

# Refractive index changes of Pd-coated magnesium lanthanide switchable mirrors upon hydrogen insertion

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The optical effect upon insertion of hydrogen into Pd-coated magnesium lanthanide switchable mirrors is investigated in terms of the changes of their complex refractive indices. A significant change in the optical constants of LnMg layers is seen between the as-deposited state and the dehydrided state after one cycle. Furthermore, the optical effect of switching the Pd cap layer to a PdH cap layer was determined. It is shown that the Pd layer mainly limits the visible transmittance of the hydrided stack to about 35%–40%. Whereas the extinction coefficient of dehydrided LnMg layers at 550 nm is between 2.2 and 3.1, it is as low as  $10^{-4}$  in the transparent state. This is of great promise to applications requiring large optical contrast (e.g., optical switches). © 1999 American Institute of Physics. [S0021-8979(99)05101-4]

## INTRODUCTION

The optical performance of electrochromic materials can be expressed in terms of transmittance and reflectance, but optical constants are required for the evaluation of the materials in thin film devices. For instance, the design of an antireflection layer is only possible if the optical constants of the electrochromic coating are known. A new class of materials in this field has recently been discovered by Huiberts *et al.*,<sup>1</sup> who showed that yttrium and lanthanum thin films capped with a Pd layer can be reversibly loaded with hydrogen. At hydrogen gas pressures above about  $10^5$  Pa the materials form the trihydride phase (LnH<sub>3</sub>) which is semiconducting and transparent. At lower hydrogen pressure (e.g., in air) the materials form the dihydride phase (LnH<sub>2</sub>), which is metallic and opaque. Based on this metal–semiconductor transition a simple gasochromic and electrochromic switchable mirror can be constructed.<sup>2</sup>

Even better optical performance can be obtained using magnesium lanthanide alloys.<sup>3</sup> These materials also form a transparent hydride at  $10^5$  Pa hydrogen gas pressure. They are neutral in color and show virtually no absorption in the visible spectrum. Thin films of magnesium lanthanide alloys transform to a metallic state when exposed to air. Contrary to the lanthanide dihydrides, they show high reflectivity and very low transmittance.<sup>3,4</sup> In this work we will characterize the optical performance of gas-phase loaded magnesium lanthanide alloy thin films capped with a Pd layer using ellipsometry. In addition, the optical constants of Pd and PdH thin films are determined.

## EXPERIMENT

Magnesium lanthanide thin films of typically 270 nm thickness were deposited on fused silica and glass substrates

in a high vacuum (HV) deposition facility (base pressure  $10^{-6}$  Pa) by codeposition from two electron-beam guns. The films were capped with an optically thin (10 nm) Pd film which is necessary to prevent the magnesium lanthanide films from oxidizing and to facilitate hydrogen dissociation in the gas-phase switching experiment.

Primary optical measurements were made from 265 to 1700 nm by variable-angle spectroscopic ellipsometry (VASE) using a rotating analyzer instrument made by the J. A. Woollam Co. This instrument measures the ratio of the complex Fresnel reflection coefficients for polarizations parallel (*p*) and perpendicular (*s* from the German “senkrecht”) to the plane of incidence in terms of the ellipsometric values  $\Psi$  and  $\Delta$ :

$$\frac{\tilde{r}_p}{\tilde{r}_s} = \tan(\Psi) \exp(i\Delta).$$

Ellipsometric measurements were taken at five angles to obtain adequate sensitivity over the full range of spectra. Standard deviations of the ellipsometric measurements could be determined experimentally by recording each data point ( $\Psi$ ,  $\Delta$ ) as the average of 30 revolutions of the analyzer. Spectrophotometric measurements from 200 to 2000 nm were added. These measurements were taken at near-normal incidence on a Perkin–Elmer lambda 19 spectrophotometer.

