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Mg–Ni–H films as selective coatings: Tunable reflectance by layered hydrogenation

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Unlike other switchable mirrors, Mg_2NiH_x films show large changes in reflection that yield very low reflectance (high absorptance) at different hydrogen contents, far before reaching the semiconducting state. The resulting reflectance patterns are of interference origin, due to a self-organized layered hydrogenation mechanism that starts at the substrate interface, and can therefore be tuned by varying the film thickness. This tunability, together with the high absorptance contrast observed between the solar and the thermal energies, strongly suggests the use of these films in smart coatings for solar applications. © 2004 American Institute of Physics.

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The discovery of the YH_x switchable mirrors by Huiberts *et al.*¹ in 1996 has been followed by extensive studies on rare-earth hydride films. Upon absorbing hydrogen, a switchable mirror transforms from a shiny metal to a transparent semiconductor. The same behavior was later observed in Mg-alloyed rare-earth hydrides² and Mg–Ni hydrides.³ However, at a low hydrogen concentration, the Mg–Ni hydrides also present a third intriguing “black” state with low reflectance and zero transmittance in the whole visible range,⁴ which immediately suggests their application as switchable smart coatings in, e.g., solar heat collectors.

Since this type of application generally involves absorption of the solar spectrum (at photon energies between 0.5 $< E < 4$ eV) and/or emission of thermal radiation (at $E < 0.5$ eV, for 100 °C),⁵ investigation of the switching behavior in the infrared is also essential. In this letter, we study the peculiar optical patterns observed in Mg_yNiH_x films ($y \sim 2$) during hydrogenation ($0 < x < 4$) in the infrared between $0.2 < E < 1$ eV ($1.2 < \lambda < 6.2$ μm), with special attention to their applicability as selective tunable absorbers.

Films of Mg_yNi ($1.4 < y < 2.4$), with a thickness between 140 and 500 nm, are deposited on CaF_2 substrates by magnetron sputtering from a Mg target with Ni additions. The background and Ar pressures are 10^{-5} Pa and 1 Pa, respectively. The films are covered with a thin (3–11 nm) Pd layer both to protect the films against oxidation and to catalyze the hydrogen uptake. Profilometry and Rutherford backscattering are used to measure the film thickness and composition. Optical measurements at near-normal incidence ($\sim 15^\circ$) are performed from the substrate side *in situ* during hydrogen loading and unloading in a Bruker IFS 66 Fourier transform infrared spectrometer. Simultaneously, the electrical resistivity of the film is recorded in a van der Pauw configuration.⁶ During loading, the hydrogen gas pressure is adjusted between 10^2 and 10^5 Pa, depending on the kinetics of the sample. For unloading, the films are exposed to air at temperatures between 30 and 120 °C.

Mg_yNi ($y \sim 2$) films exhibit metallic behavior with resistivities, ρ , of about $50 \mu\Omega\text{cm}$ and high reflectance values that vary between 0.85 at 0.2 eV and 0.6 at 1 eV. As shown in Fig. 1 for 0.85 eV ($\lambda = 1.46 \mu\text{m}$), already a small amount of H in the films (short loading times or low ρ) is enough to dramatically decrease the reflectance while the resistivity still shows clear metallic behavior. This highly absorbing state is the natural extension to infrared energies of the “black state” observed in Mg_2NiH_x films in the whole solar range.^{4,7} A further increase of the hydrogen content produces alternating recovery and loss of reflectance and reveals that the highly absorbing states are not, or not only, related to a particular hydrogen composition. Finally, Mg_2Ni is transformed into Mg_2NiH_4 , which is a semiconductor⁷ with a band gap of about 1.6 eV,⁸ and the film becomes transparent, as indicated by the onset of the transmittance T in Fig. 1. In the fully loaded state, ρ is of the order of $10 \text{ m}\Omega\text{cm}$.⁹

Figure 2 shows contour plots of the reflectance R , as a function of photon energy, E , and resistivity (an indirect

