Solar Energy Materials and Solar Cells 183 (2018) 48–51

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

# Switching properties of switchable mirrors using palladium-ruthenium catalytic layers

Y. Yamada*, M. Ohura, K. Yoshimura

*National Institute of Advanced Industrial Science and Technology (AIST), Anagahora 2266-98, Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan*

ARTICLE INFO

*Keywords:*
Switchable mirrors
Mg-Y alloys
Pd-Ru alloys
Catalytic layers
Switching properties

ABSTRACT

In preparing switchable mirrors, palladium (Pd) was used as a catalyst for hydrogenation and dehydrogenation, and to prevent oxidation of the switchable layer. To reduce the cost, Pd was alloyed with ruthenium (Ru) and used as a catalytic layer, since the price of Ru is approximately one-tenth that of Pd. Switchable mirrors of magnesium-yttrium (Mg-Y) alloy thin films coated with a Pd-Ru layer were prepared by direct-current magnetron sputtering method. Their optical switching properties between reflective and transparent states were studied using gasochromic method. The mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of up to $\alpha \approx 0.6$ showed nearly the same switching time from reflective to transparent state as those coated with pure Pd, while the mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of $0.2 \leq \alpha \leq 0.4$ showed shorter switching times from transparent to reflective state than those coated with pure Pd. Furthermore, the alloy-coated mirrors with shorter switching times had approximately 2–3 times higher switching durability than those coated with pure Pd. These shorter time and higher durability may be because Pd-Ru alloy prevents oxidation of the underlying layers more effectively than pure Pd. Thus, Pd-Ru alloy is one of the most promising catalysts for switchable mirrors.

## 1. Introduction

The use of chromogenic materials, such as electrochromic [1], thermochromic [2], and gasochromic [3] materials for smart windows has been studied extensively for many years. Recently, electrochromic devices are utilized as smart windows for airliners and buildings; however, they have not been widely used mainly because of their high installation cost.

To reduce the cost of preparing switchable mirrors, previous research has focused on gasochromic technology [4] because it does not require patterned electrodes or expensive transparent conductors such as ITO, and it does not suffer from the pinhole effect and microcrack formation [5–8]. Researchers have also attempted to prepare the mirrors on flexible plastic sheets using roll-to-roll coating to realize high throughput in fabrication. In the mirrors, Pd is used as catalyst to facilitate hydrogenation and dehydrogenation, and protect underlying layers from oxidation. Although Pd is an expensive material, the cost of the mirror is evaluated to be 1 euro/m$^2$ because the Pd layer is very thin (3 nm). However, the initial cost of a Pd sputtering target for large area deposition is extremely expensive, for example, a Pd target with the size of 1500 × 200 × 20 mm is estimated to be approximately 2 million euros.

Thus, in this study, to reduce the target cost, we alloyed Pd with cheaper metals than Pd. From the viewpoint of protection of switchable layers from oxidation, noble metals are suitable. Therefore, we have selected Ru and Ag, which are satisfied the above two requests: The price of Ru is approximately one-tenth that of Pd. In this study, we prepared switchable mirrors using Mg-Y alloy coated with Pd-Ru [9] or Pd-Ag catalyst and studied their effects on the optical switching properties of the alloy. The mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of up to $\alpha \approx 0.6$ showed nearly the same hydrogenation time as those coated with pure Pd, while the mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of $0.2 \leq \alpha \leq 0.4$ showed shorter dehydrogenation time than those coated with pure Pd. Furthermore, the mirrors coated with Pd-Ru, which showed shorter switching times, had approximately 2–3 times higher switching durability than those coated with pure Pd. In contrast, the mirrors coated with Pd-Ag showed a sharp decrease in switching speed during hydrogenation and dehydrogenation, especially dehydrogenation, with increasing Ag composition.

