



## Effect of deposition conditions on the response and durability of an Mg<sub>4</sub>Ni film switchable mirror

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### A B S T R A C T

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We are developing switchable mirror thin films based on an Mg–Ni alloy which can be switched between mirror and transparent states. The Mg<sub>4</sub>Ni alloy thin film was prepared on a glass substrate by DC magnetron co-sputtering of Mg and Ni targets and was subsequently covered *in situ* with a thin layer of Pd. The interface structure between Pd and Mg–Ni layers was found to have a crucial effect on the switching response and durability. By controlling the sputtering sequence and tailoring the interface structure, the switching response can be improved by 50–80% for the dehydrogenation process. The switching durability of the improved thin film is twice as long as that of a typical sample. We have also found that the switching response is dependent on the substrate temperature during sputtering. The dehydrogenation rate can be increased when the substrate is retained below room temperature.

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### 1. Introduction

Certain examples of metal or alloy thin films top-capped with Pd can be hydrogenated at room temperature and atmospheric pressure by alternate exposure to hydrogen-containing gas [1–3]. These alloys exhibit remarkable optical switching properties in switching from the mirror state to the transparent state. Among various switchable mirror materials, Mg–Ni alloy thin films have attracted the most attention for potential applications as smart windows, displays, optical switches, or sensors, due to the advantages of low material cost, abundance and superior hydriding and dehydriding kinetics. Since the initial discovery by Richardson et al. [4], additional investigations of the structural, optical and electrochemical properties of Mg–Ni alloy thin films have been reported [5–8]. However, additional improvements in switching response and durability will be necessary for development of practical uses of these alloy thin films.

We have investigated the layer structure and optical switching properties of Pd-capped Mg–Ni thin films with high precision and found that the interface between the Pd cap layer and the Mg–Ni layer plays an important role in the switching property. For example, X-ray photoelectron spectroscopy (XPS) measurements showed that Mg migration toward the surface occurs in the vicinity of the interface between the Pd and Mg–Ni layers by repeated switching [9,10]. When at the surface, Mg is easily oxidized by

oxygen or water in air. The resulting MgO blocks further diffusion of hydrogen into the Mg–Ni alloy layers.

To improve the optical switching properties, we investigate herein the effects of sputtering conditions including substrate temperature, working pressure, and alloy composition on the switching durability and response (hydriding and dehydriding kinetics) of Pd top-capped Mg<sub>4</sub>Ni alloy thin films using X-ray diffraction (XRD), XPS, and electrochemical methods. By controlling the sputtering conditions and tailoring the interface structure, we have succeeded in preparing samples with a greater response and durability for gasochromic switching.

### 2. Experimental

#### 2.1. Sample preparation

Ni–Mg alloy thin films were prepared on a glass substrate by DC magnetron sputtering and top-capped *in situ* with a thin layer of palladium (Pd). The experimental details for preparation of Mg–Ni alloy thin films of various compositions and apparatus used were as described in our previous papers [6,11]. The cleaned glass substrate was introduced into the vacuum chamber through a load lock system. The base pressure of the vacuum chamber was kept at  $2 \times 10^{-5}$  Pa, and the process pressure was retained at 1.2 Pa (Ar flow rate of 80 sccm). Pd/Mg–Ni thin films were prepared by co-sputtering with Mg (99.9%,  $50\phi \times 3$  mm) and Ni (99.9%,  $50\phi \times 3$  mm) targets, followed by *in situ* sputtering of Pd (99.99%,  $50\phi \times 1$  mm). The thickness of the Mg–Ni layer was 40 nm and that of the Pd layer was 4 nm. The composition of the Mg–Ni layer was

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close to that of the  $Mg_4Ni$  layer which has the moderate optical modulation range and response time [11]. The substrate temperature during deposition ( $-15\text{ }^{\circ}C$  to  $140\text{ }^{\circ}C$ ) was controlled using an electric heater or liquid nitrogen in a vacuum chamber.

## 2.2. Sample characterization

Characterization of the thin films was performed with XRD, XPS, and a scanning electron microscope (SEM). XRD measurements were used for investigation of the crystalline structures of the Mg–Ni thin films after annealing or cooling using a Rigaku RAD system. XPS depth profiling was used to obtain information about the elemental composition as well as gradients in the samples using a VG Sigma Probe. SEM observations were performed for observation of surface changes after hydrogen gas loading using an FE-SEM (Hitachi S4300). Optical transmittance changes that occur upon hydrogen loading by exposure to 4%  $H_2$  in Ar gas were measured using a semiconductor laser with a wavelength of 670 nm and a Si photo diode.

