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J. Isidorsson, I. A. M. E. Giebels, R. Griessen, and M. Di Vece

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Tunable reflectance Mg–Ni–H films

J. Isidorsson^{a)}

Faculty of Sciences, Division of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands and Solid State Physics, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

I. A. M. E. Giebels^{b)} and R. Griessen^{c)}

Faculty of Sciences, Division of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

M. Di Vece

Physics and Chemistry of Condensed Matter, Debye Institute, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands

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Mg₂NiH_x switchable mirrors, which switch from shiny metallic Mg₂Ni to transparent Mg₂NiH₄, are shown to exhibit also dramatic reversible changes in *reflectance* at remarkably low hydrogen concentrations. Already for $x \approx 0.3$ a 232 nm thick Mg₂NiH_x film has an absorptance of $\sim 90\%$ over the whole visible optical spectrum. The transition from highly reflective to black occurs in the concentration interval $0.1 < x < 0.3$. The volume changes involved are one order of magnitude smaller than in the transition from reflecting to transparent. This is expected to enhance the lifetime of future devices based on these materials. © 2002 American Institute of Physics. [DOI: 10.1063/1.1463205]

In 1996, Huiberts *et al.*¹ discovered that palladium protected metal-hydride films of yttrium and lanthanum metals could be simply, reversibly, and rapidly switched between a shiny metal and a transparent large band-gap semiconductor by hydrogen loading.² These first-generation hydrogen switchable materials (HYSWIM) were soon followed by a second generation of HYSWIMs consisting of Mg-alloyed rare-earth-hydrides^{3,4} discovered by Van der Sluis *et al.* and a third generation of Mg–Ni hydrides^{5,6} discovered in 2000 by Richardson *et al.* Contrary to bulk Mg₂Ni, films of this compound react readily (and without embrittlement) with gaseous hydrogen at room temperature and moderate pressure (well below 10⁵ Pa) to form Mg₂NiH₄. The hydrogen solubility range⁸ of the hexagonal Mg₂Ni is limited to 0.3, i.e., it extends up to a composition Mg₂NiH_{0.3}. The hydride Mg₂NiH₄ is the only stable ternary compound known for the Mg–Ni–H system.

The physics of Mg₂NiH₄ is very interesting since the nature of the ground state (metallic or semiconducting) depends crucially on the out-of-plane distance of the four H atoms⁹ covalently bound to Ni. In this picture Mg₂NiH₄ is a sort of ionic compound formed of Mg²⁺ ions and [NiH₄]^{4–} complexes. As the availability of thin films of this material makes it possible to explore in detail its basic physical properties (electrical resistivity, Hall coefficient, optical transmittance and reflectance, energy gaps, etc), Mg₂NiH₄ films have recently attracted a lot of interest.

In this letter, we report on another remarkable optical property of Mg₂NiH_x films. We show that already at low hydrogen concentration (i.e., for $x < 0.3$), Mg₂NiH_x films ex-

hibit dramatic changes in reflectance. While remaining in the metallic state, they switch from a shiny mirror to a black absorber. The great attractiveness of these variable reflectance metalhydride films is that (i) only little hydrogen is needed for optical switching, (ii) no large volume expansion occurs during switching, (iii) the switching is reversible, and (iv) they do not contain rare earths, which are highly corrosive.

Films of Mg₂Ni are prepared by sputter deposition in a Balzers UTT 400 sputter unit with Mg and Ni targets of typically 99.9% purity. The background pressure of the vacuum chamber is less than 10^{–5} Pa, and the Ar-deposition pressure is below 1 Pa. Glass substrates with a thin conducting layer of indium tin oxide, glassy carbon, and Corning 7059 are used for electrochemical, Rutherford backscattering spectrometry (RBS), optical, and electrical measurements, respectively. The films are covered *in situ* with a thin layer (≈ 2 nm) of Pd to protect them against oxidation and to promote hydrogen dissociation and absorption. The composition is determined *ex situ* with RBS to be Mg₂Ni with a little excess (0.1) of Mg. Hydrogen gas loading is carried out at room temperature at pressures between 400 and 10⁵ Pa. The pressures are chosen so as to have ample loading/unloading time for detailed measurements. X-ray experiments are performed with Cu K α radiation in a rotating anode Rigaku x-ray spectrometer. The as-deposited films do not exhibit any x-ray diffraction peaks and are therefore either amorphous or nanocrystalline. Optical measurements are carried out in a Bruker IFS66/S Fourier transform infrared spectrometer at photon energies between 0.72 and 3.5 eV corresponding to wavelengths between 1722 and 354 nm. Transmission and reflection at near normal incidence are recorded continuously during loading/unloading. The electrical resistivity is

