Optical switching properties from isotherms of Gd and GdMg hydride mirrors

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Concentration–pressure isotherms were measured together with the optical transmission in polycrystalline Gd and GdMg thin-film switchable mirrors. Formation plateaus in GdMg alloys, corresponding to gadolinium dihydride and trihydride as well as magnesium dihydride have been found. From these, the formation enthalpies could be calculated. These results show that the GdMg alloys are phase separated. From the onset of the transmission we conclude that the formation of gadolinium trihydride is the final stage in the switching process. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1499765]

Optical switching devices are of considerable technological interest. Switchable mirrors based on the rare-earth metal hydrides, discovered in 1996,[1] allow a controlled change in reflectance, absorbance, and transmittance of light. These thin films show a reversible metal-to-insulator transition on going from the dihydride to the trihydride state. The metal state is opaque, while the insulator is transparent. The lanthanide trihydrides, however, are yellow in transmission. Color neutrality, necessary for technological applications, can be achieved by alloying the metal with magnesium[2,3] or by use of multilayers;[4] the reason for this optical effect is still the subject of debate.[5]

Pressure–concentration isotherms provide information on formation enthalpies.[6] A plateau in the isotherm, corresponds to the coexistence of two different phases. Knowledge of these phases, particularly those accompanying the optical change, are important for determining the mechanism of optical switching in these alloys. From the plateau pressure it is possible to estimate the corresponding formation enthalpy of the high concentration phase with the relation[6]

$$\Delta H = \frac{RT}{2}\left[\ln p_{H_2} - \frac{S^0_{H_2}}{R}\right], \qquad (1)$$

where $S^0_{H_2} = 130.8$ J/K mol H is the standard molar entropy of hydrogen gas.

Electrochemical loading offers a double advantage: the concentration of hydrogen in the film can be controlled accurately, and extremely low pressures can be achieved.[7,8] The adsorbed hydrogen diffuses into the material; the concentration of hydrogen in the film, x, (hydrogen/metal atomic ratio) is proportional to the charge transferred in the electrochemical reaction.[7] With the galvanostatic intermittent titration technique (GITT),[9] the equilibrium potential U_e, which is measured in open circuit after a current pulse, provides us, via the Nernst equation, with the equivalent hydrogen pressure p_{H_2}:[8]

$$p_{H_2} = \exp\left[-(U_e + 0.926)\frac{nF}{RT}\right]. \qquad (2)$$

Here, F is the Faraday constant, R the universal gas constant, T the temperature, and n the number of electrons involved in the hydrogen evolution reaction ($n = 2$). The hydrogen pressure is expressed in bar. An electrochemical glass cell with a Hg/HgO reference electrode and platinum counter electrode was used for the measurements. The equilibrium potential is relative to the electrochemical potential of the reference electrode, leading to an addition factor of 0.926.

The active layers were nominally 200-nm-thick, polycrystalline Gd, $Gd_{70}Mg_{30}$, $Gd_{38}Mg_{62}$, $Gd_{26}Mg_{74}$, and $Gd_{17}Mg_{83}$ films top coated with a thin palladium layer (nominal thickness 10 nm). The palladium acts as a catalyst for hydrogenation and protects the film from oxidation. The layers were deposited on a conducting indium–tin–oxide (ITO) layer on a glass substrate. To ensure good adhesion of the GdMg alloy, a 0.5-nm-thick magnesium layer was first evaporated onto the ITO. The layers were deposited by conventional evaporation techniques at 10^{-7} mbar base pressure and analyzed with Rutherford backscattering to determine thickness and composition. A platinum lead was fixed with silver glue (2400 Circuit Works Conductive Epoxy, Agar Scientific) on the free ITO, and both the lead and the ITO were protected from the solution by Apiezon. The active surface area was 1.3 cm^2. The 1 M KOH solution was deaerated by purging with argon gas at room temperature. A potentiostat/galvanostat (EG&G Princeton Applied Research 273A) was computer controlled by in-house developed programs (LabView). Transmission was measured with a diode laser (Vector, 670 nm) and a standard photodiode. X-ray diffraction (XRD) experiments were performed with the INEL PSD 120 powder diffraction system. The GdMg alloy has previously been investigated by electrochemical[10] and photoelectrochemical[11] methods.

In Fig. 1, pressure–concentration isotherms are shown together with the transmission for a pure gadolinium film and three different gadolinium magnesium alloys. From Fig. 1(a) it is clear that the isotherm for the Gd film displays a pressure plateau up to $x = 1.2$. From the pressure of this low-