## 2. Experimental

Switchable mirrors were prepared on glass substrates by direct-current (dc) magnetron sputtering. Mg-Y alloy layers, ~50 nm thick, were deposited by co-sputtering from Mg (99.99%) and Y (99.8%) targets. Ta, ~2 nm thick, was subsequently deposited on these thin

* Corresponding author.
*E-mail address:* yasusei-yamada@aist.go.jp (Y. Yamada).

https://doi.org/10.1016/j.solmat.2018.04.007
Received 1 February 2018; Received in revised form 30 March 2018; Accepted 6 April 2018
0927-0248/ 

layers by sputtering from a Ta target (99.99%) [10,11]. Furthermore, the bilayered films were coated with Pd alloys, ~3 nm thick, by co-sputtering from Pd (99.99%) and Ru (99.99%) or Ag (99.99%) targets. These processes were carried out without breaking the vacuum. Here, $Mg_{0.4}Y_{0.6}$ was selected, because when it was used in a previous study [10], the switchable mirror showed good optical properties and a high switching durability between reflective and transparent states, of over 10,000 cycles. The compositions of the Pd-Ru and Pd-Ag alloys were controlled by adjusting the sputtering power ratio of Pd to Ru and Pd to Ag targets; the power of the Pd, Ru, and Ag targets were in the range of 0–30 W, 0–52 W and 0–20 W, respectively, and the compositions were evaluated using the sputtering rate of each target, which was estimated with X-ray reflectivity measurements. The details of the preparation conditions are described in literature [11].

The optical switching properties of the mirrors between the reflective and transparent states were studied using gasochromic switching method. They switched from reflective to transparent state when exposed to 4% $H_2$ in Ar and back to reflective state when exposed to air. The modulation in optical transmittance was monitored by measuring the light intensity of GaAs infrared emitting diodes ($\lambda$ = 940 nm) coupled with Si photodiodes.

## 3. Results

### 3.1. Hydrogenation and dehydrogenation speed

Switchable mirrors of Mg-Y alloy thin films coated with thin Pd-Ru films of various compositions ($Pd_{1-\alpha}Ru_{\alpha}$, $0 \le \alpha \le 0.8$) were prepared. All as-deposited initial films had a shiny metallic surface with low optical transmittance, indicating a reflective state of the switchable mirrors. By exposing the surface films to 4% $H_2$ in Ar gas, their transmittance increased drastically owing to hydrogenation of the Mg-Y layers, which means the optical properties changed from reflective to transparent states. By exposing the hydrogenated films to air afterward, their transmittance decreased owing to dehydrogenation. Thus, all prepared films showed optical switching properties that are similar to mirrors coated with pure Pd films. Fig. 1 shows modulations of transmittance at $\lambda$ = 940 nm as a result of hydrogenation (a) and dehydrogenation (b), as a function of elapsed time ($t$) for the mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of $\alpha$ = 0, 0.4, 0.6, and 0.7. During hydrogenation (Fig. 1a), the normalized transmittance ($T$) was respectively 0 and 1 at the start of hydrogen flow ($t$ = 0) and after hydrogenation, while during dehydrogenation (Fig. 1b), the $T$ was respectively 1 and 0 at the stop of hydrogen flow ($t$ = 0) and at the $t$ = 10,000 s. During hydrogenation, switching speed gradually decreased with increasing Ru composition, while during dehydrogenation, the mirrors with $\alpha$ = 0 and 0.4 had similar switching speeds, and the mirrors with the higher Ru composition had slower speeds as shown in the inset of Fig. 1(b). Furthermore, the mirrors stored in the atmosphere for 2 weeks had no degradation of switching properties.

In contrast, mirrors coated with Pd-Ag alloy had different switching properties from those coated with Pd-Ru alloy. Fig. 2 shows modulations of transmittance for the mirrors coated with $Pd_{1-\beta}Ag_{\beta}$ of $\beta$ = 0, 0.2, 0.5, and 0.7. With increasing Ag composition, the switching speed decreased sharply in hydrogenation and dehydrogenation, especially in dehydrogenation. Furthermore, the mirrors stored in the atmosphere for 2 weeks had much slower switching speed than as-deposited mirrors, and the mirror with $\beta$ = 0.7 did not change from the reflective to transparent state, indicating degradation of the mirrors. Thus, we have concluded that Pd-Ag alloys are not suitable catalysts for switchable mirrors.

