Contrast enhancement of rare-earth switchable mirrors through microscopic shutter effect

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In contrast to the binary switchable mirror films (YH_x, LaH_x, REH_x with RE:rare earth) which have a weak red transparency window in their metallic dihydride phase, rare-earth alloys containing magnesium are remarkable for the large contrast between their metallic dihydride and transparent trihydride phase. By means of structural, optical transmittance, and electrical resistivity measurements on a series of $Y_{1-y}Mg_yH_x$, films we show that this is due to a disproportionation of the alloy. While the yttrium dihydride phase is formed, Mg separates out, remaining in its metallic state. Upon further loading, insulating MgH_2 is formed together with cubic $YH_{3-\delta}$. In this way Mg acts essentially as a microscopic optical shutter, enhancing the reflectivity of these switchable mirrors in the metallic state and increasing the optical gap in the transparent state. © *1999 American Institute of Physics.* [S0003-6951(99)04540-4]

Recently Huiberts *et al.*[1] discovered that films of YH_x and LaH_x exhibit dramatic reversible changes in their optical properties during hydrogenation. For $x \lesssim 0.2$, α-YH_x is a shiny metal. For $x \approx 2$, metallic β-YH_2 forms with an electrical resistivity significantly lower than that of pure Y, but with a characteristic weak optical transmission[2,3] for red photons ($\hbar\omega \approx 1.8$ eV). Upon increasing the hydrogen content to $x > 2.4$, γ-YH_x reaches the hcp phase, which exhibits a continuous metal-insulator transition[4] with a pronounced optical transition. In the trihydride phase, γ-$YH_{3-\delta}$ is transparent with a characteristic yellowish color due to the optical gap of 2.8 eV [see Fig. 1(a)]. It came somewhat as a surprise in 1997 when van der Sluis, Ouwerkerk, and Duine reported that $Gd_{1-y}Mg_yH_x$ alloys could be made colorless for $y > 0.4$ over the whole visible part of the optical spectrum.[5] Moreover, the contrast between the transparent and the insulating state is enhanced due to the absence of the transparency window, which is characteristic for the binary YH_2, LaH_2, or REH_2 in their metallic state. In this letter we show that the remarkable optical properties of these Mg-containing alloys can essentially be understood in terms of a compositional disproportionation of the alloy during hydrogen absorption. In other words, Mg acts mainly as a microscopic optical "shutter." As a model substance we consider here $Y_{1-y}Mg_y$, because the physical properties of thin YH_x films[1-3,6-8] have been investigated in much more detail than those of GdH_x thin films.

Polycrystalline $Y_{1-y}Mg_y$ films of typically 400 nm thickness are coevaporated under ultrahigh vacuum (UHV) conditions (10^{-9} mbar) on Al_2O_3 substrates, Y is evaporated with an e-gun and Mg with a Knudsen cell. To protect the film against oxidation, a 15 nm thin protecting Pd cap layer is deposited *in situ*. Optical transmission measurements are performed in a Bruker IFS 66/*S* Spectrometer. Structural information is obtained from high angle x-ray scattering in a Θ–2Θ geometry. During measurements the samples are slowly hydrogenated to allow continuous recording of dif-

fraction and optical transmission spectra. In both setups, we also measure the electrical resistivity during hydrogenation. Through these resistivity measurements we relate the optical to the structural data. The maximum hydrogen gas pressure used for hydrogenation is 10^5 Pa. Although a whole series of films of alloys $Y_{1-y}Mg_y$ with $0.1 < y < 0.9$ has been prepared, in this letter we focus on $Y_{0.5}Mg_{0.5}H_x$. In Fig. 1 we compare the optical transmission spectra of a $Y_{0.5}Mg_{0.5}$ film with those of a pure Y film upon hydrogen loading. As hydrogen is continuously absorbed (at a hydrogen atmosphere of 10^5 Pa at 293 K) the time axis is qualitatively equivalent to the concentration axis $x = [H]/[Y_{0.5}Mg_{0.5}]$. The optical transmission of $Y_{0.5}Mg_{0.5}H_{2.5}$ exhibits the same characteristic features as the corresponding $YH_{3-\delta}$ spectra. In the hydrogen-rich region both $YH_{3-\delta}$ and $Y_{0.5}Mg_{0.5}H_{2.5-\delta}$ are transparent. However, there is also an important difference: The dihydride YH_2 phase has a weak optical transmission of 1% in the red part of the spectrum ($\hbar\omega \approx 1.8$ eV) while in $Y_{0.5}Mg_{0.5}H_x$ the dihydride transparency window is below the transmission detection limit (i.e., $< 10^{-4}$). Furthermore, the optical gap of $Y_{0.5}Mg_{0.5}H_{2.5}$ is significantly larger than that of $YH_{3-\delta}$.

