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Mg–Ti–H thin films as switchable solar absorbers

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ABSTRACT

The reflection and transmission spectra of Pd capped $\text{Mg}_y\text{Ti}_{1-y}$ thin films ($y = 0.7, 0.8$ and 0.9) are measured in the $0.5\text{--}5.5$ eV energy range, both in the as-prepared and hydrogenated states. Upon hydrogenation these films switch reversibly from a shiny metallic state into a “black” absorbing one. The composition and thicknesses can be tailored to achieve high solar absorptance and low thermal emittance in the hydrogenated state. The combination of these two characteristics is interesting for the application of this material as switchable absorber in solar collectors. The use of a $\text{Mg}_y\text{Ti}_{1-y}$ switchable absorber in solar collectors allows to lower the stagnation temperature from 180 to 80°C . The collector efficiency is affected only minimally.

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1. Introduction

In 1996 Huiberts et al. [1] discovered that Y and La thin films exhibit drastic optical changes upon hydrogenation. Shiny reflecting in the metallic state they become transparent during hydrogen loading. Richardson et al. [2,3] found similar behavior in Mg_2Ni thin films. Besides the reflecting and the transmitting states, Mg_2Ni films also showed an intermediate absorbing state [4] due to the preferential nucleation of the hydride phase at the film–substrate interface [5]. We have recently found that an absorbing (black) state is also present when hydrogenating $\text{Mg}_y\text{Ti}_{1-y}$ thin films, Fig. 1. The black state in $\text{Mg}_y\text{Ti}_{1-y}\text{H}_x$ thin films is; however, a final, reversible state and offers therefore interesting possibilities for technological application as switchable absorber in solar collectors [6]. In solar collectors, the absorber must have a very high absorptance in the solar spectrum (ss) ($h\nu > 0.5$ eV), while simultaneously having a very low emittance in the infrared ($h\nu < 0.5$ eV). In this way, the conversion of solar irradiation is

maximized while thermal losses are minimized. However, due to this optimization, temperatures in a solar collector can rise to above 200°C under stagnation conditions, i.e. when no heat is withdrawn from the collector. Therefore, relatively expensive materials such as copper or aluminum must be used to withstand these temperatures. This puts a fundamental lower limit on the cost of solar collectors. To structurally lower the cost, cheaper materials are needed. Polymer technology has developed several materials that can withstand temperatures up to $150\text{--}200^\circ\text{C}$ but their costs are still too high to be economically feasible for application in solar collectors. On the other hand cheap plastics cannot withstand temperatures above $\sim 100^\circ\text{C}$. We show how the use of $\text{Mg}_y\text{Ti}_{1-y}$ thin films as switchable absorbers can effectively reduce the stagnation temperature of a solar collector, without affecting the collector efficiency. We also show how it is possible to tune the solar absorptance (SA) and thermal emittance of this material, by properly tailoring alloy composition and film thickness.

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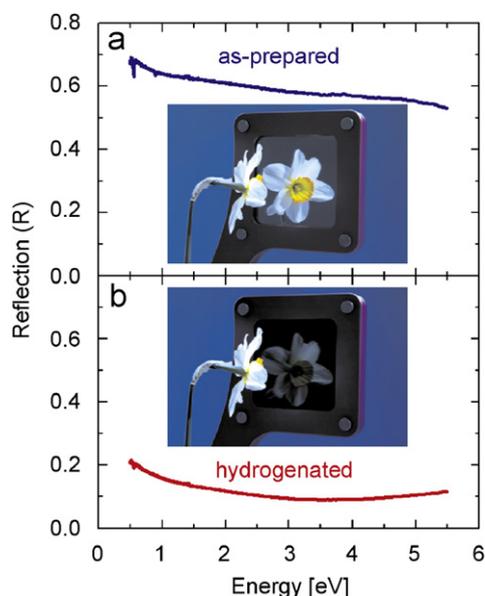


Fig. 1 – Reflection spectra and optical appearances of a 200 nm $\text{Mg}_{0.7}\text{Ti}_{0.3}$ film covered with 10 nm Pd, viewed through the glass substrate. (a) In absence of hydrogen the reflection of the $\text{Mg}_{0.7}\text{Ti}_{0.3}$ layer is mirror-like. (b) When exposed to 4% H_2/Ar mixture the reflection drops and the layer becomes black.