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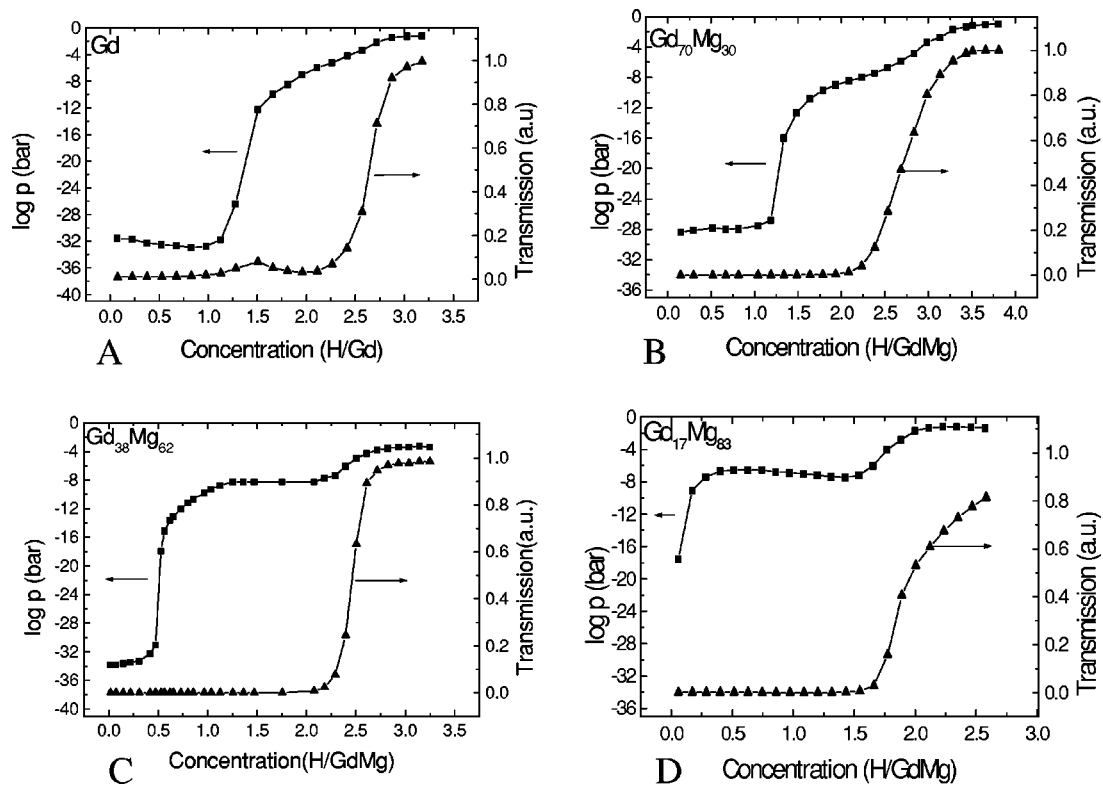a)Electronic mail: m.divece@phys.uu.nl

FIG. 1. Pressure–concentration isotherms (squares) for Gd and GdMg determined with the galvanostatic intermittent titration technique. The corresponding normalized transmission (triangles) is also shown as a function of concentration.

hydrogen concentration plateau we calculate a formation enthalpy of -107 kJ/mol H, which is in good agreement with the reported value for GdH_2 of -104 kJ/mol H.[12] We, therefore, ascribe this plateau to the $\alpha \rightarrow \beta$ transition (hcp $\rightarrow$ fcc).[12] Notten[13] found a much higher plateau pressure, possibly due to inhomogeneous loading, caused by Ohmic losses in the layer; a conducting substrate was not used in this case. The plateau pressure in our experiment agrees well with that reported for yttrium switchable mirrors.[7] This is expected since the gadolinium and yttrium dihydride formation enthalpies are almost identical. The transmission begins to increase slightly at $x = 1.3$, and decreases at $x = 1.7$. This optical window has also been observed for yttrium films.[7] Van Gogh et al.[14] explain this feature by a screening of the plasma energy and a low interband absorption coefficient, leading to lower absorption. This optical change is accompanied by a drastic increase in the pressure, as the $\alpha \rightarrow \beta$ transition (hcp $\rightarrow$ fcc) is completed. In the range after the sharp pressure increase, the $\beta \rightarrow \gamma$ (fcc $\rightarrow$ hcp) transition should occur. It is clear that a plateau cannot be distinguished; consequently, the formation enthalpy of GdH_3 cannot be established from Fig. 1(a). The transmission increases during the last part of the formation of this phase and remains constant when a pressure of 10^{-1} bar of hydrogen has been reached. This final plateau pressure is the result of the equilibrium between absorbed hydrogen in the film and hydrogen gas at the electrode/electrolyte interface. Because of hydrogen evolution, the determination of the amount of absorbed hydrogen becomes inaccurate for x values larger than 2.6.[7]

A comparison of these results with corresponding results for yttrium (Ref. 7) shows that the isotherms are similar except that the small transmission window and the onset of the

pressure increase at the end of the $\alpha \rightarrow \beta$ transition occur at higher x in the case of yttrium. The concentration difference of this feature is $\Delta x = 0.4$. For nanocrystalline metal hydrides it is known that grain size influences the isotherms;[15] the extent of the miscibility gap can differ considerably. This could be the reason for the difference between the yttrium and gadolinium studies. An error in concentration determination is caused by some hydrogen incorporation during film deposition. This can also be responsible for the concentration difference.

