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Size and stress dependent hydrogen desorption in metastable Mg hydride films

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ABSTRACT

Mg is a promising light-weight material that has superior hydrogen storage capacity. However H₂ storage in Mg typically requires high temperature, ~500–600 K. Furthermore it has been shown that there is a peculiar film thickness effect on H₂ sorption in Mg films, that is thinner Mg films desorb H₂ at higher temperature [1]. In this study we show that the morphology of DC magnetron sputtered Mg thin films on rigid SiO₂ substrate varied from a continuous dense morphology to porous columnar structure when they grew thicker. Sputtered Mg films absorbed H₂ at 373 K and evolved into a metastable orthorhombic Mg hydride phase. Thermal desorption spectroscopy studies show that thinner dense MgH₂ films desorb H₂ at lower temperature than thicker porous MgH₂ films. Meanwhile MgH₂ pillars with greater porosity have degraded hydrogen sorption performance contradictory to general wisdom. The influences of stress on formation of metastable MgH₂ phase and consequent reduction of H₂ sorption temperature are discussed.

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1. Introduction

Hydrogen is a promising alternative fuel for renewable energy applications due to its abundance, high efficiency and zero carbon emission when used in proton exchange membrane (PEM) fuel cells [2,3]. In order to economically apply hydrogen fuels for automobile applications, light-weight hydrogen storage materials with high uptake capacity and low desorption temperature are necessary. In addition, hydrogen recycling should be performed reversibly under PEM fuel cell

operation temperatures. Compared to the 700 bar gas cylinders currently used by most hydrogen vehicle manufacturers, hydrogen stored in metal hydrides offers the advantage of a much higher volumetric density [4,5]. Among numerous hydrogen storage candidates, magnesium hydride is an attractive material because of its high H₂ storage capacity (7.6 wt.%) and economical availability as the third most abundant element on earth.

Bulk Mg hydride, however, has tetragonal phase (referred to as T-MgH₂ hereafter) that is thought to be unsuitable for automotive application because of its high formation

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enthalpy ($\Delta H = -75$ kJ/mol H_2 [6]). Due to the high thermodynamic stability of Mg hydride, hydrogen absorption/desorption typically occurs at ~ 673 K in bulk Mg, much higher than practical applications (333–353 K) [2,7,8]. In order to release hydrogen at moderate temperature for PEM fuel cell applications, Mg hydride must be destabilized. Additionally hydrogen sorption kinetics must be improved to achieve practical refueling time for vehicle applications. Nanostructured materials have a large surface to volume ratio, provide more nucleation sites for hydrogen sorption, promote rapid hydrogen diffusion, and hence may lower the kinetic barriers for hydrogenation [9–11]. Recent reports showed that ball-milled nanocrystalline Mg powders can expedite hydrogen desorption process [12–14]. However, nanograins in these materials coarsen over succeeding thermal cycles and are highly susceptible to oxidation. Numerous attempts, via ball milling method, have been made to improve the kinetics of hydrogen sorption in pure Mg and Mg mixed with transition metals, with limited reduction on hydrogen sorption temperatures [10,15,16]. Vajo et al. reported thermodynamic destabilization in more complex hydrides of Mg alloys [17–20].

Besides bulk nanostructured Mg and its alloys, Mg based thin films are also actively studied as model systems to understand hydrogen sorption kinetics [1,21–24]. Among these studies, Mg–Pd is a notable thin film system with peculiar H_2 sorption properties. Pd is a noble metallic catalyst that dissociates H_2 molecules to H atoms at room temperature. It has been shown that sputtered Mg thin film with a Pd cap layer can absorb and desorb under conditions suitable for PEM fuel cells (373 K, 0.1 MPa) [1]. The authors used a “cooperative phenomenon” to explain low temperature H_2 sorption in Mg/Pd multilayer films. Basically the absorption of H_2 in Pd (catalyst) leads to tensile stress in Mg and thus facilitates the hydrogenation of Mg film. During desorption, the opposite process occurs, that is desorption of H_2 from Pd leads to compressive stress that enables rapid removal of H_2 from Mg hydride [1]. If interfacial stress indeed plays a critical role on H sorption as stated in the “cooperative phenomenon”, then one would anticipate that thinner films desorb H_2 at a lower temperature as such a mechanism implies lower H_2 sorption temperature in thinner films. However it was reported that thicker Mg films desorbed H_2 at lower temperature. On the other hand, studies on Pd/Mg/Pd trilayer films [25] revealed insignificant residual stress evolution before and after hydrogen loading. Meanwhile interfacial energy may contribute to destabilization of Mg hydride as proposed by Mooij et al. [26]. Pd-decorated Mg blades prepared by oblique angle thermal deposition also have shown a low H desorption temperature, ~ 373 K [27].

