Self-Organized Layered Hydrogenation in Black Mg_2NiH_x Switchable Mirrors

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In addition to a mirrorlike (Mg_2Ni) and a transparent (Mg_2NiH_4) state, thin films of Mg_2NiH_x exhibit a remarkable black state with low reflection over the entire visible spectrum, essentially zero transmission and a low electrical resistivity. Such a black state is not explicable for a homogeneous layer since a large absorption coefficient always yields substantial reflection. We show that it results from a self-organized and reversible double layering of metallic $Mg_2NiH_{0.3}$ and semiconducting Mg_2NiH_4.

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The discovery by Huiberts *et al.* that yttrium and lanthanum films change from shiny metallic to transparent during absorption of hydrogen [1] stimulated much experimental and theoretical research on rare-earth switchable metal-hydride films and their alloys with Mg [2]. In a search for rare-earth-free switchable mirrors Richardson *et al.* [3,4] found that Mg_2Ni also became transparent upon exposure to hydrogen. Subsequently, it was discovered that, in addition to the shiny-metallic and transparent states, Mg_2NiH_x exhibited a third optical state [5]: at intermediate hydrogen concentrations reflection is low ($R \approx 25\%$ in the visible spectrum), whereas no transmission is observed and hence 75% of the incoming light is absorbed. Such behavior is quite intriguing since a low reflection usually is accompanied by a low charge carrier density; however, the electrical conductivity is metallic and Hall effect measurements on Mg_2NiH_x films do not confirm an exceptionally large decrease of the free charge carrier density [6]. Another difficulty is that for a homogeneous thin film of 250 nm to be nontransparent the extinction coefficient k that describes the absorption needs to be quite large. But a large k also yields substantial reflection which is in contradiction to the experimental results.

In this Letter we describe the surprising mechanism responsible for the unusual physical properties mentioned above.

Mg_2Ni samples are prepared by evaporation in a ultrahigh vacuum (UHV) chamber (base pressure $<10^{-10}$ mbar) or by dc magnetron sputtering (base pressure 10^{-7} mbar). The thickness of the films varies between ~50 and ~300 nm. A Pd cap layer (5–10 nm) is added for oxidation protection as well as to promote reversible hydrogen uptake in the samples. The composition—as checked with Rutherford backscattering spectrometry—is homogeneous over the entire sample thickness and close to Mg_2Ni. Optical measurements in the visible and near infrared are performed in a Bruker IFS66 Fourier transform spectrometer equipped with a reflection and transmission unit with near normal incidence of the incoming beam. The probed photon energies were between 0.72 and 3.5 eV (corresponding to $\lambda =$ 1722–354 nm) in the visible and 0.14 to 1 eV ($\lambda =$ 8856–1240 nm) in the midinfrared.

Figure 1 shows reflection R and transmission T of a sample 250 nm Mg_2Ni/7 nm Pd at various hydrogen concentrations. As hydrogen is introduced, the resistivity increases from 0.061 mΩ cm in the metallic state

