Thermochromic and photochromic colour change in Mg-Ni-H thin films

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Abstract

Mg-Ni-H thin films were deposited by reactive magnetron sputtering. As-deposited samples were Mg-rich and annealed in air by two steps at T = 220 and 290°C in order to increase crystallinity. A reversible, thermochromic effect was detected when the crystalline yellow colour sample underwent a colour transition and changed its colour from yellow to red. The change in transmission spectra of the prepared thin films in visible range of spectra was induced by in situ heating setup. The continuous shifts of the transmission spectra at T = 200°C towards lower band gap was observed. Additionally, a photochromic effect was detected and confirmed by exposing the sample to visible light, as grey-coloured area appeared on the sample.

Keywords: chromogenic materials, metal hydride films, Mg-Ni-H films, thermochromics effect

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1. Introduction

Magnesium-based hydrides have been studied for many years as potential materials for hydrogen storage, sensors and switchable mirrors [1-3]. Mg-based switchable mirrors were investigated intensively since upon hydrogen uptake their optical appearance can be tuned from a highly reflective metallic state to a transparent insulating state over the entire optical range [2, 4-5]. Such materials can also show optical properties changes with temperature [6-7]. From a technological point of view, the investigation of materials which can change optical appearance with temperature has a great importance, as they can be used as temperature sensors or smart windows [8].

Giebels et al. reported a thermochromic effect in Mg-RE- hydrides, such as Mg$_{0.1}$Y$_{0.9}$H$_x$, which was caused by hydrogen desorption upon heating [6]. Subsequently, investigations on Mg-TM-H bilayers revealed that temperature changes triggered changes of the optical properties due to hydrogen migration between the two Pd/ Mg$_2$NiH$_x$ metal hydride layers [7]. Various colour transitions have been reported for the Mg-Ni-H system. A reversible transition, caused by exposure to air, was observed for Mg-Ni-H powders as the colour changed from orange to brown and reversed by cycling of the sample under hydrogen pressure [9].

In this work, we focus on single-layer Mg-Ni-H thin films synthesized without capping layer by reactive sputtering deposition. We report a highly reversible and continuous shift of the transmission edge as a result of the temperature increase, which differs from previous findings and is not related to H sorption.

2. Experimental
Mg-Ni-H thin films were synthesized using reactive magnetron co-sputtering at room temperature using two targets, Mg set to RF working mode and Mg$_2$Ni, which was set to DC working mode. The initial parameters of Ar and H flows and targets' power were adjusted as to obtain Mg-rich samples. The samples were deposited on microscope glass slides, sized 26 mm x 76 mm. The as-deposited samples were amorphous, or nanocrystalline with grain sizes below the detection limit of the glancing incidence X-ray diffraction instrument. Prior to the optical measurements, the samples were annealed in order to increase crystallinity. Before the measurements, the samples were annealed in air on a heating plate. The annealing consisted of two steps at $T = 220$ °C and 290 °C for 6 minutes in total. The high-temperature cubic structure of Mg$_2$NiH$_4$ was observed in the polycrystalline thin film. The thickness of the as-deposited samples was 550 nm. The heating setup used for in situ detection of the changes in the transmission spectra was assembled for the purpose of these measurements. It consisted of two heating plates on which a silicon wafer was evenly positioned. A 10 mm diameter hole in the centre of the wafer allowed a light beam (5 mm diameter) to come through. The sample was placed on the wafer and the optical transmission spectra were collected. The temperature of the wafer and the sample were kept constant at 200 °C and the sample's temperature was monitored with a thermocouple. The optical transmission of the films was measured in the visible spectral range with an Ocean Optics QE65000 optical spectrometer, while the Optical software [10] was used to estimate the band gaps.

3. Results

Figure 1 shows the changes of the optical transmission spectra recorded in situ. The total time of recording was 100 s. After placing the sample on the hot wafer, the
sample reached the temperature of 200 °C within seconds. The first collected transmission spectrum after the sample reached the temperature 200 °C, is marked with 0 s in Figure 1. Thereafter, transmission was measured after 40 s and 100 s. The heating of the sample caused a colour transition from yellow to red [inset to Figure 1], whereas the edge of the transmission spectra was shifted towards higher wavelength. This phenomenon was followed by a continuous decrease of transmission at wavelengths other than the absorption edge. The final recorded results were used to estimate the band gap. The narrowing of the band gap was 0.12 eV. The band gap of crystalline yellow colour sample at room temperature is 2.04 eV, while that of the red colour sample is 1.92 eV.

