Hydrating behavior of Mg-based nano-layers prepared by pulsed laser deposition

Z. Wiśniewski,1,* J. Bystrzycki,1 W. Mróz,2 C. Jastrzębski3

1)Faculty of Advanced Technology and Chemistry, Military University of Technology
2)Optoelectronic Institute, Military University of Technology
Kaliskiego 2 Str., 00-908 Warsaw, Poland
3)Faculty of Physics, Warsaw University of Technology
Koszykowa 75 Str., 00-662, Warsaw, Poland
e-mail: fizykcs@wp.pl

Abstract. The hydriding behavior of Mg with TiO₂ and Si nanolayers prepared by the pulsed laser deposition (PLD) was studied. The phase structure, chemical composition and hydriding properties of the obtained Mg-based nanolayers were investigated by the XRD, TEM, AFM, RS, SIMS and the volumetric Sievert method. It was shown that PLD is an excellent technique for producing the complex structures based on Mg. Both, the kinetic and destabilization topics were investigated in this paper.

1. Introduction
Magnesium is considered as a promising material for hydrogen storage because of its high hydrogen storage capacity up to 7.6 wt.%. However, the major problem of Mg is its slow reaction rate and high desorption temperature (>300°C) [1-3]. To overcome the kinetic problem, transition metal oxides such as TiO₂, Cr₂O₃ and Nb₂O₅ have been added to the nanocrystalline Mg/MgH₂ for better hydrogen absorption and desorption kinetics [4,5]. Recently, Polanski et al. [6] have reported the catalytic effect of nanoparticle metal oxides on hydrogen storage properties of MgH₂. The nanosized particles significantly decreased the activation energy for hydrogen desorption, much better as compared to their microsized counterparts. Most research was done on powders. In this work we try to show that layers can also be used for the hydrogen storage purpose and that PLD is a suitable method for fabricating both simple and complicated layers for hydrogen deposition. In our opinion the simple structure can find application as a hydrogen sensor and a complicated one can be used for academic application for studying super-structural effects.

2. Experimental
The nanolayers of Mg/TiO₂ on the ZrO₂ substrate and Mg/TiO₂/Si/TiO₂/Mg on the TiO/Mg substrate were prepared by the pulsed laser deposition. The experimental conditions used in our work for the deposition of the Mg-based nanolayers are shown in Table 1. Morphology of the obtained nanolayers was investigated with the application of the atomic force microscopy (AFM). The microstructure of multilayered samples with interlayers of the TiO₂ catalyst was conducted with a transmission electron microscopy (TEM). The specimens for TEM were prepared by the focused ion beam (FIB) technique. The phase analysis was performed by using an X-ray spectrometer with the Brag Brentano geometry. The distribution of elements in the nanolayers was investigated by using the SIMS apparatus equipped with a quadruple mass.

### 3. Results and discussions

Two different structures were deposited by PLD in our experiment. The first one is relatively simple, consisting of the ZrO₂ substrate with 100 nm of Mg on it and covered by 50 nm of TiO₂. The X-ray reflection measurements confirmed the thickness of all the investigated nano-layers. Figure 1 shows the surface of the TiO₂ nanolayer deposited on Mg in oxygen rich and deficient atmosphere.

![AFM images of the TiO₂ outer layer grown in oxygen (a) rich and (b) deficient atmosphere of the sample 1](image)

Figure 1. AFM images of the TiO₂ outer layer grown in oxygen (a) rich and (b) deficient atmosphere of the sample 1 (simple structure).

