

## Thermochromic metal-hydride bilayer devices

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### Abstract

The temperature dependent optical properties of certain thin films are used in so-called thermochromic devices. As an alternative to a single layer of, e.g. VO<sub>2</sub>, which displays a temperature dependent optical transmission, we propose the use of an encapsulated metal-hydride bilayer (i.e. a switchable mirror and a hydrogen storage layer). Due to differences in the thermodynamic properties of the two metal-hydride layers, a temperature change results in the migration of hydrogen from one layer to the other, thereby changing the optical properties of the switchable mirror metal-hydride. Depending on the materials chosen the transition can be optimized for transmission, reflection or absorption. Hence, the use of metal-hydride bilayers allows the fabrication of a thermochromic absorber. The thermodynamical background and the first results of such an all-solid-state thermochromic device are presented.

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### 1. Introduction

The optical properties of thermochromic layers are temperature dependent. As a result, such layers can be used in smart windows to control the temperature in, e.g. buildings, satellites, or cars. Thermochromic windows are usually based on VO<sub>2</sub>, which, due to a metal–insulator transition, changes at ~68 °C from reflecting at high temperature to transparent at low temperature at wavelengths larger than 600 nm (i.e.  $\hbar\omega \leq 2.1$  eV) [1].

We propose a much more versatile thermochromic device consisting of a metal-hydride bilayer. By choosing a suitable material couple the change in optical properties and the transition temperature can be adjusted to the desired requirements. For example, the use of a metal-hydride bilayer allows the fabrication of a thermochromic *absorber*. Such a coating is black and heat absorbing at low temperatures while reflecting at high temperatures. It could be used to optimize the efficiency of hybrid solar collectors – a device with a photo-

voltaic cell on top of a thermal solar collector – by keeping its operational temperature within practical limits.

For the active layer of the thermochromic device we choose a switchable mirror layer which changes its optical properties upon absorption of hydrogen. This phenomenon, the reversible change from shiny reflecting to transparent, first has been observed in Y and La thin films [2]. All rare earth (RE) metals and their alloys with Mg were found to switch optically [3] and furthermore Richardson et al. [4] demonstrated that Mg–TM (TM: Ni, Co, Mn, Fe) also act as switchable mirrors. Giebels et al. [5] showed the thermochromic effect in an open system at 1 bar H<sub>2</sub> gas pressure in RE and RE–Mg thin films capped with Pd. Here, we propose the use of an encapsulated bilayer as a closed thermochromic system with Mg<sub>2</sub>NiH<sub>x</sub> as the active layer. Beside a shiny metallic state at low hydrogen concentrations and a transparent state when fully loaded to Mg<sub>2</sub>NiH<sub>4</sub>, Mg<sub>2</sub>NiH<sub>x</sub> exhibits a third optical state at intermediate hydrogen concentrations [6]. In this state, reflection is low ( $R < 25\%$ ) and transmission is negligible ( $T < 0.01\%$ ) over the entire visible spectrum, hence the film appears black. The origin of this unusual state lies in the hydrogenation mechanism of the film: the nucleation of the hydrogen rich phase starts in an approximately 30-nm thick layer close to the film/substrate interface and not, as in-

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tuitively expected, close to the Pd cap layer [7]. For achieving the black state, only a hydrogen concentration change in the first 30 nm is necessary. Therefore,  $\text{Mg}_2\text{NiH}_x$  can be used as the active layer of a device that changes its optical appearance from black to reflecting by a small reduction of its hydrogen content. Specifically, for a 200 nm  $\text{Mg}_2\text{NiH}_x$  film to be in the black state, the average hydrogen concentration equals  $[\text{H}]/[\text{Mg}_2\text{Ni}] = 0.8$  (30 nm of  $\text{Mg}_2\text{NiH}_4$  and 170 nm of  $\text{Mg}_2\text{NiH}_{0.3}$ ).

In the following, we discuss the thermodynamic properties which determine the behavior of an all-solid-state thermochromic absorber device. To test our ideas, we consider for simplicity a device consisting of a transparent substrate, a  $\text{Mg}_2\text{Ni}/\text{Pd}$  bilayer and a hydrogen impermeable Cu cap layer. We present also the first results of its temperature dependent optical properties.

