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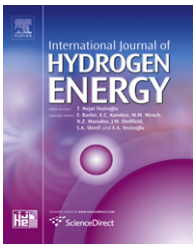

Hydrogen absorption and optical properties of Pd/Mg thin films prepared by DC magnetron sputtering

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ABSTRACT

Hydrogen storage in metallic thin films in the form of metal hydride have a great potential to solve the hydrogen storage challenges and also thin films offer an opportunity to grow new samples fast with novel structures. In the present work the ex situ study on structural, optical and hydrogen storage properties of Pd-capped Mg thin films have been investigated. The nano structured Pd-capped Mg thin films have been prepared by DC magnetron sputtering on glass substrate. The as deposited and hydrogenated samples have been characterized by XRD and FESEM. The content of hydrogen in thin films has measured by using Elastic Recoil Detection Analysis (ERDA) technique with 120 MeV_{107} Ag^{+9} ions. The temperature dependent hydrogen contents in thin film samples have been estimated and the saturation of hydrogen absorption has been observed at 250 °C among all studied samples. In the optical reflectance spectra, Mg hydride samples have been observed partially transparent in comparison to as deposited Mg film.

1. Introduction

Hydrogen is a renewable and environmental friendly source of energy which makes hydrogen storage an active area of research. Solid state storage has high volumetric efficiency and is, by far, the safest method of hydrogen storage. Magnesium hydride, MgH_2 is one of the most studied reversible hydrides, due to its high gravimetric hydrogen density (7.6 wt. %) and energy density (9 MJ/kg) [1,2]; moreover upon hydrogen absorption and hydride formation, magnesium as other hydrides shows interesting electrical and optical properties, which are reflected in a metal-to-insulator transition: this pushed the development of new Mg-based devices as gasochromic switchable mirrors, which could have technological applications as sensors, smart windows and variable reflection coatings [3,4]. Currently a lot of research effort is focused on the relation between microstructure, functional and reliability: concerning this point thin films constitute a model material, due to the easy control of microstructure and the possibility of using complementary characterization techniques [5–8].

Thin film technique is a powerful method to investigate the interaction between Mg and hydrogen because the composition, interface and crystallinity can be well defined on the nano-scale [9,10]. Thus, various attempts have been undertaken to study the hydrogen storage properties of Mg thin films [11–14]. For example, Higuchi et al. reported that Pd-capped Mg films prepared by RF sputtering on glass

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substrates absorbed, at 373 K, 2.9–6.6 wt. % hydrogen depending on the conditions of sputtering. Singh et al. have investigated the effect of catalytic coating on FeTi and TiNi thin films for hydrogen absorption [15–17]. Jianglan et al. investigated structural, optical and electrical properties of Pd-capped Mg thin films as well as the effect of annealing on these films during hydrogenation. The hydrogen absorption behaviors at 473 K for 2 h exhibited the best absorption kinetics and superior switchable mirror properties [5]. The phenomenon of hydrogenation in Pd-capped Mg films had been briefly described in the study of metal–insulator transition on an Mg–H system [18–20]. The rate at which hydrogen absorbs and desorbs is too low because of slow diffusion of hydrogen atoms through the hydride [21–23]. Pranevicius et al. studied experimentally the distribution profiles of accommodated oxygen and hydrogen atoms in Mg–Ni films after different stages of hydrogenation by Elastic Recoil Detection Analysis (ERDA) and Nuclear Reaction Analysis (NRA) techniques. The quantity of the released hydrogen after 3 h hydrogenation increases with the increase in hydrogenation temperature. The observed experimental results are explained assuming that properties of the surface barrier layer changes during hydrogenation and modify hydrogen transport mechanism. The growing hydride phase in the bulk generates stresses that induce cracks and holes in the oxide barrier formed during the initial stages of hydrogenation [25]. Recent studies revealed that in epitaxial Mg thin films the MgH_2 phase forms epitaxially relative to Mg film and that both the MgH_2/Mg and the MgH_2/Pd interfaces are nucleation sites for Mg during hydride decomposition [26–28]. A study on a real hydrogen concentration of Pd/Mg/Ni/Pd and Pd/Mg/Mg_2Ni/Pd films with the Pd/Mg/Pd base system using Elastic Recoil Detection Analysis (ERDA) technique show that, the addition of Ni or Mg_2Ni layers to base system enhances its hydrogenation and decreases the oxygen content [29,30]. The present study is to find a convenient method to evaluate the hydrogen absorbing capacities of metallic films. ERDA (Elastic Recoil Detection Analysis) is a useful tool to observe the depth profile of occluded hydrogen in thin film. Although the typical volumetric method is reliable, the expected amount of occluded hydrogen is too small to be detected by the pressure range, as already demonstrated by material scientists [31,32].