Figure 1. Heating-induced change of transmission spectra of Mg-Ni-H films: Increasing temperature gives a modulation of transmission in the visible range and red shift of fundamental absorption edge is observed. The black curve represents the transmission of the sample when it reaches $T = 200 ^\circ C$, marked with 0 s as it shows beginning of the measurement. The red line represents the transmission after 40 s spent at 200 °C, while the green curve represents the transmission after 100 s. The inset to Figure 1 shows the change in visual appearance of the sample due to the temperature increase.
To confirm that no hydrogen desorption occurred during the measurement, the same sample was measured again for 200 s. Figure 2 shows the comparison between the spectra obtained during the first and second series of measurements. Recording of the transmission spectra was performed immediately as the sample was placed on the hot wafer. The first collected transmission curve of the second series is marked with 0 s. It can be seen that the maximum of transmittance is higher than in the first series, showing that the sample undergoes the colour transition instantly before reaching the temperature of the hot stage, $T = 200 \, ^\circ\text{C}$. Moreover, it can be concluded that after different thermal treatment, shift of the transmission edge towards lower energy is same in both series. The last obtained curve was used to estimate the band gap of heated sample and it showed the same value as in the first measurement, 1.92 eV.

![Figure 2. Transmission spectra obtained by different time of heating, i.e. 100 s and 200 s. In the second measurement, the recording of the transmission spectra started immediately when the sample was placed on the hot wafer (marked with 0 s). The curves marked with 40 s represent the transmission spectra of the sample collected after 40 s from the beginning of the measurements. The curves that correspond to the last step of](image)
the recordings (green colour and orange colours) show the same shift of the transmission edge and the values of estimated band gap.

The shift in optical spectra can be attributed to deviation from periodicity due to the temperature variation of the lattice vibrations [10]. A crystal with an excess of energy experiences different electron-lattice interaction compared to the stationary state, and consequently influences the band gap width [10-11]. In addition, the arrangement of H ions in the NiH₄ complex should be taken into account for the changes observed in the band gap [12]. In this respect, one can assume that the arrangement of four H ions around Ni atom are strongly affected by the increase of the temperature and a rearrangement of ions occurs when the sample is heated. As the external perturbation is over, that is when the sample is cooled down, the crystal lattice returns to its original room-temperature equilibrium and the band gap displays again the value of the 2.04 eV.

To validate reversibility of the thermochromic effect, three continuous heating/cooling cycles were performed [Fig. 3]. The A₀ transmission curve was recorded at room temperature, before the cycles started. The curves corresponding to A₁, A₂, A₃ show spectra after cooling of the sample in cycles 1, 2 and 3, respectively. The transmission spectra at constant temperature of T = 200 °C are marked with B₁, B₂, B₃. The difference between the spectra collected at room temperature (A₁, A₂, A₃) and at high temperature (B₁, B₂, B₃) [Fig. 3], confirms the reversibility of the effect. Furthermore, the transmission spectra show the same features after each heating step. On the other hand, the comparison of A₀ and A₁, as well as A₁ and A₂, show that after each cycle the sample did not recover the same transmission spectrum as starting one, A₀ [Fig. 3]. This indicates that another effect is also contributing to band gap changes.
In fact, a grey, slightly reflective spot appeared at the place illuminated by the light beam. This can be ascribed to a photochromic effect, which can be reversed by further heating at higher temperatures ~ 250°C. The similar features observed for curves A₂ and A₃ indicate that the photochromic effect has reached a constant value. This effect has been observed after illumination of a large part of the sample by visible light at an intensity of 1 kW/m² as well. However, in the latter case, the change was permanent, as the heat transfer was not sufficient to reverse the transition to the initial optical state.

![Figure 3](image-url)  
*Figure 3. Transmission spectra of the sample after 3 cycles of heating/cooling of the sample. The curves labelled as A₁, A₂, and A₃ refer to the measurements after the sample is cooled down at room-temperature, whereas the curves labelled B₁, B₂, and B₃ are for the samples at 200 °C.*

4. Conclusion
In summary, we have studied the transmission spectra of the Mg-Ni-H system deposited by reactive magnetron sputtering. A change in optical properties was observed at $T = 200 \, ^\circ C$. A continuous shift of the transmission edge, due to a narrowing of the band gap, takes place within 200 s. The band gap narrowing was reversible and repeatable after several thermal treatments and it does not depend on thermal treatment history.

Acknowledgments. This research was financially supported by Ministry of Education and Science of Republic of Serbia, under grant III 45012, by the Research Council of Norway through the Yggdrasil mobility program 2012, 219352/F11, the ISP project 181884 and the FRINATEK project 240477/F20.
References


