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# Low-temperature cycling of hydrogenation-dehydrogenation of Pd-decorated Mg nanoblades

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## ABSTRACT

Biaxial crystalline Mg nanoblades were grown by oblique angle thermal evaporation followed by Pd deposition in a vacuum. The hydrogenation-dehydrogenation cycles of Pd-decorated Mg nanoblades was investigated *in situ* by temperature programmed desorption (TPD). It shows that hydrogen starts desorption at about 340 K and peaks around  $373 \pm 10$  K. If the dehydrogenation temperature is kept below 373 K then the cycling can be repeated up to more than 10 cycles with gradual degradation of H uptake capacity and desorption kinetics. At 373 K the hydrogen desorbs in less than 20 min. The analysis of *in situ* reflection high energy electron diffraction (RHEED) patterns of these samples reveal deterioration of Mg hydride phase, formation of Mg oxide and intermixing of Mg and Pd in a few nm scale that fundamentally limits the life time of cycling.

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## 1. Introduction

The effective storage of hydrogen is a major technical issue which has to be addressed for broader applications, especially in transportation. The onboard storage has far more stringent requirements than those of static storage outlined in the vision of hydrogen storage published by the US Department of Energy [1]. Solid state hydrogen storage has attracted intense research in recent years due to its unique features which satisfy the goals of onboard storage. The solid hydrides can be formed by physical absorption [2,3] and chemical reaction with either metals or compounds [4,5].

The key criteria for successful hydrogen storage materials are: 1. high capacity; 2. fast kinetics for both hydrogenation and dehydrogenation; 3. low-reaction temperature and pressure; 4. reversibility during cycling; 5. space-efficiency and affordable cost. Hydrogen storage materials with nanoscale grain structures that have high surface areas have emerged.

Examples are ball milling of powders [6–8], ultra-thin films on substrates [9], and nanoblades [10–12]. To further improve the hydrogenation properties various catalysts [4] have been added on the surfaces of nanoscale grains or thin films in order to dissociate the hydrogen molecules on the surfaces of storage materials.

Among pure elements, magnesium is a promising candidate material satisfying many key criteria for hydrogen storage and has been actively studied by various groups. The hydrogen desorption temperature for sputtered Pd/Mg films is affected by the degree of crystallization and ranges widely from 570 K to 420 K [13]. Recent works of binary and ternary Mg-based films alloyed with Al, Fe and Ti [14] or Mg thin film containing bimetallic Cr Ti catalyst [15] have shown over 100 absorption/desorption cycles and 10–20 min desorption kinetics at temperature of 200 °C (473 K). He et al. also investigated Mg nanoblades extensively and showed an enhanced storage properties of Mg nanoblades [16]. By either coating or

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doping Mg with V, they further improved the sorption kinetics of Mg nanoblades at temperature over 227 °C (500 K) [17,18]. Although the above desorption temperatures are dramatically reduced from 300 °C (573 K) of a pure Mg film, these temperatures are still doubled of the DOE's target temperature of 100 °C (373 K) [1]. Further lowering of the desorption temperature to as low as 92 °C (365 K) was obtained in a nanostructured Pd/Mg system with catalyst Pd decorated on vertical standing Mg nanoblades [10]. Despite of all the progress made in Pd/Mg hydride system the cycling life of hydrogenation-dehydrogenation and kinetics of desorption have not been studied.

In this work, we report the hydrogenation-dehydrogenation life cycles of Pd catalyst-decorated Mg nanoblades at low hydrogen absorption ( $\sim 333$  K) and low desorption temperatures ( $<400$  K). The Mg nanoblades are standing vertically and isolated from each other on an amorphous silicon wafer substrate. The space between nanoblades allows for volume expansion during metal to hydride transformation in hydrogenation. This differs from thin Mg films lying down on substrates where the thin film usually cracks after volume reduction in dehydrogenation. The sub-100 nm thick and a few hundred nm wide Mg nanoblades with catalyst Pd on top provide a large surface area for hydrogen dissociation and a short pathway for hydrogen diffusion in the hydrogenation and dehydrogenation process. The *in situ* temperature programmed desorption (TPD) spectra reveal that this low temperature ( $<400$  K) hydrogenation-dehydrogenation process is reversible in the first 4 cycles, and then the degradation starts. The quantitative analysis of *in situ* RHEED patterns reveals that with a cycling temperature at 373 K the structural deterioration of nanoblades occurs and the chemical composition of nanoblades also changes during repeated cycling thus preventing further cycling.

