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Optical Property of Nickel-Magnesium Alloy Switchable Mirror Thin Films

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Nickel-magnesium alloy thin films were prepared by DC magnetron sputtering with Ni, Mg and Pd targets. Basic optical switching properties by exposure to hydrogen gas and air have been investigated for the samples prepared with various deposition conditions changing induced power ratio of Mg to Ni targets, thickness of Ni-Mg layer and thickness of Pd overlayer. After the optimization of sputtering conditions, Pd capped Ni-Mg thin films showed switchable mirror property with good reproducibility. No degradation was observed after initial 10 switching cycles. However, optical transmittance of these films in the hydride state is not high enough for window applications.

Key words: Ni-Mg alloy, switchable mirror, hydride, palladium, optical transmittance

1. INTRODUCTION

After the discovery of rare earth hydride thin films, switchable mirror materials have been attracted much attention as a new kind of chromogenic material [1-4]. Ordinary electrochromic material such as WO_3 is changed from transparent state to absorbing colored state, while switchable mirror material is changed from shiny mirror state to transparent state. Switchable mirrors are supposed to have better energy efficiency when they are used for building windows than ordinary electrochromic windows because switchable mirror layer is less heated up in the nontransparent state.

Although rare earth hydride shows good optical switching by exposure to hydrogen, they have problem for window applications in the view point of resource and cost. Some other magnesium alloys such as Y-Mg [5] Gd-Mg [6], and Sm-Mg [7] are investigated as alternate switchable mirror materials, but still they have the cost problem. Recently, Lawrence Berkley National Laboratory group found that Ni-Mg alloy thin films also show switchable mirror property [8]. Nickel and magnesium are very common materials and their cost is low, which is suitable for window applications.

Ni-Mg alloy thin films are quite new material as an optical switching material, the detail of optical property dependence on deposition condition has been not clear yet. In this paper, we investigated the basic optical switching property of Ni-Mg alloy thin films prepared by various sputtering conditions. Also a brief check of durability of their siwitching behavior has been done.

2. EXPERIMENTAL

Ni-Mg alloy thin films were prepared by DC magnetron sputtering. Figure 1 shows the schematic diagram of deposition apparatus. This deposition chamber has three magnetron sputtering guns (MightyMak). Metal targets of magnesium, nickel and palladium were set to each gun. Personal computer controlled DC power supplies were used for discharge. The personal computer monitors the cathode voltage and discharge current, and it keeps the induced power to sputtering gun constant.

The base pressure was 2 x 10^{-5} Pa. Introducing Ar gas was controlled by computer controlled mass flow controller. Substrate is glass with the size of 15x15 mm and thickness of 1mm. All depositions have been done in unheated condition. Sample holder was rotated in horizontal plane with 5 rpm during deposition.

After evacuation, co-sputtering of Ni and Mg targets has been done for deposition of Ni-Mg alloy thin films. Ni power was fixed to 27W. Mg power was varied from 25W to 35W. Then very thin Pd layer was coated onto the alloy film *in situ* condition and the sample was taken out from the chamber. Typical deposition rates were about 0.5 nm/s for Ni-Mg deposition and 0.2 nm/s for Pd deposition, respectively. The deposition conditions are summarized in Table I.

Element composition was determined by X-ray fluorescence spectrometer (Shimadzu XRF-1700WS). Crystallinity of deposited films were analyzed by X-ray diffractometer (Rigaku RAD system). Film thickness was measured by stylus profilometer (Kosaka ET-350).