## 2. Thermodynamic model

An all-solid-state thermochromic device consists of two metal-hydride layers, of which at least one is a switchable mirror. The system is sealed by a hydrogen impermeable cap layer. As the temperature is raised, the chemical potential of the hydrogen increases together with the dissociation pressure, albeit differently in the two metal-hydride layers due to a different formation enthalpy  $\Delta H$ . Note, that in general, the temperature dependence of the plateau pressure is proportional to  $\Delta H$ . In an open system, hydrogen would leave the two layers, however this is prevented by the hydrogen impermeable cap. As a result, hydrogen is redistributed among the metal-hydride layers until the chemical potentials of the two layers in contact are equal. Fig. 1 presents a schematic picture of the mechanism. The migrating hydrogen induces a change in optical properties of the switchable mirror layer.

For a quantitative description, we consider the thermodynamic properties of the two layers involved in the hydrogen

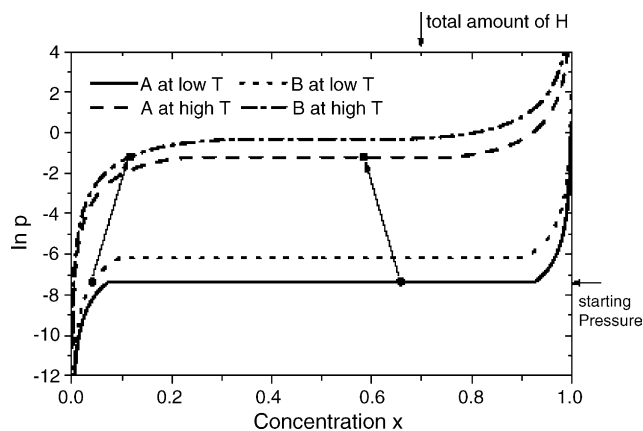


Fig. 1. Schematic pressure–composition isotherms of metal-hydrides A and B showing the hydrogen redistribution upon temperature increase in a closed system as a result of the different  $\Delta H$  of the metal-hydrides. The redistribution is only symmetric if  $N_A = N_B$ .

transfer process. In equilibrium, the chemical potentials  $\mu_A$  and  $\mu_B$  of the two layers A and B are equal:

$$\mu_A = \mu_B \quad (1)$$

Using the Bragg–Williams approximation [8], the chemical potential of hydrogen inside metal A can be described by:

$$\mu_A = kT \ln \left( \frac{x_A}{x_{f,A} - x_A} \right) + \epsilon_A + a_A \left( \frac{x_A}{x_{f,A}} \right) \quad (2)$$

Here,  $x_A$  is the number of H-atoms dissolved per formula unit and  $x_{f,A}$  is the number of the relevant interstitial sites per formula unit, i.e.  $x_{f,A}$  is equal to the value of  $x_A$ , when the saturation composition is reached.  $\epsilon_A$  is the energy of a H-atom in the metal host A and  $a_A$  is the H–H pair interaction.  $k$  denotes the Boltzmann constant and  $T$  the absolute temperature.

The parameters  $a_A$  and  $\epsilon_A$  can be roughly estimated from pressure–composition isotherms, since the pressure  $p$  can be described [9,10] by:

$$\ln(p) = 2 \ln \left( \frac{x_A}{x_{f,A} - x_A} \right) + \frac{2}{kT} t \left( \epsilon_A + a_A \left( \frac{x_A}{x_{f,A}} \right) - \frac{1}{2} \epsilon_b \right) + \ln(p_0(T)) \quad (3)$$

Here,  $\epsilon_b$  represents the binding energy of the  $\text{H}_2$  molecule ( $\epsilon_b = -4.46$  eV). In the case of hydrogen, we can approximate  $p_0(T)$  by [11]:

$$p_0(T) = \left( \frac{T}{9.13} \right)^{7/2} \quad (4)$$

where  $p_0(T)$  is in bar and  $T$  in Kelvin.

In a sealed bilayer consisting of a layer A and a layer B, the total amount of hydrogen  $N_{\text{Htot}}$  is constant and equal to the sum of the hydrogen content in layer A and B, i.e.:

$$N_{\text{Htot}} = x_A N_A + x_B N_B \quad (5)$$

where  $x_{A,B}$  is the concentration of hydrogen in layer A or B and  $N_{A,B}$  is the amount of material A or B in formula units. Using Eqs. (1), (2) and (5), the hydrogen concentration  $x_{A,B}$  in one of the sublayers can be numerically calculated. This calculation is based on materials behaving as a lattice gas such as Pd, but we use it also as an approximation for complex hydrides like  $\text{Mg}_2\text{NiH}_x$ .