In Figs. 1(b) and 1(c) it is clear that for $Gd_{70}Mg_{30}$ and $Gd_{38}Mg_{62}$ a pressure plateau at low hydrogen concentration is also observed with the gadolinium magnesium alloy. The formation enthalpies calculated from this first plateau, -96 and -108 kJ/mol H for $Gd_{70}Mg_{30}$ and $Gd_{38}Mg_{62}$ respectively, are close to the literature value of -104 kJ/mol H (Ref. 12) and our experimental value of -107 kJ/mol H for $Gd \rightarrow GdH_2$. The fact that a GdH_2 formation plateau is found at the gadolinium bulk pressure level suggests disproportionation of these GdMg alloys, resulting in gadolinium dihydride and magnesium clusters. EXAFS studies on the GdMg alloy[16] show that on hydrogen loading the coordination number of gadolinium by magnesium decreases markedly, indicating segregation. Nagengast et al.[3] reported disproportionation in a $Y_{50}Mg_{50}$ film, during the first loading with hydrogen in the gas phase. This results in magnesium and yttrium clusters of very small size.

In Fig. 1(b) there is an indication of a second plateau after which the pressure continues to rise up to the hydrogen evolution plateau. In Fig. 1(c), a second plateau from $x = 1$ to $x = 2.1$ is clearly visible. The formation enthalpy of -41 kJ/mol H calculated from this plateau is in good agree-

ment with the reported value of -42 kJ/mol H for MgH_2 in a thin stressed film.[3] Since the formation enthalpies of GdH_3 [-46 kJ/mol H (Ref. 12)] and MgH_2 are similar, it is not surprising that we do not find a pressure separation in this second range. This second plateau extends over a range $\Delta x = 1.1$, too large for that corresponding to GdH_3 formation ($\Delta x = 0.4$) only. The plateau can be ascribed largely to the formation of MgH_2. It is, however, difficult to determine the exact extent since a large part of the isotherm is considerably curved, probably due to the presence of hydrogen sites of different energies.

The first plateau is completely absent in the isotherms with 26% gadolinium (not shown) and 17% gadolinium [Fig. 1(d)]. There is, nevertheless, a jump from low to higher pressures, indicating that a small amount of gadolinium dihydride is still being formed. The range of the MgH_2 plateau for the $Gd_{17}Mg_{83}$ film [Fig. 1(d)] is $\Delta x = 1.4$; this should be $\Delta x = 1.7$. This difference is probably due to grain size effects.[15] The small increase in transmission when the hydrogen evolution plateau has been reached ($x = 2.2$) is probably due to incomplete loading of alloys with high magnesium concentration.[17]

The optical transmission window at low hydrogen concentration is absent in the magnesium alloy films.[2] For the yttrium magnesium alloy, Nagengast et al.[3] suggested that the magnesium clusters act as a microscopic optical shutter. They also suggested that the yttrium clusters switch optically to the trihydride state before the magnesium clusters, since the yttrium trihydride formation enthalpy is a little lower. From our isotherms we conclude that gadolinium dihydride clusters are being formed for a gadolinium content of more than 38%. Magnesium dihydride is also clearly detectable for a magnesium content of more than 30%. XRD experiments on the virgin $Gd_{38}Mg_{62}$ and $Gd_{17}Mg_{83}$ samples do not show crystalline magnesium or gadolinium. This could be caused by the high signal strength of the ITO, masking gadolinium and magnesium or the crystallites may be very small (< 10 nm).

Since the transmission is measured as a function of hydrogen concentration for different GdMg alloys, it is possible to link the sequence of hydride formation steps to the optical changes. The relation between the partial and total hydrogen concentrations is given by

$$r_{Gd}x_{Gd} + r_{Mg}x_{Mg} = x, \tag{3}$$

in which r_{Gd} and r_{Mg} are the composition ratios and x_{Gd} and x_{Mg} are the partial hydrogen concentrations. Assuming that the magnesium is completely transformed to magnesium dihydride before the transmission increase ($x_{Mg} = 2$), we find by Eq. (3) that the onset of the transmission calculated for $Gd_{70}Mg_{30}$ and $Gd_{38}Mg_{62}$ corresponds to $x_{Gd} = 2$ (gadolinium dihydride). If it is assumed that gadolinium forms the trihydride ($x_{Gd} = 3$) before the onset of the transmission increase,

different values are found for the magnesium concentration (x_{Mg}) at the transmission onset for the two alloys. This suggests strongly that the final process causing the transmission increase in these alloys is the formation of gadolinium trihydride. This procedure is not valid for the high magnesium alloy ($Gd_{17}Mg_{83}$), probably due to considerably fewer gadolinium clusters.

Pressure–concentration isotherms of GdMg clearly show formation plateaus. The corresponding formation enthalpies indicate a segregation of the elements. The formation enthalpies are in good agreement with values reported for experiments on thin films and bulk materials. From the onset of the transmisson in the isotherms we conclude that the formation of gadolinium trihydride coincides with the transmission increase, and it is therefore the final process to occur during optical switching.

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