In order to measure the optical properties in the transparent hydrided state special sample holders had to be designed. Ellipsometric data of the hydrided films were taken from the backside through the substrate. The rare earth hydride with the Pd layer faced a black painted aluminum block separated by an O-ring. Two small holes had been drilled in the aluminum block. Through one of them hydrogen gas flowed slowly at slightly overatmospheric pressure. The other one served as an outlet hole. This very simple construction proved to yield perfectly repeatable optical data in the transparent and reflective states. Backside reflections

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from the aluminum block did not have to be considered, since the 1 mm thick O ring shifted the reflection from the aluminum versus the reflection from the  $\text{Gd}_{0.4}\text{Mg}_{0.6}/\text{Pd}$  layer by 3.8 mm at the minimum angle of incidence of  $59^\circ$ . A 2 mm narrow detector iris diameter was sufficient to suppress the signal from the aluminum.

A similar sample holder was constructed for transmittance measurements. Here a quartz window had to be inserted into the aluminum block. To eliminate the influence of the sample holder an identical device was placed in the reference beam of the double beam spectrophotometer.

A thickness measurement of the LnMg layer by ellipsometry was only possible in the hydrided transparent state. Thickness measurements of the Pd layer and composition measurements of the LnMg layer were done using inductive coupled plasma spectrometry (ICPS) by dissolution of the complete film in  $\text{HCl}/\text{HNO}_3$  solution. The total thickness of the stacks was verified in the dehydrided state by profiling them with a Tencor alpha stepper and they agreed with the first method within 5%.

## OPTICAL MODEL

A Lorentz oscillator model was used to represent the dispersion for Pd of  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Sm}_{0.48}\text{Mg}_{0.52}$  and  $\text{Er}_{0.42}\text{Mg}_{0.58}$  in order to guarantee the Kramers–Kronig consistency of the spectral optical indices. Only time-dependent dynamic data, which were taken at a single wavelength, were fitted point by point. Ellipsometric and radiometric data were fitted together weighting both data types according to their standard deviations. The numerical iteration was performed utilizing a Levenberg–Marquardt algorithm.<sup>5</sup>

## RESULTS

In order to analyze the magnesium lanthanide hydrides under a Pd coating, first Pd thin film optical constants had to be determined, which below 50 nm thickness proved to be somewhat different from data reported in the literature on bulk Pd.<sup>6</sup> The optical constants of Pd on the LnMg alloys were investigated by depositing Pd layers of 5, 10, and 50 nm thickness on indium–tin–oxide (ITO) coated glass by electron beam evaporation. It was assumed that the optical properties of Pd on LnMg resemble those of Pd on ITO. The complex refractive index of the ITO substrate had been measured previously.<sup>7</sup> A Lorentz oscillator model with a Drude free electron contribution fitted to literature Pd optical constants for bulk material served as the starting guess in the optical model. Figure 1 shows the spectral extinction coefficient of Pd films of different thickness compared to bulk literature data. Whereas the real parts of the refractive index are rather similar, the extinction coefficient apparently approaches the bulk value for  $d > 10$  nm. This is due to the increasing Drude free electron contribution in the dispersion model with increasing thickness of the thin film. Figure 2 illustrates the change in reflectance of the Pd thin films on ITO coated glass as a function of their thickness.

Before measuring  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Sm}_{0.48}\text{Mg}_{0.52}$ , and  $\text{Er}_{0.42}\text{Mg}_{0.58}$  in reflective and transparent states the optical properties of the Pd thin films had to be investigated at