In this paper, we reported an ex situ study of catalytic behavior of Pd on Mg in the formation of magnesium hydride. We have also studied structural, hydrogen absorption and optical properties on nano structured Pd-capped Mg thin films, hydrogenated at different temperatures.

2. Experimental details

2.1. Deposition of Pd/Mg thin films

The Pd/Mg thin films were deposited on glass substrate using Mg (99.95% purity) and Pd (99.95% purity) target (2 inch diameter and 5 mm thick) by DC magnetron sputtering in a custom built (Excel Instruments, India) sputtering chamber which was initially evacuated to high vacuum (2.5×10^{-6} Torr). Thereafter, high purity (99.99%) inert gas (Ar) was used in sputtering. The substrates were cleaned by rinsing in ultrasonic bath of acetone. All depositions were carried out at fixed substrate temperature of 100 °C with substrate to target distance of 45 mm. The targets were pre-sputtered for 5 min before starting deposition. The sputtering parameters for all Samples are shown in Table 1.

Table 1 – Sputtering parameters for Pd/Mg films.

Sputtering parameters	
Target	Mg, Pd
Base pressure	2.5×10^{-6} Torr
Gas used	Ar
Deposition power	50 W (Mg), 30 W (Pd)
Deposition time	5 min (Mg), 5 s (Pd)
Sputtering pressure	5 m Torr
Substrate	Glass
Substrate temperature	100 °C
Target-substrate distance	4.5 cm

2.2. Hydrogenation of the samples

Hydrogenation was carried out with hydrogen gas (purity: 99.99%) in a custom built chamber (Excel Instruments, India). The Pd-capped Mg thin films were activated up to a certain temperature (100 °C–300 °C) for 2 h in a fine vacuum of 2×10^{-3} Torr after which the hydrogen gas was bled into the chamber to create a pressure of 1 bar. The samples were kept there for 12 h at different temperatures so that the hydrogenation (annealing in hydrogen atmosphere) of Pd/Mg films takes place. The sample hydrogenated at 100 °C is marked as H100, at 150 °C is marked as H150, at 200 °C is marked as H200, at 250 °C is marked as H250 and at 300 is marked as H300. After annealing all samples were cooled down to room temperature for the structural and ERDA studies.

2.3. Characterization

The room temperature XRD measurements were carried out using CuK_α radiation in X-ray diffractometer (Bruker AXS, D8 Advance) in ($\theta - 2\theta$) geometry. FESEM (FEI, Quanta 200F) was

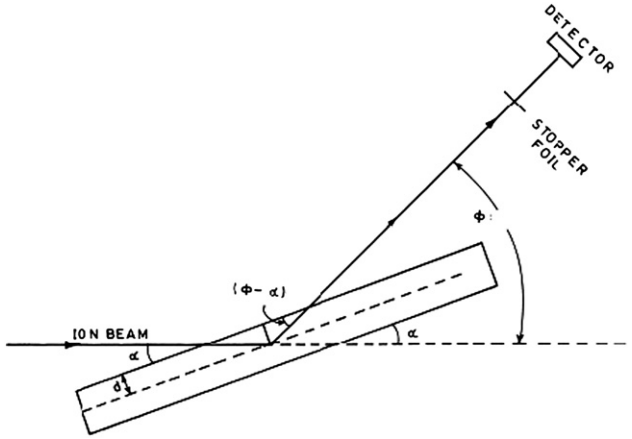

Fig. 1 – A schematic of experimental set up of ERDA indicating path of ion beam and the positions of sample and detector.