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Solar Energy Materials
& Solar Cells

Solar Energy Materials & Solar Cells 90 (2006) 485–490

www.elsevier.com/locate/solmat

Metal hydride switchable mirrors: Factors influencing dynamic range and stability

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Received 11 November 2004; accepted 14 February 2005

Available online 9 June 2005

Abstract

Palladium-coated magnesium–manganese–nickel films behave as gasochromic switchable mirrors, becoming transparent on exposure to dilute hydrogen, and reverting to a mirror state on exposure to air. The cycling stability of the optical switching depends upon preservation of the integrity of the Pd catalyst overlayer. Alloying between Mg and Pd causes interdiffusion of the two elements, and leads to degradation in switching speed and eventual deactivation. Incorporation of a thin niobium oxide barrier layer between the active magnesium alloy film and the Pd layer substantially improves the cycling stability of the mirror.

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Keywords: Switchable mirrors; Thin films; Metal hydrides

1. Introduction

Switchable mirrors offer significant advantages over traditional electrochromic devices for control of incident light in architectural and aerospace applications due to their large dynamic ranges in both transmission and reflection in the visible and near-infrared regimes. Magnesium-transition metal alloy films on transparent

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substrates behave as gasochromic switchable mirrors [1,2]. A thin palladium overlayer catalyzes the absorption and desorption of hydrogen when the film is exposed alternately to dilute hydrogen and air. Formation and decomposition of Pd–Mg alloys during cycling results in interdiffusion of Pd and Mg, which leads to lower catalytic activity and oxidation of Mg near the air-exposed surface. These factors act to degrade the optical switching speed and dynamic range of the mirror. Effects on the optical dynamic range, switching speed, and cycling stability of alloy composition, catalyst structure, and barrier layers are discussed.

2. Experimental

Fifty nanometer thick alloy films of $\text{Mg}_x(\text{Ni}_{0.75}\text{Mn}_{0.25})_{1-x}$ were deposited on plain glass and ITO-coated glass substrates by dc magnetron co-sputtering from separate 50 mm diameter Mg and $\text{Ni}_{0.75}\text{Mn}_{0.25}$ targets. To optimize the experimental conditions, films were deposited with variable parameters of Ar pressure (1.25–20 mTorr), deposition time (45–100 s) and composition ($x = 0.79$ – 0.91). Composition was controlled by varying the power applied to each target. The base pressure was kept below 5×10^{-5} Pa. Pd layers 5 nm thick were deposited over the alloy films at 2 mTorr Ar pressure and constant power (13 W). The Pd layer deposition rate was 0.2 nm/s. NbO_x films 1–5 nm thick were deposited by sputtering from an Nb_2O_5 target at Ar pressures ranging from 5 to 40 mTorr. All films were mirror-like in appearance and had very low visible transmittance. Total film thickness was measured by surface profilometry (Dektak II). Films were characterized by atomic force microscopy, Rutherford backscattering spectroscopy (RBS), and Auger electron spectroscopy. Gasochromic mirror-to-transparent state switching was carried out by exposing the films to flowing 4% H_2 in Ar. Switching time was defined as the time to reach 90% of the maximum transmittance. The return to the mirror state was effected by exposure to flowing dry air, with switching time defined as the time to reach 10% of the maximum transmittance. Photopic transmittance was monitored using a filtered silicon detector (International Light).

3. Results and discussion

The change in photopic transmittance of a typical sample during 2 switching cycles is shown in Fig. 1. There is a delay of 5–60 s, depending upon the Mg content, after the first exposure to hydrogen before any change is observed. The mirror-to-transparent transition is rapid, and the maximum transparency is achieved in a few minutes. The dehydrating reaction is somewhat slower, though there is an almost immediate response to the introduction of air. On the second cycle, hydrating occurs with essentially the same speed, but the delay before switching begins is nearly absent, and the maximum transparency is diminished. Dehydrating is considerably faster in the second cycle. Subsequent cycles resemble the second in shape, with a gradual decrease in dynamic range (within the same time period) and transition