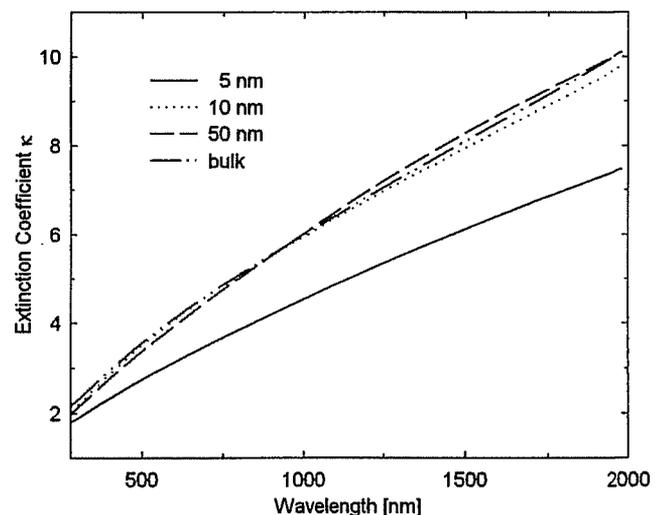


FIG. 1. Spectral extinction coefficient of Pd films of different thicknesses compared to bulk literature data.

$10^5$  Pa hydrogen gas pressure. The optical properties of Pd itself undergo a less dramatic, but nevertheless significant, reversible change under the influence of hydrogen. The extinction coefficient at 550 nm decreases from 3.78 to 2.78 upon hydration. The corresponding optical constants are shown in Fig. 3.

The same experiments were performed on Pd coated  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Sm}_{0.48}\text{Mg}_{0.52}$ , and  $\text{Er}_{0.42}\text{Mg}_{0.58}$  on fused silica. The films switch from completely opaque (transmittance  $< 10^{-6}\%$ ) to visibly transparent (Fig. 4). (The extremely low transmittance of  $10^{-6}\%$  was not measured, but calculated from the refractive index data. It is far below the experimental error of our transmittance measurements, which is about 0.1%.) The lower visible transmittance and smaller apparent optical gap of  $\text{Sm}_{0.48}\text{Mg}_{0.52}$  vs  $\text{Gd}_{0.42}\text{Mg}_{0.58}$  and  $\text{Er}_{0.42}\text{Mg}_{0.58}$  in the trihydride state are probably due to its lower Mg content.<sup>3</sup>

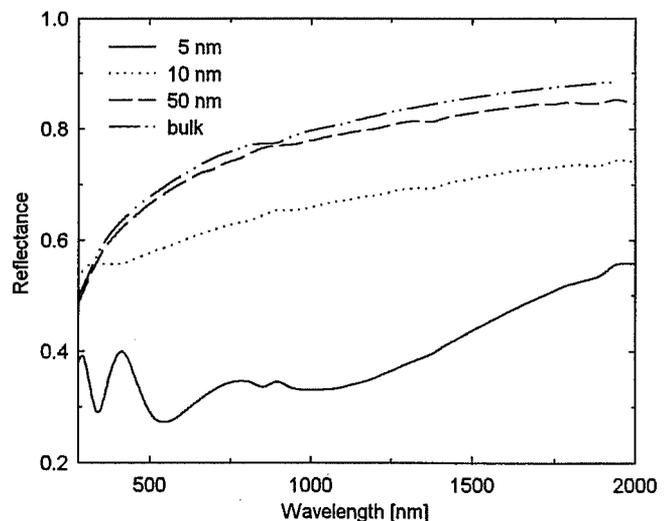


FIG. 2. Reflectance of Pd films of different thicknesses on ITO coated glass compared to reflectance calculated from bulk literature optical constants.

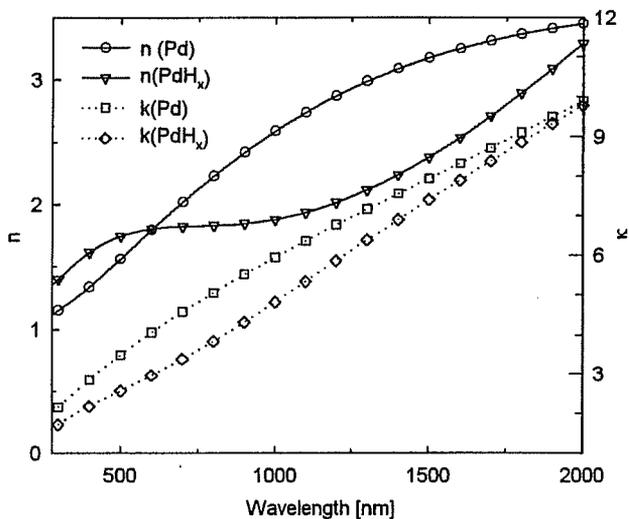


FIG. 3. Optical constants of 10 nm thin Pd in the unhydrided and hydrided states.

