Thin film metal hydrides for hydrogen storage applications

Andrea Baldi and Bernard Dam*

Thin film technology is a powerful exploratory technique in the search for advanced hydrogen-storage systems. Thin films of metal hydrides allow one to perform high-throughput screening of large materials libraries, discover new metastable phases inaccessible by bulk preparation methods, and model the finite-size effects occurring at the nanoscale.

Hydrogen is a promising energy carrier, thanks to its high energy density and clean combustion process. Hydrogen is the lightest element and can be stored either in molecular (H_2) or atomic (H) form. Storage of molecular hydrogen has the disadvantage of requiring high pressures and/or low temperatures. In contrast, if the H–H bond is broken with the use of a proper catalyst, hydrogen atoms are readily absorbed into several metals at standard pressures and temperatures. The hydrogenation of a metal usually undergoes the following steps:[1] *i)* at low hydrogen pressure only a small amount (typically H/M < 0.1) of hydrogen is dissolved in the metallic lattice as a solid solution (α phase); *ii)* when the hydrogen pressure is increased up to the equilibrium
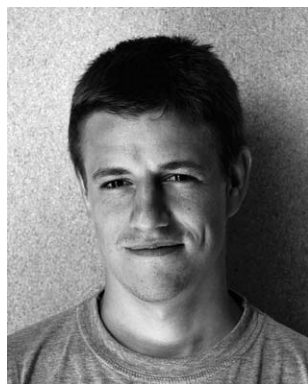
pressure, p_{eq}, the attractive elastic H–H interaction triggers the nucleation of a hydrogen-rich phase (β phase) which coexists with the solid solution.[2] At p_{eq} the hydrogen concentration H/M increases, while the hydrogen pressure in equilibrium with the metal hydride remains constant; *iii)* above p_{eq} the metal hydride is constituted only by the β phase and the hydrogen concentration in the metal increases only slightly upon further increases in pressure. These steps are highlighted in the Pressure-Composition-Isotherms (PCIs) shown in Fig. 1a. The logarithm of the equilibrium pressure is inversely proportional to the absolute temperature, T, according to the Van't Hoff equation (Fig. 1b):

$$\ln \frac{p_{eq}}{p_0} = \frac{\Delta H}{RT} - \frac{\Delta S_0}{R}$$

where ΔH is the enthalpy of hydride formation, usually assumed to be temperature independent, R is the gas

constant and ΔS_0 is the entropy of hydride formation at $p_0 = 10^5$ Pa which, in most cases, is given by the loss of entropy when H_2 gas is absorbed into the solid metal ($\Delta S \approx -130.7 J/(K\ mol H_2)$). An ideal hydrogen storage material should be characterized by large volumetric and gravimetric capacities and fast and reversible (de)hydrogenation kinetics. Furthermore, in order to be used in combination with fuel cells, it should have an equilibrium H_2 pressure of about 10^5 Pa at room temperature (*i.e.* $\Delta H \approx -40 kJ/mol H_2$). Unfortunately no known material fulfills all these requirements at once and a lot of effort is currently being made to engineer advanced materials with optimal thermodynamic and kinetic properties. The most promising metal from a hydrogen storage perspective is Mg. Magnesium can store up to 7.6wt% of hydrogen as MgH_2 and it is cheap and abundant. The (de)hydrogenation kinetics are however slow and several

Department of Chemical Engineering, Delft University of Technology, Julialaan 136, 2628 BL, Delft, The Netherlands. E-mail: B.Dam@tudelft.nl; Fax: +31-(0)15-2787421; Tel: +31-(0)15-2784342

Andrea Baldi

Andrea Baldi received his Ph.D. from the VU University Amsterdam in March 2010. He is currently a postdoctoral researcher in the MECS (Materials for Energy Conversion and Storage) group at the Delft University of Technology, where he studies the hydrogen sorption properties of Mg-based thin films and multilayers, with a special focus on the effects of stress and surface energy on the thermodynamic properties of very thin layers. In July 2010 he has been awarded the Fellowship for Young Energy Scientists (YES!) from the Dutch Foundation for Fundamental Research on Matter (FOM).