2. Experimental

200 nm thick $\text{Mg}_y\text{Ti}_{1-y}$ ($y = 0.7, 0.8$ and 0.9) films covered with 10 nm of Pd are prepared by DC/RF magnetron co-sputtering of Mg and Ti, on quartz substrates. The palladium layer is needed to prevent oxidation and to promote hydrogen dissociation. The film composition and thickness are measured ex situ by Rutherford backscattering and profilometry, on samples prepared during the same deposition run, but on carbon substrates. The reflection (R) and transmission (T) spectra of the films are measured in a Perkin Elmer Lambda 900 diffraction grating spectrometer ($0.5 < h\nu < 6.5$ eV) and in a Bruker IFS 66 Fourier transform infrared spectrometer ($0.2 < h\nu < 1.1$ eV). The spectra are measured through the substrate, at near normal incidence, on films in the as-prepared state and during hydrogenation (H_2 pressures up to 1 bar).

3. Results and discussion

Absorption ($A = 1 - R - T$) spectra of 200 nm $\text{Mg}_y\text{Ti}_{1-y}$ films covered with 10 nm Pd are shown in Fig. 2. In the as-prepared states the films have a high (metallic) reflection and no transmission and consequently low absorption. When exposed to 1 bar H_2 at room temperature the absorption increases for all compositions: the reflection decreases dramatically and a significant transmission is observed only for $y = 0.9$ [6]. In order to evaluate the total SA of these films we convolute the absorption (A) spectra with the SS in the 0–4 eV range. In addition we calculate the ratio (Z) between

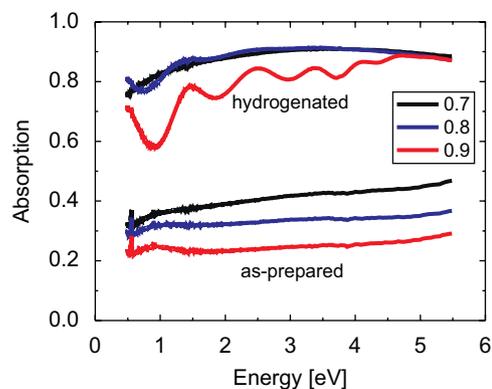


Fig. 2 – Absorption spectra of 200 nm $\text{Mg}_y\text{Ti}_{1-y}$ thin films ($y = 0.7, 0.8, 0.9$), covered with 10 nm Pd, measured in the as-prepared and hydrogenated (1 bar H_2 at room temperature) states.

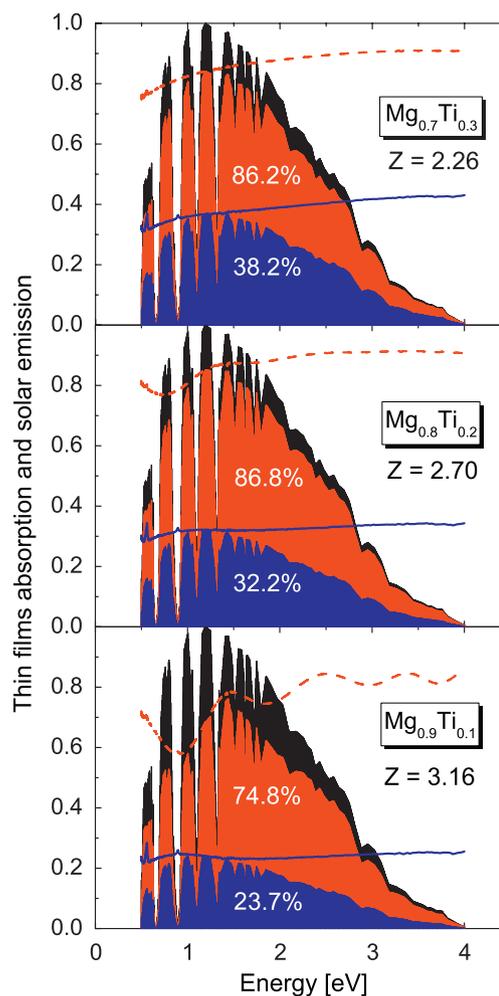


Fig. 3 – Lines: absorption spectra of the as-prepared (solid line) and hydrogenated (dotted line) states for 200 nm $\text{Mg}_y\text{Ti}_{1-y}$ thin films ($y = 0.7, 0.8, 0.9$), covered with 10 nm Pd. Areas: solar spectrum (black) and its convolutions with the absorption spectra of the as-prepared and hydrogenated states.