The switching speeds during hydrogenation and dehydrogenation was dependent on Ru composition as shown in Fig. 1. We studied the switching times during hydrogenation and dehydrogenation as a function of Pd-Ru composition. Each switching time for hydrogenation and dehydrogenation was defined respectively as the elapsed time ($t$) when

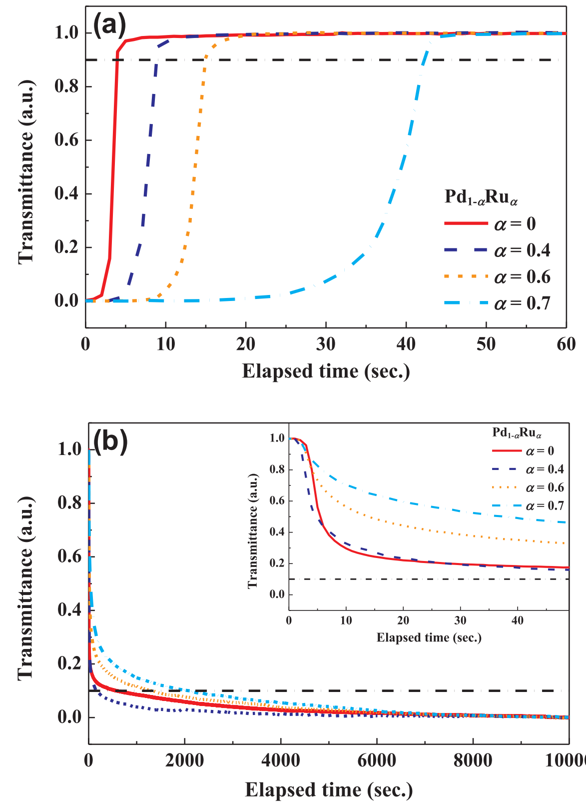


**Fig. 1.** Modulation of transmittance at 940 nm due to hydrogenation (a) and dehydrogenation (b) as a function of elapsed time ($t$) for the prepared Mg-Y switchable mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of $\alpha$ = 0, 0.4, 0.6, and 0.7 with inset showing elapsed time up to 50 s. The dashed-dotted lines indicate $T$ = 0.9 (a) and 0.1 (b) of normalized transmittance.

$T$ increased to 0.9 and when $T$ decreased to 0.1. The dashed-dotted lines indicating $T$ = 0.1 and 0.9 are shown in Figs. 1 and 2. Fig. 3 shows switching time of hydrogenation (a) and dehydrogenation (b) as a function of Ru composition. The mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of up to $\alpha \approx 0.6$ showed nearly the same switching times from reflective to transparent state as those coated with pure Pd; however, the time slightly increased with increase in Ru composition. The hydrogenation time of the mirrors with $Pd_{1-\alpha}Ru_{\alpha}$ of $\alpha > 0.6$ increased sharply with increase in Ru composition. The mirror coated with pure Ru did not switch from the reflective to transparent states, indicating that pure Ru has no catalytic effect on hydrogenation. Therefore, the catalytic effect of the alloy degraded sharply due to excess Ru composition. In addition, the mirrors coated with $Pd_{1-\alpha}Ru_{\alpha}$ of $0.2 \le \alpha \le 0.4$ showed shorter switching times from transparent to reflective state than those coated with pure Pd. The dehydrogenation time of the mirrors with $Pd_{1-\alpha}Ru_{\alpha}$ of $\alpha > 0.5$ increased sharply with increased Ru composition. Thus, we show that it is possible to reduce the cost of the Pd target by alloying with Ru of $\alpha \le 0.4$ without a reduction of switching speed during hydrogenation and dehydrogenation.

### 3.2. Switching durability

We examined the effect of alloying with Ru on switching durability, which is a very important factor for practical applications. Because Mg-Y switchable mirrors have a high switching durability, it takes a very long time to evaluate their switching durability. Therefore, in this experiment, we carried out an accelerated deterioration test by decreasing the thickness of the catalytic layer from 3 to 2 nm and dehydrogenation period from 900 to 100 s. Fig. 4 shows the modulation of transmittance at 940 nm due to hydrogenation and dehydrogenation as a function of switching cycles of the Mg-Y switchable mirror coated with $Pd_{1-\alpha}Ru_{\alpha}$ of