Bernard Dam

Bernard Dam has been the head of the MECS (Materials for Energy Conversion and Storage) group at the Delft University of Technology since 2009. This group specializes in photoelectrochemical water splitting, the defect chemistry of oxide semiconductors and the application of metal hydrides for sustainable energy applications. Using a thin film combinatorial approach, hydrogen storage materials, hydrogen sensors and hydrogen separation membranes are being investigated.
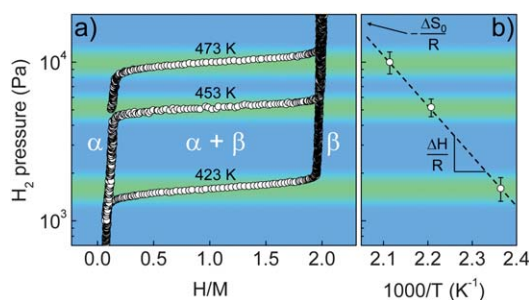
Fig. 1 a) Typical Pressure-Composition-Isotherms measured at various temperatures for a thin Mg film and b) corresponding Van't Hoff plot.

methods, such as addition of catalysts[3] and nanostructuring,[4] are being explored to enhance the rate of hydrogen uptake and release. Furthermore, MgH_2 is thermodynamically too stable, with an equilibrium hydrogen pressure of 10^5 Pa at around 573 K. Strategies to reduce the stability of MgH_2 include alloying with various elements[5] and nanostructuring.[6]

After the discovery of the reversible hydrogen storage properties of $NaAlH_4$[7] a lot of effort has been devoted to finding complex metal hydrides with higher weight densities. So far, however, no compounds could be found that show the required equilibrium hydrogen pressure at room temperature, in conjunction with high storage capacity.

Although the ultimate goal is the production of large amounts of hydrogen storing material to be used in the transport sector, research is conducted also on thin film metal hydrides (typically <1 μm). Thin films have several advantages with respect to their bulk counterparts as they allow one to: i) tune the microstructure by simply changing the film deposition parameters; ii) co-deposit two or more elements to synthesize metallic mixtures at room temperature. This can lead to the synthesis of metastable phases, which are inaccessible by bulk (equilibrium) preparation methods; iii) produce films with compositional gradients, allowing one to perform combinatorial research on thousands of different samples at once; iv) explore the behavior of metal hydrides at the nanoscale, thus allowing one to probe the effect of size confinement and surface energy contributions on the hydrogenation thermodynamics.

Thin film technology has also been successfully applied to the *in situ* deposition of complex hydrides such as

$MgNiH_4$[8] and (Ti-doped) $NaAlH_4$.[9] However, due to the stringent vacuum conditions this field is still in its infancy.

1 High-throughput screening techniques

Many Mg-based thin films exhibit "switchable mirror" properties:[10] upon exposure to hydrogen they undergo an optical transition from shiny reflecting metals to transparent semiconducting hydrides. The optical transmission of thin metallic films can therefore be used as an indication of their hydrogen content: in first approximation, from the Beer–Lambert law, the logarithm of the optical transmission through a thin film is

directly proportional to the layer thickness times its hydrogen content. Gremaud and co-workers recently developed "Hydrogenography",[11] a technique in which the amount of light transmitted through a thin film is measured as a function of hydrogen pressure at constant temperature. Hydrogenography allows one to build Pressure-optical Transmission-Isotherms (PTIs) which are equivalent to the standard PCIs. A scheme of the hydrogenography setup is shown in Fig. 2a: a white light source illuminates a transparent hydrogenation cell kept at constant temperature. The H_2 partial pressure in the cell is varied between 10^{-1} and 10^6 Pa, while simultaneously recording the amount of light transmitted through the thin films by means of a 3CCD camera. PTIs of thousands of different samples can be measured simultaneously. Fig. 2b shows an image of a $Mg_yNi_zTi_{1-y-z}$ gradient film, deposited by magnetron sputtering on a 3 inch wafer, taken at a pressure of 3 kPa at 333 K. Upon measurement of the PTIs at various temperatures it is possible to build Van't Hoff plots and determine the thermodynamic parameters of all the compositions at once (Fig. 2c). With this method a composition with optimal enthalpy of hydride formation
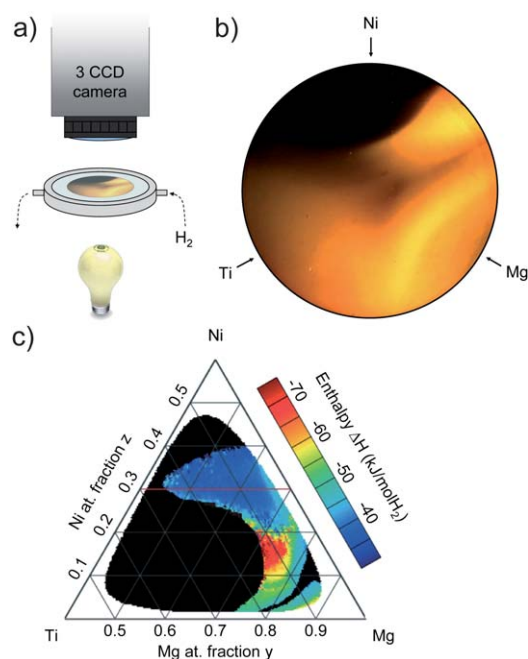

