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Optical transmission of magnesium hydride thin film with characteristic nanostructure

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Abstract

Optical and structural properties of rare-earth free and pure Mg thin film coated with Pd have been investigated. Optical examination indicates that the fully hydrogenated films are in a color-neutral transparent state. With increasing temperature up to 453 K in air, nontransparent scratch-like parts that correspond to dehydrogenated Mg precipitate in macroscopic scale, and their number gradually increases and grows sharply along specific orientations. The structural characterization indicates that the Mg layer is composed of epitaxial columnar grains whose widths are less than 100 nm with a *c*-axis preferred orientation for the Mg layer. The columnar grains are restructured to grains with 50–100 nm diameter during hydrogenation–dehydrogenation (optical switching) cycles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen storage; Optical transmission; Nanostructure; Magnesium hydride; Transmission electron microscopy

1. Introduction

From both fundamental and practical viewpoints, much attention has been paid to the metal–hydrogen system. In 1996, an interesting phenomenon on the optical properties, i.e. optical transmission due to hydrogenation, was discovered by Huiberts et al. [1]. The rare-earth metal hydride thin films show dramatic changes in the optical properties depending on the hydrogen content [1–6]. The optical transmission of those films can be switched between shiny mirror and transparent state in a fraction of a second at room temperature by changing the hydrogen gas pressure [1–3,6] or by electrochemical means [4–6]. Thus, since the optical switching occurs at ambient conditions, rare-earth metal hydride thin films are very attractive materials as optical switching devices, for example, for optical shutter, mirror with variable transmission, sunroof and so on.

Such a phenomenon has also been recently observed in RE–Mg (RE=rare-earth metals) alloy hydride thin films, especially Gd–Mg [7], Sm–Mg [8] and Y–Mg hydride [9]. In this work, it has been found that the absorption edges in the transmission spectra of the alloy hydrides shift to shorter wavelength for higher Mg contents in the alloys, and that the transmissions of the alloy hydrides are higher than those of the pure rare-earth metal hydrides. Nagengast et al. [9] concluded that the remarkable optical properties of these RE–Mg alloys can essentially be understood in terms of a compositional disproportionation of the alloy during hydrogen absorption, and that the Mg clusters act mainly as a microscopic optical shutter, enhancing the reflectively in the metallic state and increasing the optical gap in the transparent state. For pure Mg hydride thin films, however, this phenomenon has been insufficiently studied, because it is difficult to load enough hydrogen into pure Mg thin film. To our knowledge, few experimental results have been reported on the optical transmission of pure Mg films caused by gas-phase hydrogenation, although this phenomenon had been briefly described in [10] and predicted from the study of metal-insulator transition on a Mg–H system [11].

Recently, we found that the Mg thin films coated with Pd, which was fabricated using an in situ system, have the following noticeable hydriding properties [12]. The 200 nm Mg thin film coated with 25 nm Pd absorbed a large amount of hydrogen (5.6 mass% in the Mg layer) at 373 K under a hydrogen pressure of 0.1 MPa, and all the hydrogen atoms absorbed in the film were desorbed below

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463 K in vacuum. Moreover, it is to be noted that the films changed from a shiny mirror state into an optical transparent state upon the hydrogen absorption. From the viewpoint of hydrogen applications, it is important to mention that not only the hydriding–dehydriding properties but also the optical properties of pure Mg thin films with characteristic nanostructure are of interest. We consider that the Mg thin films are applicable as a base material not only to hydrogen storage but also to sensors, sunroof and other optical switching devices. The purpose of this study is to clarify the nature of the optical transmission caused by gas-phase hydrogenation of pure Mg thin film coated with Pd. We also focused on the structural properties because the notable hydriding–dehydriding properties of the film used in this study would have originated in the structural properties [12,13].

