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Quasifree Mg–H thin films

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The thermodynamics of hydrogen absorption in Pd-capped Mg films are strongly dependent on the magnesium thickness. In the present work, we suppress such dependency by inserting a thin Ti layer between Mg and Pd. By means of optical measurements, we show that the surface energy contribution to the destabilization of MgH_2 is negligible. The inserted Ti layer prevents Mg–Pd alloy formation at the Mg/Pd interface, leading to quasifree Mg films and enhancing the kinetics of hydrogen desorption. Our observations are important for the development of thin film devices. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3210791]

The thermodynamic and kinetic properties of metal-hydrides need to be drastically improved to make them a viable solution for hydrogen storage. Thanks to its relatively high volumetric and gravimetric capacities and its low cost, magnesium hydride has been proposed as an excellent hydrogen storage system.[1] However, the kinetics of hydrogen uptake and release in magnesium are poor and the thermal stability of its hydride, MgH_2, is too high. For practical applications in fact, assuming that the only relevant entropic contribution is due to the entropy loss of gaseous hydrogen, an ideal hydrogen storage system should have an enthalpy of hydride formation of about -40 kJ/mol H_2, in order to release hydrogen at a pressure of 10^5 Pa at room temperature. The formation of MgH_2, however, releases 74.4 kJ/mol H_2, leading to an equilibrium pressure of 10^5 Pa at ~300 °C. Tuning the thermodynamics of hydrogen absorption in Mg has so far been achieved by means of proper doping,[2,3] although this generally results in a reduction of the material's storage capacity. Some destabilization upon reduction of the Mg particle size has also been observed experimentally[4] and predicted theoretically.[5,6] In our group, we have recently demonstrated the possibility of tuning the thermodynamics of hydrogen absorption in Mg thin films by means of elastic clamping.[7] By "sandwiching" thin Mg films between layers of elements which form stable alloys with Mg (such as Pd or Ni), we were able to increase the equilibrium pressure of hydrogen absorption by more than two orders of magnitude with respect to pure Mg in bulk. This destabilization is of elastic nature and it originates from the formation of Mg–Pd (or Mg–Ni) alloy at the interface between the two elements. On the contrary, Mg films sandwiched between layers of elements which are immiscible with Mg (such as Ti, Nb, and V) do not feel significant elastic clamping. In the present work, we compare the absorption isotherms already obtained for "Pd-capped" Mg films of different thicknesses, in which the elastic clamping has a significant effect, with layers of identical thickness but in which the Pd/Mg interface has been removed by the insertion of a thin layer of Ti, which we will call "Ti-buffer" samples. The samples are deposited in a ultra-high vacuum system (base pressure of 10^{-6} Pa) by dc/rf magnetron sputtering of Mg (99.95%), Ti (99.999%), and Pd (99.98%) targets in argon atmosphere, on transparent substrates kept at room temperature. The films are covered with Pd to prevent oxidation and promote hydrogen dissociation and absorption. In all the samples discussed in the present work a 10 nm layer of Ti is deposited before Mg in order to reduce clamping effects from the substrate.[7] Hydrogen loading isotherms are measured at 333 K by means of hydrogenography,[2] an optical technique in which the amount of light transmitted through a thin film is continuously monitored while slowly increasing the hydrogen pressure at

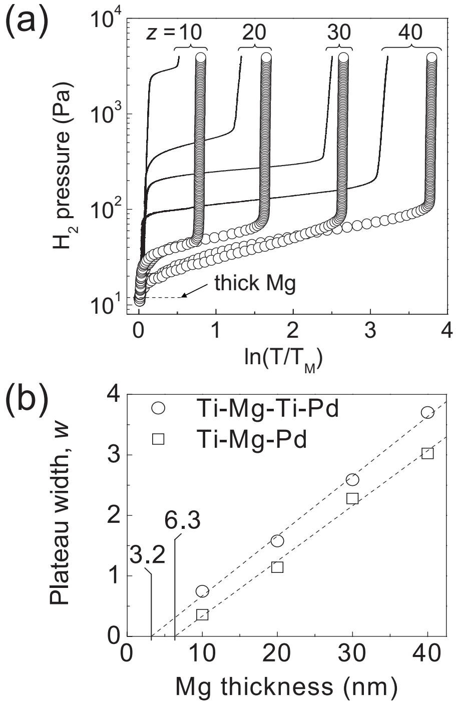

FIG. 1. Effect of a Ti buffer layer on the thermodynamic properties of Mg thin films. (a) PTIs measured at 333 K for (lines) Pd-capped Ti(10 nm)Mg(z nm)Pd(40 nm) samples, as already published in Ref. 7 and (symbols) Ti-buffer Ti(10 nm)Mg(z nm)Ti(10 nm)Pd(40 nm) samples. The Mg thicknesses are in both cases $z = 10$, 20, 30, and 40 nm. (b) Thickness dependence of the plateau width, w, expressed in optical transmission, of Pd-capped and Ti-buffer samples.