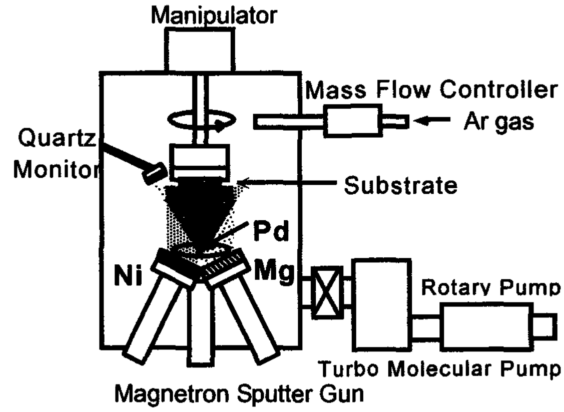


Fig. 1 Schematic diagram of sputtering apparatus.

Table I. Sputtering conditions.

Method	DC Magnetron Sputtering
Targets	Mg(99.9%) 50Φx3mm, Ni(99.9%) 50Φx3mm Pd(99.99%) 50Φx1mm
Base Pressure	2 x 10^{-5} Pa
Ar Flow Rate	200 sccm
Total Pressure	1.2 Pa
Discharge Power	Ni:27W Mg:25-35W Pd:14W
Target-Substrate Distance	150 mm
Sample Size	15 x 15 x 1 mm

There are two kind of methods to make switching for switchable mirror materials. One is using electrolyte like electrochromic materials. Another way is using hydrogen gas like gasochromic materials [9]. In this work we investigate the gasochromic property of Mg-Ni alloy thin films, because gasochromic switching is more prominent for these materials compared with electrochromic switching [8].

Figure 2 shows our characterization system of optical switching using hydrogen gas. Sample surface was facing the small vacuum chamber with silicon rubber O-ring. Firstly the inside of the chamber was evacuated by rotary pump, then 0.1 MPa hydrogen gas was introduced to the chamber. The change of optical transmittance was measured by the combination use of semiconductor laser (λ = 670 nm) and Si photodiode. Monitoring the output current of the photodiode, optical transmittance at the wavelength of 670 nm can be measured every 10 seconds very precisely. In this paper, transmittance means the total transmittance of glass substrate, Ni-Mg and Pd layers.

Optical transmittance and reflection spectra in the

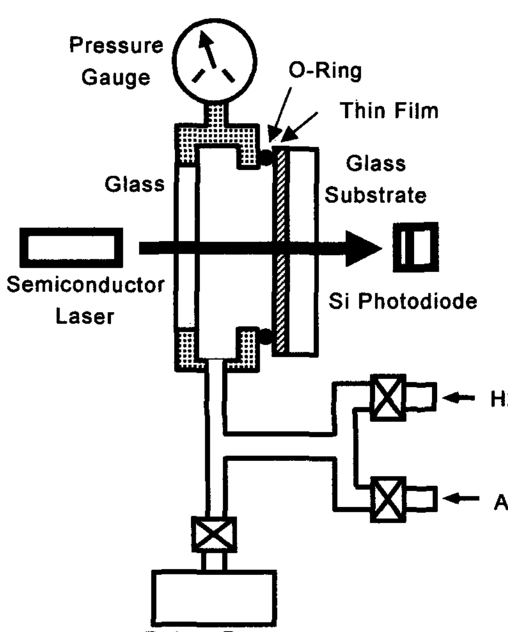


Fig. 2 Schematic diagram of optical characterization system.

metallic and hydride states were measured by UV-VIS-NIR optical photometer (JASCO V570). At measurements, the small chamber was set in the optical path of the photometer.

3. RESULTS AND DISCUSSION

3.1 Composition Dependence

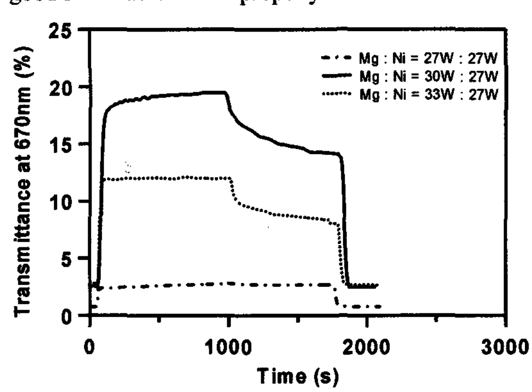
Firstly we investigated the composition dependence of alloy thin films. We prepared the samples with various power ratio and measured their optical switching properties.