The complex refractive indices of the lanthanide magnesium alloys in the as-deposited, the dehydrided, and the hydrided states are depicted in Figs. 5, 6, and 7, respectively. The optical constants in the unhydrided, as-deposited states show a clearly metallic character with the extinction coefficient rising towards higher wavelengths due to free electron contribution. The hydrided state shows a dielectric optical response in the visible. Residual free electron contribution in the hydrided state seen in  $\text{LaH}_3$  could not be identified up to 2000 nm.<sup>8</sup>

The complex refractive index in the reflective state changes significantly from the as-deposited, virgin state to the dehydrided state after one cycle and stays constant after subsequent cycles. This effect is presumably related to the significant residual hydrogen that can be found in the samples after one hydrogenation cycle. For instance, in  $\text{Gd}_{0.5}\text{Mg}_{0.5}$  it is observed that hydrogen is trapped up to a

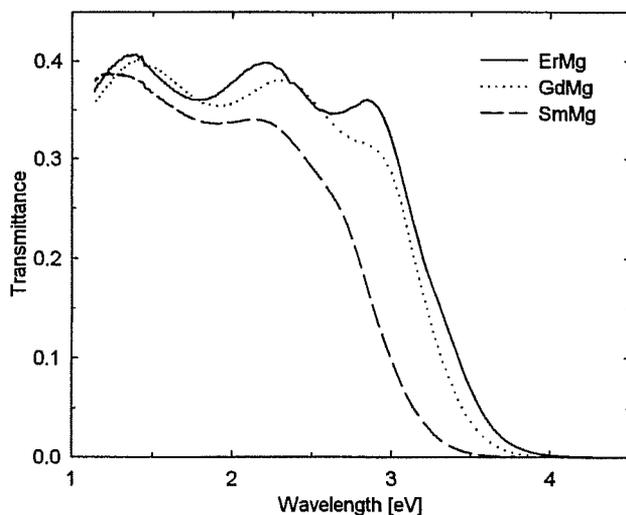


FIG. 4. Spectral transmittance of 200 nm  $\text{Er}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ , and  $\text{Sm}_{0.48}\text{Mg}_{0.52}$  capped with 10 nm Pd on fused silica as a function of photon energy.

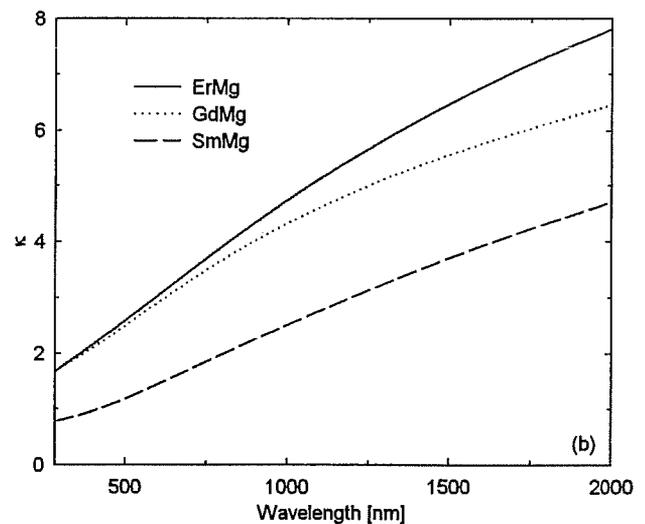
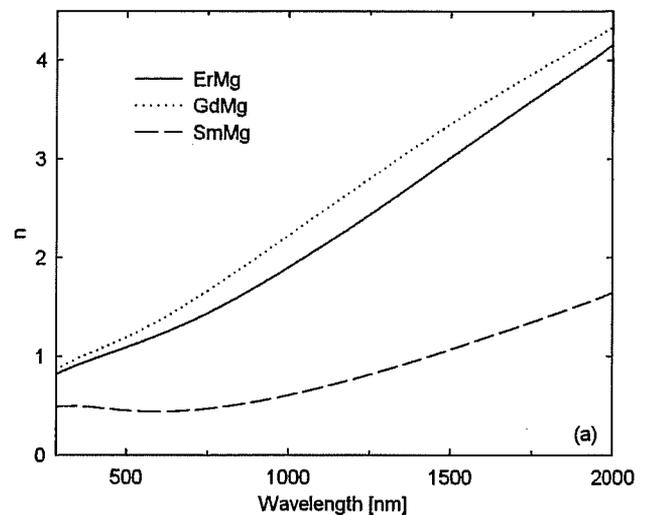