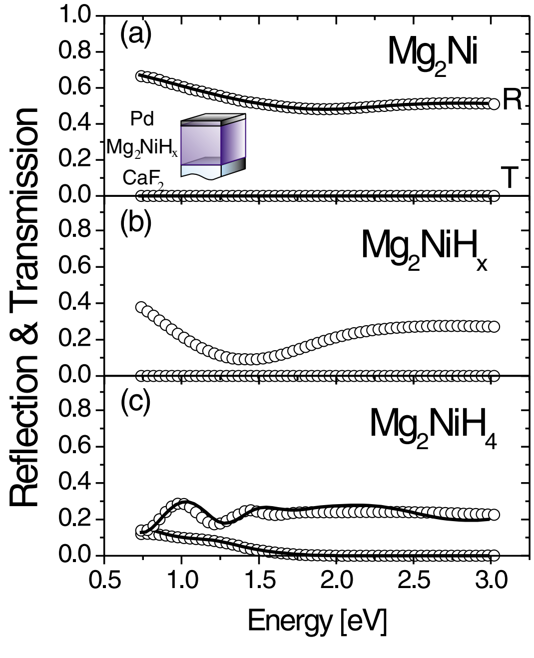

FIG. 1 (color online). Reflection R and transmission T of a 250 nm Mg_2Ni/7 nm Pd film on CaF_2. (a) As deposited Mg_2Ni, (b) black Mg_2NiH_x, and (c) fully loaded Mg_2NiH_4. The reflection is measured through the substrate. At intermediate hydrogen concentrations, R exhibits a deep minimum at about 1.5 eV and stays below 25% over the entire visible range while T is very low ($T < 10^{-4}$). The solid lines are calculations (see text) using known dielectric functions for Mg_2Ni and Mg_2NiH_4. The curves in (b), corresponding to the black state, cannot be fitted with any choice of the refraction index n and extinction coefficient k for the Mg_2NiH_x layer.

[Fig. 1(a)] to 1.37 mΩ cm for semiconducting, transparent Mg_2NiH_4 [Fig. 1(c)], the latter value being mainly limited by the metallic Pd layer on top. At intermediate hydrogen concentrations, R decreases dramatically over the entire visible spectrum, whereas T remains extremely low as shown in Fig. 1(b). At about 1.5 eV a broad minimum ($R \leq 10\%$) is observed. In a simple Drude model a decreasing reflection R is due to a decreasing plasma energy $\omega_p^2 = n_e e^2/\epsilon_0 m$ (n_e, effective charge carrier density; ϵ_0, vacuum permittivity; e, electron charge; and m, electron mass). Such a simple analysis gives a decrease of the charge carrier density by a factor of 25 [5]. However, Hall effect measurements do not confirm such an abrupt decrease of n_e. On the contrary, over the whole range $0 \leq x \leq 4$ each added hydrogen removes one electron from the conduction band of the host metal [6].

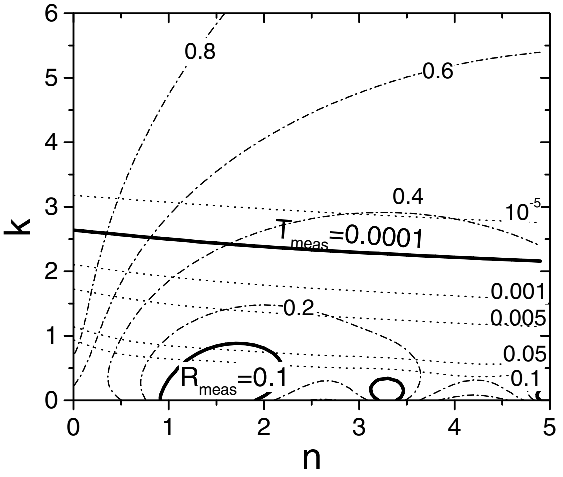

FIG. 2. Contour maps of the reflection (dot-dashed lines) and transmission (dotted lines) calculated for a sample 250 nm Mg_2NiH_x/7 nm Pd on a CaF_2 substrate. The incoming beam ($\hbar\omega = 1.5$ eV) reached the layer through the substrate and (n, k) are those of the Mg_2NiH_x layer. The contours of the experimentally obtained values R_{meas} and T_{meas} are indicated (thick lines). There exists no couple (n, k) that describes simultaneously the experimentally observed reflection R_{meas} and transmission T_{meas}; i.e., these contours never cross.

There is another difficulty: The observed R and T values cannot be explained assuming a homogeneous Mg_2NiH_x layer. This follows directly from