## 3. Results and discussion

As an example, we study an all-solid-state thermochromic device consisting of a  $\text{Pd}/\text{Mg}_2\text{Ni}$  bilayer and a Cu cap layer. For  $\text{PdH}_x$  we use  $x_{f,\text{Pd}} = 0.6$ ,  $a_{\text{Pd}} = -0.20$  eV [9] and  $\epsilon_{\text{Pd}} = -2.36$  eV, obtained from a fit of  $\text{PdH}_x$  isotherms [12] in the temperature and pressure region considered here. We obtain  $x_{f,\text{Mg}_2\text{Ni}} = 4$ ,  $\epsilon_{\text{Mg}_2\text{Ni}} = -2.42$  eV and  $a_{\text{Mg}_2\text{Ni}} = -0.14$  eV from a fit of  $\text{Mg}_2\text{NiH}_x$  isotherms [13] as shown in Fig. 2

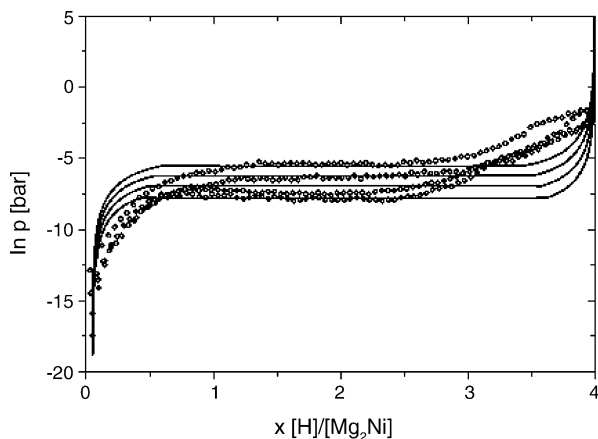


Fig. 2. Pressure–composition isotherms of  $\text{Mg}_2\text{NiH}_x$  at 20 °C, 30 °C, 40 °C and 50 °C (from bottom to top). The experimental isotherms are determined electrochemically. The saturation of the isotherms near  $x = 4$  is due to  $\text{H}_2$  evolution during electrolytic charging. The full lines are obtained from Eq. (3) and the values of the parameters are  $x_{f,\text{Mg}_2\text{Ni}} = 4$ ,  $\epsilon_{\text{Mg}_2\text{Ni}} = -2.42$  eV and  $a_{\text{Mg}_2\text{Ni}} = -0.14$  eV.

(note that  $\Delta H(\text{eV/atom}) = \frac{1}{2}(2\epsilon_A + a_A - \epsilon_b)$  and 1 eV corresponds to 96.5 kJ/mol H giving  $\Delta H_{\text{Pd}} = -22.0$  kJ/mol H and  $\Delta H_{\text{Mg}_2\text{Ni}} = -25.1$  kJ/mol H). Using these parameters the distribution of the hydrogen over the two metal-hydride layers can now be calculated at various temperatures. At room temperature (RT) we want the bilayer to be in the black state. Hence, for a 200-nm layer, the hydrogen concentration is fixed to  $\text{Mg}_2\text{NiH}_{0.8}$ . Since we prepare the bilayer at RT,  $x_{\text{Pd}}$  is fixed, leaving  $N_{\text{Pd}}$  as a free parameter. Fig. 3 shows the calculated change of hydrogen concentration in the  $\text{Mg}_2\text{NiH}_x$  layer of a 200-nm  $\text{Mg}_2\text{Ni}/3000$  nm Pd bilayer as a function of temperature. In the same figure, we include the expected change in reflection at a photon energy of 1.25 eV taking experimental data from Lohstroh et al. [13]. Increasing the temperature from 300 K to 400 K results in a reflection  $R$  increasing from 14% to 23%. Since the metal-hydride bilayer device is non-transparent, this is accompanied by a change in absorption  $A = 1 - R$  from 86% to 77% at 1.25 eV. In comparison, the reflection of a 100-nm thick  $\text{VO}_x$  layer increases from  $\approx 30\%$  to  $\approx 36\%$  (at 1.25 eV) by heating the sample from 293 K to 353 K [1].