Table 1. Experimental conditions used in our investigation for the deposition of Mg-based nanolayers.

| Sample designation | Sample 1 | Sample 2 |
|--------------------|----------|----------|
| Substrate          | ZrO₂     | TiO₂/Mg  |
| Targets            | Mg, TiO₂ | TiO₂, Mg, Si |
| Laser wavelength   | λ = 193 nm | λ = 193 nm |
| Energy of impulse  | 320 mJ   | 320 mJ   |
| Frequency of impulses | 5 Hz    | 5 Hz     |
| Impulse duration   | 15-20 ns | 15-20 ns |
| Substrate temperature | Room temperature | Room temperature |
| Distance target sample | 60 mm | 60 mm |
| Vacuum             | 5*10⁻⁵ mbar | 5*10⁻⁵ mbar |
| Atmosphere         | O₂ - optional | O₂ - 5 cm³/min |
The surface morphology presented in figure 1a is rather smooth and homogenous and the one presented in figure 1b is rough showing large irregular islands. It points out that the amount of oxygen in the chamber is an important parameter determining the morphology of the deposited microstructure.

Figure 2 presents the Raman spectrum of the Mg/TiO$_2$ sample hydrogenated under 100 bar of hydrogen pressure. In the Raman profile one broad line is visible around 200 cm$^{-1}$ and the second one much wider around 1400 cm$^{-1}$. The former can be attributed to Ruthil, probably partially the amorphous phase of TiO$_2$ but the origin of the latter maximum is much more difficult to explain. Its character, however, suggests the presence of some amorphous components of MgO. The peak around 120 cm$^{-1}$ can be attributed to hydrogen. This results show that the Raman spectroscopy can be used to detect the hydrogen presence in described structures. Because the Raman spectroscopy sees mainly the outer parts of a sample, the Raman spectra of the second structure is practically the same.

Desorption behavior of the hydrogenated Mg/TiO$_2$ sample measured by the TPD is shown in Figure 3. There are two dehydrogenation peaks, the first one at 370°C (marked as NC) and the second one is at 470°C (marked as MC). It may suggest that there are two populations of crystalline grains in the sample as regard to their size. In the microcrystalline areas of the layer dehydrogenation may take place at the higher temperature (450°C) while in nano-crystalline areas desorption occurs at the lower temperature (350°C). The presence of small grains with a diameter of nanometers can significantly lower the hydrogen absorption temperature. It is consisted with the results shown in [12,13] where the similar behavior was observed for the Mg/Pd layers. Moreover, recently the theoretical calculations carried out on metal clusters have shown that the decomposition temperature of the MgH$_2$ clusters essentially decreases when the diameter of clusters shifts to the nanometer range. The obtained temperatures are still higher as compared to the Pd/Mg/Pd nanolayers where temperatures about 150°C were observed.
Figure 3 Thermal desorption spectrum of hydrided Mg/TiO$_2$ sample.

Some theoretical works suggest that the destabilization of MgH$_2$ with Si forming the Mg$_2$Si intermetallic compound is possible even at room temperature [9]. Therefore it is useful to study the interaction between both elements in nanoscale by using the Mg-Si layers. Figure 4 shows TEM image depicting the cross section of a multilayer sample after the pulsed laser deposition.

The microstructure consists of different nano-layers showing crystals in the Mg layers. The multilayer sample was immersed in hydrogen for 48 h. In order to increase the incorporation rate of hydrogen through all the layers high pressure (1 GPa) was applied. Fig.5 presents SIMS spectra of the hydrogenated multilayer sample.
As it can be seen the hydrogenation of the sample really took place although bigger density of absorbed hydrogen is in the outer layers than in Mg. The largest amount of hydrogen is observed in the regions where the gradient of Ti concentration reaches the highest values. Some correlation between hydrogen and Si concentration can also be observed.

4. Summary
The nanolayers of Mg/TiO$_2$ on the ZrO$_2$ substrate and Mg/TiO$_2$/Si/TiO$_2$/Mg on the TiO$_2$/Mg substrate were successfully prepared by the pulsed laser deposition. Hydrating behavior of the obtained nanolayers were studied. The PLD and Raman spectroscopy techniques exhibit a considerable potential for further investigations of hydrogen storage properties in nano-layered materials.

The SIMS method can also be used for a hydrogen presence determination in the described structures but it is a destructive method what is a considerable disadvantage.

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