Electrochemical Properties of Pd-capped Mg-Ni Switchable Mirror Thin Films

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Switchable mirrors composing magnesium-nickel thin films with a palladium top layer are prepared by dc magnetron sputtering. Electrochromic properties of the switchable mirrors are investigated by means of various electrochemical methods. Electrochemical switching conditions influenced by the composition of the Mg-Ni alloy thin film and the thickness of palladium and Mg-Ni layers are investigated to obtain optimal switching behavior and transparent films using cyclic voltammetry and optical measurements. The values of the diffusion coefficients of hydrogen in Mg-Ni, MgNi, and Mg-Ni films are estimated using a potential-step method.

Key Words : Switchable Mirror, Electrochromic Switching, Metallic Hydride, Mg-Ni Alloy Thin Film

1 Introduction

The discovery of remarkable optical switching properties of rare-earth hydrides has had the result of focusing attention on switchable mirrors as a new class of chromogenic materials.1,2 Although pure rare-earth switchable mirrors such as yttrium and lanthanum are yellow in the transparent state, these optical properties can be improved by doping magnesium into a rare-earth metal film.3,4 However, such materials are generally not practical due to the low natural abundance and high cost of materials. Magnesium-nickel alloy thin film switchable mirrors, which were discovered by Richardson,5,6 are less expensive and comprised of naturally abundant metals. Pd-capped Mg-rich Mg-Ni alloy thin films demonstrate excellent optical switching properties with wide optical modulation ranges and color neutrality indicated by gasochromic switching.6 A thin film of Pd/Mg-Ni is brown in the hydride state. As for electrochromic (EC) switching, Richardson et al.5,7 Isidorsson et al.,7 and Lohstroh et al.5,6 have reported on the basic electrochemical properties of these films. It is understood that Mg-Ni alloy thin films also undergo switching in an alkaline electrolyte solution and can function as EC devices. Advanced studies of EC switching of Mg-Ni based devices have yet to be carried out.

The electrochemical hydriding/dehydriding reactions for the interface and the inside of the Pd/Ni-Mg alloy switchable mirrors in an alkaline solution during hydriding and dehydriding steps occur as a result of the hydrogen adsorbing (Hads) to the surface of the Pd film and diffusing into the host lattice of Pd film to produce absorbed hydrogen (Hads).

\[
Pd + H_2O + e^{-} \rightarrow PdH_{ads} + OH^- \quad (1)
\]

\[
PdH_{ads} \rightarrow PdH_{bds} \quad (2)
\]

The Pd thin film acts as a catalyst layer and promotes the hydriding and dehydriding processes of the Mg-Ni alloys, it also functions as a protective layer, preventing the oxidation of magnesium in air. On the other hand, the hydriding reaction of the Mg-Ni type alloy occurs according to the following reactions.8

\[
Mg + H_2 \rightarrow MgH_2 \quad (3)
\]

\[
Mg_2Ni + 2H_2 \rightarrow MgNiH_4 \quad (4)
\]

The added nickel forms MgNi and has a catalytic effect on the formation of MgH2. Thus, the Ni content and the thickness of the Pd layer both play an important role in the transmission, switching speed and durability of switchable mirrors.

In this paper, various preparative parameters including the composition of the Mg-Ni alloy thin film, the thickness of the catalytic palladium top layer, and the thickness of the Mg-Ni layer are investigated to obtain switchable mirrors with optimal switching behavior, faster hydriding/dehydriding properties and higher transparency. Three types of switchable mirrors including MgNi, MgNi and MgNi alloy thin films are produced and characterized by cyclic voltammetry and optical measurements. The hydrogen diffusion coefficients of Mg-Ni alloy thin films, capped with a thin film of palladium, were measured by electrochemical means.

