Solid-State Gadolinium-Magnesium Hydride Optical Switch

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Abstract

The optical switching properties of gadolinium-magnesium hydride have been demonstrated in a solid-state electrochromic device. With positive polarization of the hydride electrode, the visible reflectance approaches 35% with virtually zero transmission, while with negative polarization, the visible transmission exceeds 25% at 650 nm. The switching is reversible, with intermediate optical properties between the transparent and reflecting states.

A remarkable discovery by Huiberts *et al.*[1] initiated interest in metal hydride optical switches. As the hydrogen content in palladium-capped (5-20 nm) yttrium and lanthanum films (200-500 nm) was varied with H_2 pressure, they switched reversibly from opaque metals at lower H content (H/M ~2) to transparent semiconductors at high H content (H/M ~3). A theoretical discussion of this transition was given by Ng *et al.*[2] Optical switching in yttrium hydride required less than a minute at 10^5 Pa H_2. The Pd cap prevented oxidation and catalyzed H_2 adsorption and H absorption at room temperature.

Lanthanide-magnesium alloys possess improved optical properties, as reported by van der Sluis *et al.*[3] The H-rich phase of gadolinium-50% magnesium has $E_g > 3$ eV, yielding a color neutral window with transmission limited almost entirely by the Pd layer, while the reflecting H-deficient phase has virtually zero transmission[3,4]. Thus hydrides allow variable transmission windows with mirror states, which cannot be attained using conventional electrochromics[5].

Optical switching has also been demonstrated by varying the H content of hydride films using electrolytic cells with liquid electrolytes[4,6]. The Pd layer catalyzes the reaction of protons from the electrolyte with electrons from the potential source, forming H atoms then absorbed into the hydride. While this method allows control of the optical properties with electrochemical potential, the liquid electrolyte is inconvenient. From a practical standpoint, an all-solid device is most desirable.

In this letter we report a prototype solid-state switching mirror. This metal hydride device switches reversibly from reflecting (~35% R, <0.05% T) to transparent (>25% T at 650 nm). Intermediate properties are observed between these extremes. The

transmission and reflectance are comparable to those obtained with gas and liquid cycling of this material.

The metal in the device is $Gd_{0.44}Mg_{0.56}$ deposited by DC magnetron sputtering from an alloy target. The Gd-Mg thickness is 220 nm, and the Pd cap 15 nm. The Gd/Mg ratio was determined by Rutherford backscattering. The metal film was initially hydrided using a 4% H_2, 96% Ar mixture at 2.4×10^5 Pa.

The device is based on a glass substrate coated with indium-tin oxide (ITO), followed by Gd-Mg hydride, Pd, hydrated zirconium oxide electrolyte, H storage layer, and ITO stacked as shown in Figure 1. The H storage layer is the electrochromic material WO_3, which switches from transparent to blue when protonated,[5] complementing the transition in the hydride. With the stored H fully transferred to the hydride, all layers except the Pd are transparent. This occurs with the hydride at -3.0 V relative to the WO_3. In the reverse process at +3.0 V, H is transferred to the WO_3 layer. Viewed through the substrate, the device becomes absorbing, then reflecting. The H content in the hydride varies as the potential scales through this range, yielding intermediate optical properties.

Figure 2 shows the device's transmission in three optical states: absorbing without polarization, intermediate after equilibrating at -2.0 V, and transparent at -3.0 V. The transmission of a hydrogen saturated Pd-capped Gd-Mg film of approximately the same thickness and composition as in the device is shown for comparison. This test film was deposited on ITO coated glass and hydrided in an electrolytic cell as described in ref. 4. Aside from interference due to its several thin layers, the maximum transmission of the device is slightly below that of the similar film. This is expected, as the WO_3 and $ZrO_2 \cdot H_2O$ are not 100% transparent, and there is scattering at the optical interfaces. The

absorbing state has a low but measurable transmission. Further reducing the H content in the hydride makes the device reflecting, and the transmission falls below the spectrophotometer uncertainty (0.05% T).

Figure 3 shows the reflectance of the device in the reflecting and absorbing states, measured through the substrate. The device was equilibrated at +3.0 V for the reflecting state and without polarization for the absorbing state. Figure 3 also shows data for a comparable H-deficient film. The interference results from the reflecting hydride/ITO interface. No interference is observed for the test film as it was deposited on glass without ITO.

The large and reversible reflectance changes indicate the hydride is switching, and transmission modulation results from varying hydrogen content, not another process such as formation of transparent Gd-Mg oxides.