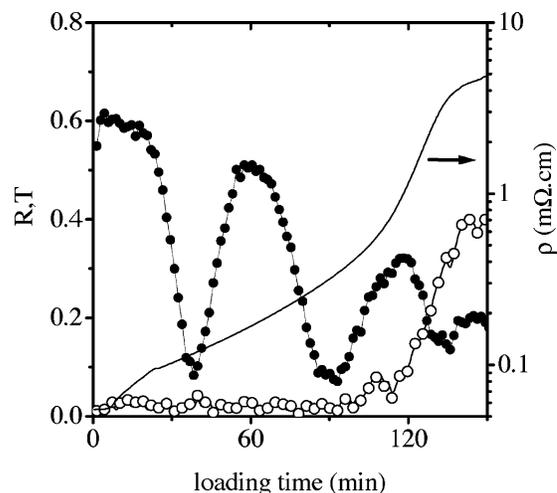


FIG. 1. Reflectance (●), transmittance (○), and resistivity (—) as a function of hydrogen loading time of a 420 nm $\text{Mg}_{1.80}\text{Ni}$ film with a 3 nm Pd cap layer at $E=0.85$ eV ($\lambda = 1.46 \mu\text{m}$). The reflectance is measured from the substrate side of the sample.

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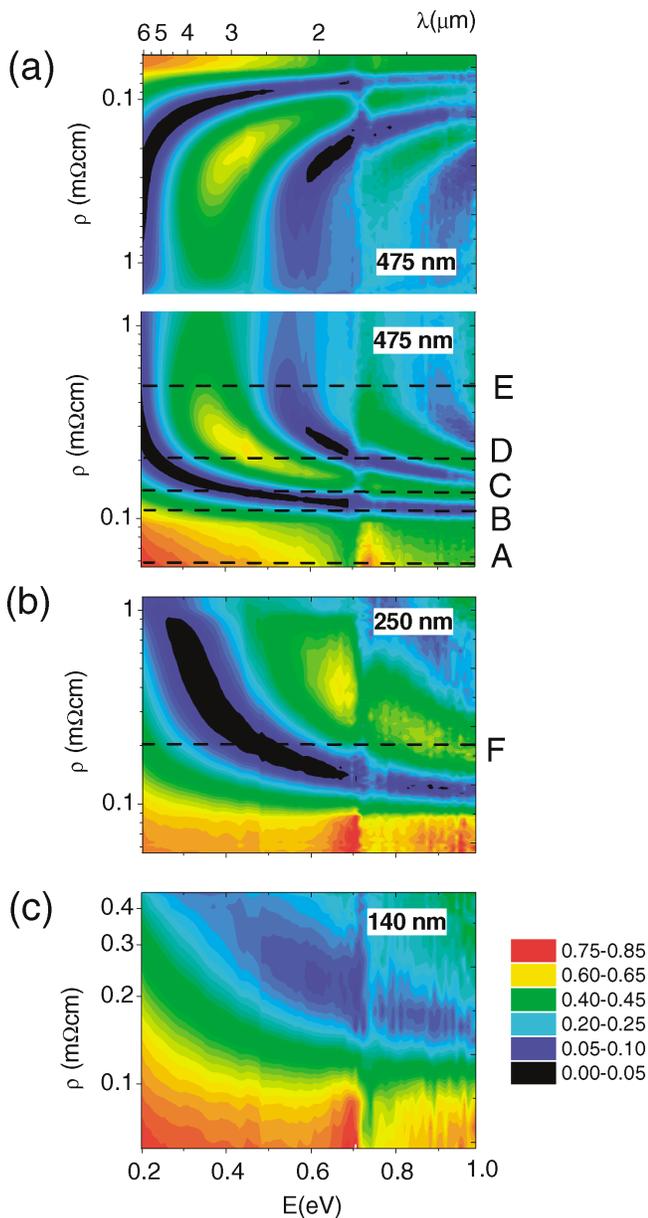