2 Experimental

Ni-Mg alloy thin films were prepared by DC magnetron cosputtering of Mg (99.9%) and Ni (99.9%) targets in pure Ar plasma. Subsequently, the films were top-capped in situ with Pd (4 nm) as a catalytic and protective layer. The base pressure was 2.0 × 10−5 Pa and the process pressure was 0.6 Pa. The sputtering powers for magnesium and nickel were set to 30 W and 9 (MgNi), 16 (MgNi), and 30 W (MgNi), respectively. The thickness of MgNi (x = 2, 4, 6) thin film were 20 –
120 nm, and that of the Pd layer was about 2 – 10 nm. Thickness was measured with a Stylus Profilometer (Kosaka ET-350). The Pd top layer was deposited using 14 W. Experimental details for preparation of various compositions of Mg-Ni alloy thin films and apparatus used have been described in our previous papers. The MgNi (x = 2, 4, 6) thin film composition was identified by Rutherford backscattering. All alloy thin films were deposited on ITO (20 Ω/□) coated glass substrates of 35 mm × 35 mm. The effective area of the electrode was 5.94 cm². The glass substrates were cleaned ultrasonically with cleaning fluid (Furuuchi SemiClean 50), acetone and deionized water for 30 min, 10 min, and 10 min, respectively, and preserved in the deionized water before use.

Electrochemical measurements were carried out using a GPIB potentiostat/galvanostat (HA501G, HOKUTO DENKO Ltd) in an open cell at 25 °C. A conventional three-electrode glass cell (Pt counter electrode, HgO/Hg as reference electrode filled with 1 M NaOH solution (ALS Co., Ltd), and Ni-Mg alloys thin film as working electrode) was used to electrochemically characterize the thin films in an alkaline solution (1 M KOH). The potential range for cyclic voltammetry was set in a potential region between +0.5 V and −1.20 V vs the HgO/Hg reference. Scan rate was set to 5 mV s⁻¹. Galvanostatic charging and discharging experiments were carried out at a constant current of 0.5 mA. The currents and transmittances were recorded simultaneously after a step from 0.3 V to −1.2 V. Before each measurement, the electrolyte solution was purged with an argon gas to obtain stable voltage readings. Optical characteristics were obtained in situ by optical photometry using a semiconductor laser of with a wavelength of 670 nm and a Si photo diode.

3 Results and Discussion

3.1 Galvanostatic loading and unloading

Electrode potential and optical transmittance changes of Pd (6 nm)/Mg-Ni (40 nm) thin films for galvanostatic loading and unloading are shown in Fig. 1. The charging current was set to −0.5 mA. At loading, two plateau structures are observed on the potential curve of Pd/Mg-Ni. At the first plateau region (E = −0.2 V), the transmittance is not changed. Because MgNi can absorb hydrogen into the lattice up to H/MgNi = 0.3, observations in this region may indicate formation of MgNiH₃. In the second plateau region (E = −0.85 V), the transmittance increases with time, which indicates transformation from MgNi to MgNiH according to reactions (3) and (4). Both of the plateaus are narrow on the potential curve of Pd/MgNi relative to that of Pd/MgNi. This may indicate that less MgNi exists in the film. On the potential curve of Pd/MgNi, the plateaus are not clear. This behavior may originate from two types of reactions (3) and (4) which subsequently occur in the film.

At unloading, an apparent plateau is seen around E = −0.6 eV on the potential curves of Pd/MgNi and Pd/MgNi, which corresponds to the transformation from MgNiH₄ to MgNi in the films. On the contrary, a small inflection point is seen instead of a plateau on the potential curve of Pd/MgNi, at E = 0 V.