$$R = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2}, \tag{1}$$

$$T = e^{-2(\omega k d/c)}, \tag{2}$$

which give the reflection of a thick film (that is with a larger thickness than the optical absorption depth) with thickness d, refraction index n, and extinction coefficient k for light coming from a transparent medium with refraction index n_0. The energy and the velocity of the incoming light are $\hbar\omega$ and c, respectively. To reproduce the low transmission ($T < 10^{-4}$) for a 250 nm thick film on, e.g., CaF_2 ($n_0 = 1.43$), Eq. (2) requires $k > 2.4$ (for $\hbar\omega = 1.5$ eV). From Eq. (1) it then follows that R should exceed 30% which is clearly in contradiction to the experimental data. These conclusions are confirmed by an exact calculation of R and T for the entire sample by means of a transfer matrix method that considers reflection and transmission at each interface and absorption in each layer (i.e., 7 nm Pd–250 nm Mg_2NiH_x on Ca_2F). The refraction indices for Ca_2F and Pd are known (Ref. [7]) and R and T are then calculated for a dense grid of (n, k) values for the Mg_2NiH_x layer [8]. Possible solutions for (n, k) are found when R and T coincide with the experimental values. Figure 2 gives the results of such a calculation for incoming light with an energy of $\hbar\omega = 1.5$ eV. There is no couple (n, k) that simultaneously describes the measured values R_{meas} and T_{meas} (indicated by thick lines). The discrepancy is quite serious since a 10^3 larger transmission would be necessary for the lines to cross and it persists for all energies between 0.8 and 2.5 eV. Although the particle size D ranges from ≈ 30 nm for the metallic sample to nanocrystalline (too small to be detected with x rays) in the fully loaded state and hence $D \ll \lambda$ (λ: wavelength of light), effective medium theories [9] fail to explain the optical properties. Measurements of the total reflection and transmission coincide within experimental errors with the measured specular reflection and transmission hence confirm that the diffuse scattering is negligible and can be excluded as a reason for low reflection.

We show now that the highly absorbing state in Mg_2NiH_x is caused by a subtle interplay of the effective dielectric function $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ (which is related to the refractive index n and extinction coefficient k by $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$) and a self-organized double layering of the Mg_2NiH_x film. Even though hydrogen enters through the Pd cap layer, the nucleation of the hydrogen-rich phase starts deep in the sample near the film-substrate interface. This unusual loading sequence is nicely demonstrated when the sample is observed simultaneously from both sides: once through the transparent substrate and once from the Pd cap layer side. Figure 3 displays photographs taken from two pieces of the same sample (a) in the metallic state and (b) black Mg_2NiH_x, respectively. On the left-hand side the view is through the substrate, and on the right-hand side the Pd cap layer faces the front. Without hydrogen, both sides are shiny reflecting, and the small difference in appearance is mainly due to the different media for the incoming light (sapphire, which is optically thick, and air). After hydrogen is introduced at a pressure of 16 mbar, it takes a couple of minutes for Mg_2NiH_x to become black when viewed through the substrate. Surprisingly, at the same time Mg_2NiH_x keeps a metallic appearance when observed from the Pd side. Note that the Pd cap layer (5 nm) has a rather high transparency ($T > 40\%$) and

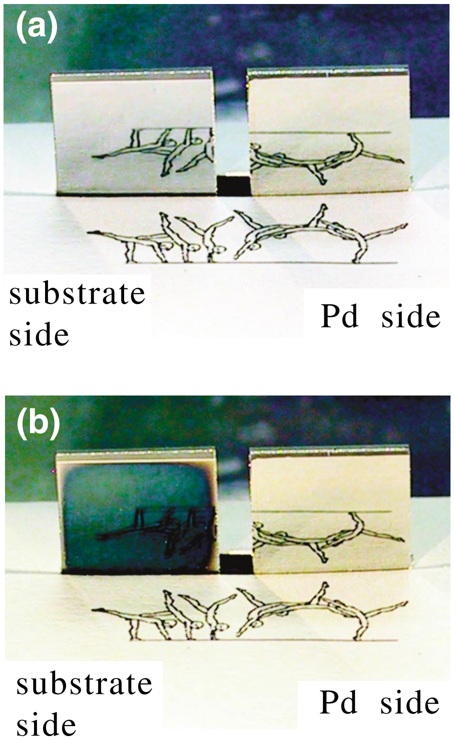

FIG. 3 (color). Photographs of two identical films 200 nm $Mg_2Ni/5$ nm Pd on sapphire. On the left-hand side we look at the film through the substrate and on the right-hand side from the Pd layer side. (a) As deposited: both sides appear metallic as can be seen from the reflection of the test pattern in front of the samples. (b) Upon exposure to hydrogen (16 mbar H_2 at room temperature) the "substrate" side of the sample becomes black while the "Pd" side stays metallic. The difference in appearance is not due to the thin metallic Pd cap layer but to the nucleation of the hydrogen-rich phase Mg_2NiH_4 at the film-substrate interface.