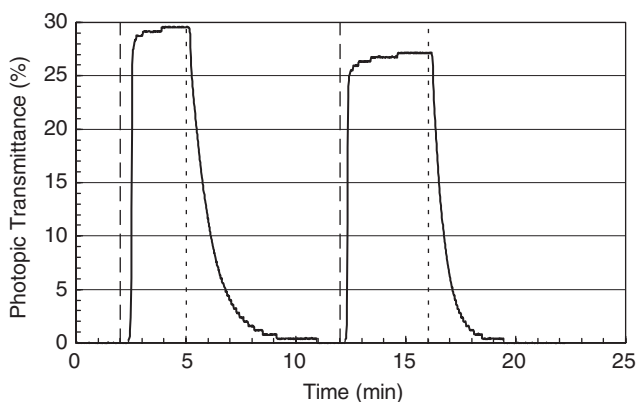


Fig. 1. Photopic transmittance vs. time of 50 nm $\text{Mg}_{0.90}(\text{Ni}_{0.75}\text{Mn}_{0.25})_{0.10}$ film on plain glass with 5 nm Pd overlayer. The times at which H_2 was introduced are designated by vertical lines with long dashes, air introduction by lines with short dashes.

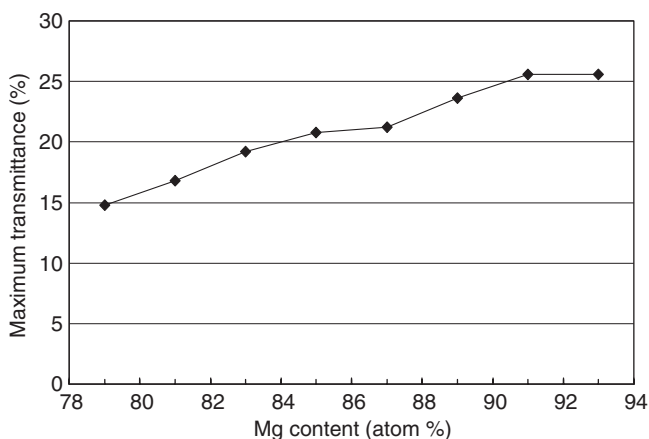


Fig. 2. Maximum transmittance in hydride state of 50 nm $\text{Mg}_x(\text{Ni}_{0.75}\text{Mn}_{0.25})_{1-x}$ films on ITO-coated glass with 5 nm Pd overlayer as a function of composition.

speed. The maximum transparency (first cycle) varied considerably with film composition (Fig. 2), increasing with Mg content. This is expected, since the switching mechanism involves conversion of the metals to the red–orange ternary hydrides Mg_2NiH_4 and Mg_3MnH_7 , along with the binary hydride MgH_2 , which is colorless and highly transparent in the visible range. The switching time, however, was shortest for samples containing about 87% Mg, and increased sharply beyond this level, as shown in Fig. 3. This can be understood in terms of the catalytic behavior of the transition metals for conversion of Mg to MgH_2 . When insufficient catalyst is available, Mg takes up hydrogen very slowly.

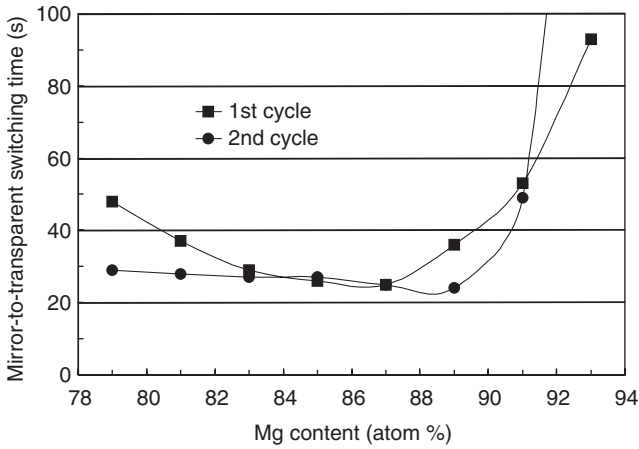


Fig. 3. Mirror-to-transparent switching times for 50 nm $Mg_x(Ni_{0.75}Mn_{0.25})_{1-x}$ films on ITO-coated glass with 5 nm Pd overlayer as a function of composition.

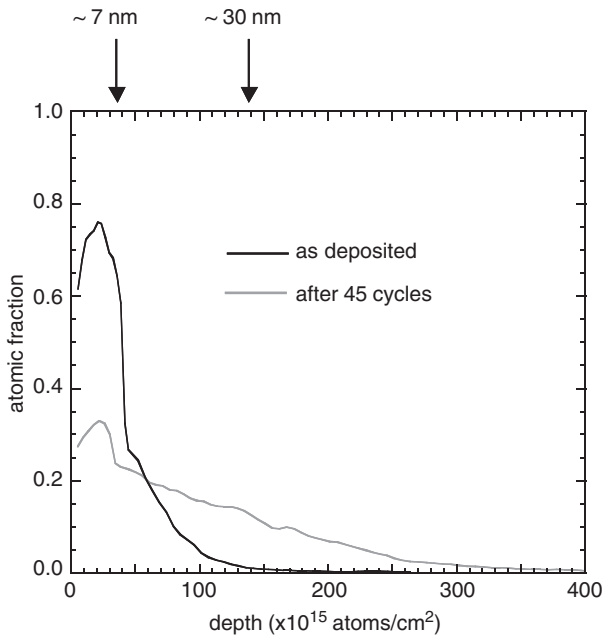


Fig. 4. PBS depth profiles (atomic fraction Pd vs. depth from surface) in composite film before and after cycling.