## 2. Experimental

The experimental setup consists of two connected stainless steel chambers, one hydrogen reaction chamber and one RHEED chamber. A transfer rod was used to move the sample back and forth from the RHEED chamber to the reaction chamber. The Pd-decorated Mg nanoblades were grown on native oxide covered Si substrates by oblique angle deposition (OAD) in the RHEED chamber equipped with Mg and Pd thermal evaporation sources. The size of oxide covered Si substrate is about  $1'' \times 1''$ , and an amount of Mg estimated from SEM images is in the order of microgram. We used 99.95% pure Mg pellets ( $1/4''$  diameter  $\times$   $1/4''$  length) in an alumina crucible wrapped by a Ta filament and 99.99% pure Pd wire of 0.05 mm diameter wrapped around a W filament. During a deposition the Mg vapor flux was incident on the substrate at 75° with respect to the substrate normal, resulting in nearly vertically standing nanoblades with an angle slightly tilted away from the flux [19]. The Pd was deposited along the substrate normal on the as-prepared Mg nanoblades, so that the vertical Mg nanoblades were approximately aligned with the Pd incident flux direction. During the growth of Mg and Pd the base pressure increased from  $3.0 \times 10^{-9}$  Torr to  $1.0 \times 10^{-8}$  Torr. The evaporation rates of Mg and Pd were monitored *in*

*situ* by a quartz crystal monitor (QCM). Later an *ex situ* SEM image of Mg was taken for thickness calibration and the rate was found to be about 30 nm/min. The Pd growth rate was 0.12 nm/min and a total of about 5 nm Pd was deposited on Mg nanoblades based on the reading from the QCM.

After the Pd deposition, the Mg nanoblades were transferred *in situ* from the RHEED chamber to the reaction chamber. The Pd-decorated Mg nanoblades were hydrogenated under a hydrogen pressure of 1 bar for about 15 h at 333 K as measured by a type K thermocouple touching the top of the sample surface. The hydrogen gas used is ultra high purity in a compressed cylinder and is connected to the reaction chamber through a stainless steel gas handling system. The TPD was performed, after evacuating the hydrogen partial pressure in the reaction chamber to lower than  $2.0 \times 10^{-8}$  Torr. The sample surface was heated by a halogen lamp outside the reaction chamber. The light beam reaching the sample surface through an ultra high vacuum (UHV) view port was focused down to about 2 cm diameter using optical lenses. The temperature was measured by a thermocouple pressed on the top of the sample surface, and the programmed heating rate for most TPD measurements up to 400 K was 3 K/min. In the kinetic study the temperature was raised quickly from room temperature to  $\sim 373$  K, and then kept at 373 K until the sample stopped releasing hydrogen. A residue gas analyzer (RGA) was used to measure the partial pressure of major residue gases as a function of time.

RHEED patterns were taken *in situ* at room temperature before and after each hydrogenation and dehydrogenation cycle by transferring the sample between the RHEED chamber and the reaction chamber. The RHEED gun was operated at 9 kV primary voltage and 0.2 mA emission current. The diffraction patterns scattered from the sample were displayed on a phosphorous screen. The RHEED patterns were then captured by a single-lens reflex camera with 14 bits dynamic range. The raw image data from the camera was analyzed using our program codes. The SEM images of Mg nanoblades were taken using scanning electron microscopy (SEM) (Zeiss model SUPRA 55).

## 3. Results

Fig. 1(a) and (b) show SEM side views of two samples. Fig. 1(b) shows a side view of SEM image taken from Pd-decorated Mg nanoblades that have gone through 15 cycles of hydrogenation and dehydrogenation when the highest sample temperature used was  $\sim 373$  K. A visual inspection of this image shows that nanoblades are intact but some part have a less smooth morphology compared with that of pure Mg nanoblades that has never gone through any hydrogenation and dehydrogenation process, as seen in Fig. 1(a). The dimensions of the nanoblades are about sub-100 nm thick and a few hundred nm wide.

Fig. 2 shows TPD spectra of hydrogen from Pd-decorated Mg nanoblades under hydrogenation and dehydrogenation cycles when two different highest sample temperatures were used during dehydrogenation in vacuum. Fig. 2(a) is for two cycles when the highest sample temperature used was over 500 K and Fig. 2(b) is a different sample prepared under

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