Fig. 2 a) Scheme of the hydrogenography setup. b) Optical transmission image of a $Mg_yNi_zTi_{1-y-z}$ gradient sample during loading at 333 K. c) Hydride formation enthalpies of the Mg–Ni–Ti–H system, determined from the Van't Hoff plots for each pixel of the $Mg_yNi_zTi_{1-y-z}$ gradient film (ref. 11).

($\Delta H = -40$ kJ/molH$_2$) has been found: Mg$_{0.69}$Ni$_{0.26}$Ti$_{0.05}$. Such a ternary alloy has a reversible hydrogen content of 3.2 wt%, as determined by electrochemical galvanostatic measurements.

Thanks to its fast acquisition rate, hydrogenography also allows the characterization of the (de)hydrogenation kinetics of compositional gradients, such as Mg–Pd,[12] Mg–Al[13] and Mg–Ni[14] thin film alloys. Other optical combinatorial approaches make use of *infrared* (instead of *visible*) imaging of thin film compositional gradients, deposited by a combination of pulsed laser deposition and magnetron sputtering[15] or by electron beam evaporation.[16] Ludwig and co-workers recently presented a high-throughput method for the characterization of thin films of metal hydrides by means of micromachined Si cantilevers.[17] Thin metallic films are deposited on an array of 24 Si cantilevers and exposed to H$_2$ gas. The volume expansion occurring upon hydrogen absorption induces in-plane stresses and out-of-plain strains, which result in the bending of the cantilevers. The deflection is detected simultaneously for all the cantilevers allowing a combinatorial characterization of all the samples at once (Fig. 3). Such a technique has been successfully applied to the characterization of the (de)hydrogenation properties of a Mg$_y$Ni$_{1-y}$ (0.6 < y < 0.8) thin film compositional gradient.[18] The Mg–Ni system has also been used to validate a different combinatorial technique, which relies on a Si-based MEMS array with 49 independent heaters.[19] Such an array allows both Temperature Programmed Desorption (TPD) and Infrared Thermography experiments, resulting in the determination of the temperature of hydrogen desorption and the hydrogen capacity of the materials.

2   New phases

Typical thin film deposition techniques, such as magnetron sputtering and electron-beam evaporation, allow the deposition of more than one element at the time. Metallic mixtures with positive enthalpies of mixing, which are not easily accessible by bulk preparative methods, are therefore easily synthesized and their hydrogenation properties can be studied.[20] In 2005 Niessen and Notten presented a comprehensive study of the hydrogen storage characteristics of several metastable Mg$_{0.8}$X$_{0.2}$ (X = Sc, Ti, V, Cr) thin film alloys, deposited by electron-beam at room temperature (Fig. 4a).[21] These crystalline single-phase mixtures show high reversible hydrogen storage capacities and, especially in the cases of Sc and Ti doping, remarkably faster kinetics of hydrogen absorption and desorption with respect to pure Mg. Similar properties have been observed by Borsa *et al.* in magnetron sputtered Mg$_y$Ti$_{1-y}$ (0.55 < y < 0.95) thin film alloys. These films have been studied with respect to their optical, structural and electrical properties.[22] For Ti concentrations higher than 13 at% fast (de)hydrogenation kinetics are observed, due to the stabilization of a face-centered cubic Mg–Ti–H phase in the hydrogenated (loaded) state, instead of the usual tetragonal MgH$_2$ (Fig. 4b).[22,23] Upon hydrogen absorption many binary alloys of Mg with immiscible elements such as Y,[24] Gd,[25] La[26] and V[27] show strong segregation into the constituting elements. Notwithstanding the positive enthalpy of mixing of Mg and Ti, however, Mg–Ti thin film alloys are both structurally and optically reversible upon hydrogen cycling (Fig. 4b). The microstructural origin of this remarkable behavior lies in the distribution of Mg and Ti atoms into Mg-rich and Ti-rich domains.[28,29] Fig. 4c shows 3D Monte Carlo simulations of the atomic distribution of Mg and Ti atoms, as measured by means of Extended X-ray Absorption Fine Structure (EXAFS) on Mg$_y$Ti$_{1-y}$ (y = 0.53, 0.59, 0.70, 0.81, 0.9) thin films. The chemical short-range order parameter, s, is used to quantify the amount of segregation, s = 0 corresponding to random atomic distribution and s = 1 to a completely segregated system. Such a "spinodal" microstructure originates during thin film deposition, due to the rapid quenching of Mg and Ti atoms at the substrate, which is kept at room temperature. Triggered by the remarkable properties observed for Mg–Ti thin films, many groups are currently trying to synthesize bulk Mg–Ti alloys with correspondingly fast and reversible (de)hydrogenation characteristics.[30]