the SA in the hydrogenated and as-prepared states, Fig. 3. The maximum SA (87%) is obtained for the hydrogenated state of $\text{Mg}_{0.8}\text{Ti}_{0.2}$, while the best contrast (highest Z) is found in the $y = 0.9$ composition. However the speed of hydrogen absorption and desorption are strongly dependent on the metal ratio in the initial alloy and films with higher Ti content have the best kinetics. These layers have absorptances only slightly lower than those found in commercially available absorbers (91–96%) [8], but they have the great advantage of being switchable. In order to increase the efficiency of a solar absorber, it is also necessary to reduce the thermal emittance as much as possible [9]. The thermal emittance of a layer stack can be tuned by changing the thicknesses of the layers and it depends on the dielectric functions of the materials. From the reflection and transmission measurements we have calculated the dielectric functions of our $\text{Mg}_y\text{Ti}_{1-y}$ thin films through a Drude–Lorentz parametrization [7]:

$$\begin{aligned} \varepsilon(\omega) &= \varepsilon_1 + i\varepsilon_2 \\ &= \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{j=1}^3 \frac{f_j}{\omega_{0j}^2 - \omega^2 - i\omega\beta_j}, \end{aligned} \quad (1)$$

where ε_∞ accounts for high energy excitations, the second term in the sum is the free-carrier absorption (Drude) and the last term is a sum of three Lorentz oscillators. With the dielectric functions obtained we have calculated the absorption spectra for different thicknesses of hydrogenated $\text{Mg}_y\text{Ti}_{1-y}$ films, covered with 40 nm of Pd. The thermal emittance is then derived by convoluting the calculated absorption spectra with the black body radiation at 100 °C in the 0–0.5 eV range. The absorption spectra in this range are obtained by linearly extrapolating to zero energy the spectra obtained in the 0.5–5.5 eV range [6]. The results are shown in Fig. 4. It is clear that in order to reduce the thermal emittance, the film thickness should not exceed a critical value, depending on composition: in fact, from an analysis of the dielectric functions we have seen that the higher the amount

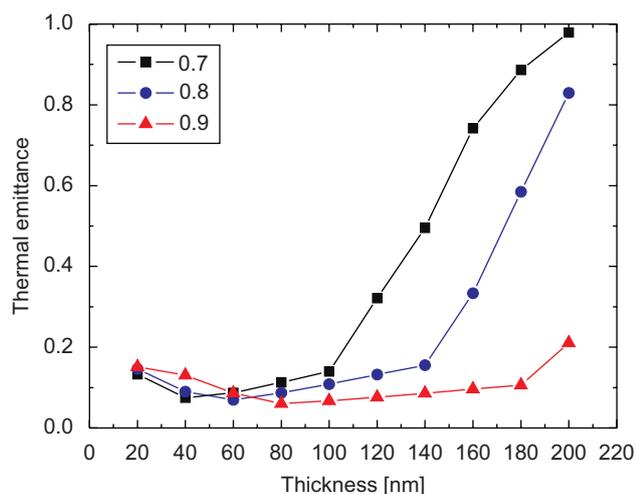


Fig. 4 – Thickness dependence of the calculated thermal emittance of hydrogenated $\text{Mg}_y\text{Ti}_{1-y}$ thin films ($y = 0.7, 0.8, 0.9$), covered with 40 nm of Pd.