2. Experimental details

2.1. Sample preparation

Mg thin films coated with Pd were prepared using an in situ system with RF-assisted magnetron sputtering and an analysis chamber to study the hydriding–dehydriding process. Details about this in situ system were described elsewhere [12]. The Mg layer of 200 nm thickness was deposited onto glass or quartz-glass substrates at an argon pressure of 0.7 Pa with a target DC current of 0.05 A and an RF coil power of 200 W without supplemental heating. The quartz-glass substrate was used for the measurement of optical transmission. Then, a Pd layer of 10–50 nm thickness was deposited onto the Mg layer at argon pressure of 0.07 Pa with a target DC current of 0.10 A and an RF coil power of 50 W without supplemental heating. The Pd layer serves as a protection layer against oxidation of the Mg layer as well as a catalyst for hydrogenation. After the film formation, the films were hydrogenated at 373 K under a hydrogen pressure of 0.1 MPa for 24 h in an in situ system.

2.2. Sample characterization

The optical properties were measured from the substrate side by ultraviolet and visible spectrophotometry at room temperature in air, using a Shimadzu UV-160A. The measurements were carried out as soon as possible after taking the samples out of the in situ system to prevent hydrogen desorption and oxidation of the samples. The structural properties were characterized by X-ray diffraction (XRD) with CuKα radiation, using a Mac Science MXP18VA, and transmission electron microscopy (TEM), using a JEOL JEM-3000F operated at 300 kV. TEM specimens were prepared by the focused ion beam thinning technique with 30 kV Ga^+ ion, using a Hitachi FB-2000H. The thinning technique was described previously [14]. The hydriding–dehydriding properties were evaluated from thermal desorption spectroscopy (TDS) with a Q-mass spectrometer in an in situ system. The TDS analysis was carried out under heating of 4 K min^{-1} from room temperature up to 773 K.

3. Results and discussion

3.1. Optical properties

Fig. 1 shows the photographs in transmitted light for a hydrogenated 200 nm Mg thin film coated with 10 nm Pd. After hydrogenation in an in situ system, it is obvious that the film is in an optical transparent state, as seen in Fig. 1a. As seen in Fig. 1b and c, with increasing temperature up to 453 K, nontransparent macroscopic scratch-like parts precipitate, and their number gradually increases and grows sharply along specific orientations in the film. As is evident from Fig. 4, it is reasonable to assume that these

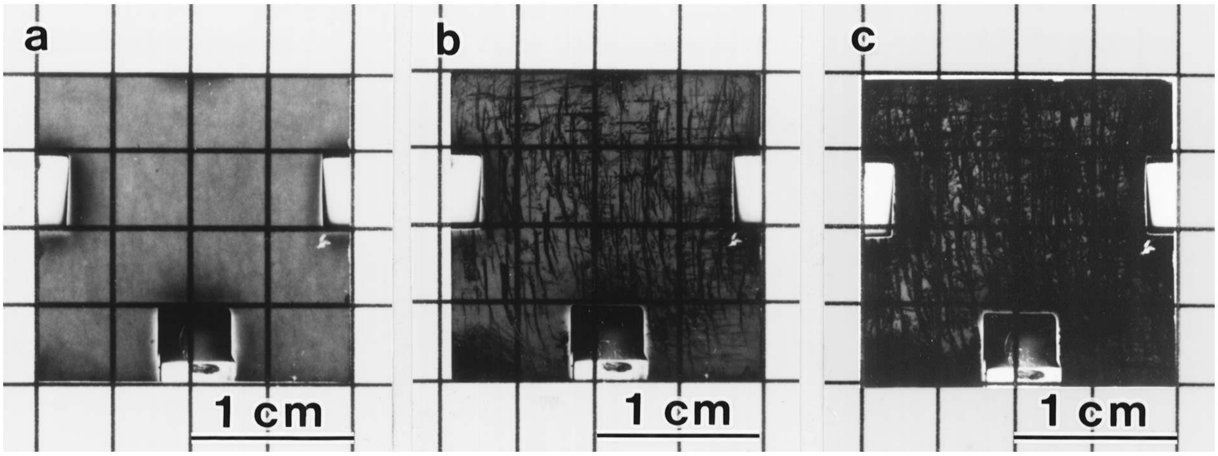

Fig. 1. Photographs in transmitted light for a hydrogenated 200 nm Mg thin film coated with 10 nm Pd, (a) after hydrogenation at 373 K under a hydrogen pressure of 0.1 MPa for 24 h in an in situ system, and after heating at (b) 393 K and (c) 453 K for 300 s in air.

