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Remarkable hydrogen storage properties in three-layered Pd/Mg/Pd thin films

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Abstract

We have investigated hydrogen storage and structural properties in nano-composite three-layered Pd(50 nm)/Mg(x nm)/Pd(50 nm) films with $x=25$, 50, 200, 400 and 800 prepared by an RF-associated magnetron sputtering method. After hydrogenation under a hydrogen gas pressure of 0.1 MPa at 373 K for 24 h, the TDS profiles indicated that the Pd layers contain only 0.15–0.30 mass% hydrogen, whereas the Mg film contains ~5.0 mass% hydrogen for all the films. The most striking feature is that the temperature corresponding to maximum dehydrogenation rate remarkably shifts to low temperature with increasing the thickness of Mg film, which decreased from 465 K at $x=25$ nm to 360 K at $x=800$ nm. These improvements could be understood by the concept of cooperative phenomenon which hydrogen shows in nano-scale composite regions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thin film; Magnesium; Palladium; Hydrogen storage; Multi-layer

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1. Introduction

Hydrogen storage materials are one of the important key materials for the future clean energy systems. Current problems for the utilization of hydrogen storage materials are that almost all the alloys reveal either suitable hydrogen absorption/desorption temperatures but too low hydrogen capacities or suitably high hydrogen capacities but too high desorption temperatures. To achieve high performance with high hydrogen absorbing capacity and suitable absorption/desorption temperature, we have proposed that it is possible to design nano-composite hydrogen absorbing material which are made from two kinds of alloys/metals with contrasting hydrogen storage properties [1] and to extract advantageous hydrogen storage properties in both materials using cooperative phenomena that hydrogen reveals in nano-composite regions. The best way to make suitable nano-composite for hydrogen storage is to form thin film by sputtering or evaporation method because it is easy to control the thickness of film layers in nano-meter scales.

In the previous work, we have investigated hydrogen storage properties of nano-composite two-layered Pd/Mg films prepared by a RF-associated magnetron sputtering method [1] to check whether the above cooperative phenomena are realized or not. As is well known, Mg is a hydrogen storage material with its very high capacity of 7.6 mass%, but with a high desorption temperature (573 K), while Pd has just the opposite properties. The results obtained were summarized as follows: (i) the dehydriding properties of Pd-coated Mg (Pd/Mg) films were strongly dependent on the Mg sputtering condition, (ii) the Pd/Mg film prepared under higher Ar pressure and higher RF power revealed better dehydriding properties, (iii) the temperature corresponding to complete dehydrogenation was 465 K, and (iv) the desorbed hydrogen content was ~5.6 mass%. This indicated that hydrogen storage properties could be remarkably improved by controlling the Mg sputtering conditions and the formation of finer structure in Mg film in nano-meter scales leads to better hydrogen storage properties.

Until now, some investigations of thin films with Mg and Pd for hydrogen storage materials have been per-

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formed by Krozer and co-workers [2,3], Fischer and co-workers [4,5] and Spatz et al. [6]. The some interesting features have been reported, but such improvement in hydrogen storage properties that we mentioned above has not been reported yet.

In this work, we studied hydrogen storage and structural properties in nano-composite three-layered Pd/Mg/Pd films as a series of continuous researches. The results indicate that the advantageous hydrogen storage properties which Mg and Pd could be extracted in the three-layered nano-composite films suitably controlled with nano-meter scales. Finally, a scenario for understanding how hydrogen induces low temperature desorption in this system is presented on the basis of cooperative elastic interaction model.

2. Experimental details

An in situ system was used in this work [1], by which we prepare nano-composite thin films and examine the hydrogen storage properties without exposing in the air. Pd/Mg/Pd films were prepared on a glass substrate (Corning #7059; 20×20×0.5 mm) by a RF-associated magnetron sputtering method without additional heating. Before sputtering, the inside of sputtering chamber was baked out and a residual gas pressure was kept in the order of 10^{-7} Pa. Mg and Pd targets with 4 N purity and Ar gas with 6 N purity were used for the sputtering. Pd films were prepared at an Ar pressure of 7.0×10^{-2} Pa with a target DC current of 0.10 A and a RF coil power of 50 W, which leaded to most smooth film surface on Pd. On the other hand, Mg films were prepared at an Ar pressure of 7.0×10^{-1} Pa with the target DC current of 0.05 A and the RF coil power of 200 W, the condition of which gave the best dehydriding properties in two-layered Pd/Mg films. The thickness of the Pd layer was 50 nm, while those of the Mg layers were 25, 50, 200, 400 and 800 nm.