All as-deposited films had shiny metallic surface and optical transmittance was very low. We set the prepared samples to the characterization system and observed the optical switching by exposure to 0.1 MPa hydrogen gas.

Optical transmittance changes at 670 nm for the different composition samples are shown in Fig. 3. Every sample consists of 50 nm Ni-Mg layer and 5 nm Pd layer. The chamber is evacuated at t = 0, and 0.1 MPa hydrogen is introduced at t = 70 s. After the exposure, hydrogenation occurs and transmittance of the sample is increasing rapidly within about 30 second. Then the transmittance is increasing gradually. The chamber is evacuated again at t = 950 s. In the vacuum state, the transmittance is decreasing. After the introduction of 0.1 MPa air at t = 1750 s, the transmittance goes back to the initial level rapidly (within about 30 sec).

The dynamic range of optical switching shows strong dependence on element composition of the prepared samples. The sample with the Mg:Ni power ratio of 30W:27W shows the largest switching level. The transmittance in the hydride state is getting smaller with increasing Mg power from 30 W. Also the transmittance in the hydride state is decreasing rapidly with decrease of Mg power from 30 W.

The element composition of prepared film is determined by the X-ray fluorescence spectrometer. The results are summarized in Table II. It shows that the sample whose composition is close to Mg_2Ni has good switchable mirror property.



Fig, 3 Optical switching of samples prepared with different power ratio of Mg to Ni targets.

Table II Compositions of the samples.

Power ratio of Mg:Ni	Composition ratio of Mg:Ni
27W : 27W	1.82 : 1
30W : 27W	2.05 : 1
33W : 27W	2.21 : 1

3.2 Crystalline Structure

Crystalline structure of prepared films were examined by XRD measurements. There is no specific peak in the XRD patterns for all samples prepared in this work. It means that all samples have amorphous structure.

3.3 Switching Mechanism

Although the switching mechanism of Ni-Mg thin films has been not well understood yet, Mg_2NiH_4 and MgH_2 are supposed to be formed in the hydride state. Our Mg_2Ni thin film looks dark brown in the hydride state. Mg_2NiH_4 is a red solid [10], while MgH_2 is a colorless insulator [11]. Hence we think that Mg_2NiH_4 is the dominant material in the hydride state.

In this case, the reaction formula is considered to be described as following;

$$Mg_2Ni + 2H_2 \longrightarrow Mg_2NiH_4 \quad \text{----(1)}$$
$$Mg_2Ni + 2H_2O \longleftarrow Mg_2NiH_4 + O_2 \quad \text{----(2)}$$

(1) is for hydrogenation and (2) is for dehydrogenation.

The composition dependence shown in Fig. 3 means that excess and insufficient Mg from stoichiometric Mg_2Ni may block the formation of Mg_2NiH_4 in the film.

3.4 Thickness Dependence

Next we investigated the dependence of switching properties on thickness of Mg_2Ni layer. Figure 4 shows the optical transmittance of Mg_2Ni films with different thickness. Every sample has 5 nm Pd overlayer. The switching sequence is the same as that described in 3.1.

The optical transmittance of the sample of 70 nm in the hydride state is much lower than that of the sample of 50 nm. It may because hydrogen can not penetrate the inside of thicker film and Mg_2Ni remains in the film.

The transmittance of the sample of 30 nm in the hydride state is higher than that of the sample of 50 nm. However the transmittance in the metallic state is also high and not completely metallic.

From these results, we select the thickness around 50 nm as a suitable condition for gasochromic switching of Mg_2Ni thin film.