Migration of the Pd catalyst layer into the Mg alloy film is believed to be one cause of deterioration in the performance of samples over many cycles. The Pd depth profile from RBS (Fig. 4) in a sample before and after 45 gasochromic cycles shows

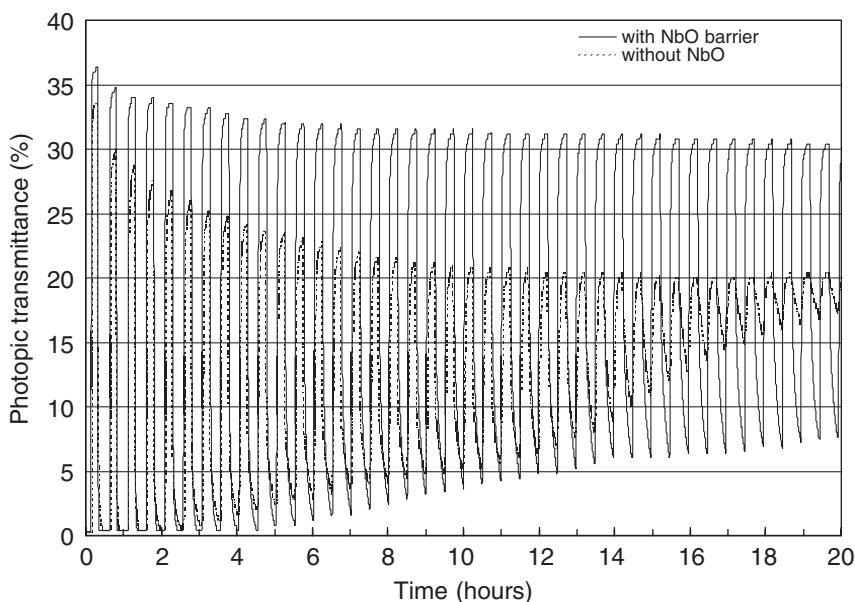


Fig. 5. Gasochromic cycling of 50 nm $\text{Mg}_{0.89}(\text{Ni}_{0.75}\text{Mn}_{0.25})_{0.11}$ films on plain glass with 5 nm Pd overlayer, with and without 1 nm NbO_x barrier layer.

significant penetration into the alloy film, with nearly complete disappearance of the boundary between the two layers. AES data show a similar Pd profile, and also show migration of Mg, but not the transition metals, toward the surface (i.e., into the Pd layer). These phenomena are likely due to formation of Mg–Pd alloys such as Mg_6Pd and Mg_5Pd_2 , which have been found by X-ray diffraction in Mg films coated with Pd and stored at 45 °C [3]. The alloys dissociate on exposure to hydrogen, but may reform during or after dehydrogenating. To test the effect of a barrier layer, samples were prepared with a thin (1–5 nm) niobium oxide layer between the Pd and Mg alloy layers. This material was chosen because it has been reported to catalyze hydrogen uptake and release by Mg powder [4], and because NbO_x thin films are transparent for $x \sim 2.5$. Fig. 5 compares the cycling behavior of otherwise identical samples with and without a 1 nm NbO_x barrier layer. Note that the apparent loss of dynamic range with cycle number is due to slower kinetics rather than to a change in the actual limits of switching. The maximum transmission achieved was slightly improved by the addition of the oxide layer, and the deterioration in switching speed was much slower.

4. Conclusions

The dynamic range and transition kinetics of gasochromic switchable mirrors based on hydrogen absorption and desorption by magnesium–manganese–nickel

films depend upon the film composition and structure. The stability of reversible optical switching is degraded by interdiffusion of Pd and Mg. The presence of a thin niobium oxide barrier layer between the optically active Mg alloy and Pd catalyst layers was found to be highly beneficial to the gasochromic cycling stability of these films.

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, State and Community Programs, Office of Building Research and Standards of the US Department of Energy under contract no. DE-AC03-76SF00098.

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