nontransparent precipitates correspond to dehydrogenated Mg. Similar morphological changes in the film occurred after several days exposure to air at room temperature. This feature leads to a characteristic pattern for the dehydrogenation process from Mg hydride. It is not clear at present why the nontransparent precipitates appear scratch-like during the dehydrogenation process.

Fig. 2 shows the transmission spectra as a function of wavelength for a hydrogenated 200 nm Mg thin film coated with 10 nm Pd. The maximum transmission is limited by the reflection and absorption in the Pd layer. After correction for the quartz-glass substrate, as shown in Fig. 2a, the transmission of the hydrogenated film reaches 20–26% in the range of 400–1000 nm. Furthermore, the transmission reaches 82% at nearly 900 nm after correction for the quartz-glass substrate with 10 nm Pd thin film, as shown in Fig. 2b. Here, the quartz-glass substrate with 10 nm Pd thin film was used as the reference, because the Pd layer reverts from the hydride to metal states in air (see Fig. 3b). These indicate that the hydrogenated Mg thin film coated with Pd is in a color-neutral transparent state. The transmission gradually dropped below 400 nm, and vanished near 205 nm. This value is consistent with the results of the Gd–Mg alloys in [7].

3.2. Structural properties

Fig. 3 shows the XRD profiles for 200 nm Mg thin films coated with 50 nm Pd. Before hydrogenation, we can see the Mg (002) and Mg (004) diffraction peaks from the Mg layer, and the Pd (111), Pd (200) and Pd (220) peaks from the Pd layer in Fig. 3a. Here, the broad peak around 25 degrees is due to the glass substrate. Thus, the profile reveals that the Mg grains epitaxially prefer the *c*-axis orientation for the Mg layer, but no preferred orientation occurs for the Pd layer. After hydrogenation in an in situ system, as shown in Fig. 3b, the peaks which are related to the *c*-axis orientation of Mg disappear, and the broad peaks related to the *ab*-plane orientation of MgH_2, i.e. MgH_2 (110) and MgH_2 (220) peaks, appear. These results suggest that almost all of Mg is hydrogenated, and the MgH_2 grains form some nanostructure. Furthermore, these results imply that small displacement of Mg atoms due to hydrogenation satisfies the orientation relation that the hexagonal Mg (00*l*) plane corresponds to the tetragonal MgH_2 (*hk*0) plane. The hydrogen content in the Mg layer was estimated to be 6.0 mass% by TDS with a Q-mass spectrometer, and all the hydrogen atoms absorbed were desorbed nearly 453 K in vacuum. Therefore, we conclude that at least 79% of the Mg layer is fully hydrogenated under the experimental conditions in this study. These results are in good agreement with previous work by Higuchi et al. [12]. After dehydrogenation in an in situ system at 453 K, that is the endpoint of hydrogen desorption temperature in the TDS profile, the MgH_2 peaks disappear, and the Mg (002) peak reappears although the peak intensity is weak, as shown in Fig. 3c. This indicates that the epitaxiality of the Mg layer remains intact during the hydrogenation–dehydrogenation (optical switching) process. This feature is similar to that of the epitaxial Y film [15]. In this case, the structure changes from *fcc* YH_2 to *hcp* $YH_{3-\delta}$ during the optical switching process.