^{a)}Electronic mail: jcisidor@nat.vu.nl

^{b)}Electronic mail: giebel@nat.vu.nl

^{c)}Electronic mail: griessen@nat.vu.nl

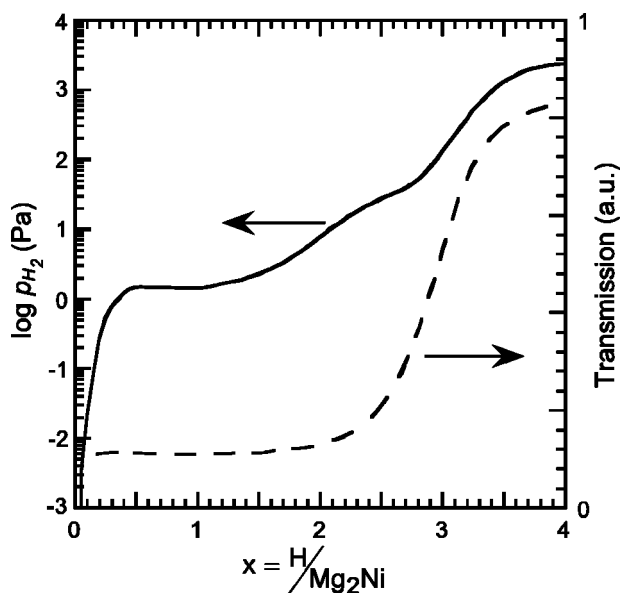


FIG. 1. Room temperature hydrogen pressure-composition isotherm evaluated from electrochemical GITT measurements on a 232 nm thick Mg_2NiH_x protected with a 2 nm thick Pd capping layer. The transmission measured with a laser with $\hbar\omega = 1.85$ eV is given in arbitrary units. The plateau corresponding to the two-phase region between $\text{Mg}_2\text{NiH}_{0.3}$ and Mg_2NiH_4 starts approximately at $x = [\text{H}]/[\text{Mg}_2\text{Ni}] \approx 0.3$. The large changes in reflection in Figs. 2 and 3 occur at $x < 0.3$.

measured in a Van der Pauw¹⁰ configuration simultaneously with x-ray scattering and optical spectra.

Electrochemical loading is carried out with an EG&G PAR 273A potentiostat/galvanostat in 1 M KOH in a standard three-electrode configuration with a Pt counter electrode and an Hg/HgO reference electrode. Optical transmission is measured simultaneously with a laser at 1.85 eV. The galvanostatic intermittent titration technique (GITT) is used to determine the equilibrium potential U_{eq} as a function of hydrogen concentration in the sample.¹¹ With these data and Nernst's equation (with p_{H_2} in units of 10^5 Pa and U_{eq} in volts)

$$\ln p_{\text{H}_2} = -\frac{2F}{RT}(U_{\text{eq}} + 0.926), \quad (1)$$

we obtain the pressure-composition isotherm shown in Fig. 1. In Eq. (1), F is the Faraday constant, R is the molar gas constant, and T is the absolute temperature. The pressure-composition isotherm exhibits a plateau near $p_{\text{H}_2} \approx 2$ Pa that corresponds to the coexistence region of $\text{Mg}_2\text{NiH}_{0.3}$ and Mg_2NiH_4 . For $x = [\text{H}]/[\text{Mg}_2\text{Ni}] > 3.3$, development of gaseous H_2 on the electrode surface leads to a spurious saturation in p_{H_2} and transmission. The large changes in reflectance described below occur in the α - Mg_2NiH_x phase for $x < 0.3$, i.e., before the plateau in the pressure-composition isotherm is reached.