Without sufficient H_2 pressure or applied potential, metal hydride test films are unstable for H/M ratios above 0.8 in $Gd_{0.5}Mg_{0.5}$ alloys[3]. Within a few minutes, excess hydrogen escapes to the ambient as H_2 and the film becomes opaque. In the device this transition occurs slowly. The $ZrO_2 \bullet H_2O$ above the Pd cap layer apparently hinders H_2 permeability. With no electric potential to ionize the hydride's H atoms to H^+ and drive their motion, diffusion along the concentration gradient to the WO_3 is limited, hence the relative stability.

Figure 4 compares the transmission at -3.0 V with a subsequent measurement after the device was maintained at open-circuit conditions and room temperature for 48 hours. The maximum transmittance decreased only ~0.05 over this extended period, implying minimal performance loss for typical operating intervals of 12 hours.

Although the optical characteristics and stability of the prototype are encouraging, the switching speed is not. The reflecting-transparent-reflecting cycle time is under 3 minutes for electrochemically cycled Gd-Mg hydride films,[4] but the device requires 16 hours. This difference is surprising. As switching in WO_3[5] is faster than in Gd-Mg, it is unlikely the H storage layer is the limiting factor. The $ZrO_2 \bullet H_2O$ solid electrolyte has a lower conductivity (~10^{-4} S/cm) than the 5 N NaOH (0.07 S/cm) used for liquid cycling, but the path lengths are of the order 1 μm and 1 cm, respectively. Thus we expect speeds of the same order of magnitude for the device and liquid cell.

The switching currents and voltages are also surprisingly high. In a liquid electrolytic cell, the switching voltage range is ~1 V, with peak currents under 10 mA for a potential sweep at 10 mV/s.[4] In the solid state device, the potential range is 6 V and the currents exceed 40 mA. This suggests the speed is limited by shorting and unexpectedly high resistance in the proton conductor, not kinetics of the Gd-Mg hydride or WO_3. Only a small fraction of the applied potential performs electrochemical work, with the rest wasted in electronic currents through shorts. We expect correcting these problems would reduce the switching time to the order of 5 minutes, sufficient for window applications.

In summary, our device exhibits the remarkable reflecting-to-transparent optical switching of Gd-Mg hydride in an all-solid configuration. The device is stable for many hours when transparent, unlike films tested in the gas and liquid modes. Although the switching speed is unacceptable for applications, it is not limited by the hydride material.

References

[1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot and N.J. Koeman, Nature (London), **380**, 231 (1996)

[2] K.K. Ng, F.C. Zhang, V.I. Anisimov, and T.M. Rice, Physical Review B, **59**, 5398 (1999)

[3] P. van der Sluis, M. Ouwerkerk, and P.A. Duine, Appl. Phys. Lett. **70**, 3356 (1997)

[4] K. von Rottkay, M. Rubin, F. Michalak, R. Armitage, T. Richardson, J. Slack, and P.A. Duine, Electrochimica Acta, **44**, 3093 (1999)

[5] C. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, (1995)

[6] P.H.L. Notten, M. Kremers, and R. Griessen, J. Electrochem. Soc. **143**, 3348 (1996)

Figure Captions

Figure 1. Cross-section schematic of the Gd-Mg hydride optical switch. Dimensions are

not shown to scale. With the hydride at maximum H content, all layers except the Pd are

visibly transparent.

Figure 2. Transmission of the device in transparent, absorbing, and intermediate optical

states, along with the maximum transmission of a similar Pd/Gd-Mg hydride film.

Figure 3. Reflectance (measured through the substrate) for the device in the reflecting

and absorbing states, and a comparable Pd/Gd-Mg film in the hydrogen-deficient phase.

Figure 4. Transmission of the device immediately after switching to the transparent state,

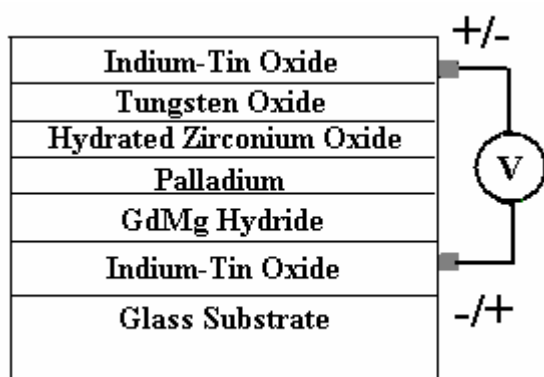and later after 48 hours at open-circuit conditions.