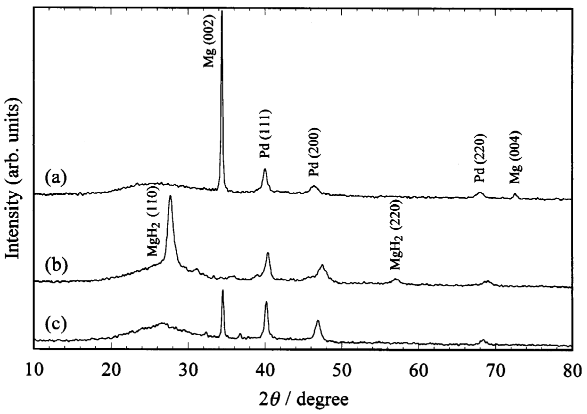

Fig. 3. XRD profiles for 200 nm Mg thin films coated with 50 nm Pd, (a) before hydrogenation, (b) after hydrogenation at 373 K under a hydrogen pressure of 0.1 MPa for 24 h and (c) after dehydrogenation at 453 K for 300 s in an in situ system. The profiles are obtained using CuKα radiation at room temperature in air.

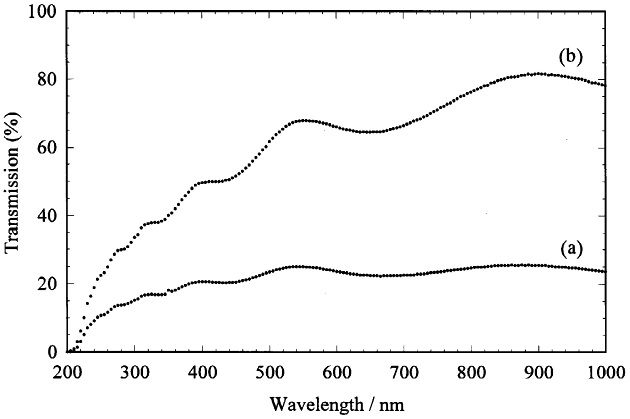

Fig. 2. Transmission spectra as a function of wavelength for hydrogenated 200 nm Mg thin films coated with 10 nm Pd, (a) after correction for the quartz-glass substrate and (b) after correction for the quartz-glass substrate with 10 nm Pd thin film. The spectra were measured in air at room temperature.

Typical examples of TEM images for 200 nm Mg thin films coated with 50 nm Pd are shown in Fig. 4, corresponding to Fig. 3. Here, the region above the Pd layer is the protection layer (epoxy resin and tungsten deposited) against the irradiation damage introduced by focused ion beam during thinning of TEM specimens. Before hydrogenation, as seen in Fig. 4a, the Mg layer is composed of epitaxial columnar grains whose widths are less than 100 nm. Judging from the results of XRD analysis shown in Fig. 3a, it is clear that there is preferential orientation for the columnar Mg grains in the Mg layer. After hydro-