In Fig. 4 first experimental results of a device consisting of a sputtered 100-nm  $\text{Mg}_2\text{Ni}/1500$ -nm Pd bilayer capped with 300 nm Cu are shown. The reflection was monitored in an optical microscope equipped with an RGB camera. The sample is viewed through the transparent substrate, hence we observe the side of the active switchable absorber layer. Before capping with Cu by pulsed laser deposition, the  $\text{Mg}_2\text{Ni}/\text{Pd}$  double layer is loaded with H approximately to the black state at RT. After deposition of the Cu, the sample appears still dark. In Fig. 4, we show the average signal (channel green and blue) of the RGB camera at different temperatures. As the temperature is raised, the reflection increases and the sample appears shiny metallic. Cooling down to RT brings back the low reflection and the dark appearance.

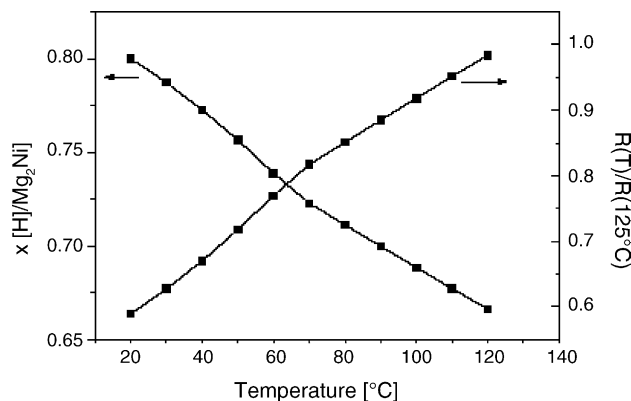


Fig. 3. Calculated change in concentration in the  $\text{Mg}_2\text{NiH}_x$  layer of a 200-nm  $\text{Mg}_2\text{Ni}/3000$ -nm Pd bilayer as a function of temperature together with the accompanying change in normalized reflection at a photon energy of 1.25 eV as taken from [13].

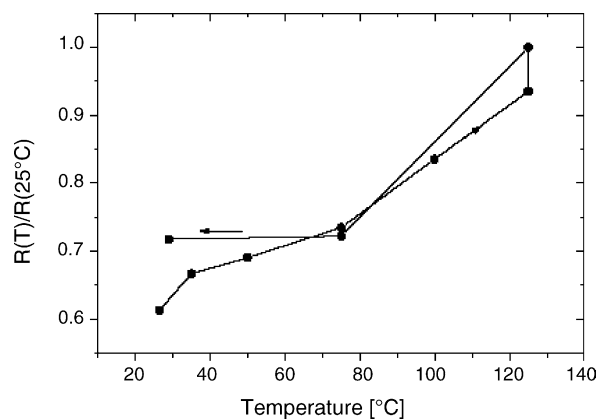


Fig. 4. Average normalized reflection signal (channel green and blue) of the RGB camera at various temperatures through the substrate of an all-solid-state thermochromic device with  $\text{Mg}_2\text{Ni}$  (100 nm) as the switchable mirror, Pd (1500 nm) as the H storage layer and Cu as the H impermeable layer.

#### 4. Conclusion

The proposed metal-hydride bilayer thermochromic device is a versatile system. Its optical properties can be adjusted to the desired requirements by choosing a suitable switchable mirror layer. If hydrogen *desorption* from the switchable mirror layer upon temperature increase is desired, the storage metal-hydride layer should have a less negative formation enthalpy  $\Delta H$  than the switchable mirror layer. In that case, the increase of the dissociation pressure with increasing temperature is smaller for the storage layer than for the switchable mirror layer and then hydrogen migrates from the switchable mirror to the storage layer upon a temperature increase. However, in order to have a large amount of transferred hydrogen, the dissociation pressures should not be too different.

Using  $\text{Mg}_2\text{Ni}/\text{Pd}$  we have demonstrated the feasibility of an all-solid-state thermochromic metal-hydride bilayer device, which could be used for temperature control of, for example, hybrid solar collectors.

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