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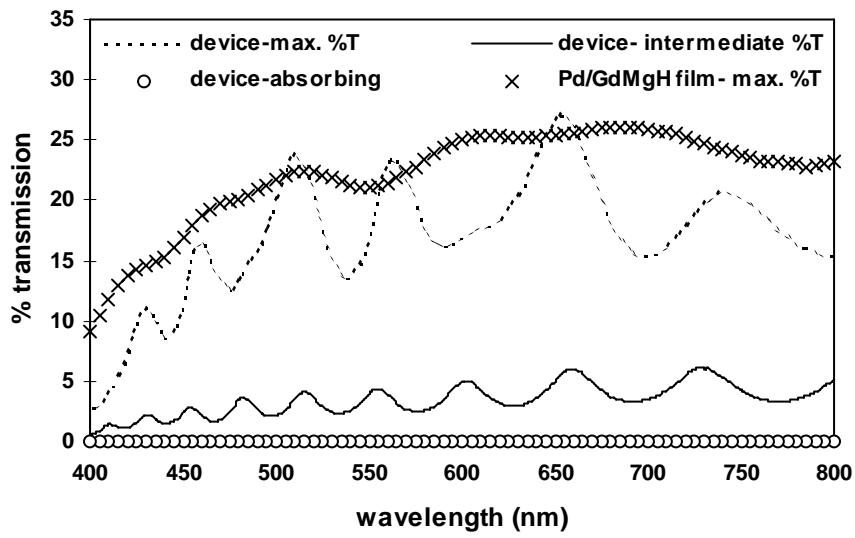Applied Physics Letters

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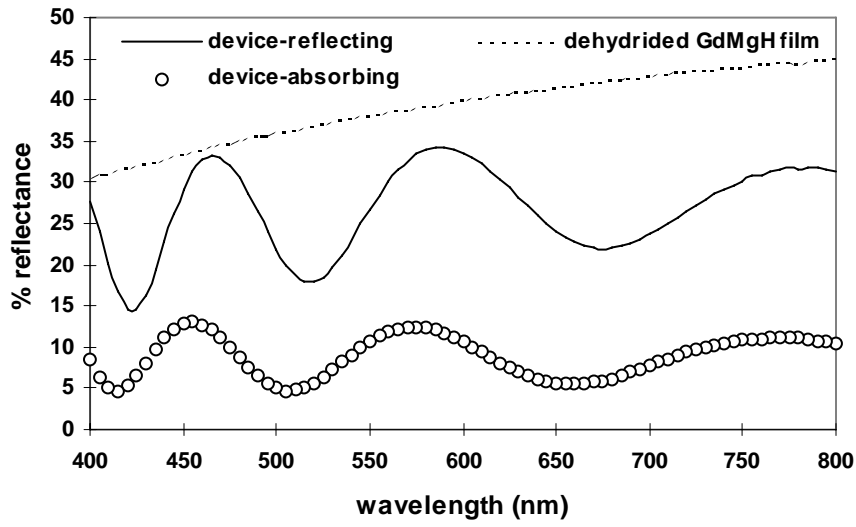
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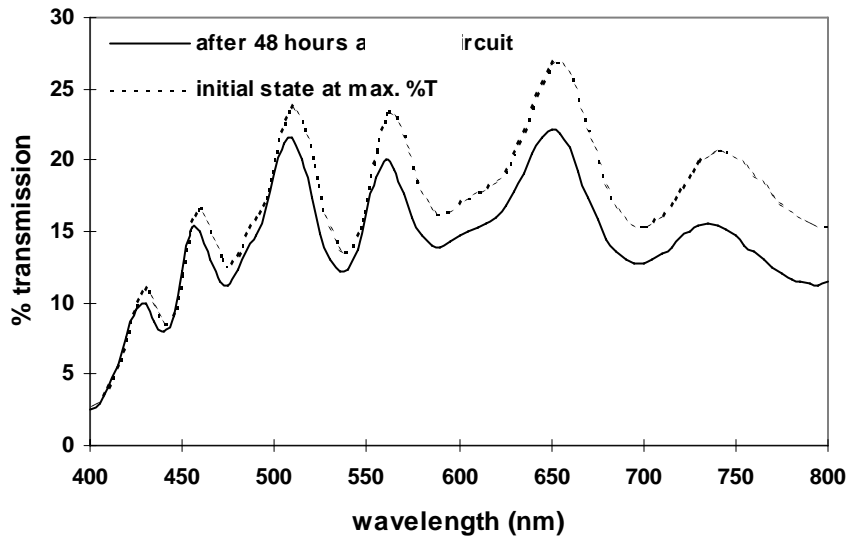
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