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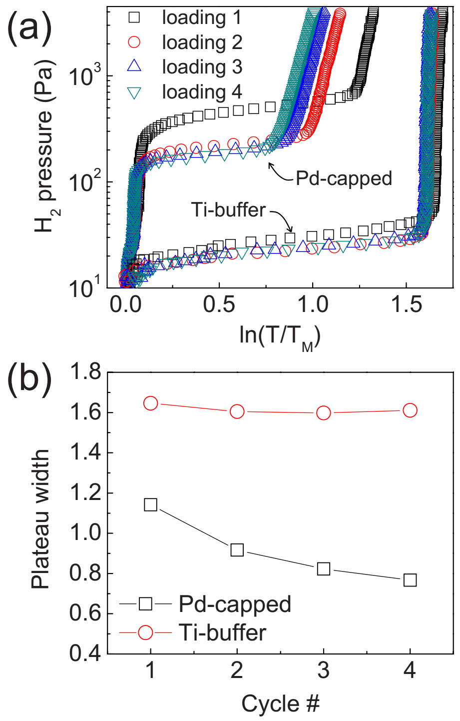

FIG. 2. (Color online) (a) PTIs of 20 nm thick Mg films both in the Pd-capped (top bundle of curves) and Ti-buffer (bottom bundle) geometries, for the first 4 hydrogenation cycles at 333 K. Note that the plateau pressures for all the cycles, except the first one, remain unchanged. (b) Evolution of the plateau width upon cycling.

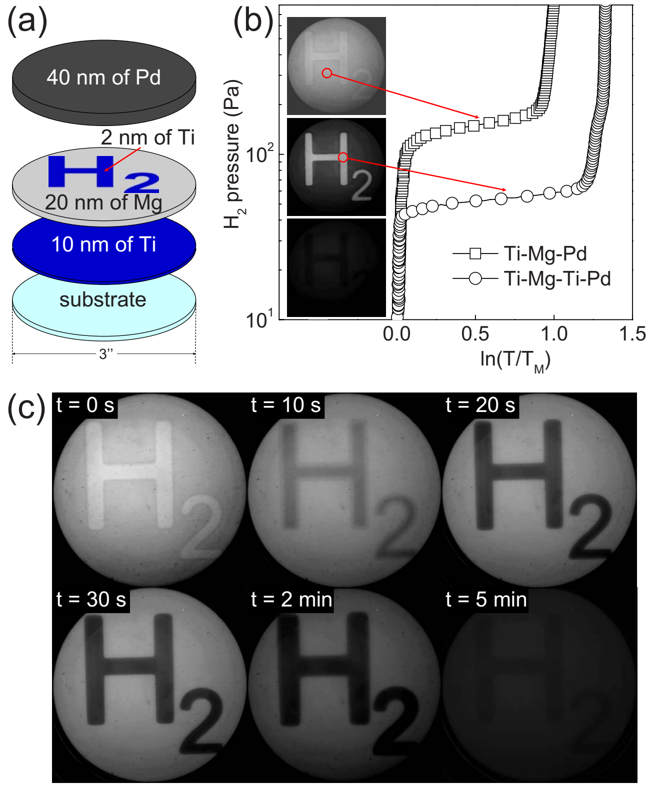

FIG. 3. (Color online) Mg sample deposited on a glass wafer and partially covered with a 2 nm thin Ti layer. (a) Sketch of the sample architecture. (b) PTIs measured during loading at 333 K. (c) Unloading sequence of the same sample when exposed to 10^5 Pa of 20%O_2/Ar mixture at 333 K.