FIG. 5. (a) Real and (b) imaginary parts of the refractive index of  $\text{Er}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ , and  $\text{Sm}_{0.48}\text{Mg}_{0.52}$  in the as-deposited state.

ratio of 0.8 H/M.<sup>3</sup> As a consequence, the visible reflectance of the magnesium rich alloy films is lowered from about 65% to about 60%.

In order to “quantify” the switching time of the magnesium lanthanide hydride/Pd structure we also had to investigate the time scale of the Pd optical response alone. Therefore *in situ* ellipsometric data were taken on Pd on ITO at 500 nm while the hydrogen gas supply was opened and closed. Pd changes its optical properties almost instantaneously upon exposure to hydrogen overpressure. Figure 8(a) shows the ellipsometric parameter  $\Delta$ , whose changes at constant film thickness correspond to a varying complex refractive index between the two curves in Fig. 3. Dehydridation (in air) is much slower and it takes more than 1 min after shutting down the hydrogen supply for Pd to reach its initial optical state.

The reaction speed for magnesium lanthanide alloy hydrides is much slower than for Pd [Fig. 8(b)]. This is fortunate, because it allows us to relate changes in the overall optical properties mainly to the rare earth hydrides. However, it must be stressed that the kinetics of the switching strongly depends on the thickness of the Pd layer, the switch-

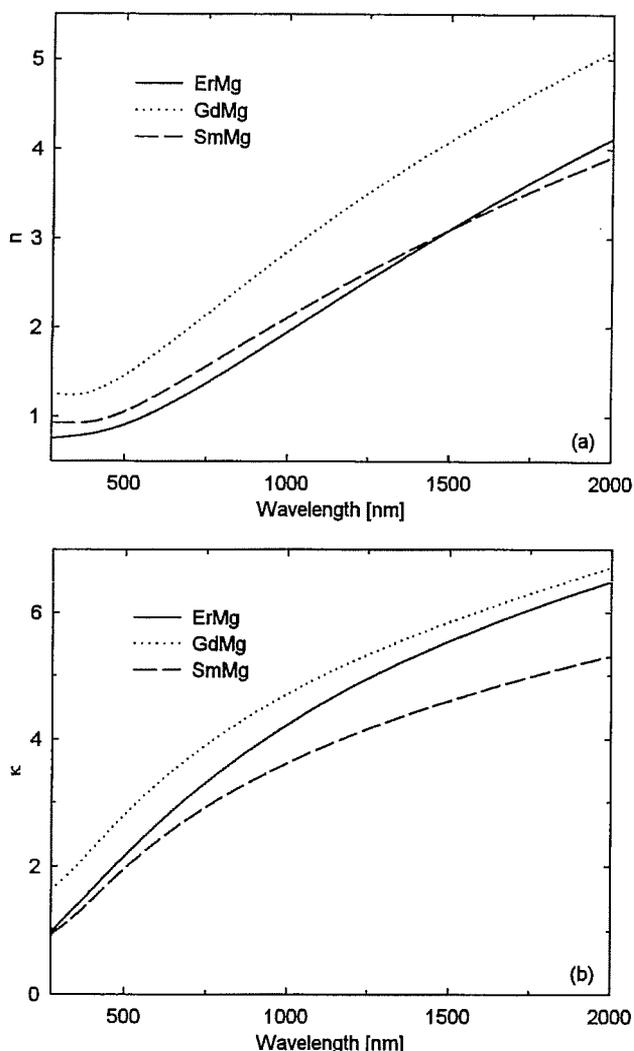


FIG. 6. (a) Real and (b) imaginary parts of the refractive index of  $\text{Er}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ , and  $\text{Sm}_{0.48}\text{Mg}_{0.52}$  in the dehydrated state after switching.