The structural measurements on this $Y_{0.5}Mg_{0.5}$ alloy film are shown in Fig. 2. For the as-deposited sample (a) we only find ($hh0$)-reflections corresponding to a cubic intermetallic γ-YMg phase with a lattice constant $a_0 = 0.3806$ nm, in agreement with the bulk Y–Mg phase diagram.[9] As no other intermetallic phase reflection peaks in the Θ–2Θ region from $20°$ to $80°$ were found we conclude that the as-deposited film consists of a preferentially (110)-oriented, single-phase alloy. Upon loading the film in a 10^3 Pa hydrogen pressure we distinguish three stages. In stage A at low hydrogen concentration, the shift of the ($hh0$) reflection toward smaller angles (curve b) indicates that the crystal lattice is expanded coherently. With increasing hydrogen concentration (curves c–f) the intensity of the γ-YMg-($hh0$) peak decreases. Simultaneously, the asymmetric broadening of the γ-YMg (110) reflection peak around $32°$ indicates the formation of pure Mg[hcp α-Mg-(100) at $32.2°$[10]] and possibly pure Y.
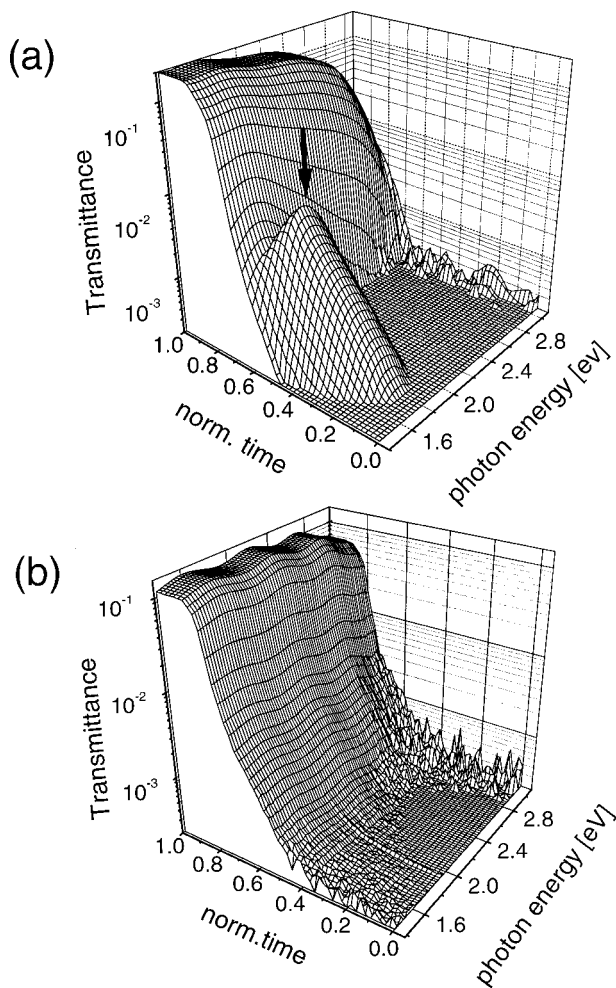
FIG. 1. Variation of the optical transmission as a function of time during hydrogen loading from the gas phase at room temperature: (a) for a 300-nm-thick Y film, covered with a 15 nm Pd cap layer hydrogenated at 10^3 Pa H_2, and (b) for a 400-nm-thick $Y_{0.5}Mg_{0.5}$ film covered with a 15 nm Pd cap layer, hydrogenated at 10^5 Pa. The optical spectra are continuously recorded at a rate of one spectrum per 40 s. For comparison the time axes are normalized: time $t=0$ corresponds to an H concentration of 0, $t=0.7$ to $x\approx 2$ for YH_2, in $Y_{0.5}Mg_{0.5}H_x$ the concentration is $x=1$ at $t=0.4$, $x=2.5$ at $t=0.7$ and for $t=0.9$ is $x=2.5$. Note, that the small dihydride transmission window at a photon energies around 1.8 eV [indicated by an arrow in (a) is not present for the alloy in (b)].
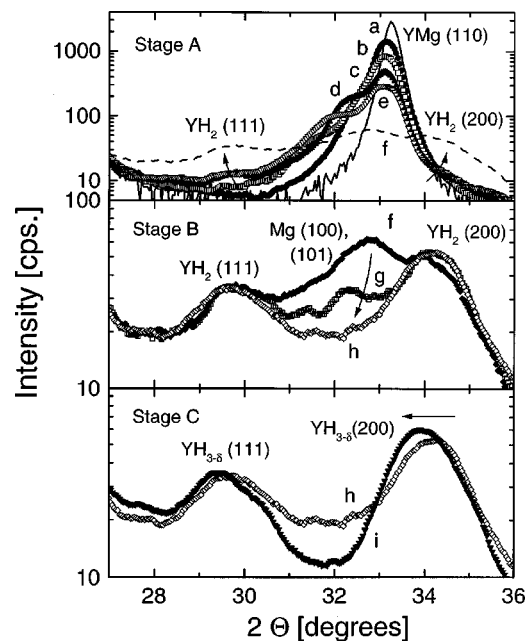