In Fig. 2, the evolution of the resistivity of a 232 nm thick Mg_2NiH_x film is displayed together with the optical reflection and transmission recorded at 1.24 eV (i.e., 1000 nm). The sample is exposed to hydrogen (1.2×10^3 Pa H_2) at $t = 350$ s. On the high hydrogen concentration side ($t > 4000$ s), one observes large variations of the electrical resistivity and the optical transmittance. The resistivity increases from $260 \mu\Omega \text{ cm}$ to $9 \text{ m}\Omega \text{ cm}$ when a composition

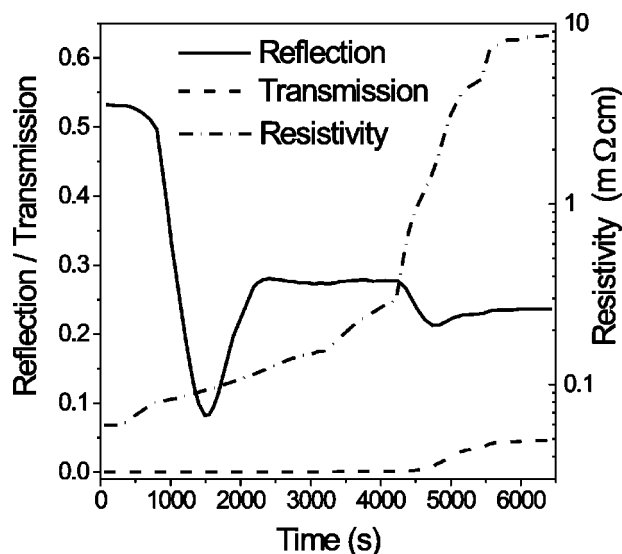


FIG. 2. Optical transmission and reflection at $\hbar\omega = 1.24$ eV recorded simultaneously together with the electrical resistivity during hydrogen loading of a 232 nm thick Mg_2NiH_x protected with a 2 nm thick Pd capping layer. At 3200 s, the pressure is increased from 1500 to 2500 Pa, at 4200 s to 9200 Pa, at 5400 s to 0.250×10^5 Pa, and at 5800 s to 10^5 Pa.

close to Mg_2NiH_4 is reached. These changes are associated with a metal-insulator transition. The (optical) band gap of the transparent Mg_2NiH_4 is 1.6 eV, and increases with increasing Mg content. The transmission is lower than that of more Mg-rich films.^{5,6}

The most interesting feature in Fig. 2 and, at the same time, the central result of this letter, is the dramatic drop in the optical reflectance on the low hydrogen concentration side. Between $t = 700$ and 1500 s, which correspond approximately to $x \approx 0.2$ and 0.3 , the reflectance drops by a factor of 6 while the electrical resistivity remains metallic: at $x \approx 0.3$, it is $94 \mu\Omega \text{ cm}$. As the $\text{Mg}_2\text{NiH}_{0.3}$ film is nontransparent, the film has an absorbance larger than 90% in the minimum reflectance state. Note that the intrinsic absorbance of $\text{Mg}_2\text{NiH}_{0.3}$ is even higher since the reflectance has not been corrected for the reflectance of the glass substrate, which is $\approx 3.5\%$. Furthermore, as seen in Fig. 3, the concentration at which the minimum in reflectance occurs (i.e., $t \approx 1500$ s) is essentially independent of the photon energy for $\hbar\omega > 1.25$ eV. This implies that a low reflectance occurs over the entire visible spectrum in a narrow range of hydrogen concentration around $x \approx 0.3$, i.e., around $t = 1500$ s in Fig. 3.

A Drude-Lorentz fit to the data in Fig. 3 suggests that the density of free charge carriers decreases rapidly between $t = 700$ and 1500 s (i.e., for x between 0.2 and 0.3) since the fitted plasma energy $\hbar\omega_p$ decreases from approximately 10 eV in Mg_2Ni to approximately 2 eV in $\text{Mg}_2\text{NiH}_{0.3}$. Such a large shift, which corresponds at least to a decrease by a factor of 25 in charge carrier density n , ($\hbar\omega_p \propto \sqrt{n}$) can not be understood within a rigid-band structure model since each added hydrogen can at most bind one host electron to form an H^- ion. For $x = 0.3$, one would then expect that the four conduction electrons of Mg_2Ni have been reduced to 3.7 in $\text{Mg}_2\text{NiH}_{0.3}$. This 7.5% reduction in charge carrier density is much lower than the factor of 25 mentioned herein. The large drop in $\hbar\omega_p$ might, however, be indicative of a Peierls transition triggered by the rearrangement of the H ions in the

