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Hydrogenation of Mg nanofilms catalyzed by size-selected Pd nanoparticles: Observation of localized MgH_2 nanodomains

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ABSTRACT

We utilized gas-phase condensation to deposit size-selected Pd nanoparticles (NPs) on Mg nanofilms and systematically studied the catalytic conversion to localized MgH_2 nanodomains upon exposure to hydrogen. Atomic force microscopy (AFM), aberration corrected transmission electron microscopy (TEM), and electron energy-loss spectroscopy (EELS) experiments were applied to map localized embryonic hydride nanodomains protruding from the Mg surface as a function of hydrogenation time, NP surface coverage, applied hydrogen pressure, and NP size. The results show that Pd NPs dissociate hydrogen and create atomic hydrogen pathways for hydrogenating the Mg nanofilm. The Pd NPs also inhibit oxidation of the underlying Mg nanofilm. Interestingly, the Mg nanofilm could be fully hydrogenated with a small quantity of Pd NPs at room temperature and modest hydrogen pressures. The localized hydrogenation enables improved control over the spatial distribution of hydride nanodomains making this configuration promising for future on-board hydrogen storage applications.

1. Introduction

Nanofilms can serve as useful model systems to understand hydrogen sorption behavior of corresponding bulk systems [1,2]. Additionally, owing to their high surface area, nanofilm hydrides have been proposed as a solution to store hydrogen in the form of coils [3]. As is well known, magnesium hydride (MgH_2) has a high reversible hydrogen mass capacity ($MgH_2 \leftrightarrow Mg + H_2$, 7.6 wt.%), but the activation barrier for dissociative chemisorption of hydrogen is very high (>1.0 eV), which results in slow hydrogen sorption kinetics [4,5]. Moreover, bare Mg nanofilms are prone to oxidation, easily forming a thin MgO layer, even under high vacuum, due to reaction with residual water vapor. Once formed, this MgO layer is stable and unreactive [6,7], and creates a very high activation energy barrier (2.34–2.94 eV) to the dissociative adsorption of hydrogen, thus inhibiting hydride formation [8–10]. To overcome such obstacles, a common solution is to cover the Mg nanofilm with a nanolayer of Pd (~10 nm), which both facilitates hydrogenation and also prevents oxidation of the underlying Mg nanofilm [11–15]. Nevertheless, use of a Pd capping film has several shortcomings. Specifically, Pd-capped Mg nanofilms suffer from a "blocking-effect" of MgH_2 at the Pd–Mg interface, and usually a high sorption temperature is required to accelerate the kinetics. However, use of high temperatures results in Pd inter-mixing with Mg, which typically forms intermetallic compounds such as Mg_5Pd_2, Mg_3Pd, and Mg_6Pd [16]. Moreover, the Pd capping layer often delaminates after a few sorption cycles, resulting in reduced hydride formation [17]. Also, Pd-capped Mg nanofilms exhibit a large number of nucleation centers (at the Pd–Mg interface), which accelerates the fusion of adjacent hydride nanodomains [18]. In such cases, important information, for example, the role of the underlying Mg grain structure is often suppressed and cannot be clearly determined.

Using Pd nanoparticles (NPs) instead of continuous Pd capping layers presents a number of potential advantages. NPs are generally well-known to exhibit enhanced catalytic activity, compared to bulk or nanofilm systems [19–21]. Moreover, compressive stress and delamination, which arise with continuous Pd capping layers, can also be prevented by using Pd NPs. Additionally, monodispersed Pd NPs can potentially reduce the degree of alloy formation at high temperature because there is less Pd in contact with

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the Mg film. Thus, the interaction of hydrogen with nanostructured Pd has received significant attention [22–24]. On the theoretical front, Du et al. performed ab initio density functional theory calculations and reported that the Pd-dopant provides a much lower activation barrier for both dissociation of molecular hydrogen and diffusion of atomic hydrogen on the Mg surface. Specifically, effective activation barriers for dissociation of molecular hydrogen and diffusion of the first and second H atoms are 0.305, 0.247, and 0.195 eV, respectively [25]. This implies easy dissociation and fast migration of hydrogen over a Pd-doped Mg surface, even under ambient conditions [14]. However, lack of control of the size, morphology, and chemistry of materials has impeded understanding of hydride nucleation and growth. Experimentally, Chung et al. recently explored hydride formation using SEM and optical measurements [26]. They reported the 'nanoportal' role of Pd NPs deposited on epitaxial Mg nanofilms; in which hydride nucleation occurs only under the Pd NPs. This study also demonstrated the effect of Pd NP number density on the hydrogenation of Mg films. However, to better understand the hydrogenation mechanism, other researchers mentioned the necessity to study the metal–hydride interface at the nanoscale and the topographical changes that occur after hydride formation, which cannot be clearly resolved using optical methods [18,27].

In the present study, we have used atomic force microscopy (AFM), aberration corrected TEM, and EELS to investigate the catalytic effect of mono-dispersed Pd NPs on hydride formation in Mg nanofilms and the Pd–Mg hydride interface under different experimental conditions. The experimental findings facilitate understanding of the hydrogenation mechanism. In particular, we suggest that by understanding the important factors controlling the catalytic hydrogenation of Mg nanofilms by Pd NPs one should be able to tune the parameters to achieve the desired catalytic activity required for the hydride formation.