ing pressure, and also on the time between deposition and measurement. Therefore the presented switching times are relative rather than absolute values.

Whereas most of the switching from the reflective to the transparent state occurs within seconds, it takes minutes before the optical properties stabilize. This leads to a more continuous change in the refractive index and becomes stable only after almost 15 min.

## DISCUSSION

The extinction coefficient at 550 nm in the hydrided state is about  $10^{-2}$  for  $\text{Sm}_{0.48}\text{Mg}_{0.52}$ ,  $10^{-3}$  for  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ , and  $10^{-4}$  for  $\text{Er}_{0.42}\text{Mg}_{0.58}$ . That means that it is mainly the Pd cap layer that limits the visible transparency. The effect of the switching of Pd can be estimated to be about 5%–8% visible transmittance for the whole stack of layers, i.e., the transmittance of a Pd coated  $\text{Er}_{0.42}\text{Mg}_{0.58}$  film would be reduced from 35% to below 30% if Pd did not form a hydride.

The visible transmittance of the approximately 270 nm thick lanthanide magnesium alloys on a fused silica substrate without the Pd cap-layer lies between 60%–90% and is de-

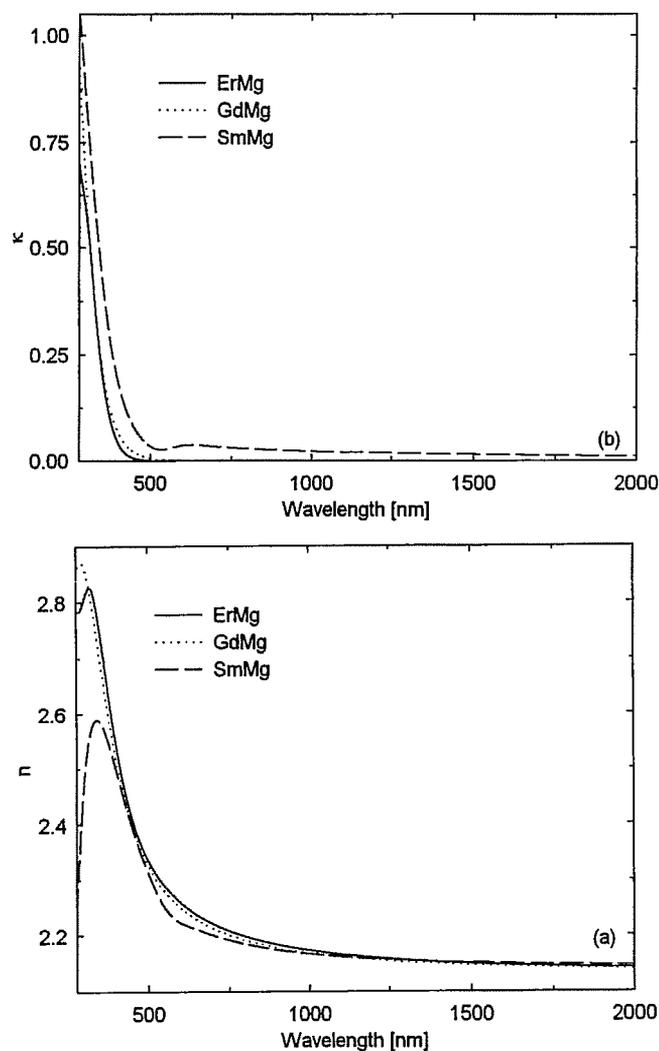


FIG. 7. (a) Real and (b) imaginary parts of the refractive index of  $\text{Er}_{0.42}\text{Mg}_{0.58}$ ,  $\text{Gd}_{0.42}\text{Mg}_{0.58}$ , and  $\text{Sm}_{0.48}\text{Mg}_{0.52}$  in the hydrided state.

pendent on the spectral position of interference fringes. For maximum visible transparency together with complete opacity in the reflective state a single film of a lanthanide magnesium hydride should be about 240 nm thick.