3   Model nanoscale structures

Nanosized metal hydrides present several advantages over their bulk counterparts, from the perspective of their application as hydrogen storage materials.[31] They provide shorter paths for hydrogen diffusion and hence faster (de)hydrogenation kinetics. Furthermore, when size is
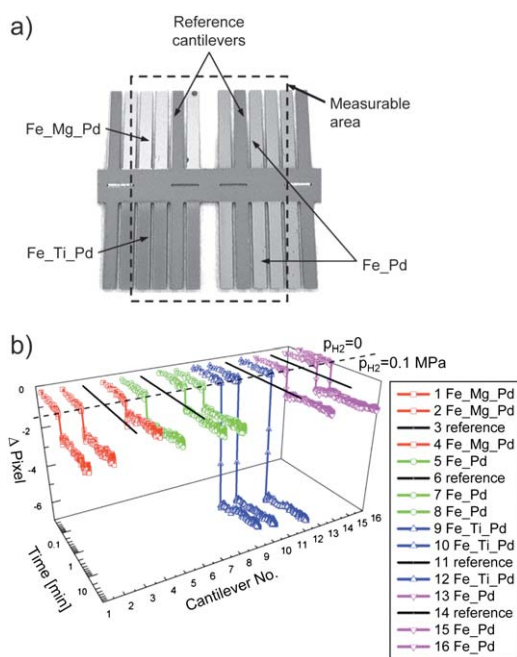
Fig. 3 a) Picture of a cantilever material library composed of 24 cantilevers. b) Results from the simultaneous measurement of the bending of 16 thin film/cantilever combinations, during hydrogenation at room temperature: cantilever/Fe(5 nm)/X(80 nm)/Pd(10 nm), with X = Ti and Mg (ref. 17).
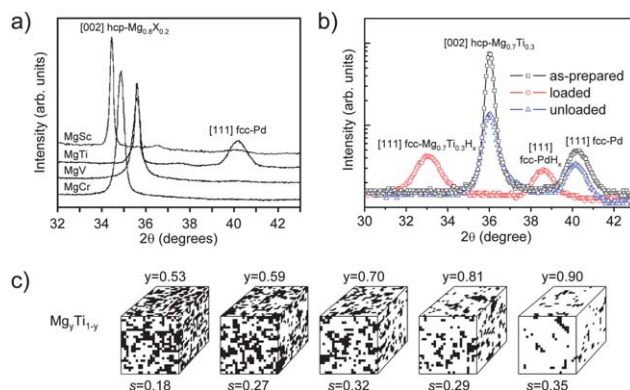
Fig. 4 a) X-ray diffraction patterns of 200 nm thick $Mg_{0.8}X_{0.2}$ films (X = Sc, Ti, V, Cr) capped with 10 nm of Pd (rearranged from ref. 21). b) X-ray diffraction patterns of a Pd-capped 200 nm thick $Mg_{0.7}Ti_{0.3}$ film in the as-prepared, loaded and unloaded states (ref. 22). c) 3D-representation of Mg_yTi_{1-y} alloys with chemical short-range order parameters, s, as measured with EXAFS (ref. 29).

reduced to the nanoscale, energy contributions which are typically negligible in bulk may become relevant, if not dominant, and be exploited to tailor the thermodynamics of hydrogen absorption. Typical finite-size effects include the interaction of the sample with the support/substrate, surface or interface energies and quantum-size effects.[32] All these contributions can be fruitfully addressed by studying the hydrogenation properties of thin films. In our group we recently reported a large increase in the equilibrium hydrogen pressure of thin Mg layers, covered with Mg-alloy-forming elements such as Pd and Ni, while no such effect is observed when the Mg layers are in contact with "immiscible" elements such as Ti, V and Nb.[33] Furthermore,