3.2 Diffusion constant

The diffusion coefficients of hydrogen in bulk alloys have been studied by many researchers using electrochemical methods and nuclear magnetic resonance (NMR). For example, Goren and Korn measured the nuclear spin-lattice relaxation time T₁ of protons in MgNiH₄ and determined the activation energy Eₐ = 10.6 kcal mol⁻¹ and a jump attempt frequency ν₀ = 6.6 × 10¹³ in the temperature range of 210-480 K. The hydrogen diffusion coefficients were calculated from the following Arrhenius equation:

\[ D = \frac{d^2}{3 \pi} \exp \left( \frac{-E_a}{RT} \right) \]  

where d is the distance between nearest neighbors in the MgNi lattice, ν₀ is the jump attempt frequency, Eₐ is the activation energy and T is the temperature. The diffusion coefficient of hydrogen in the bulk sample of MgNi alloy is calculated to be 8.7 × 10⁻¹⁰ cm² s⁻¹.

Electrochemical measurements are conventionally used to determine the hydrogen diffusion coefficients in metals or alloys. The diffusion coefficients of hydrogen in alloys can be estimated from the following equation, where the discharge curve is expressed as

\[ 1nI = 1n (2FAcD_n/L) - (\pi^2D_n/4L)t \]
where \( I \) is the potentiostatic discharge current density, \( c \) is the hydrogen concentration, \( L \) is the film thickness, \( A \) is the active surface area, \( F \) is the Faraday constant, and \( D_h \) is the diffusion coefficient. The diffusion coefficient of hydrogen in a Mg$_2$Ni alloy powder sample (powder below 400 mesh) was estimated by Cui et al., based on equation \( (6) \). The values were in the range of \( 1.2 \times 10^{-11} \) to \( 1.57 \times 10^{-10} \) cm$^2$s$^{-1}$. In this study, we evaluate the diffusion coefficients of hydrogen in Mg-Ni alloy thin films capped with a Pd top layer using the some electrochemical methods at room temperature.

Figure 2 shows the optical transmission shift for Pd (6 nm)/Mg-Ni (120 nm) thin films during the discharge process. To estimate the hydrogen diffusion coefficients in Mg-Ni film, we prepared a sample with a thickness three times greater than that of a typical sample (40 nm). Transmission spectra were measured at a wavelength of 670 nm. A negative potential of \(-1.2 \) V was applied at \( t = 10 \) s and positive potential of \( 0.3 \) V was applied at \( t = 610 \) s for each sample. Mg$_2$Ni and MgNi thin films capped with Pd at a thickness of 6 nm reach the maximum transmittance in 60 s. The Mg$_2$Ni alloy thin film reaches the maximum transmittance in about 470 s and the rate of dehydrogenation of the MgNi film is very slow. As shown in Fig. 2, the dehydrogenation rate for electrochromic switching follows the trend of Mg$_2$Ni > MgNi > Mg$_2$Ni for 60 s, 320 s, and 760 s. These results are in agreement with gasochromic switching behavior.

Figure 3 shows typical potentiostatic discharge curves of Mg$_2$Ni, Mg$_2$Ni and Mg$_2$Ni (film thickness is 120 nm) capped with Pd of a thickness of 6 nm in 1 M KOH solution at a discharge potential of 0.3 V. As observed in the transmission spectra the point at which the anodic current returns to zero depends on the Mg content where higher Mg content slows the return of the current to zero. According to equation \( (6) \), the average diffusion coefficients of hydrogen in the Mg-Ni alloys thin films were obtained from the slope of the linear response of the corresponding plots in \( \ln(I) \) vs \( t \) graph. We considered the result of Fig. 2 and determined the linear regions of the corresponding plots as 60 s, 320 s, and 760 s for Mg$_2$Ni, Mg$_2$Ni and Mg$_2$Ni, respectively. The values of \( D_h \) for Mg$_2$Ni, Mg$_2$Ni and Mg$_2$Ni are \( 8.5 \times 10^{-12} \) cm$^2$s$^{-1}$, \( 3.1 \times 10^{-13} \) cm$^2$s$^{-1}$, and \( 9.5 \times 10^{-14} \) cm$^2$s$^{-1}$, respectively. These diffusion coefficients of hydrogen in Mg-Ni film are in agreement with the dehydrogenation behavior of Mg-Ni films estimated by optical measurements and are one to two orders of magnitude less than the coefficients reported by Goren\(^1\) and Cui\(^2\). The hydrogen diffusion coefficients we have calculated have discrepancies with known values but these differences may arise from differences of measurements made in bulk sample vs. measurements made in thin films.

