

Double layer formation in Mg–TM switchable mirrors (TM: Ni, Co, Fe)

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Abstract

The optical properties of Mg–TM (TM: Ni, Co, Fe; Mg:TM \approx 2) thin films during hydrogenation are investigated using reflection and transmission measurements. Mg–Ni and Mg–Co show an unusual behavior upon exposure to hydrogen. The nucleation of the hydride starts at the film substrate interface and not – as intuitively expected – at the Pd covered top side of the film. Consequently, a double layer structure is formed. Reflection measurements are used to identify the loading behavior as the double layering yields to an remarkable optical black state at intermediate hydrogen concentrations. Photometric measurements on samples loaded at H_2 -pressures of 10^5 Pa show that in Mg–NiH_x and Mg–CoH_x the complex hydrides Mg₂NiH₄ and Mg₂CoH₅ are formed, whereas in Mg–Fe_x the formation of MgH₂ is prevalent.
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1. Introduction

Mg-based hydrogen storage materials belong to the most promising candidates for application as light weight storage materials in a future hydrogen economy. Among the materials under consideration are the complex hydrides Mg₂NiH₄, Mg₂CoH₅ and Mg₂FeH₆ with hydrogen storage capacities of 3.6 wt.% [1] (Mg₂NiH₄), 4.5 wt.% [2] (Mg₂CoH₅) and 5.5 wt.% [3] (Mg₂FeH₆). Recently, it has been shown that Mg–Ni, Mg–Co and Mg–Fe can be prepared as thin films (capped with Pd) which readily react with hydrogen at room temperature and moderate pressures ($\leq 10^5$ Pa H₂) [4]. Since the hydrogen uptake is accompanied by a metal-to-semiconductor transition which changes the optical appearance from metallic to transparent, these films act as switchable mirrors.

In this paper, we discuss the optical properties of Mg–TM (Ni, Co, Fe) thin films with an approximate composi-

tion Mg:TM \approx 2 upon hydrogenation. Although only Mg–Ni forms a stoichiometric compound Mg₂Ni [5], single phase hydrides exist for all three Mg–TM materials: Mg₂NiH₄ [6], Mg₂CoH₅ [2] and Mg₂FeH₆ [3]. The complex hydrides are semiconductors with band gaps E_g of 1.6 eV [7] (Mg₂NiH₄) and 1.9 eV [8] (Mg₂CoH₅). For Mg₂FeH₆, E_g was calculated to be 1.74 eV [9].

In Mg₂NiH_x thin films an unusual loading behavior has been observed. Beside the two 'normal' optical states of a switchable mirror – reflecting and transparent – at intermediate hydrogen concentrations, Mg₂NiH_x exhibits a black state with low reflection ($R < 0.25$) and zero transmission ($T < 10^{-4}$) over the entire visible spectrum [7]. The transition between metallic, black and transparent is reversible. This peculiar optical state originates from a preferred nucleation of Mg₂NiH₄ close to the film-substrate interface [10–12] that causes a self-organized double layering of the originally homogeneous film. The loading sequence of Mg₂NiH_x thin films, is schematically shown in Fig. 1. Upon exposure to hydrogen an initially homogeneous layer absorbs hydrogen in solid solution and Mg₂NiH_{0.3} is formed (a). The nucle-

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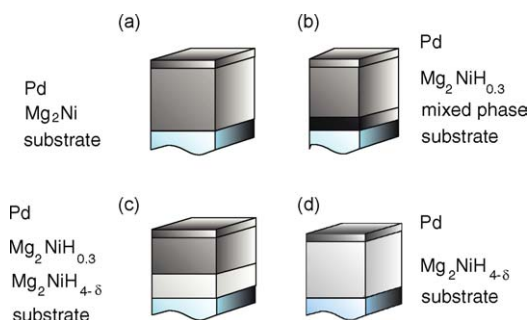


Fig. 1. Schematic picture of the hydrogenation sequence in Mg_2NiH_x thin films covered with Pd.

ation of Mg_2NiH_4 starts in a layer of ≈ 30 nm thickness at the film–substrate interface (b). Viewed through the substrate this state appears black. This double layer structure persists and upon further loading Mg_2NiH_4 grows in thickness (c) until the entire film has switched to Mg_2NiH_4 (d). In the following we will show that Mg–Co exhibits a similar double layering during hydrogenation. In contrast, in Mg–Fe the indications for a double layer formation are less clear. Transmission and reflection measurements on fully hydrogenated Mg–TMH_x suggest that the complex hydride is only partially formed for Mg–Co and Mg–Fe, while in Mg–Ni the entire film has reacted to form Mg_2NiH_4 .