2. Experiment section

2.1. Materials

Un-doped silicon (5 × 5 mm, MTI Corporation, CA, USA) was used as a substrate for fabrication of Mg nanofilm-support Pd nanoparticle films. Magnesium magnetron-sputtering targets (Purity >99.95%) 50 mm in diameter × 3 mm thick and Pd magnetron sputtering targets (Pd, purity >99.95%) 25 mm in diameter × 3 mm thick were purchased from Kurt J. Lesker (PA, USA). TEM grids required for TEM/STEM measurements were purchased from Ted Pella Inc. (CA, USA).

2.2. Pd NP decorated Mg nanofilm synthesis

Supported nanoparticle samples were prepared by sequential deposition of Mg nanofilms and Pd nanoparticles, using (1) an RF sputtering source and (2) a NP source, respectively. First, Mg nanofilms were fabricated by RF-sputtering (Fig. 1a) on (3) silicon substrates and TEM grids at ambient temperature. The base pressure was below 4×10^{-8} mbar and the Ar pressure was 1.6×10^{-3} mbar during Mg film deposition. The total thickness of the Mg film was about 25 nm for each sample. The Mg deposition rate was measured using a quartz crystal thickness monitor to control the thickness of the nanofilms. Next, Pd NPs were formed in the gas phase using sputtering and inert-gas condensation in the same ultra-high vacuum system described in detail in [28–32] and shown schematically in Fig. 1a, which illustrates the method of preparing Mg nanofilm-supported NP samples. A quadrupole mass filter (QMF) allowed in situ monitoring of particle sizes (Fig. 1b). For 5 nm Pd NP deposition, magnetron power and Ar gas flow rate were set to 15 W and 60 sccm, respectively. For 2.5 nm Pd NP deposition, magnetron power and Ar/He gas flow rate were set to 6 W and 50/10 sccm, respectively. Aggregation zone length was set to 100 mm and 40 mm for 5 nm and 2.5 nm Pd NPs, respectively. During deposition of the two sizes of NPs, pressures were $\sim 6.7 \times 10^{-4}$ and $\sim 2.0 \times 10^{-1}$ mbar in the deposition chamber and in the aggregation zone, respectively. Variable Pd NP surface coverage on the Mg nanofilm (ca. approximately 1.3%, 2.5%, 3.6%, and 14.1% coverage) was achieved by varying the deposition time. Substrate table rotation was set at 2 rpm for all depositions to ensure uniform coverage.

2.3. Hydrogenation measurements

As-deposited Mg nanofilms decorated with Pd NPs were hydrogenated in a PCT (pressure-composition isotherms) Sieverts-type apparatus (Setaram PCTpro 2000). Prior to hydrogenation, Mg nanofilm-supported Pd NP samples were intentionally exposed to air for 5 min to create a very thin $MgO/Mg(OH)_2$ layer in order to simulate the real-world application conditions. Subsequently, these films were loaded into the micro-doser holder that has a volume of 0.49 mL. Owing to the high reactivity of the samples with hydrogen, no activation step was performed. All catalyzed hydrogenation reactions were conducted at room temperature (ca. 298 K) under various hydrogen exposure pressure and time conditions. After hydrogenation, samples were kept inside the glove box to avoid contamination and for further characterization.

2.4. Characterization techniques

AFM measurements were conducted in the glove box (<0.1 ppm O_2 and <1 ppm water) using a Multimode 8 AFM (Bruker, Santa Barbara, CA). The AFM system is equipped with a NanoScope-V controller in tapping mode using a silicon probe (tip radius <10 nm, force constant of 9 N/m, resonant frequency of 150 kHZ, and OLYMPUS optics). The AFM system height "Z" resolution and noise floor were less than 0.030 nm. Scanning probe processor software (SPIP from Image Metrology, Hørsholm, DK) was employed for AFM image analysis. The obtained images were used to measure roughness and to evaluate the % conversion to the metal hydride. Here, 100% conversion is defined by the hydrogenated sample where hydride nanodomains completely cover the surface. Thus % conversion refers to the surface coverage of hydride nanodomains relative to complete conversion. Also, the root mean square (RMS) roughness (R_q) of the film surfaces was measured over an area of 5 × 5 μm^2 using SPIP software. For the same measuring area, the RMS roughness (R_q) was found to be 0.3 nm for Si (100) substrates.

Grazing incidence X-ray diffraction (GIXRD) measurements were performed using Cu K_α radiation (40 kV/40 mA, λ = 1.5418 Å) at a fixed incident angle of 0.5°. XPS measurements were performed in a Kratos AXIS Ultra DLD Photoelectron Spectrometer equipped with a Mg K_α anode (1253.6 eV), and a base pressure of 2×10^{-9} mbar. The Pd *3d*, Mg *2p*, and O *1s* core level narrow spectra were recorded using pass energy of 20 eV for high resolution.

Transmission Electron Microscopy (TEM)/Scanning Transmission Electron Microscopy (STEM)/Selected Area Electron Diffraction (SAED) studies were carried out using an FEI Titan microscope, operated at 300 kV, equipped with a spherical aberration corrector for TEM imaging. In TEM mode, spherical and chromatic aberrations were <5 μm and 1.4 mm, respectively, with an optimum resolution of better than 0.09 nm. Electron energy-loss spectroscopy (EELS) experiments were performed with a post-column Gatan Quantum 966 energy spectrometer.