hence the Mg_2NiH_x layer underneath contributes significantly to the observed reflection. These photographs demonstrate vividly that the originally homogeneous film starts to react with hydrogen at the substrate-film interface. Further H uptake causes the hydrogen-rich layer to grow at the expense of the metallic part until eventually the entire film has switched to Mg_2NiH_4. Because of the double layering and the transparency of Mg_2NiH_4, the reflection exhibits typical interference fringes when the optical path of the light reflected between the two interfaces fits a multiple of the wavelength (see Fig. 4). With increasing hydrogen concentration the increasing Mg_2NiH_4 thickness yields to a shift of the interference fringes towards lower energies as well as to a smaller difference between adjacent maxima. In contrast, the reflection viewed from the Pd side is unchangingly high. The hydrogen concentration for the different optical states and the loading sequence has been independently established [6] by means of electrochemical loading. Upon hydrogen loading, the samples dissolve hydrogen homogeneously up to $Mg_2NiH_{0.3}$ which still has a metallic appearance. The dramatic decrease of R coincides with the nucleation of Mg_2NiH_4. Especially, ^{15}N hydrogen depth profiling [10] confirmed the formation of a hydrogen-rich layer close to the substrate interface. The average hydrogen concentration in the black state was estimated to be $x \approx 0.8$ [11]. The increasing thickness of the evolving Mg_2NiH_4 layer can be directly determined from the experimental reflection data as shown in Fig. 5. The solid lines are model calculations of R in accordance with the above described scenario. The dielectric function of Mg_2Ni, $Mg_2NiH_{0.3}$, and Mg_2NiH_4 have been determined independently [10]. In Figs. 5(b) and 5(c) a self-organized double layer $Mg_2NiH_{0.3}/Mg_2NiH_4$ is assumed for the transfer matrix calculation (see sketch in Fig. 5). The only free parameter is the thickness of Mg_2NiH_4 which varies from $d \approx 30$ nm to the total thickness 250 nm. In Fig. 5(a) (in the black state), the bottom layer close to the substrate (~30 nm) is presumed to consist of a mixture of $Mg_2NiH_{0.3}$ and Mg_2NiH_4. This mixture of metallic and semiconducting particles ($D \ll \lambda$) can be described within the effective medium Bruggeman approximation for spherical particles [9] and an effective dielectric function for a volume ratio 20 vol% $Mg_2NiH_{0.3}$–80 vol% Mg_2NiH_4 was assumed in the 30 nm layer close to the substrate with 220 nm metallic $Mg_2NiH_{0.3}$ on top. The agreement of