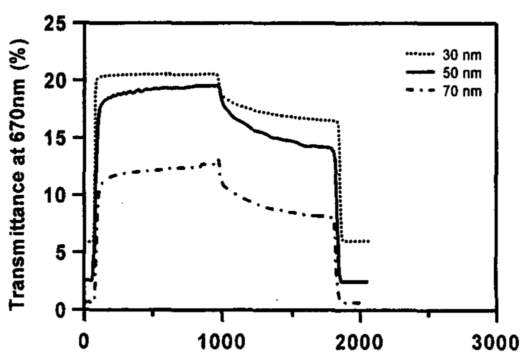


Fig. 4 Optical switching of Mg_2Ni thin films prepared with different thickness.

3.5 Pd Layer Dependence

To investigate the effect of Pd coating, the samples with different thickness of Pd overlayer were prepared. Transmittance changes of the samples with four kind of thickness of Pd layer are shown in Fig. 5.

The transmittance of the sample with 7 nm Pd layer in the hydride state is lower than that of the sample with 5 nm Pd layer. It may be because the total transmission of the sample is affected by the transmittance of Pd layer. The transmittance of the sample with 3 nm Pd layer is a little bit higher than that of the sample with 5 nm. But transition speed to the metallic state by exposure to air is apparently slow. Therefore we think that the sample with the 5 nm Pd layer is the best one.

It should be noted that the Mg_2Ni film without Pd overlayer (Pd = 0 nm) showed no switching change at all. It means overcoated Pd layer is essential for gasochromic switching as a catalyst.

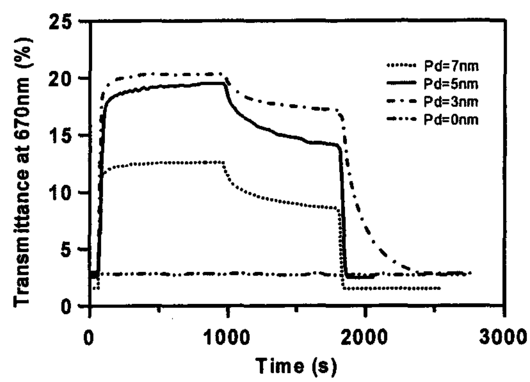


Fig. 5 Optical switching of Mg_2Ni thin films overcoated with different thickness of Pd.

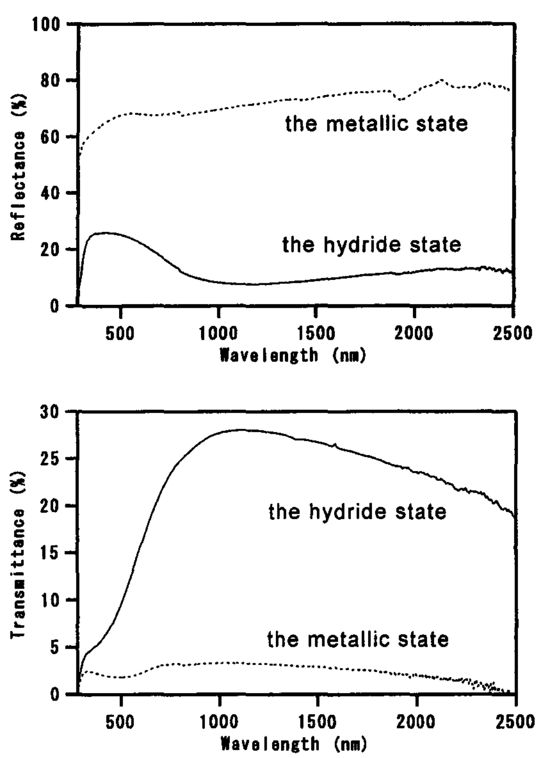


Fig. 6 Reflectance (upper) and transmittance (lower) spectra of Mg_2Ni thin films in the metallic (broken line) and hydride (solid line) states.