constant temperature. The output of a hydrogenography experiment is therefore a pressure-optical transmission-isotherm (PTI). A PTI is equivalent to a standard pressure-composition-isotherm,[8] thanks to the Beer–Lambert law, according to which the logarithm of the optical transmission, normalized to the transmission of the film in its metallic state, is proportional to the hydrogen concentration in the film, c_H, times the film's thickness, d. Thus, $\ln(T/T_M) \propto c_H \cdot d$. In a PTI the width of the pressure plateau, indicating the magnitude of the optical change occurring in the film upon hydrogen absorption, is therefore directly proportional to the film's thickness. Figure 1(a) shows the isotherms obtained at 333 K for Ti-buffer samples, together with the results already obtained for Pd-capped ones.[7] The samples have the following geometries: Ti-buffer=substrate/Ti(10 nm)/Mg(z nm)/Ti(10 nm)/Pd(40 nm), Pd-capped=substrate/Ti(10 nm)/Mg(z nm)/Pd(40 nm), with z=10, 20, 30, and 40 nm in both cases. The dashed line in Fig. 1(a) represents the pressure at which the MgH_2 phase begins to nucleate in thick, bulklike Mg layers.[9] The insertion of a Ti layer drastically reduces the equilibrium pressure, leading to "quasifree" Mg. The equilibrium pressure of the Ti-buffered films is independent on the thickness of the Mg layers, indicating that surface energy effects, which would produce a thickness dependence similar to the one observed for the Pd-capped samples, are negligible.[10] The plateaus shown in Fig. 1(a), corresponding to the regions of the isotherms at almost constant pressure, have widths, w, expressed in terms of optical transmission and proportional to the nominal thickness of the Mg films, d_{Mg}. In Pd-capped samples we found a relation of the type $w = A(d_{Mg} - d_0)$, with $d_0 \approx 6$ nm.[7] These "missing" 6 nm are due to the formation of Mg–Pd alloy at the Mg/Pd interface. Figure 1(b) shows the thickness dependence of the plateau width for both the Pd-capped[7] and the Ti-buffer samples. Although the nominal thickness of the Pd-capped and Ti-buffer samples is the same, the plateau width of the former ones is constantly larger: the presence of a Ti layer between Mg and Pd leads to a smaller d_0, indicating either a reduction of interalloying or a smaller roughness at the Mg/Cap interface. A flatter interface in the Ti-buffer samples is reasonable, considering that Mg and Ti are thermodynamically immiscible, while Mg and Pd form stable intermetallic compounds for a wide range of compositions. Figure 2 shows the PTIs for four subsequent hydrogen loadings of a 20 nm thick Mg layer, both in the Pd-capped=Ti(10 nm)Mg(20 nm)Pd(40 nm) and Ti-buffer=Ti(10 nm)Mg(20 nm)Ti(10 nm)Pd(40 nm) geometries. The plateau width of the Pd-capped sample shrinks upon cycling indicating that the alloying between Mg and Pd, triggered by the absorption of hydrogen, continues even after the first hydrogen absorption. On the contrary in the Ti-buffer sample the Ti layer acts as a blocking barrier for atomic diffusion, preventing the formation of Mg–Pd alloy and resulting in pressure plateaus of practically constant width. The decrease in plateau pressure observed for the Pd-capped sample between the first and second cycle is most likely due to the partial release of stresses generated by the Pd clamping. Such relaxation is in fact absent in the Ti-buffer sample. In Fig. 3 we show the loading isotherms measured on a Mg sample deposited in the following way: 10 nm of Ti are deposited on a 3 in. wide glass wafer, then 20 nm of Mg are added on top of Ti, subsequently 2 nm of Ti are deposited with the use of a mask only on certain regions of the wafer in order to write "H_2", finally 40 nm of Pd are added to protect the film from oxidation [Fig. 3(a)]. With this sample architecture we are able to compare the behavior of a Pd-capped and a Ti-buffer Mg film, in the same specimen and under identical experimental conditions. When exposed to increasing hydrogen pressures at 333 K the film exhibits the following loading sequence [Fig. 3(b)]: (1) for hydrogen pressures $p_{H_2} < 40$ Pa the film is everywhere metallic and no light is transmitted through it; (2) for $40 < p_{H_2} < 150$ Pa the regions of the sample containing a Ti-buffer layer load completely, forming the transparent MgH_2, while the Pd-capped regions remain metallic; (3) for $p_{H_2} > 150$ Pa also the Pd-capped regions form the hydride and the sample becomes completely transparent. The plateau width for the loading isotherms of the Ti-buffer areas in Fig. 3(b) is wider than for the Pd-capped regions. This indicates that Mg–Pd alloy has been significantly formed only in the latter. A Ti layer as thin as 2 nm is apparently thick enough to prevent Mg–Pd alloy formation and to produce remarkably different thermodynamic properties. The presence of a Ti-buffer layer also induces different kinetics of hydrogen desorption, as shown in Fig. 3(c). When the sample is exposed to oxygen in a $20\% O_2/Ar$ mixture at 333 K, the Ti-buffer regions unload much faster than the Pd-capped ones. This kinetic effect is on one end due to the absence of Mg–Pd alloy at the Mg/Pd interface. Doping Mg with Pd, in fact, enhances the kinetics of hydrogen absorption, but the desorption rates for these alloys are very low.[11] On the other hand it is well known[12] that a hydrogen absorbing material (M) covered with a transition metal (TM) exhibits a fast unloading rate when the enthalpies of hydride formation for the two materials are such that $\Delta H_{TM} < \Delta H_M < 0$. In our samples, Mg covered with Ti ($\Delta H_{Ti} = -130$ kJ/mol$H_2 < \Delta H_{Mg} = -74.4$ kJ/molH_2) shows indeed faster kinetics than Mg covered with Pd ($\Delta H_{Pd} = -38$ kJ/mol $H_2 > \Delta H_{Mg} = -74.4$ kJ/mol H_2).