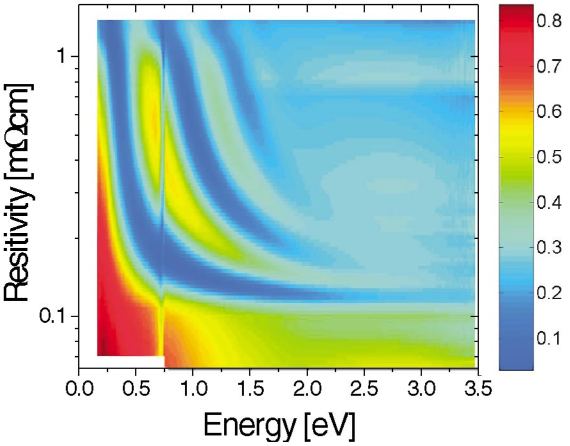

FIG. 4 (color). Intensity map of the reflection R (measured through the substrate) during hydrogen uptake of a sample 250 nm $Mg_2Ni/7$ nm Pd. The resistivity is a measure for the hydrogen concentration, upon loading ρ increases from 0.061 mΩ cm (metallic Mg_2Ni) to 1.37 mΩ cm (semiconducting Mg_2NiH_4). At low resistivity (that is, in the metallic state) R is high. At about $\rho = 0.13$ mΩ cm, R exhibits a deep minimum over the entire visible wavelength regime. A double layer system $Mg_2NiH_{0.3}$-Mg_2NiH_4 is formed, and subsequently interference minima and maxima appear. As the transparent layer increases in thickness these interference fringes shift to lower energies. The feature at about 0.75 eV is an artifact of the measurement due to an absorption line in the background.

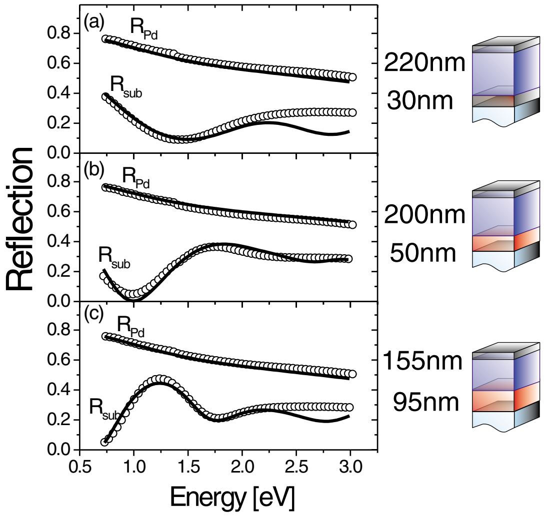

FIG. 5 (color online). Reflection spectra R (○) of a 250 nm Mg_2NiH_x/7 nm Pd on a CaF_2 sample measured through the substrate (R_{sub}) and from the Pd side (R_{Pd}) at various H concentrations [at (a) $\rho = 0.13$, (b) 0.14, and (c) 0.18 mΩ cm; compare Fig. 4]. The solid lines are model calculations that assume a self-organized double layer, as sketched schematically on the right. The thicknesses used in the calculations for the evolving bottom layer Mg_2NiH_4 are 30, 50, and 95 nm. The remaining part of the film (220, 200, and 155 nm) is assumed to be $Mg_2NiH_{0.3}$.

the calculated curves with the experimental data confirm that black Mg_2NiH_x can be understood as the result of the interplay of the composition dependent effective dielectric function of the mixed layer and the self-organized layering of the system. The composite layer near the substrate effectively suppresses the reflection, whereas the metallic $Mg_2NiH_{0.3}$ on top inhibits any transmission and ensures a metallic conductivity. The discrepancy between the experimental data and theory at higher energies is most likely due to nonideally flat interfaces of the self-organized double layer. It is also noteworthy to mention that the self-organized layering process described above is fully reversible. During hydrogen unloading reflection, transmission and resistivity go through the same stages as during loading but, of course, in reversed order.

The "impossible" black state described above is not an exotic peculiarity of the Mg_2NiH_x system. Similar behavior has been observed in other Mg-based alloys (Mg-Co, Mg-Fe). The spatial separation of the hydrogen uptake (in the catalytic Pd layer) and the nucleation of the new phase in the vicinity of the film-substrate interface seems inherent to these systems. The black state is robust in the sense that it appears in sputtered films as well as in UHV evaporated films and the choice of the substrate is also not crucial, i.e., Al_2O_3, ITO, SiO_2, and CaF_2 were used. Scanning tunneling microscopy studies suggest that the growth mode during the initial stages of deposition plays an important role for the preferential nucleation [12]. This suggests new strategies for the optimization of these materials for the use in hydrogen storage applications [13]. Finally, the switching from mirror to a black absorber offers interesting possibilities for applications as smart coatings in solar collectors and antiglare rearview mirrors or as a sensing layer in optical fiber hydrogen detectors.

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