### 3.3 Composition dependence in cyclic voltammetry

Electrochemical switching measurements were carried out by means of cyclic voltammetry in an aqueous alkaline solution (1 M KOH). Typical cyclic voltammograms and optical transmittances of 40 nm thick Mg$_2$Ni, Mg$_2$Ni and Mg$_2$Ni alloy thin films capped with a 6 nm thick layer of Pd are shown in Fig. 4a. Two anodic peaks are observed for all samples at \(-0.67 \) V and at approximately \(-0.40 \) V. The position of the anodic peak at \(-0.40 \) V shifts to the lower potential side and the peak height diminishes for films with more Mg content in the alloy. The electrochemical dehydriding reaction for Mg-Ni thin films in an alkaline solution during discharging can be represented as follows:\(^7\)

\[
\text{H}_2\text{ad} + \text{OH}^- \rightarrow \text{H}_2\text{O} + e^-.
\]

The anodic peak centered at \(-0.67 \) V in Fig. 4(a) is attributable to the oxidation of adsorbed hydrogen by the Pd layer,\(^5\) because in this position, the thin film does not change to the mirror-like state. In these films, the anodic peak centered at \(-0.40 \) V is related to the process of dehydriding of Mg$_2$NiH$_x$ and the peak position and height are dependent upon the Mg content in the alloy, while peaks at \(-0.67 \) V have little dependence on compositions. In addition, the position of the reduction peak at
approximately -1.1 V slightly shifts to the lower potential side and the peak height decreases as the Mg content increases.

Figure 4b is a re-plot of the transmittance in an electrode potential-course. Figure 4c is a re-plot of the transmittance in a time-course. The speeds of switching from the metallic state to the transparent state are almost the same for all types of mirrors. These results correspond to the potentiostatic loading of MgNi (x = 2, 4, 6) as shown in Fig. 2. The reverse switching from the transparent state to the metallic state can be achieved in 80 s, 130 s and 350 s for Mg2Ni, Mg4Ni and Mg6Ni films respectively. There is a tendency for the rate of the dehydriding reaction to decrease with increasing Mg content. The same behavior is observed by gasochromic switching using hydrogen gas.18

The transmittances of Mg2Ni and Mg4Ni in the electrochemical switching process are almost the same at approximately 45% while the transmittance of Mg6Ni is only 30% (Fig. 4b). The dehydrogenation speed of Mg2Ni mirror, however, is very slow compared to other samples. This difference may arise from the difference of the content of MgH2 in the film because, in bulk, Mg2NiH4 is red and MgH2 is transparent,59 and also hydrogen diffusion speed is very slow in MgH2 layer. So in conclusion on the transmittance and switching response, the composition of Mg2Ni mirror is most suitable as optical switching devices. We also investigated the effect of scan rate on the transmittance of the Pd/Mg2Ni switchable mirror. The results showed that the same transmittance of 45% can be achieved at a scan rate of 2 mVs⁻¹, 5 mVs⁻¹ and 10 mVs⁻¹, although the transmittance is reduced to 30% when the scan rate is increased to 20 mVs⁻¹.

3.4 Dependence of palladium thickness

Figure 5 shows the cyclic voltammograms of Mg2Ni, Mg4Ni and Mg6Ni thin film switchable mirrors of 40 nm thickness while varying the thickness of the top Pd layer (2, 6, 10 nm). The cyclic voltammograms of all types of switchable mirrors with a 2 nm Pd top layer were different from the others. It is possible that the thin layer of Pd allows the hydriding and dehydriding processes to
occur at a fast rate.