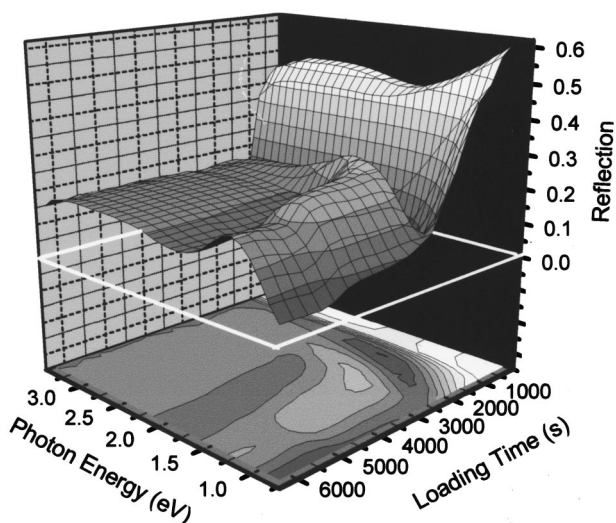


FIG. 3. Optical reflection spectra of the same film as in Fig. 2 during slow hydrogen uptake at room temperature. The hydrogen gas pressure is successively increased from 10^3 to 10^5 Pa. The contour plots show that a pronounced minimum in reflectance occurs after hydrogen loading for 1500 s for all photon energies larger than 1.25 eV at essentially the same hydrogen composition, i.e., $\text{Mg}_2\text{NiH}_{0.3}$. This implies that the film is black over the entire visible spectrum.

Mg_2Ni lattice. This idea is consistent with the high sensitivity of the $\text{Ni}-d_{x^2-y^2}$ antibonding state on the exact H position found by García *et al.*⁹ in Mg_2NiH_4 . Unfortunately, band structure calculations for $\alpha\text{-Mg}_2\text{NiH}_{0.3}$ do not exist yet.

An important parameter for the lifetime of a device is the volume change induced by absorption of hydrogen. The switching from Mg_2Ni to transparent Mg_2NiH_4 involves a huge volume increase of 32%. In order to estimate the volume increase involved in our films between mirror-like Mg_2Ni and black $\text{Mg}_2\text{NiH}_{0.3}$, we post-annealed a film at 300°C in 10^{-7} Pa for 4 h and obtained a highly oriented sample with only the (003)- and (006)-reflections of the Mg_2Ni hexagonal-close-packed (hcp) structure (P6₂22). This corresponds to a unit cell with a c axis of 13.22 Å, in excellent agreement with values found for bulk samples.^{8,12} The hcp Mg_2Ni can adsorb a small amount of hydrogen and is stable up to the composition $\text{Mg}_2\text{NiH}_{0.3}$. At this composition, we find that the c axis is extended to 13.62 Å. This corresponds to a 3% increase (which corresponds also to a 3% volume expansion since the film is laterally clamped) in good agreement with 2.3% reported by Schefer *et al.*⁸ and 3.3% reported by Darriet *et al.*¹³

The large tunability of the reflectance of Mg_2NiH_x is expected to be technologically important for the following reasons: (i) It occurs at low concentrations ($x < 0.3$) in sharp contrast with HYSWIMs for which the large optical changes occur typically for H to metal ratios above 2, (ii) it is easily tunable at room temperature and reversible,¹⁴ (iii) it involves only a small volume expansion (3% in volume), and (iv) Mg_2NiH_x remains metallic (for x up to 0.3 the resistivity is lower than $94 \mu\Omega\text{cm}$). It is thus a very attractive electrode

material for an all-solid-state heterostructure¹⁵ consisting of a hydrogen-ion conductor (solid electrolyte) and a counter electrode. This should lead to variable reflectance devices with unique properties.¹⁶

The possibility to transform a good metallic mirror into a black layer offers also entirely possibilities for electronic paper and is interesting for all applications where the thermal state of a system needs to be controlled (for example in buildings and in satellites) or the reflectance needs to be adapted to external circumstances (for example, in antiglare rear-view mirrors).

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¹⁴Although the optical and electrical properties of Mg_2NiH_x with $x < 0.3$ are similar to those of $\text{Sc}_{1-y}\text{Ti}_y\text{N}$ films with $y > 0.3$ [D. Gall, I. Petrov, and J. E. Greene, *J. Appl. Phys.* **89**, 401 (2001)], cerium monpnictides [R. Pittini, J. Schoenes, F. Hulliger, and P. Wachter, *Phys. Rev. Lett.* **76**, 3428 (1996)], and rare-earth hydrides with $x < 2.1$ [Ref. 2], Mg_2NiH_x has the enormous advantage to be easily, and reversibly, tunable at room temperature.

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¹⁶The coloration efficiency and electrical conductivity are, for example, much better than for a H-intercalated WO_3 film of the same thickness.