Figure 9(a) shows the reflectance from the backside of a 10 nm Pd coated  $\text{Er}_{0.42}\text{Mg}_{0.58}$  film on silica before and after hydration together with data calculated from the optical model. Due to the influence of the substrate the backside reflectance in the reflective state is lowered by about 10% versus the frontside reflectance. Experimental reflectance of the transparent, hydrided state is not shown because of the difficulty of properly accounting for the sample holder at near-normal incidence. However, excellent fits of calculated data to ellipsometric and transmittance data in the hydrided state assure an accurate prediction of reflectance.

The transmittance behavior of the same sample is shown in Fig. 9(b). It can be seen how dramatically the optical properties change upon the transition from the shiny dehydrated to the transparent hydrided state. At 550 nm the optical contrast is theoretically in the order of  $10^9$ . For comparison the optical contrast achievable with conventional electrochromic tungsten oxide layers (of 400 nm thickness)

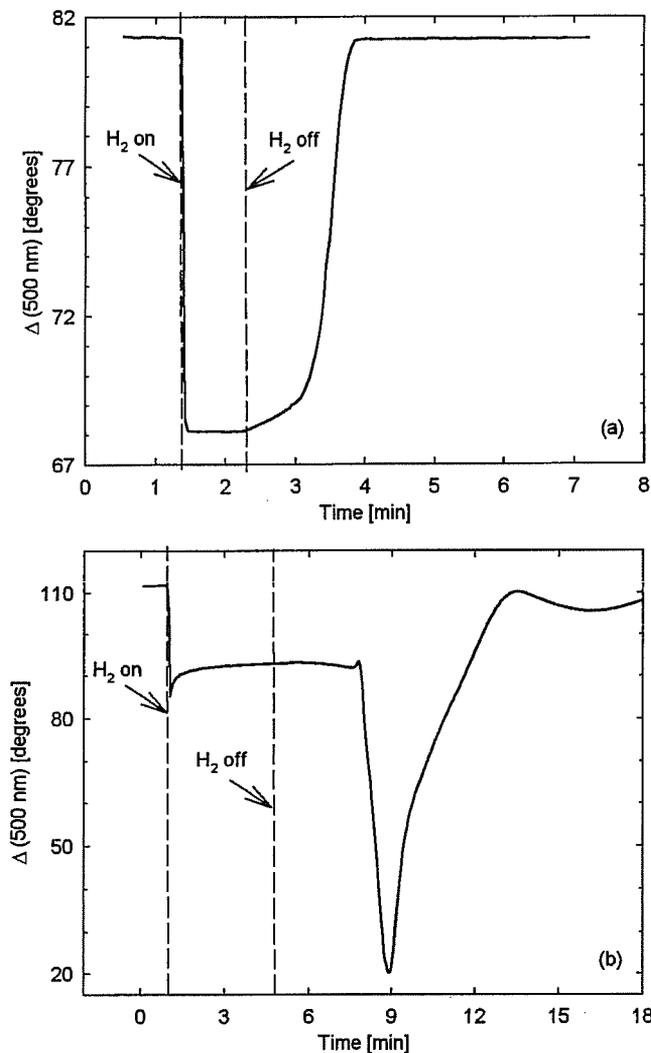


FIG. 8. *In situ* ellipsometric data at 500 nm of (a) Pd on ITO coated glass and (b) of  $\text{Sm}_{0.3}\text{Mg}_{0.7}$  on silica. The vertical dashed lines correspond to the opening and closing of the hydrogen gas supply.

is about eight orders of magnitude lower. However, the maximum visible transmittance is about 80% for a  $\text{WO}_3$  film on ITO versus 40% for Pd capped magnesium lanthanide hydrides.