After the film preparation, their films were hydrogenated with a hydrogen pressure of 0.1 MPa at 373 K for 24 h, and the dehydriding properties were examined by thermal desorption spectroscopy (TDS) method during heating at 4 K min^{-1} from room temperature up to 773 K. The amount of desorbed hydrogen gas was measured by throughput method with mass spectroscopy [1] and hydrogen contents were calculated using the thickness and specific gravity of Mg and Pd.

The films were characterized by X-ray diffraction (XRD) using Cu Kα radiation just after the films were prepared. The structures of the films were examined by transmission electron microscopy (TEM). Prior to TEM observation, the films were cut into slices with thickness less than hundred nanometer along the cross section of the films using a focused ion beam thinning technique with 30 kV Ga^{+} ion. The thinning technique was described in detail in Ref. [7]. The TEM observation was operated at 300 kV using a JEOL JEM-3000F.

3. Results

3.1. Hydrogen storage properties of three-layered Pd/Mg/Pd films

The TDS spectra of the hydrogenated three-layered Pd/Mg/Pd films are shown in Fig. 1. We notice that each spectrum exhibits two peak structures in low and high temperature sides for all the films. The low and high temperature side peaks correspond to those due to hydrogen desorption from the palladium and the magnesium hydrides, respectively, because hydrogen in palladium is less stable and easier to be desorbed than that in magnesium, and the peak area of high temperature side increases with increasing the Mg thickness. Similar spectra were observed in the Pd/Mg films [1]. It is of interest that the peak position in the TDS spectrum remarkably shifts toward low temperature side with increasing the thickness of Mg films. We can deduce that the peak temperature due to hydrogen desorption from magnesium decreases from 463 to 360 K with increasing the Mg thickness, while that from palladium hydride decreases from 375 to 320 K. It is to be noted that the peak temperature due to hydrogen desorption from magnesium in the Pd/Mg/Pd films are significantly lower than that of the Pd/Mg films in the same condition.

The estimated hydrogen contents measured by throughput method in Mg in the three-layered Pd/Mg/Pd films were ~5.0 mass%, being almost independent of the Mg thickness. This is contrast with the results that those in the

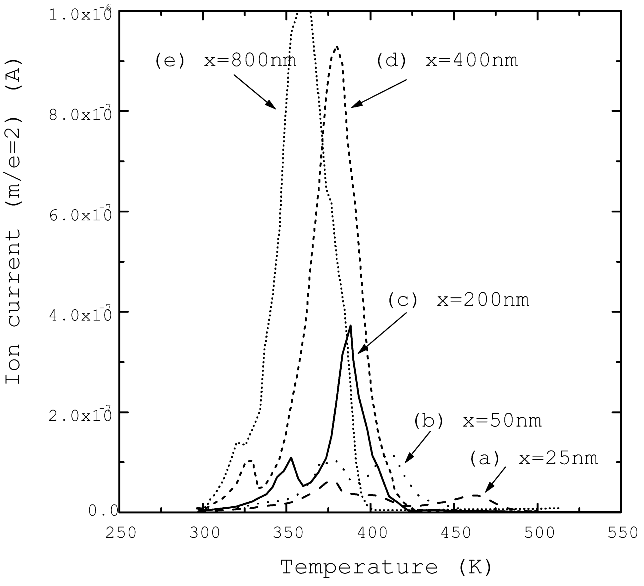

Fig. 1. TDS spectra of several hydrogenated Pd (50 nm)/Mg (x nm)/Pd (50 nm) films with x=25, 50, 200, 400 and 800 nm.

two-layered Pd/Mg films rapidly decreased with increasing the Mg thickness. It is noteworthy that H/Mg in three-layered Pd/Mg (800 nm)/Pd film was about two times larger than that in two-layered Pd/Mg (800 nm) film in the same hydrogenation condition. This suggests that the Mg layer in the Pd/Mg films is hydrogenated through only one Pd layer [8] after hydrogen molecule is dissociated into atomic state, whereas Mg in Pd/Mg/Pd films is hydrogenated through the two up and down Pd layers after hydrogen dissociation. The hydrogen contents in the Pd layers were estimated to be 0.15–0.3 mass%, irrespective of the Mg thickness for both the films.

3.2. Structural characteristics of three-layered Pd/Mg/Pd films

To clarify the origin of remarkable hydrogen storage properties in the three-layered Pd/Mg/Pd films, we performed the X-ray diffraction experiments and TEM image-figure observations.