of Ti in the film, the higher is the extinction coefficient (k) and therefore the lower will be the thickness at which the thermal emittance starts to increase. On the other hand a too thin layer would compromise the SA due to an increase in transmission in the visible range. A thickness of 65 nm is a good compromise for all compositions both in terms of high SA and low thermal emittance. The hydrogenation process is both fast and reversible: upon exposure to 5% H_2/Ar mixture a 65 nm $\text{Mg}_{0.7}\text{Ti}_{0.3}$ film covered with 40 nm of Pd undergoes an optical transition from shiny metallic to black absorbing in a few seconds. By subsequent exposure to a 20% O_2/Ar mixture the films dehydrogenate in less than 200 s [6] recovering the initial state both from an optical and a structural point of view [7]. The reversibility has been demonstrated for over 150 cycles. In order to evaluate the applicability of a $\text{Mg}_y\text{Ti}_{1-y}$ layer as a switchable absorber in a real solar collector we consider the model collector depicted in Fig. 5a. The model consists of a glass cover, an air gap and the switchable absorber which is in thermal contact with the water pipes. The light shines from above onto our film, through its substrate. In order to achieve an optical switch we have either to expose our absorber to hydrogen (gasochromic loading) or to integrate it into an all-solid state electrochromic device (electrochromic loading). In our simulation, however, we consider the absorber as a single layer. We did not take into account the effects due to the substrate, the eventual hydrogen gas reservoir or the additional layers needed in an electrochromic device. This is reasonable both from an optical and a thermal point of view: the major optical changes happen at the substrate–film and film–palladium interfaces and the optical properties of the substrate do not have a significant influence on them. Furthermore the films are very thin, assuring a high thermal conduction to the water pipes even in presence of additional layers. The stagnation temperature of the whole collector is plotted as a function of the SA and thermal emittance of our absorber in Fig. 5b. The calculation is based on the method described by de Vries [10] and Zondag et al. [11]. As an example of the behavior of a $\text{Mg}_y\text{Ti}_{1-y}$ layer we have taken a 65 nm thick $\text{Mg}_{0.8}\text{Ti}_{0.2}$ covered with 40 nm of Pd and calculated its SAs and thermal emittances both in the as-prepared and hydrogenated states. From Fig. 5b we see that, by switching the layer between these two states, the stagnation temperature can be lowered from ~ 180 to ~ 80 °C. The calculations have also shown that the collector efficiency is affected only minimally.

4. Conclusions

We have studied the optical properties of $\text{Mg}_y\text{Ti}_{1-y}$ thin films covered with 10 nm of Pd in the 0.5–5.5 eV range. Highly reflecting in the as-prepared state these films become highly absorbing upon exposure to hydrogen. The hydrogenated “black” state is a final, reversible state. The SA and thermal emittance of these layers can be tailored by changing the metal ratio in the initial alloy and the thickness of the films. These optical properties are ideal to be used in a solar collector, in order to reduce the stagnation