## CONCLUSION

Upon hydridation  $\text{Gd}_x\text{Mg}_y$ ,  $\text{Sm}_x\text{Mg}_y$ , and  $\text{Er}_x\text{Mg}_y$  undergo an optical transition, changing their appearance from reflective to transparent. Their spectral complex refractive indices were determined in the reflective dehydrided and transparent hydrided phases from 280 to 2000 nm. The optical constants are very different between the as-deposited reflective state and the dehydrided reflective state after the first switching. Thin film optical constants of Pd were measured in the as-deposited and hydrided states. It was found that the optical properties of Pd itself change upon hydridation. The response time of Pd is much shorter than that of the examined magnesium lanthanide hydrides.

In the hydrided state the extinction coefficients of the lanthanide magnesium alloys are between  $10^{-2}$  and  $10^{-4}$  vs 2.78 for hydrided Pd. That means that if the protective layer

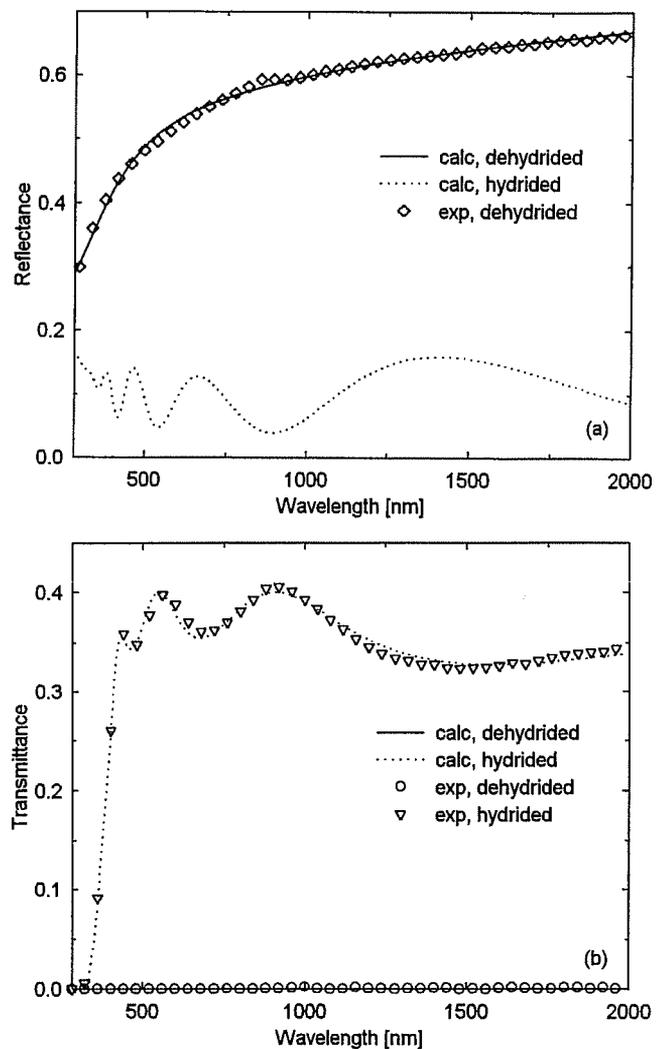


FIG. 9. Spectral (a) reflectance from the backside and (b) transmittance of Pd coated  $\text{Gd}_{0.4}\text{Mg}_{0.6}$  on glass in the reflective, unhydrided and transparent, hydrided states. The symbols depict experimental data and lines correspond to calculated data from the optical constants in Figs. 6 and 7.

of Pd could be eliminated (e.g., in a sealed device), a visible transparency of close to 90% seems to be achievable with 240 nm thick lanthanide magnesium alloy films.

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