In the case of Mg$_3$Ni and Mg$_2$Ni alloy thin films, the absorbed hydrogen peaks at ~0.40 V are at almost the same position for samples with 6 nm Pd and 10 nm Pd as shown in Fig. 5a. The anodic peaks are centered at ~0.6 V where oxidation of absorbed hydrogen by Pd thin films occurs. However, these are shifted to more positive directions with increasing Pd thickness. This observation may reflect a difference in the quantity of adsorbed hydrogen in Pd films. On the other hand, the absorption peak in the sample with 10 nm Pd almost disappears for the Mg$_3$Ni alloy thin film. This may be caused by the fact that the discharge of hydrogen is very slow for this sample.

Figure 6 shows the relationship between the transmittance and the thickness of the Pd layer on Mg$_3$Ni, Mg$_2$Ni and Mg$_3$Ni alloy switchable mirrors with varying thickness of the Pd layer (2, 4, 6, 8, 10 nm). The transmittance of the switchable mirrors increases as the thickness of the Pd layer decreases for all types of mirrors. The electrochemical hydriding/dehydriding reaction speeds are fast for the 2 nm thick Pd top layer capped mirrors as indicated by the cyclic voltammograms and transmittances. However, the transmittances of the 2 nm Pd-capped Mg$_3$Ni ($x = 2, 4, 6$) mirrors are larger than 10% in the metallic state. XPS measurements were performed on the Mg$_3$Ni thin film mirrors with various compositions. Depth profiling of XPS indicates that when the Mg content increases, Pd is diffusing toward the interlayer or Ni is diffusing toward the substrates. As the Mg content increases in the Mg$_3$Ni thin films, Mg: Pd is formed in increasing amounts. From the transmittance modulation of metallic and hydride states, Pd top layer with 4 – 6 nm thick are most suitable for electrochromic switching.

3.5 Dependence of Mg-Ni layer thickness

We also investigated the effect of thickness of the Mg$_3$Ni alloy thin film on the transmittance in a 1 M KOH solution. Figure 7 shows the relationship between the transmittance and thickness for a Mg$_3$Ni layer. The current density increases as the thickness of the Mg$_3$Ni increases. It is characteristic that the anodic peak at approximately ~0.4 V (which is related to dehydriding of Mg$_3$NiH$_4$) is very small for the sample with 20 nm thick Mg$_3$Ni (Fig. 7a). Transmittance in the transparent state decreases with increasing thickness of Mg$_3$Ni layer (Fig. 7b), as well as transmittance in the metallic state. From the viewpoint of the optical modulation range (which is important for practical applications), samples with a 40 – 60 nm thick Mg$_3$Ni layer are most suitable for optical switching.

4 Conclusions

We prepared Pd-capped Mg-Ni alloy thin films by DC magnetron sputtering and investigated their electrochemical and optical properties. Values for the diffusion coefficients of hydrogen determined by a potential step method for 120 nm Mg$_3$Ni, Mg$_2$Ni and Mg$_3$Ni alloy thin films top-capped with palladium of 6 nm are $8.5 \times 10^{-12}$ cm$^2$s$^{-1}$, $3.1 \times 10^{-11}$ cm$^2$s$^{-1}$ and $9.5 \times 10^{-11}$ cm$^2$s$^{-1}$, respective-
ly. The hydrogen diffusion coefficients we have calculated have discrepancies with known values\cite{12,14} but these differences may arise from differences of measurements done on bulk sample vs. measurements done on thin films. Electrochemical hydrogen loading and unloading properties indicate that Mg-rich Mg-Ni alloy thin films consist of Mg2Ni and Mg. The optical modulation range depends upon the composition of alloy films. Mg-rich films demonstrate improved optical switching behavior and gasochromic switching behavior.\cite{15} In conclusion, Pd-capped Mg-Ni alloy thin films of compositions of Mg2Ni with a Pd thickness of about 6 nm and a Mg-Ni thickness of 40-60 nm have superior optical switching properties.

References