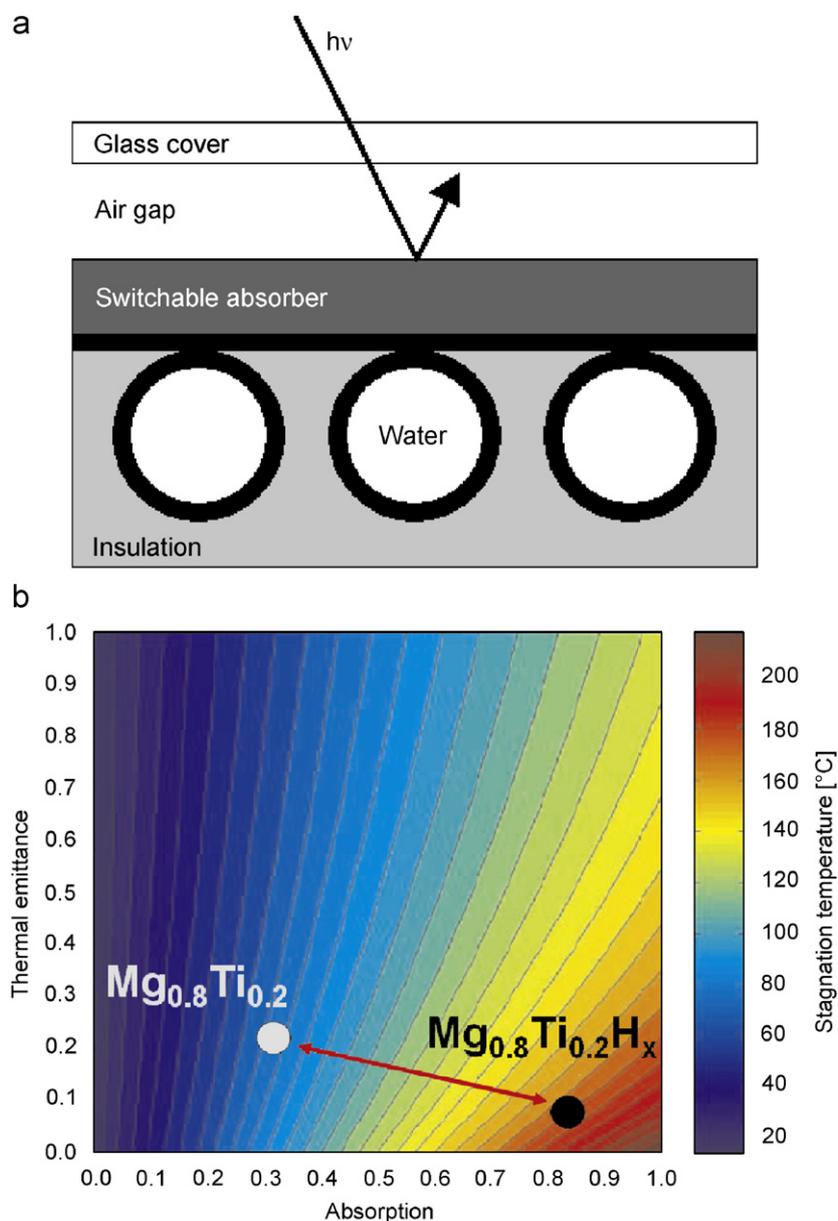


Fig. 5 – (a) Model of the solar collector. (b) Stagnation temperature map as a function of solar absorptance and thermal emittance of the absorber. The dots indicate the stagnation temperature for a 65 nm thick $\text{Mg}_{0.8}\text{Ti}_{0.2}$ film covered with 40 nm of Pd, both in the as-prepared (white dot) and hydrogenated (black dot) states.

temperature, without significantly decreasing the efficiency of the device.

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REFERENCES

- [1] Huiberts JN, Griessen R, Rector JH, Wijngaarden RJ, Dekker JP, de Groot DG, et al. Yttrium and lanthanum hydride films with switchable optical properties. *Nature* 1996;380:231.
- [2] Richardson TJ, Slack JL, Armitage RD, Kostecki R, Farangis B, Rubin MD. Switchable mirrors based on nickel-magnesium films. *Appl Phys Lett* 2001;78:3047.
- [3] Richardson TJ, Slack JL, Farangis B, Rubin MD. Mixed metal films with switchable optical properties. *Appl Phys Lett* 2002;80:1349.
- [4] Isidorsson J, Griessen R, Di Vece M, Giebels IAME. Tunable reflectance MgNiH films. *Appl Phys Lett* 2002;80:2305.
- [5] Lohstroh W, Westerwaal RJ, Noheda B, Enache S, Dam B, Giebels IAME, et al. Self-organized layered hydrogenation in black Mg_2NiH_x switchable mirrors. *Phys Rev Lett* 2004;93(19):197404.
- [6] Borsa DM, Baldi A, Pasturel M, Schreuders H, Vermeulen P, Notten PHL, et al. Mg–Ti–H thin films for smart solar collectors. *Appl Phys Lett* 2006;88:241910.
- [7] Borsa DM, Gremaud R, Baldi A, Schreuders H, Rector JH, Kooi B, et al. Structural, optical, and electrical properties of $\text{Mg}_{0.8}\text{Ti}_{1-y}\text{H}_x$ thin films. *Phys Rev B* 2007;75:205408.

- [8] Zhao S, Ribbing CG, Wäckelgård E. New method to optimize a solar absorber graded film profile. *Sol Energy* 2005;78:125–30.
- [9] Chen J, Yan Z, Chen L, Andresen B. Efficiency bound of a solar-driven stirling heat engine system. *Int J Energy Res* 1998;22:805–12.
- [10] de Vries DW. Design of a photovoltaic/thermal combi panel. Eindhoven University of Technology Thesis; 1998.
- [11] Zondag HA, de Vries DW, van Helden WGJ, van Zolingen RJC, van Steenhoven AA. The yield of different combined PV-thermal collector designs. *Sol Energy* 2003;74:253–69.