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# Pd distribution of switchable mirrors based on Mg–Y alloy thin films

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ABSTRACT

Pd-capped magnesium–yttrium alloy switchable mirrors were found to have high switching durability of over 10,000 cycles between reflective and transparent states. However, the durability decreased with the decreasing Pd thickness. Switchable mirrors with various Pd thicknesses were then prepared by a direct-current magnetron sputtering method, and the degradation in durability was studied by observing the distribution of each element of the switchable mirrors from the film surface to the substrate. X-ray photoemission spectroscopy and transmission electron microscopy showed that Pd with a short sputtering time (corresponding to layer thickness of 3 nm) resulted in surface oxidation of Mg and Y, and no Pd was present at the surface. The deposited Pd was alloyed with the Mg–Y layer and after taking the sample out from the vacuum chamber a Pd-rich layer appeared between the surface oxides and the Mg–Y layers. With increasing deposition time, a Pd layer was formed on the oxide layer and the Pd layer thickness increased. The mirror with switching durability of over 10,000 cycles had a sufficiently thick Pd top layer of ~7 nm and a very thin oxide layer. This thick Pd layer is believed to be the reason for the high switching durability.



## 1. Introduction

Reducing cooling load in buildings is an important issue with respect to global warming. Metal hydride switchable mirrors [1–9] are promising materials as the switchable glazing in smart windows to contribute to saving energy for air-conditioning because these mirrors can control the optical transmittance by changing their optical reflectance [10].

One of the most serious bottlenecks of these mirrors for window applications is the low switching durability between the reflective and transparent states. Recently, we have found that switchable mirrors using Mg–Y alloy had high switching durability of over 10,000 cycles [9]. However, the transmittance in the transparent state was not so high, only ~35%. We then attempted to improve the transmittance by decreasing the Pd layer thickness because the Pd hydride shows opaque metallic appearance although the hydride of the Mg alloy shows transparent appearance. The switchable mirrors with thinner Pd layer improved the transmittance in the transparent state but the switching durability decreased sharply with the decreasing Pd thickness.

In this paper, we prepared switchable mirrors with various Pd thicknesses and studied the degradation in durability by observing the distributions of each element of the switchable mirrors from the film surface to the substrate.

## 2. Experimental

Mg–Y alloy thin films with a thickness of ~40 nm were prepared on glass substrates using direct-current (dc) magnetron co-sputtering of Mg (99.99%) and Y (99.8%) targets. Pd was subsequently deposited on these thin films without breaking the vacuum by sputtering a Pd (99.99%) target for three different deposition times corresponding to a thickness from 3 to 7.5 nm. In this study, the composition of $Mg_{0.4}Y_{0.6}$ was chosen, because the switchable mirror with this composition had high switching durability between the reflective and transparent states of over 10,000 cycles from our previous study [9]. The details of the deposition conditions are described elsewhere [9].

X-ray photoemission spectroscopy (XPS: Thermo Scientific Sigma Probe) was utilized to determine the distribution of each element that are included in the switchable mirrors, such as Mg, Y, Pd, and O, and the chemical-bonding state of the samples from the film surface to the substrate. The cross-sections of the sample were observed using a scanning transmission electron microscope (STEM: Hitachi High-Technologies HD-2700). The optical switching durability of the mirrors between the reflective and transparent states was estimated by measuring the change in optical transmittance at 940 nm by alternately exposing to 4% $H_2$ in Ar and air using GaAs infrared emitting diodes. The duration time of

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exposure of hydrogen and air was 95 s and 900 s, respectively and one cycle of switching was defined as a set of exposure to hydrogen and subsequent air [9].

## 3. Results

The prepared switchable mirrors using a $Mg_{0.4}Y_{0.6}$ alloy thin film covered with Pd with thicknesses of 3, 4, and 7.5 nm, are hereafter called samples A, B and C, respectively. The mirror with Pd corresponding to a layer thickness of 7.5 nm (sample C) had a high switching durability of over 10,000 cycles [9], while that of 4 nm (sample B) showed a drastically decreased durability of less than 100 cycles, although the transmittance of sample B in the transparent was much higher than that of sample C as shown in Fig. 1. Furthermore, the mirror with 3 nm (sample A) never changed from the reflective to transparent states. Thus, the durability decreased drastically with the decreasing deposition time of Pd.

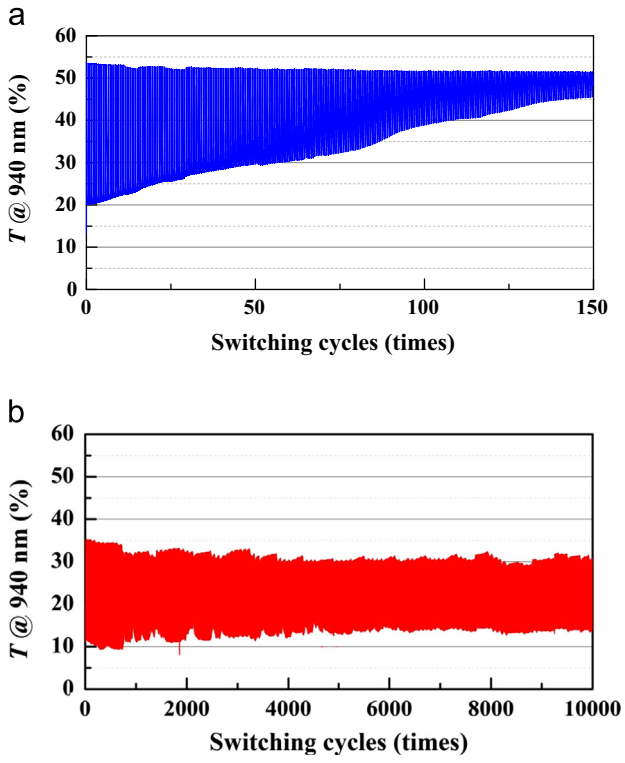


**Fig. 1.** Variation in transmittance at 940 nm due to hydrogenation and dehydrogenation as a function of number of switching cycles for sample B (a) and sample C (b).

