Pd/Mg/Pd thin films prepared by pulsed laser deposition under different helium pressures: Structure and electrochemical hydriding properties

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ARTICLE INFO

ABSTRACT

Three-layered Pd/Mg/Pd thin films were prepared by pulsed laser deposition in the presence of helium gas. For Pd layer deposition, the He pressure was fixed at 200 mTorr whereas different pressures of He were used for Mg layer deposition (50, 200 and 600 mTorr). The degree of crystallinity and of (001) texture in the Mg layer increase with increasing He pressure. In addition, the increase in He pressure upon Mg deposition greatly accentuates the roughness of the Mg layer, which induces an extension of the outer Pd/Mg interface region. In contrast, the inner Pd/Mg interface is sharp for all the Pd/Mg/Pd films. The electrochemical hydrogen sorption properties of the Pd/Mg/Pd films are improved by increasing the He pressure for Mg layer deposition. However, the maximum H-solubility in the Mg layer remains low (H/Mg ~ 0.26) and is not significantly increased by the presence of the inner Pd layer, indicating that Mg hydride phase is confined in the outer Pd/Mg interface region.

1. Introduction

Much attention has been paid to the magnesium–hydrogen system from both fundamental and practical viewpoints [1]. Magnesium is a very interesting hydrogen storage material because of its high hydrogen storage capacity (7.6 wt.% for MgH$_2$), low density and low cost. However, its operating temperature is typically over 600 K, because of the presence of a native surface oxide preventing the access to metallic magnesium, the high energy barrier for H$_2$ dissociation on Mg and the slow hydrogen diffusion through the MgH$_2$ phase. Moreover, the high thermodynamic stability of MgH$_2$ (enthalpy of decomposition of about 70 kJ mol^{-1} H$_2$) results in a low partial hydrogen pressure at ambient temperature. This strongly restricts the practical applicability of magnesium as H-storage material.

However, it was shown that hydrogen uptake by Mg can occur at room temperature for Pd-capped Mg thin films aided by the high H$_2$ dissociation rate and high hydrogen diffusivity of the Pd outermost layer [2–5]. Unfortunately the saturation level of hydrogen in the Mg film is low and decreases with increasing H$_2$ pressure. This is attributed to the formation of a Mg hydride layer at the Mg/Pd interface that blocks further hydrogen uptake due to the slow hydrogen diffusion in the magnesium hydride (β) phase. This kinetic limitation can be circumvented by working at low H$_2$ pressure (typically, lower than 0.1 MPa) in the temperature range 330–370 K, leading to an average H/Mg atomic ratio in the Mg layer as high as 0.8 [3,4]. At higher temperatures, H content in the Mg layer decreases due to thermodynamic considerations. Significant Pd–Mg intermixing or alloying can also occur at temperatures above 390 K. X-ray photoelectron spectroscopy studies on Mg

thin films evaporated onto a hydrided Pd foil [6–9] confirmed that the hydride phase is preferentially formed at the Pd–Mg interface and that H diffusion in Mg is very slow with a diffusion coefficient $D_H = 1.1 \times 10^{-20}$ m^2 s^{-1} at $T = 305$ K [8].

The preparation of four-layered films (Pd/Mg/Pd/Mg) instead of two-layered films (Pd/Mg) leads to a three-fold increase in the amount of absorbed hydrogen [4]. This is due to the formation of a hydride layer at each Pd–Mg interface although two of these interfaces are "buried" in the film so that hydrogen must go through a magnesium layer to reach them. The advantages offered by the multi-layered Pd/Mg films for the H-storage properties have been confirmed by Fujii et al. [10–12] and it was explained by cooperative phenomena due to elastic interactions between nanostructured Mg and Pd layers.

Some studies have also shown that the hydrogen storage properties of two or more layered Pd/Mg films are strongly dependent on the Mg deposition method and parameters [10,13–19]. For instance, Pd/Mg films prepared by sputtering under higher Ar pressure and higher RF power exhibited better dehydriding properties due to the lower degree of crystalline Mg [10,13]. It has also been shown on air-exposed Mg films prepared by thermal evaporation that the kinetics of H-sorption are faster as the evaporation rate increases, which may be related to the c-axis preferred orientation of the Mg structure [14]. In addition, depending on the deposition conditions, an extension of the Pd/Mg interface region may occur and affect positively the hydrogenation process [15–19]. It was associated with alloying between Pd and Mg layer and/ or with the penetration of Pd atoms in the pores of the Mg sublayer.