2. Experimental

The samples are prepared either by evaporation in an UHV-chamber (base pressure 10^{-8} Pa) or by sputtering from two sources in a vacuum chamber (base pressure 10^{-6} Pa). Quartz is used as substrate and the films are covered with 5–10 nm Pd for oxidation protection and to promote further hydrogen uptake. The reflection and transmission measurements were done in a Bruker IFS66 Fourier transform spectrometer between 0.72 and 3.5 eV (corresponding to wavelengths $\lambda = 1722$ –354 nm) and in a Perkin Elmer Lambda 900 diffraction grating spectrometer with an energy range 0.495–6.51 eV ($\lambda = 2500$ –190 nm). The reflection measurements are done during hydrogen uptake through the transparent substrate. In the Fourier transform spectrometer, the reflection from the Pd capped top of the film was additionally monitored at one fixed wavelength by means of a laser diode ($\hbar\omega = 1.95$ eV).

3. Results and discussion

Fig. 2 shows the reflection R at the photon energy $\hbar\omega = 1.95$ eV for the switchable mirrors Mg–TM (TM = Ni, Co) while the H_2 -pressure is increased to 10^5 Pa. R is measured both through the transparent substrate (R_{sub} , solid line) and from the Pd capped top side of the film (R_{Pd} , dashed line). R_{sub} , R_{Pd} are plotted as a function of the resistivity ρ ,

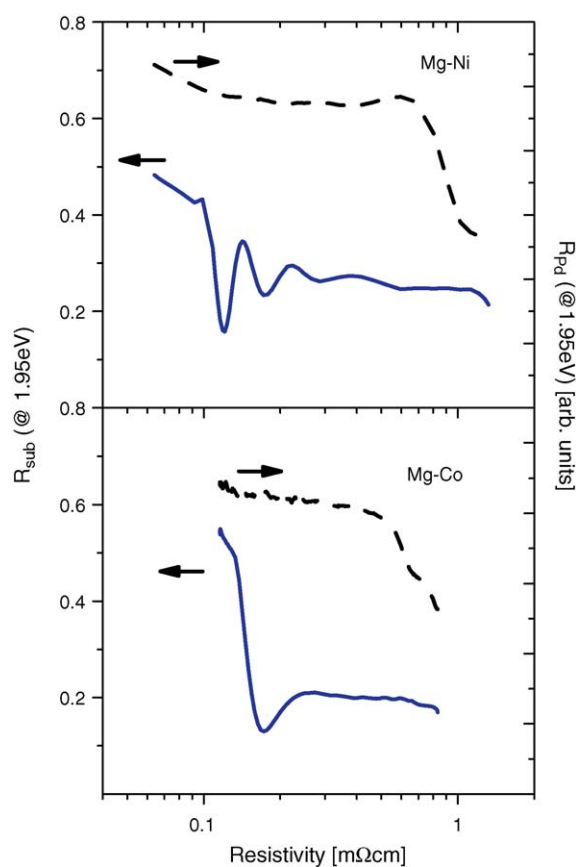


Fig. 2. Reflection R at $\hbar\omega = 1.95$ eV for Mg–TM switchable mirrors (TM: Ni, Co) as a function of resistivity which is a measure for the hydrogen concentration. At $\rho \geq 1$ m Ω cm, the samples are fully loaded with hydrogen. The sample compositions after deposition are 250 nm $\text{Mg}_{1.7}\text{Ni}$ capped with 7 nm Pd and 200 nm Mg_2Co capped with 10 nm Pd, respectively.

which is a measure of the hydrogen concentration. As hydrogen is introduced into Mg–Ni and Mg–Co, R_{sub} observed through the substrate decreases rapidly and goes through a minimum at low resistivity. In contrast, R_{Pd} remains unchangingly high up to higher hydrogen concentrations (i.e., high resistivity). Furthermore, transmission remains low (i.e., $T < 2 \times 10^{-4}$ at $\hbar\omega = 1.95$ eV up to $\rho_{\text{Mg–Ni}} = 0.54$ m Ω cm and $\rho_{\text{Mg–Co}} = 0.45$ m Ω cm). This course of reflection fits nicely to the layered hydrogenation shown in Fig. 1. The nucleation of the semiconducting hydride in the vicinity to the film–substrate interface yields to a dramatic decrease of R_{sub} while R_{Pd} still reflects the metallic appearance of the metallic layer on top (compare Fig. 1(b)) [12]. Upon further loading, the thickness of the hydrogen rich layer increases. The oscillating R_{sub} corresponds to interference oscillations due to light reflected at the two interfaces of the transparent hydride layer (compare Fig. 1(c)). For Mg–NiH_x, two subsequent minima are observed indicating that the spontaneously formed double layer is very well ordered. In Mg–CoH_x, the layering is more distorted and the oscillations in R_{sub} are damped out more quickly. The reflection observed from the Pd top side only decreases when the film is almost completely loaded, i.e. at high resistivity [13]. Only then, the part of the film that is