The X-ray diffraction (XRD) profiles of the Pd/Mg/Pd films before hydrogenation are shown in Fig. 2. We can see the Mg(002) and Mg(004) diffraction peaks, and Pd(111), Pd(200) and Pd(220) peaks as being similar to those in the two-layered Pd/Mg films. The profiles indicate the *c*-axis preferred orientation for the Mg films, but no preferred orientation for the Pd layers. We can see that the intensity of the Mg(002) peak decreases with decreasing Mg thickness and no Mg peak is observed in the film (a) with a Mg thickness of 25 nm. The broad maximum around 25° is due to the glass substrate.

After hydrogenation under a hydrogen pressure of 0.1 MPa at 373 K for 24 h, the XRD diffraction experiments were performed for the Pd/Mg/Pd films, the profiles of which are shown in Fig. 3. We notice that the XRD profiles with thinner Mg films than 200 nm are completely different from those with thicker Mg films than 400 nm. To outward seeing, we noticed the peeling off of films (d) and (e) from the glass substrate at interface of palladium and substrate, where the adhesive force is weakest in the sample. Because the adhesive force between the substrate and the Mg film is larger than that between the substrate and the Pd film [9]. Degradation of peeling by appearances increases with increasing Mg thickness. This may be due to the fact that the stress induced between the substrate and Pd films increases with increasing the Mg thickness.

We can see that the $PdH_{0.6}$(111) and $PdH_{0.6}$(200) hydride peaks are strong for the films (a), (b) and (c), whereas the intensity are very weak for the films (d) and (e). This suggests that Pd has completely absorbed hydrogen to form $PdH_{0.6}$ after hydrogenation at 373 K for 24 h for all the films, but a part of hydrogen in $PdH_{0.6}$ is desorbed for the films (d) and (e) during their removal from the chamber because of peeling off the films from the substrate. On the contrary, the Pd(111) peak with no hydrogen is not observed in the films (a), (b) and (c), while the Pd(111) peak are mainly observed in the films (d) and (e).

As is well known, Mg metal transforms from the h.c.p. structure to the rutile-type tetragonal one (MgH_2) upon hydrogenation. After hydrogenation, the MgH_2(110) peak is observed for all the films except the film (a), but the

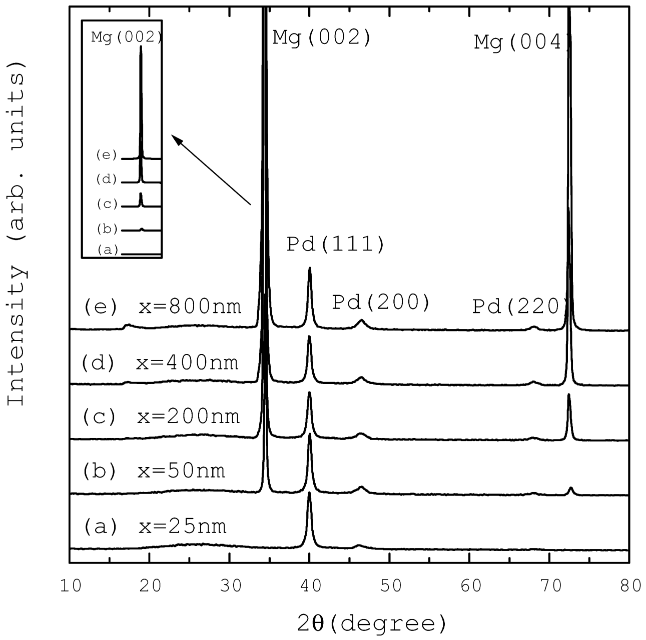

Fig. 2. X-ray diffraction profiles of the Pd (50 nm)/Mg (*x* nm)/Pd (50 nm) films with $x=25$, 50, 200, 400 and 800 nm before hydrogenation. The broad peak near the range 20–30° is that of glass substrate.