Pd-capped Mg thin films show equilibrium pressures which are strongly dependent on their thickness, the thinner layers hydrogenating at higher pressures (Fig. 5). We explained this effect by invoking an elastic clamping exerted by the Pd cap layer, due to the formation of an intermetallic alloy at the Mg/Pd interface. We developed a bidimensional elastic model that allows us to qualitatively understand the thickness dependence of the equilibrium hydrogen pressures shown in Fig. 5. Although hydrogenography does not allow a direct determination of the hydrogen concentration in our films, the optical properties of the Pd-capped Mg layers can be reproduced using the MgH_2 dielectric function, indicating that the storage

capacity is not significantly influenced by clamping.[33]

Upon nanostructuring the surface area-to-volume ratio increases and surface energy effects might become large enough to significantly reduce the thermodynamic stability of MgH_2. Surface energy differences between Mg and MgH_2 have been theoretically predicted to be very small for layers thicker (or nanoparticles larger) than 3–5 nm.[35] Given the high sensitivity of the hydrogenography technique, however, loading isotherms of Mg layers as thin as few (4–6) atomic layers are easily measured and our group recently found strong evidence for interface energy-driven destabilization of MgH_2 films thinner than 10 nm.[36]

The possibility of tuning the hydrogenation thermodynamics of nanosized metal hydrides by means of elastic and surface energy effects is intriguing from the perspective of their hydrogen-storage application. Furthermore, the destabilization observed for "bidimensional" Mg thin films is expected to be larger in nanosized 3D systems, such as core-shell[37] and carbon-supported[38] Mg nanoparticles. Thanks to their ease of deposition, high sensitivity for hydrogen absorption and accurate control over thickness, composition and microstructure, thin films can therefore be used as model systems in the search for bulk materials, with optimal hydrogen storage properties.

4 Limitations and challenges

Notwithstanding the advantages highlighted in the previous sections, a thin film approach to hydrogen storage faces some limitations and presents some scientific and technological challenges.

Thin films are used as model systems for bulk hydrogen storage materials. However, to reproduce the phase and defect structure of the film in a bulk sample may not always be easy. As an example, while Mg–Ti thin films hydrogenate readily and reversibly at standard hydrogen pressures and room temperature,[39] mechanically milled Mg–Ti bulk samples typically display much slower kinetics, diminished structural stability and reduced storage capacities.[40]

The possibility of depositing thin films of complex hydrides allows to study their optical properties, which can be used as
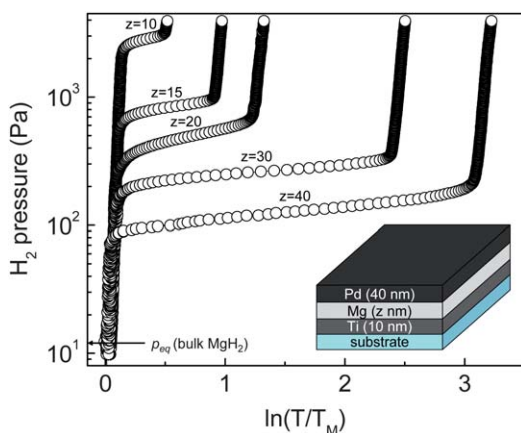

Fig. 5 Pressure-optical Transmission-Isotherms measured by hydrogenography at 333 K for Ti(10 nm)Mg(z nm)Pd(40 nm) thin films, with z = 10, 15, 20, 30, and 40 nm (ref. 33). The x-axis shows the logarithm of the optical transmission (T), normalized by the transmission in the initial metallic state (T_M), which according to the Beer–Lambert law is proportional to the hydrogen concentration in the film. The bottom Ti layer does not influence the equilibrium loading pressure.[34]

powerful tools to study the reaction pathways, the role of catalysts and the phase segregation phenomena occurring during hydrogen absorption and release. However, although the deposition of thin films of sodium alanate has been recently demonstrated,[9] the use of thin film technology to deposit and study other light-weight hydrogen storage materials such as borohydrides and amides is challenging: due to the high reactivity of these compounds and the constraints imposed by their hydrogenation thermodynamics, ultra-high vacuum deposition chambers need to be interfaced with high-pressure and high-temperature loading chambers.

Finally the hydrogenation properties of very thin layers, especially for thicknesses of the order of few nanometres, can be strongly modified by the interaction with the substrate[41] and with the adjacent layers.[33] How plastic deformations and surface energy contributions affect exactly the properties of very thin films remains to be investigated. The ultimate challenge, especially from a physics perspective, is the hydrogenation of a single unit-cell metal hydride layer.

Acknowledgements

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