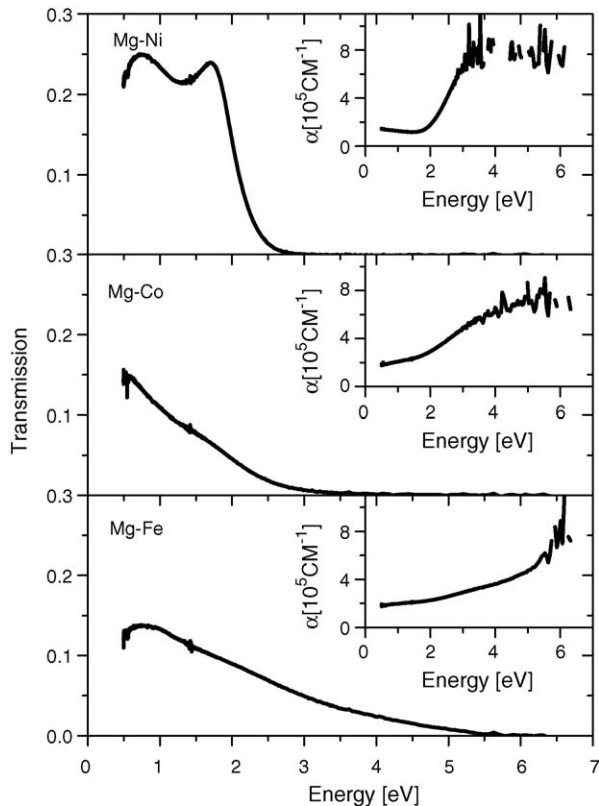


Fig. 3. Transmission T of Mg–TM (TM: Ni, Co, Fe; Mg:TM = 2:1) switchable mirrors after hydrogenation in 10^5 H₂ (at 80 °C).

close to the Pd capping layer also switches to the transparent hydride and the films become transparent.

Compared to Mg–NiH_{*x*} and Mg–CoH_{*x*}, the hydrogen loading behavior of Mg–FeH_{*x*} is different. Similar to R_{sub} , the reflection observed from the Pd side decreases already at low hydrogen concentration (i.e., low resistivity) and no interference oscillations are observed in R_{sub} . This points to a more homogeneous hydrogen uptake throughout the entire film thickness.

Fig. 3 shows the transmission T and absorption coefficient α of Mg–TM (TM: Ni, Co, Fe; Mg:TM = 2:1) switchable mirrors after exposure to H₂-pressures of 10^5 Pa for 12 h in 80 °C. In each case, the film thickness is 100 nm covered with 10 nm Pd. α was obtained from

$$\alpha = -\frac{1}{t} \ln \left(\frac{T}{1-R} \right) \quad (1)$$

where t is the thickness of the layer, and R and T , reflection and transmission of the fully loaded film. No correction for the Pd layer is included. The absorption coefficient is distinctively different for the three Mg–TMH_{*x*} layers. Mg–NiH_{*x*} exhibits a sharp increase of α around 2 eV indicating the onset of absorption above the band gap of Mg₂NiH₄ (1.6 eV [7]). For Mg–CoH_{*x*} the absorption edge is far less pronounced and only a small kink is observed around 2 eV. For Mg–FeH_{*x*}, α exhibits a gradual increase over the accessible photon energy regime with a steeper slope only around 6 eV. For the var-

ious Mg–TM-hydrides the fraction of the formed complex hydride apparently depends on the transition metal. Enache et al. [14] found a hydrogen concentration of $x \approx 3.95$ in Mg₂NiH_{*x*} under similar loading conditions. In comparison, Mg–CoH_{*x*} appears to react less completely, although the kink in α around 2 eV presumably belongs to the absorption edge of Mg₂CoH₅. In Mg–FeH_{*x*} the formation of Mg₂FeH₆ is less evident. T extends to high energies and the steep increase of α_{Fe} around 6 eV points to the formation of MgH₂ with a band gap of 5.6 eV [15].

4. Conclusion

We have shown that the hydrogenation of Mg–TMH_{*x*} switchable mirrors (TM: Ni, Co) takes place in an unusual double layer structure where the nucleation of the hydrogen rich phase preferentially takes place at the film–substrate interface. In contrast, Mg–Fe shows a more homogeneous hydrogen uptake. From the photometric data in the fully loaded state, it appears that in Mg–FeH_{*x*}, MgH₂ is predominantly formed, while in Mg–NiH_{*x*} and Mg–CoH_{*x*} the signature of Mg₂NiH₄ and Mg₂CoH₅ is clearly visible. Possible reasons for the different loading behavior is the absence of any intermetallic compound in the Mg–Fe system, consequently the atomic movements to form the complex hydride Mg₂FeH₆ is considerably higher than in Mg–Ni or Mg–Co. The understanding of the enhanced hydrogen affinity at the film–substrate interface and the study of the complex hydride formation in thin films might give valuable information for the use of these Mg–TM alloys as hydrogen storage materials.

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