Figs. 2–4 show the contour plots of intensities of photoelectrons based on the XPS spectra of Pd 3d, Mg 1s, and Y 3d, and the Auger electron spectra of O KLL transition as a function of etching time with $Ar^+$ ions for samples A, B, and C, respectively. Fig. 2(e)–(h) shows the normalized basic XPS spectra and the Auger electron spectrum at various etching times as marked with a white line in (a)–(d). In the contour plots, the top position at etching time of 0 s and bottom position at the time of ~450 s correspond to the surface of the films and the interface between films and substrates, respectively. Although Pd 3p and O 1s spectra are usually utilized to examine the distribution and chemical bonding of the elements, in this study we used the Pd 3d and O KLL Auger electron spectra because the Pd 3p and O 1s spectra overlap.

For sample A of Fig. 2, Pd 3d peaks were not observed in the surface region with an etching time within ~150 s, although Pd was deposited on top of the Mg–Y layer. In contrast, a Mg 1s peak with a binding energy of ~1304.5 eV was observed at the surface and in the surface region, and Y 3d peaks with binding energies of ~157.5 (5/2) and ~159.5 (3/2) eV were observed from just below the surface in the surface region. These binding energy values indicate Mg–O [11] and Y–O [12] bonds, respectively, and the bonds were supported from the fact that the O KLL peak was also observed in the surface region. Pd peaks, which were not observed at the surface region, appeared inside of the film, indicating that the Pd diffused deeply into the Mg–Y layer all the way down to the substrate. In the region to which Pd diffused, the O KLL peak was not observed and the Mg–Y layer was not oxidized because the peak positions of the binding energy for Mg 1s and Y 3d were ~1303 eV and ~155.5 and 157.7 eV, indicating Mg–Mg [11] and Y–Y [12] bonds, respectively. Thus, the metallic Mg–Y layer including Pd in sample A was covered with MgO and/or $Mg(OH)_2$ and $Y_2O_3$, and without Pd.

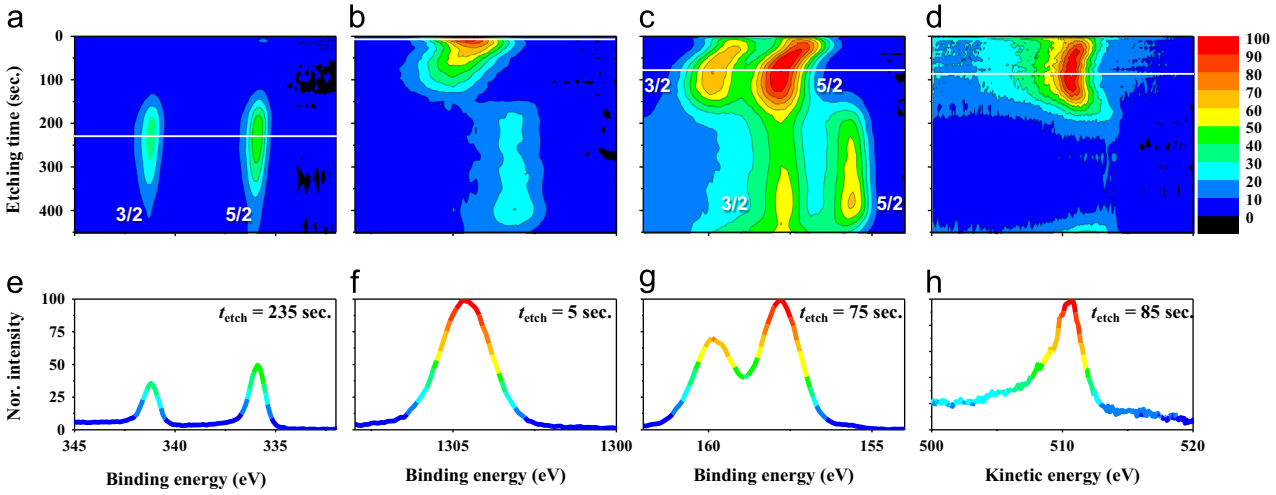


**Fig. 2.** Contour plots of the intensity of photoelectrons based on XPS spectra of Pd 3d (a), Mg 1s (b), and Y 3d (c), and Auger electron spectra of O KLL transition (d) as a function of etching time with $Ar^+$ ions for sample A. Basic XPS spectra and Auger electron spectrum at the various etching time ($t_{etch}$): Pd 3d at $t_{etch}$=235 s (e), Mg 1s at $t_{etch}$=5 s (f), Y 3d at $t_{etch}$=75 s (g), and O KLL at $t_{etch}$=85 s (h). These intensities were normalized using the largest value of each element in the three samples after removing constant background using count rate of binding energy of 330 eV for Pd 3d, 1298 eV for Mg 1s, 152 eV for Y 3d and kinetic energy of 526.6 eV O KLL. Sample A has a Pd thickness of 3 nm.