In the present work, it is shown that the pulsed laser deposition (PLD) is a suitable technique to prepare nanostructured Pd/Mg/Pd thin films with variable microstructures depending of the deposition parameters. It is demonstrated that the increase of the pressure of the background helium gas in the PLD chamber during Mg deposition increases the roughness of the Mg layer, which induces an extension of the Pd/Mg interface region. This extension has a positive influence on the electrochemical hydriding properties of the films.

2. Experimental

2.1. Film preparation

Three-layered Pd/Mg/Pd films were prepared at room temperature using a pulsed KrF excimer laser ($\lambda = 248$ nm, pulse width $= 20$ ns, repetition rate $= 50$ Hz). The thickness of the layers (determined from SEM observations) was ca. 15 and 170 nm for the Pd and Mg layers, respectively. Prior to deposition, the chamber was evacuated to a pressure of ca. 10^{-4} Pa. Depositions were made in the presence of helium (4.8 grade) at a partial pressure of 200 mTorr (~ 27 Pa) for the Pd layers and a partial pressure ranging from 50 (~ 7 Pa) to 600 mTorr (~ 80 Pa) for the Mg layer. The He pressure has no major influence on the Mg deposition rate in this pressure range (~ 0.012 nm/pulse). The Pd deposition rate is ~ 0.002 nm/pulse. The targets for ablation were alternatively a magnesium foil (99.95%; Alfa Æsar) and a palladium foil (99.9%; Alfa Æsar). The

laser beam was focused at a 45° angle on the target with a spot area of 1.7 mm^2. The targets were continuously moved via a dual rotation and translation motion during ablation to ensure uniform ablation of the target. During the deposition, the laser fluence was kept at 5.0 ± 0.1 J/cm^2 (250 MW/cm^2). The substrate holder was spun around its normal axis during deposition. The target and the substrate holder were parallel and the distance between them was set to 4 cm. Films were deposited on mirror-polished nickel disks (S $= 1$ cm^2). Eight substrates were placed symmetrically around the center of the substrate holder at a radial distance of 2 cm.

The samples are designated as Pd–Mg(X)–Pd, where "X" is the helium gas pressure (mTorr) in the PLD chamber upon Mg deposition.

2.2. Film characterization

X-ray diffraction (XRD) measurements were performed by means of a Bruker-AXS D8 ADVANCE X-Ray diffractometer using (CuKα radiation). The diffractograms were fitted without smoothing using a pseudo-Voigt function. The crystallite size was estimated from XRD peak broadening using the Scherrer's formula.

Scanning electron microscopy (SEM) observations were made using a Hitachi SE4300 SE/N with secondary electrons imaging at 20 kV operating voltage. Atomic force microscopy (AFM) investigations were carried out under ambient conditions with a Nanoscope III microscope from Digital Instruments in contact mode using standard Si$_3$N$_4$ tips.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab 220I-XL with an Al Kα monochromatic source (1486.6 eV). The binding energy scale was calibrated using the C 1s binding energy on Pd at 284.66 eV. Depth profiling was done by sputtering the sample by means of argon ions incident at 40° to the film normal with an energy $E = 5$ keV and an ion current $I = 100$ nA. The spot area was 1 mm^2. The peaks considered for quantification are Mg 1s (~ 1304 eV, RSF $= 11.18$) and Pd 3d$_{5/2}$ (~ 335 eV, RSF $= 9.48$).

The electrochemical experiments were carried out using a Voltalab40 (Radiometer Analytical) potentiostat/galvanostat. Tests were performed at room temperature in 1 M KOH solution with a three-electrode cell. The counter-electrode was a Pt wire and the reference electrode was an Hg/HgO electrode (Koslow). All potentials are given with respect to Hg/HgO.

3. Results and discussion

3.1. Structure and morphology of the films

Fig. 1A shows a typical XRD pattern of a Pd/Mg600/Pd film deposited on Ni substrate. Peaks related to pure hcp Mg and fcc Pd phases are clearly discernable. Note that no MgO peak is detected in contrast with that currently observed during PLD deposition under ultra-high vacuum conditions of Mg-based thin films such as Mg–Ni–Ti [20] or MgB$_2$ [21,22]. Actually, our various PLD experiments on Mg-based films clearly indicate that the presence of an inert gas in the PLD chamber is a key parameter to avoid Mg oxidation during the deposition