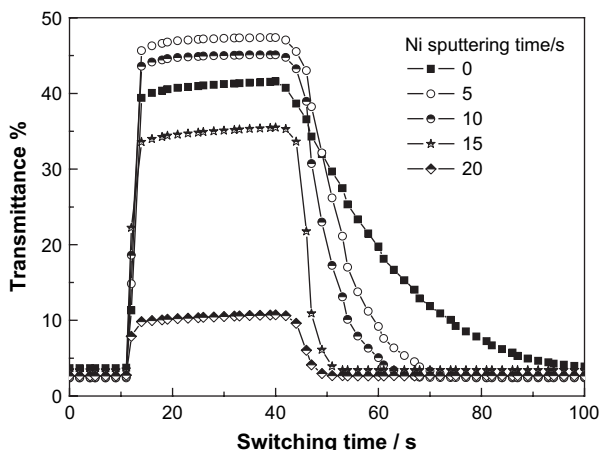
## 2.3. Electrochemical measurements

Electrochemical measurements were carried out using a GPIB potentiostat/galvanostat (HA501G, HOKTO DENKO Ltd.) at  $25\text{ }^{\circ}C$  using a conventional three-electrode glass cell with a Pt counter electrode, an HgO/Hg reference electrode and a Ni–Mg alloy thin film working electrode in alkaline solution (1 M KOH). The cyclic potential range for cyclic voltammetry was set in the potential region between  $+0.5\text{ V}$  and  $-1.20\text{ V}$  vs HgO/Hg reference. Currents and transmittances of  $Mg_4Ni$  thin films were recorded as a function of electrode potential simultaneously. Optical characteristics were obtained *in situ* by optical photometry using a semiconductor laser of 670 nm and a Si photo diode.

## 3. Results and discussion

### 3.1. Sputtering sequence and switching kinetics

Exposure of the thin film to 4%  $H_2$  in Ar causes a marked change from the metallic state to the transparent state upon hydrogenation. The thin film reverts to the metallic state upon exposure to air due to dehydrogenation. The black squares in the plot shown in Fig. 1 represent the optical switching response of Pd/ $Mg_4Ni$  samples. The dehydrogenation speed of Pd/ $Mg_4Ni$  thin films is slower



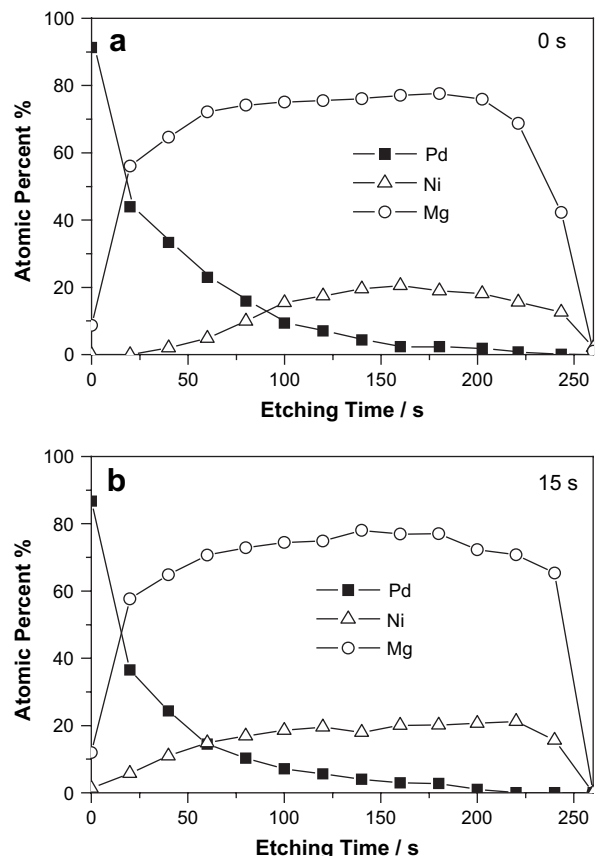
**Fig. 1.** Hydriding and dehydriding kinetics of the Ni-compensated Pd/ $Mg_4Ni$  thin films (the designated time indicates the sputtering time of additional Ni deposition). The thickness of the  $Mg_4Ni$  film is 40 nm and the top layer of Pd is 4 nm.

than the hydrogenation rate [11]. As shown in Fig. 1, the transition from the transparent state takes 2–3 s, while the reverse transition takes 60 s.

We characterized the depth profile of the deposited sample by XPS measurements and found that the slow rate of dehydrogenation is related to a characteristic interface structure between the Pd and  $Mg_4Ni$  layers. Fig. 2 shows the depth profile of Pd/ $Mg_4Ni$  thin films determined by XPS measurements. The uppermost graph in Fig. 2(a) clearly shows that the interface between the Pd and Mg–Ni layers is not sharp. Pd is distributed within the Mg–Ni layer and Mg is distributed within the Pd layer. The diffusion and migration of metallic Mg to surface of thin films in deposition and switching processes have been reported [12]. These phenomena have been interpreted by thermodynamics calculations which indicate that the total energy is reduced by segregation of Mg to the surface [12].

It should be noted that there is a region which contains almost no nickel, even after 30 s of etching time. In this region, only  $MgH_2$  is formed and may block the diffusion of hydrogen in the dehydrogenation of the hydride state, because the rate of hydrogen diffusion in the  $MgH_2$  layer is very slow [13].

To compensate for the deficiency of Ni near the surface region, we carried out an additional Ni deposition after the Mg–Ni deposition and before the Pd deposition. Fig. 2(b) shows the depth profiles of the Ni-compensated samples. The Ni-deficient region decreases in size with additional Ni sputtering. The optical switching responses of corresponding samples are shown in Fig. 1. As additional Ni sputtering time increases, the dehydrogenation rate increases, while the additional sputtering time is less than 10% when the Ni sputtering time exceeds 20 s. This may be due to the formation of the Ni layer at the surface. Additional sputtering of Ni for approximately 5–10 s provides optimal sputtering time.



**Fig. 2.** Depth profiling of normal Pd/ $Mg_4Ni$  (a) and Ni-compensated Pd/ $Mg_4Ni$  thin films (b). The XPS Mg 1s, Ni 2  $p_{3/2}$ , and Pd 3d $_{5/2}$  peaks were normalized to a calculation of atomic percentage of Pd/ $Mg_4Ni$  thin films.

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