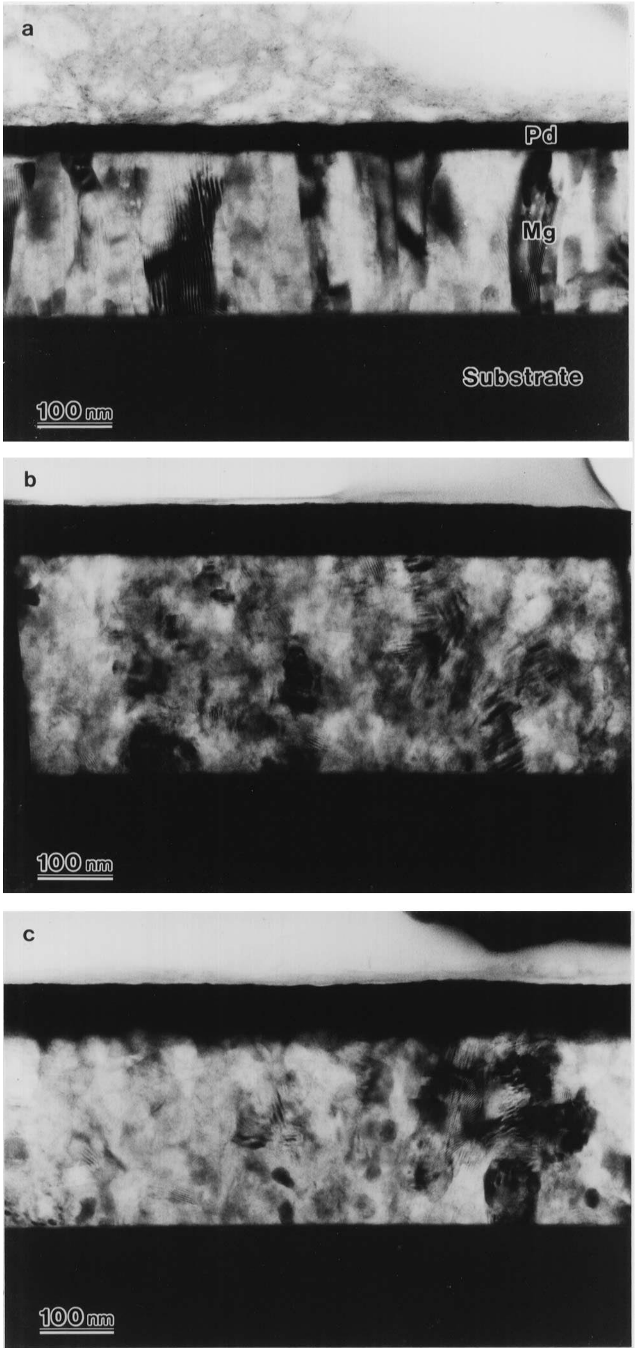

Fig. 4. Typical examples of TEM images for 200 nm Mg thin films coated with 50 nm Pd corresponding to Fig. 3. Only in (a), the thickness of Pd layer is 25 nm.

genation (see Fig. 4b), the Mg layer is composed of grains 50–100 nm in diameter, and the boundaries of the columnar grains seem to be partly maintained. We assume that the diameter of grains formed after hydrogenation are restricted by the width of columnar grains before hydrogenation. As the result of this restriction, the grains become less than 100 nm in diameter. After dehydrogenation (Fig. 4c), the nanostructure of Mg layer exhibits no prominent difference with that of the Mg layer after hydrogenation shown in Fig. 4b, while the interface between the Pd and Mg layers becomes slightly fuzzy. From XRD measurement and TEM observation after dehydrogenation induced by excessive heating above 453 K, we have confirmed that the Mg_6Pd phase was formed at the interface.

4. Conclusions

In order to clarify the optical switching caused by gas-phase hydrogenation of rare-earth free and pure Mg thin films coated with Pd, the optical and structural properties of such films have been investigated in detail. The results obtained are summarized as follows:

1. The films change from shiny mirror state into a color-neutral transparent state during hydrogenation. The transmission reaches to 82% at nearly 900 nm wavelength after correction for the quartz-glass substrate with 10 nm Pd thin film, and the absorption edge occurs at 205 nm.
2. With increasing temperature up to 453 K in air, nontransparent scratch-like parts corresponding to dehydrogenated Mg precipitate on a macroscopic scale, and their number gradually increases and grows sharply along specific orientations in the film.
3. The Mg layer is composed of epitaxial columnar grains whose widths are less than 100 nm with a *c*-axis preferred orientation. The columnar grains are restructured to grains with 50–100 nm in diameter during hydrogenation–dehydrogenation (optical switching) cycles.
4. Since small displacement of Mg atoms due to hydrogenation satisfies the orientation relation that the hexagonal Mg (00*l*) plane corresponds to the tetragonal MgH_2 (*hk*0) plane, the epitaxiality of the Mg layer remains intact during the optical switching process.

It is believed that the change in optical transmission depends strongly not only on the electronic structure but also on such remarkable nanostructure. For the understanding of the optical phenomena and for technological applications, further fundamental studies are required for pure Mg and Mg-based alloy thin films.

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