FIG. 2. Detail of a representative *in situ* x-ray measurement on a 400-nm-thick $Y_{0.5}Mg_{0.5}$ film covered with a 15 nm Pd cap layer during hydrogen loading at 10^3 Pa at room temperature. The intensity [cps] is continuously recorded. The various letters (a)–(i) specify the measurements at times in increasing order [(a) unloaded 0 min, (b) 20 min, (c) 40 min, etc.]. Three stages A, B, and C of hydrogenation are distinguished (note the difference in scale).

Additionally, in curve f we observe new reflections at $\sim 29.6°$ and $\sim 34.1°$ due to the formation of the cubic YH_2 phase. All this indicates that upon absorption of H in γ-YMg, YH_2 is formed and the host metal essentially disproportionates in YH_2 and Mg clusters. This is consistent with the fact that the enthalpy of formation of YH_2 ($\Delta H_{\alpha\to\beta} = -110$ kJ/mol H)[11] is much more negative than that of MgH_2 ($\Delta H_{\alpha\to\beta} = -37.2$ kJ/mol H).[12] In stage B the intensity of the YH_2 reflection peak hardly changes. However, the intensity of the Mg-(100) reflection is reduced. Additional x-ray measurements show that this is due to the formation of an orthorhombic primitive MgH_2 structure.[13] So far orthorhombic MgH_2 has only been reported for bulk samples[13] under high pressure (8 GPa at room temperature). This is not in contradiction with our observations as we estimate from the x-ray measurement that the hydrogenation process induces a stress of approximately 3.2 GPa.

Upon further increase of the hydrogen concentration (stage C), the shift of the diffraction peaks to smaller angles

reflects a gradual expansion of the cubic $YH_{2+\delta}$ structure. By electrochemical H loading we have determined that in the final state (curve i) the composition is $Y_{0.5}Mg_{0.5}H_{2.5}$. Apparently, *cubic* $YH_{3-\delta}$ is formed, with $a=0.525$ nm. The surprising result is that we do not find any evidence for the formation of the *hexagonal* $YH_{3-\delta}$ phase, which is observed in bulk and YH_x films. The volume expansion of 8% that we find in the *cubic* phase is somewhat less than the volume change involved in the transition from bulk fcc YH_2 to hcp $YH_{3-\delta}$ ($\delta V/V=9.9\%$). Possibly, the *cubic* $YH_{3-\delta}$ phase is also stabilized by internal stress.

The phase disproportionation induced by the hydrogenation process is also reflected in the electrical resistivity ρ as a function of hydrogen loading. In Fig. 3(a) both ρ and its derivative (in arbitrary units) are shown. The increase in ρ at low hydrogen concentration is similar to that in α-YH_x (Ref. 6) and is mainly caused by electron scattering from the randomly distributed hydrogen atoms. In stage A, YH_2 starts to form. In a pure rare-earth (RE) film this leads to a decrease of ρ. However in γ-$Y_{0.5}Mg_{0.5}H_x$ the formation of YH_2 induces a concomitant increase in the disorder of the host metal lattice which leads to a further overall increase in ρ. In stage B the formation of the insulating MgH_2 phase causes a further increase in resistivity, while the change in the slope of the resistivity at high H concentration (stage C) is caused by the formation of cubic $YH_{3-\delta}$. The final value for the resistivity is due to the thin Pd-cap layer, which shortcuts the underlying $Y_{0.5}Mg_{0.5}H_x$ layer. The resistivity of uncapped γ-YMg samples loaded *in situ* in the deposition system is of the order of ohm meter, in agreement with the fact that both YH_3 and MgH_2 are insulators.[1,14]