FIG. 2. (Color) Contour plots of reflectance vs photon energy and ρ for (a) 475 nm $\text{Mg}_{1.96}\text{Ni}$, (b) 250 nm $\text{Mg}_{1.70}\text{Ni}$, and (c) 140 nm $\text{Mg}_{1.43}\text{Ni}$ films.

measure of x),⁷ during loading, for films of various thicknesses, d . For a specific E , the R pattern as a function of ρ produces a plot similar to that in Fig. 1. In Fig. 2(a), the reflectance is also depicted during unloading, showing the reversibility of the hydrogenation process. It is clearly observed that the reflectivity oscillations during loading (or unloading) evolve into the interference fringes of the fully loaded transparent state, which already points to a common origin for both of them. Since the measurements are performed from the substrate side, the existence of interference already in the first stages of the hydrogenation process, when there is still no transmission through the film, can only be explained by the formation of a well defined transparent layer, presumably Mg_2NiH_4 , at the substrate–film interface.¹¹ This layer, of thickness $t(x) < d$, grows during H loading and finally reaches the total thickness of the film, d . The two main features observed in Fig. 2, namely, the hyperboliclike bending of the minima and maxima as a function of the energy, and the increment of the number of reflectance

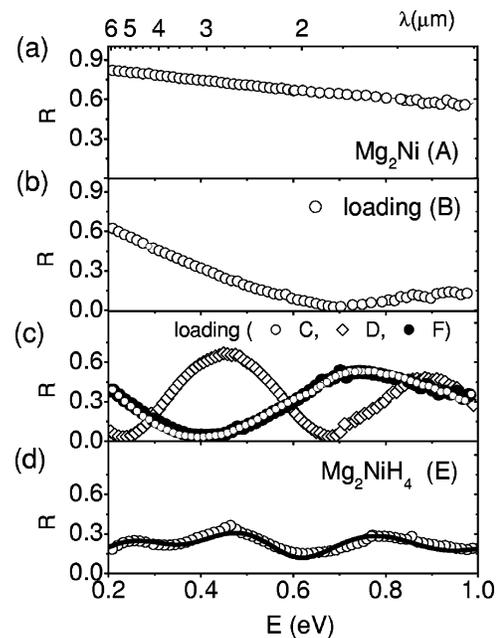


FIG. 3. Reflectance spectra for the 475 nm $\text{Mg}_{1.96}\text{Ni}$ film shown in Fig. 2(a) at different stages (A to E) of the H loading. The letters refer to those in Fig. 2(a). The solid circles in (c) correspond to the 250 nm $\text{Mg}_{1.7}\text{Ni}$ film. The line in (d) is the fit to the data with $n \approx 3.7$ and $k \approx 0.5$, both weakly depending on energy in the studied range.

oscillations with increasing thickness, are consistent with this model. This can be qualitatively understood from the interference condition $2t(x)n = N\lambda \propto N/E$, where n and N are the refractive index and interference order, respectively.¹⁰ Quantitative evidence of this phenomenon has been obtained by modeling the reflection and transmission of a three-layer stack ($\text{Pd-Mg}_2\text{NiH}_{0.3}\text{-Mg}_2\text{NiH}_4$) at various hydrogenation stages.¹¹ It is worth noticing that the same self-organized layered mechanism occurs during unloading in a completely reversible way [see Fig. 2(a)].

The observed fringes lead to a switchable and highly tunable reflectance, R , or absorptance, A (during loading, when there is no transmission through the film, $A = 1 - R$), and strongly suggest the use of these films as smart coatings. Figure 3 shows the reflectance as a function of photon energy for different loading stages [A to E in Fig. 2(a)], in a film with $d = 475$ nm. The metallic reflectance of the unloaded film (stage A), as high as 0.85 at 0.2 eV, is plotted in Fig. 3(a). With only a small amount of hydrogen added, at a composition of about $\text{Mg}_2\text{NiH}_{0.6}$ (the average H content depending on d),¹¹ the film becomes black. The reflectance decreases drastically at $E > 0.5$ eV ($\lambda < 2.5$ μm), and varies between 0.05 and 0.3 at $0.5 < E < 4$ eV [see Fig. 3(b) and Refs. 4 and 11], while it is still reflecting ($R > 0.6$) in the thermal range. By linearly extrapolating the reflectance of Fig. 3(b) to low energies and convoluting $A = 1 - R$ with the blackbody radiation at 100 °C, one can estimate the thermal emittance in this state to be about 0.16. Similarly, a solar absorptance of about 0.84 is estimated by using the data at $E > 0.5$ eV in the Fig. 3(b) together with those obtained for similar films at energies up to 4 eV.^{4,11} These high solar absorptance and low thermal emittance are comparable to those recently reported for films of $a\text{-Si:H/Ti}$ on Al substrates,¹² proposed as good candidates for selective coat-