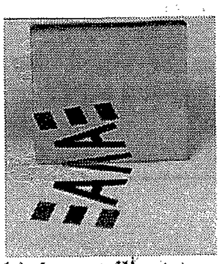
3.6 Optical Spectra

After the optimization of deposition conditions, optical spectra were studied for the best sample. This sample was prepared with Mg-Ni power ratio of 30W:27W, 50 nm Ni-Mg layer and 5 nm Pd layer.

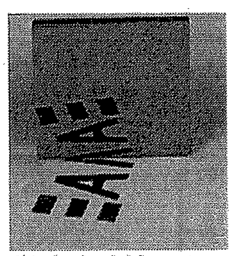
Optical reflectance and transmittance spectra were measured by optical photometer in the metallic and hydride states. Reflectance spectra were measured from the backside. Figure 6 shows the transmittance and reflectance spectra of Mg_2Ni thin film in both states. Reflectance change between both states is more than 50% in the infrared region, while transmittance change is about 22% at the wavelength of 1000 nm.

Figure 7 shows the photographs of Mg_2Ni thin films in the metallic and hydride states for the same sample. In the metallic state, the sample looks shinny metallic. However, as shown in Fig.7 (b) and (c), this film is not so transparent in the hydride state. It has dark brown color. As mentioned above, this color comes from the Mg_2NiH_4 which is formed in the film.

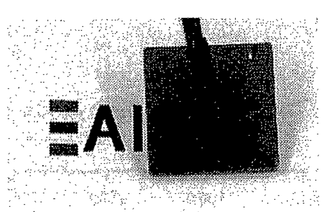
From the transmittance spectrum in Fig. 6, we calculate the visible transmittance of Mg_2Ni thin film in the hydride state, and the result is 16%. For the practical use of this material as window coating, this visible transmittance is too low. The most important subject of this material for the window applications is to raise the transmittance in the hydride state.



(a) the metallic state



(b) the hydride state



(c) front view of the hydride state

Fig. 7 Photographs of Mg_2Ni thin film in the metallic and hydride states.

3.7 Durability Test

Durability is very important for practical use of this material. We briefly studied the durability for repeating gasochromic switching of Mg_2Ni thin films in the small chamber shown in Fig. 2. Figure 8 shows the change of transmittance at 670 nm by alternate exposure of hydrogen and air every 10 minutes. Hydrogen and air were introduced to the small chamber with the pressure of 0.1 MPa after evacuation.

Transmittance in the metallic state is not changed during repetition. Transmittance in the hydride state is a little bit increased after 5 cycles. Up to the first 10 cycles, this material shows rather good durability for switching.

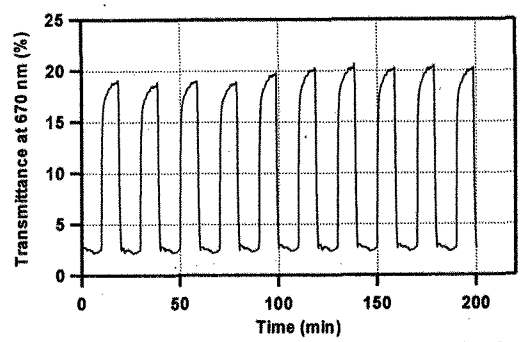


Fig. 8 Initial durability test of the switching of Mg_2Ni thin film.

4. CONCLUSIONS

Ni-Mg alloy thin films have been prepared using DC magnetron sputtering and their gasochromic switching properties were investigated.

After optimization of deposition conditions, Mg-Ni thin films whose composition is close to Mg_2Ni with 50 nm Mg-Ni layer and 5 nm Pd ovelayer showed the best switchable mirror property. After exposure to 0.1 MPa hydrogen, Mg_2Ni thin film changed from the metallic to the absorbing hydride state.

The Mg_2Ni thin film showed good durability for the initial 10 switching cycles. However, the optical transmittance in the hydride state should be improved for the practical window applications.

5. ACKNOWLEDGEMENT

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