With the structural and electrical data presented above we have the necessary ingredients to interpret the hydrogen
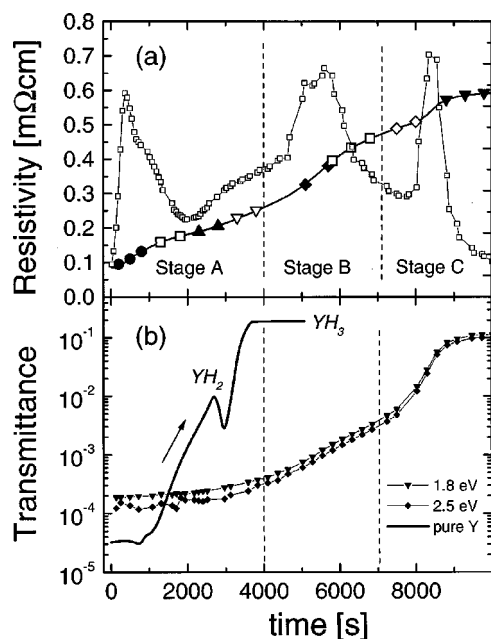
FIG. 3. (a) Time dependence of the electrical resistivity measured on a 400-nm-thick $Y_{0.5}Mg_{0.5}$ film during hydrogen loading at 10^3 Pa at room temperature in the x-ray and optical setups. The small open squares represent the derivative of the resistivity. The various symbols label the resistivity measurements corresponding to the x-ray measurements in Fig. 2. Vertical dotted lines separate the various stages A, B, and C in accordance with Fig. 2. (b) Time dependence of the optical transmittance at photon energies of 1.8 eV (solid inverted triangles) and 2.5 eV (solid diamonds) during loading at 10^5 Pa at room temperature. For comparison, the transmittance of the Y film [Fig. 1(a)] for photon energy of 1.8 eV is shown as a solid line. Note the dihydride window for the YH_2, which does not appear (stage A) in the YMg sample. The difference in the loading time is due to disproportionation.

concentration dependence of the optical transmission in Fig. 1(a). In Fig. 3(b) we concentrate on the optical transmission of $Y_{0.5}Mg_{0.5}H_x$ at photon energies $\hbar\omega = 1.8$ eV (where the optical transmission window occurs in pure YH_x) and $\hbar\omega = 2.5$ eV. Unlike in pure YH_x we do not see any indication that, before opening in the visible range, the film exhibits a transparency window in the red part of the spectrum.[3] The transmittance increases during the formation of MgH_2 as MgH_2 is an insulator with an optical absorption edge at 5.16 eV.[14] Other than the larger optical gap in the YMg alloy, the optical opening after MgH_2 is formed is very similar to what is observed in pure Y films. These results are in agreement with the x-ray measurements. Both support an interpretation based on the existence of two essentially independent materials, one of them, Mg, acting as a *microscopic optical shutter*: As long as metallic Mg material is present, the film is highly reflective and the transmission is negligible. As soon as the highly transparent MgH_2 is formed, the optical transmission of $Y_{0.5}Mg_{0.5}H_x$ is essentially the same as that of pure YH_x.

At first sight, this interpretation seems to be inconsistent with the fact that the enthalpy of formation of YH_3 ($\Delta H_{\beta\to\gamma}$) from YH_2 is about 7 kJ/mol more negative[11,15] than that for MgH_2 ($\Delta H_{\alpha\to\beta}$).[12,16] This means that YH_3 should be formed before MgH_2 during hydrogen absorption. However, ΔH depends strongly on the host metal volume.[17] A dilatation of the lattice induces a lowering of $d\Delta H/d\ln V = BV_H$ with V_H the molar volume of hydrogen

and B the bulk modulus of the hydride. By using the observed lattice volume change of YH_2 ($\delta V/V = -0.069$) and Mg ($\delta V/V = 0.076$) and $B_0 = 81$ kJ/cm^3 for YH_2 (Ref. 18) and $B_0 = 35.4$ kJ/cm^3 for Mg, we estimate that the actual formation enthalpy equals: $\Delta H_{\beta\to\gamma} = -31$ kJ/mol H for $YH_{3-\delta}$ and $\Delta H_{\alpha\to\beta} = -42$ kJ/mol H for MgH_2. Therefore in our stressed films MgH_2 will form *before* the YH_3.

In conclusion, x-ray results and optical transmission and electrical resistivity data show that the absence of a YH_2 transmission window (photon energy around 1.8 eV) in Mg-containing switchable mirrors can be understood in terms of a two-step disproportionation of the $Y_{0.5}Mg_{0.5}$ alloy during hydrogen absorption. In the first step YH_2 is formed, leaving pure Mg clusters in the matrix. In the second step the concentration of YH_2 increases gradually but the optical transmission remains low until the Mg clusters are transformed into highly transparent MgH_2. From there on the optical properties of $Y_{0.5}Mg_{0.5}H_x$ are similar to those of YH_x. Thus Mg acts as a kind of microscopic optical shutter. Remarkably, YH_x remains *cubic* for all values up to $x \approx 3$. The suppression of the transparency window of the β-YH_2 phase leads to a significant enhancement in contrast between the optically opened and optically closed phase in $Y_{0.5}Mg_{0.5}H_x$ (and other $Y_{1-y}Mg_y$ alloys).

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