.