ings in solar collectors. The main advantage of the Mg_2Ni films is that their behavior is switchable. Moreover, the small amount of H needed, which involves minimal morphology changes and thus little aging, makes the switching between A and B very attractive from the applications point of view. The self-organized nature of the absorbing double layer means that it is more easily incorporated as a *single* active layer in an electrochromic device.

Upon increasing the H content (stage C), a very different reflectance pattern is measured with a narrow highly absorbing state at ~ 0.4 eV ($\lambda \approx 3.1$ μm), whose energy and width can be tuned by varying the film thickness. Due to the layered loading mechanism, the reflectance spectrum at this state of the loading process is identical to that of a later loading stage in a thinner 250 nm film (*F*), as shown in Fig. 3(c). A larger H content in a thick enough film gives rise to more than one *R* minima (*D*).

As shown above, a transparent Mg_yNiH_x ($x=4$ for $y=2$) growing layer determines the reflectance spectra, even at the initial loading states. The spectrum in Fig. 3(d) shows the interference pattern observed when the whole film is transparent. The solid line in Fig. 3(d) is the result of fitting *R* and *T* (*T* is not shown for clarity) to those of a Mg_yNiH_x film with a Pd cap layer, both of known thickness and unknown *n* and absorption coefficient, *k*.¹¹ The optical constants obtained for the transparent layer from the fits of the films under study are in between $2.5 \leq n \leq 4.0$ and $0.01 \leq k \leq 1.5$, depending on composition, in the investigated energy range. The lowest *k* values are desirable since they produce the largest interference contrast. This can be observed by comparing the high contrast of the film in Fig. 1, with $k \approx 0.03$ and the lower contrast of the film in Fig. 2(c) with $k \approx 1$.

Nucleation of the transparent layer at the film–substrate interface is observed for all compositions under study, however the Mg/Ni ratio influences the growth of the transparent layer. In slightly Mg-rich films with $2.0 < y < 2.4$, only the first minimum and maximum are observed, in agreement with Isidorsson *et al.*⁴ The contrast is also found to greatly decrease with the Mg content for $2.0 \leq y < 2.4$, pointing to the formation of a hydride layer with ill-defined interfaces. Whether the role of the Mg/Ni ratio is direct, e.g., due to the

catalytic properties of Ni, or indirect, e.g., due to the low degree of crystallinity of the Ni-rich films¹³ is not clear yet. Work is in progress to elucidate the catalytic properties of the substrate–film interface and the role of the Mg/Ni ratio during loading.

In summary, Mg_yNiH_x films with $y \approx 2$ are particularly suitable as smart coatings due to their energy tunability, high reflectance contrast, and switching capabilities. While the metallic state reflects about 60% of the incoming solar radiation, a small amount of H is enough to change from reflective to black, absorbing 84% of the solar spectrum. As the film in this state emits only 16% of the 100 °C blackbody radiation, it can be used as a switchable solar absorber in solar collectors. Such absorbers can be temperature controlled, which makes them also ideally suited for integration with photovoltaic cells.

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⁹Measured values include the Pd cap layer. Therefore, measured ρ and *T* are lower than those of the Mg_2NiH_4 film itself.

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¹³Only films with $\text{Mg/Ni} > 2$ have shown x-ray diffraction peaks.