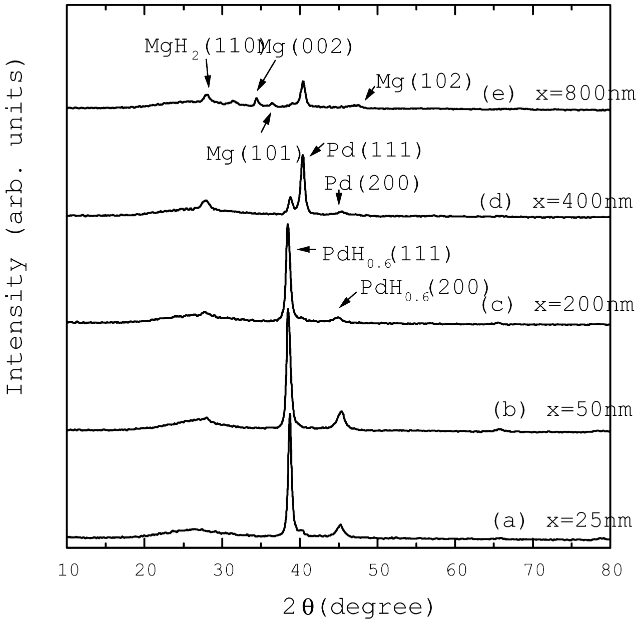

Fig. 3. X-ray diffraction profiles of the Pd (50 nm)/Mg (*x* nm)/Pd (50 nm) films with $x=25$, 50, 200, 400 and 800 nm after hydriding under a hydrogen pressure of 0.1 MPa at 373 K for 24 h. The broad peak near the range 20–30° is that of glass substrate.

intensity is too small. This suggests that the orientation preference in Mg films partly disappears in the three-layered Pd/Mg/Pd films by hydrogenation absorption. This is contrast to the case of two-layered films, in which Mg in the Pd/Mg films reveals such a martensite-like transformation upon hydrogenation that the h.c.p. Mg (00*l*) plane corresponds to the MgH_2 (*hh*0) plane. Therefore, we speculate that Mg in the three-layered Pd/Mg/Pd films reveals an amorphous-like displacement upon hydrogen uptake. On the other hand, the Mg peaks are observed only in the film (e), in which the *c*-axis preferred orientation is not apparently induced. This may be due to complete peeling off of the film (e) from the substrate.

TEM images for the cross section of the Pd (25 nm)/Mg (200 nm) and Pd (50 nm)/Mg (200 nm)/Pd (50 nm) films before hydrogenation are shown in Fig. 4. The boundary between the Mg and Pd layers is very clear, and the Mg layer in the both films is composed of columnar grains, the widths of which are ~70 and ~30 nm for the Pd/Mg and Pd/Mg/Pd films, respectively. It is of interest that the latter is much smaller than the former. This indicates that the structure of Mg layer is remarkably changed by its foundation (Pd or glass) and the thinner Mg columnar grain leads to lower dehydrogenation temperature.

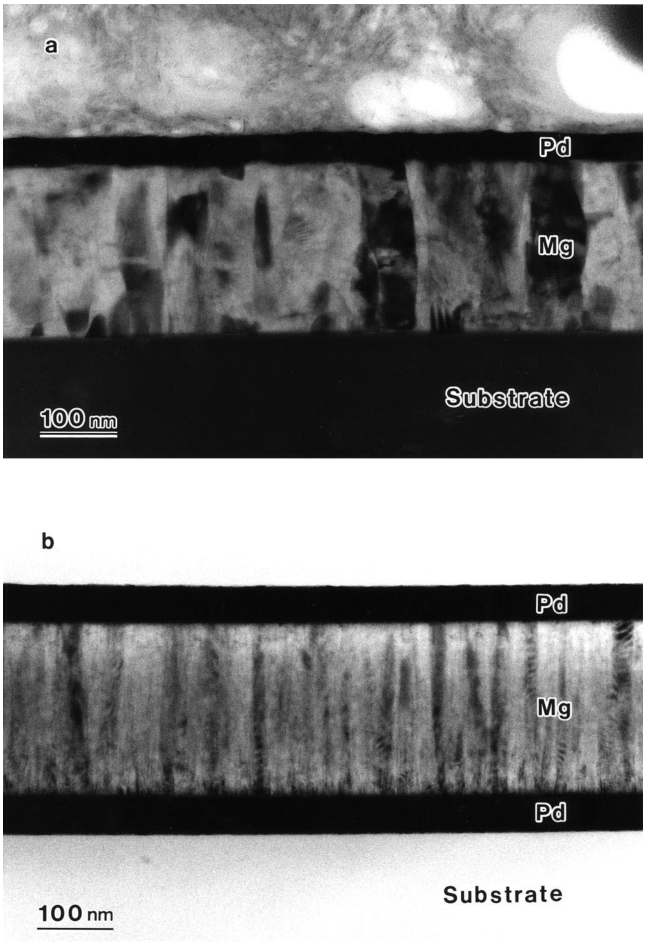

Fig. 4. TEM micrographs for the cross section of (a) Pd (25 nm)/Mg (200 nm) and (b) Pd (50 nm)/Mg (200 nm)/Pd (50 nm) films before hydrogenation.