Other than noble metal catalyst (such as Pd), transition metal catalysts were added to Mg films to expedite H_2 sorption kinetics in T-MgH₂ [28–34]. Furthermore certain transition metal catalysts incorporated by co-sputtering with Mg have led to reduction of the hydrogen formation energy [35–38]. Co-sputtered Mg–Ti thin film showed cyclic capability, but hydrogen formation energy is unknown [37–39]. Mg–Ni–Ti ternary thin film exhibited hydride formation energy of -40 kJ/mol H_2 [40,41]. Co-sputtered Mg-25 at.% Nb thin film showed the formation of a metastable bcc alloy with the hydride formation enthalpy of -52 kJ/mol H_2 [42]. However, the

hydrided Mg–Nb film desorbed hydrogen only at 448 K and deterioration of the Mg and Nb (a gradual segregation) was observed after extended cycling studies. We have recently reported that H_2 sorption in 1.6 μm Mg film grown on rigid SiO_2 substrate and free standing Mg/Nb multilayers led to the formation of a metastable orthorhombic MgH₂ (O-MgH₂) phase, which has an ultra-low hydride formation energy, -37 kJ/mol H_2 [43], compared to -75 kJ/mol H_2 of stable T-MgH₂. Thus O-MgH₂ desorbs H_2 at ~ 373 K or lower. These experimental results compared well with those obtained by first principle calculations [43]. In parallel TEM studies have shown that bcc metastable Mg formed on top of Nb [44] and DFT calculations were performed to gain insight on the stabilization of such a metastable bcc Mg phase [45]. The potential tie between bcc Mg and the formation of O-MgH₂ requires further investigations.

In this paper we show that thinner Mg films indeed desorb H_2 at lower temperature than thicker films. Film thickness has a direct influence on porosity of Mg films, namely thinner film (~ 200 nm) formed a continuous dense layer, beyond which it evolved into a porous columnar structure. Mg pillars with different porosity also have drastically different H_2 sorption performance. Contradictory to our intuitive anticipation, greater porosity degrade H_2 sorption performance of Mg pillars. The evolution of stress during H_2 sorption and stress-induced formation of O-MgH₂ play major roles on hydrogen sorption properties of Mg films. This study provides an important step forward towards in-depth understanding of destabilization of Mg hydride via stress-driven formation of metastable phases.

2. Experimental

Mg films with layer thickness t varying from 200 to 1600 nm were deposited by DC magnetron sputtering on oxidized Si (100) substrates with 1 μm thermal oxide layer at room temperature. All Mg films were protected by 25 nm Pd cap layer, which catalyzes the dissociation of hydrogen molecules and protect Mg films from oxidation. Mg and Pd targets with 99.99% purity were used for magnetron sputtering. The base pressure of the chamber was better than 6.6×10^{-6} Pa prior to deposition. The films were grown under ~ 0.8 mTorr Argon pressure with 99.999% purity. The deposition rates for Mg and Pd were ~ 2 and 0.3 nm/s, respectively. To fabricate Mg nanopillars, Si wafers were mounted on a custom-designed substrate holder at an angle of 5° relative to the direction of the sputtering source (i.e. using a configuration of glancing angle deposition). During glancing angle deposition, the substrate was not rotated. In parallel, inclined deposition at 45° was also performed without substrate rotation. After deposition, samples were transported directly into an attached high vacuum chamber for hydrogen absorption and desorption studies. The base pressure of hydrogen chamber was $\sim 6.66 \times 10^{-7}$ Torr before hydrogen loading. All Mg films were hydrided at a pressure of 0.25 MPa with ultra high purity gas mixture (96% Ar + 4% H_2) at 373 K for 24 h. Hydrogen desorption studies were performed by thermal desorption spectroscopy (TDS) technique enabled by a quadruple mass spectrometer in a residual gas analyzer (RGA). During

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