In conclusion, we have shown that it is possible to dramatically change the thermodynamic properties of a thin metallic film by means of very little changes in the architecture of the samples. Surface energy effects are to be ruled out as a possible source of destabilization in clamped Mg films. The insertion of a buffer layer suppresses the formation of Mg–Pd alloy at the Mg/Pd interface. This effect is responsible for the enhanced cycling stability and improved performances reported for buffer-layer-inserted switchable mirrors.[13–15] Our results provide insights into the microstructural, thermodynamic, and kinetic aspects of Pd-capped hydrogen-absorbing thin films used in technological applications, such as switchable mirrors[16] and optical hydrogen sensors.[17]

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[1] L. Schlapbach and A. Züttel, Nature (London) **414**, 353 (2001).
[2] R. Gremaud, C. Broedersz, D. M. Borsa, A. Borgschulte, P. Mauron, H. Schreuders, J. H. Rector, B. Dam, and R. Griessen, Adv. Mater. **19**, 2813 (2007).
[3] J. J. Vajo, F. Mertens, C. C. Ahn, R. C. Bowman, and B. Fultz, J. Phys. Chem. B **108**, 13977 (2004).
[4] R. Varin, T. Czujko, C. Chiu, and Z. Wronski, J. Alloys Compd. **424**, 356 (2006).
[5] R. Wagemans, J. H. van Lenthe, P. E. de Jong, A. J. van Dillen, and K. P. de Jong, J. Am. Chem. Soc. **127**, 16675 (2005).
[6] J. Liang, Appl. Phys. A: Mater. Sci. Process. **80**, 173 (2005).
[7] A. Baldi, M. Gonzalez-Silveira, V. Palmisano, B. Dam, and R. Griessen, Phys. Rev. Lett. **102**, 226102 (2009).
[8] R. Gremaud, M. Slaman, H. Schreuders, B. Dam, and R. Griessen, Appl. Phys. Lett. **91**, 231916 (2007).
[9] A. Krozer and B. Kasemo, J. Less-Common Met. **160**, 323 (1990).
[10] V. Berube, G. Chen, and M. S. Dresselhaus, Int. J. Hydrogen Energy **33**, 4122 (2008).
[11] M. Pasturel, M. Slaman, H. Schreuders, J. H. Rector, D. M. Borsa, B. Dam, and R. Griessen, J. Appl. Phys. **100**, 023515 (2006).
[12] M. Pasturel, R. J. Wijngaarden, W. Lohstroh, H. Schreuders, M. Slaman, B. Dam, and R. Griessen, Chem. Mater. **19**, 624 (2007).
[13] A. T. M. van Gogh, S. J. van der Molen, J. W. J. Kerssemakers, N. J. Koeman, and R. Griessen, Appl. Phys. Lett. **77**, 815 (2000).
[14] J. L. Slack, J. C. W. Locke, S. W. Song, J. Ona, and T. J. Richardson, Sol. Energy Mater. Sol. Cells **90**, 485 (2006).
[15] S. Bao, Y. Yamada, M. Okada, and K. Yoshimura, Jpn. J. Appl. Phys., Part 2 **45**, L588 (2006).
[16] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature (London) **380**, 231 (1996).
[17] M. Slaman, B. Dam, M. Pasturel, D. Borsa, H. Schreuders, J. Rector, and R. Griessen, Sens. Actuators B **123**, 538 (2007).