4. Discussion

As mentioned above, some significant improvement in hydrogen storage properties is induced in the Pd/Mg/Pd films with thicker Mg layers. Here, we discuss the origin of such improvement on the basis of the concept of cooperative phenomena which hydrogen reveals in nano-composite regions.

In Fig. 5, we illustrate a schematic diagram for understanding the cooperative phenomena. The scenario of dehydrogenation is drawn as follows: Now, we assume that the Pd/Mg/Pd film with thicker Mg layer is fully hydrogenated and peels off from the substrate. When the temperature is increased, (1) hydrogen in Pd films becomes unstable and easily desorbs from the up and down Pd films. As a result of hydrogen desorption from both the Pd films, (2) the compression stress is induced on the up and down surface of the Mg film. This stress strongly influences the Mg films, by which (3) hydrogen in the Mg film becomes unstable and leads to low temperature dehydrogenation. Therefore, hydrogen in Mg can be dehydrogenated as soon as hydrogen in Pd films is desorbed at lower temperature below 370 K. This phenomenon is the so-called 'cooperative phenomena which hydrogen exhibits in nano-composite system by elastic interactions' [10,11]. Otherwise, the Pd/Mg/Pd with thinner Mg layer and Pd/Mg films did not peel off from the substrate by hydrogen uptake. In this case, Mg in the films might exhibit such a martensite-like transformation upon hydrogenation that the h.c.p. Mg (00*l*) plane corresponds to the MgH_2 (*hh*0) plane. As a result of such transformation, we can deduce that the distance between Mg atoms are expanded 22% along the direction perpendicular to the substrate plane, while the Mg–Mg distance are expanded only 6% in substrate plane. Therefore, since such an anisotropic deformation brings only a small compression

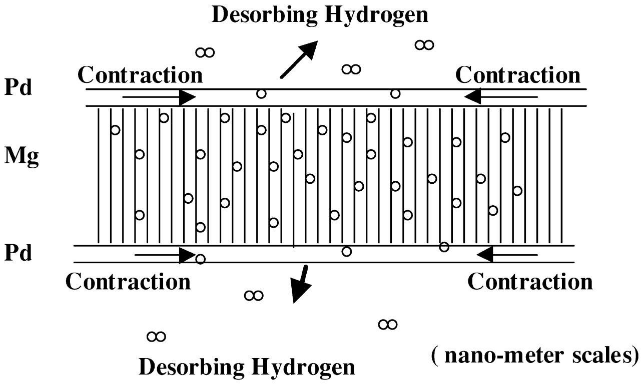

Fig. 5. Schematic diagram of hydrogenated Pd/Mg/Pd film with thicker Mg layer.

stress on the Mg film plane, the cooperative interaction is weak in the films without peeling off. This leads to worse hydrogen storage properties for the films with the thinner Mg layers without peeling off.

In addition, since the width of Mg columnar grains in the Pd/Mg/Pd film is smaller than that in the Pd/Mg film, the number of grain boundaries (hydrogen path way) in the Pd/Mg/Pd films is larger than that in two-layered Pd/Mg films (shown in Fig. 4). Therefore, we can deduce that the smaller width of Mg columnar grains leads to the lower dehydrogenation temperature as well.

From the above experimental results, we conclude that Mg hydride with hydrogen capacity of ~5.0 mass% is formed at 373 K and the hydrogen is desorbed at temperature lower than 373 K in the nano-composite three-layered Pd/Mg/Pd films. Some advantageous hydrogen storage properties that Mg and Pd metals have could be extracted in this system.

5. Summary

We have investigated the hydrogen storage and structural properties in three-layered Pd/Mg/Pd thin films. The results obtained are summarized as follows:

1. Hydrogen capacity of Mg in the Pd/Mg/Pd films are almost ~5.0 mass%, irrespective of the thickness of Mg layers, which is about two times larger than that in the Pd/Mg film with thicker Mg layer.
2. The hydrogen desorption temperature rapidly decreases with increasing the Mg thickness in Pd/Mg/Pd films. The desorption temperature from the magnesium hydride is lower than 373 K in the Pd/Mg (800 nm)/Pd film.
3. The structure of Mg in Pd/Mg/Pd film is composed of columnar grains, whose width is ~30 nm. The smaller width leads to better hydrogen storage properties.
4. Significant improvement in the dehydriding properties of the Pd/Mg/Pd films can be explained by cooperative phenomena due to elastic interactions between nano-structured Mg and Pd layers.

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