Structural evolution of Pd capped-Mg thin films under H₂ absorption

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INTRODUCTION

It is well known that slow absorption/desorption kinetics, high temperatures, and need of activation processes prevent the use of magnesium hydride as a hydrogen storage material suitable for automotive applications. In last years there has been a strong effort to overcome these problems: improvements in kinetics at useful temperatures have been achieved thanks to reducing materials microstructures to the nanometer scale [1]. However we are still far from requirements set by the U.S. DoE and more research is needed, in particular on the relation between microstructure, functional properties and reliability.

Concerning this point thin films constitute a model material, due to the easy control of microstructure and the possibility of using complementary characterization techniques [2-4].

EXPERIMENTAL

Magnesium thin films, with a Cr buffer layer, were deposited on Si and glass substrates by r.f. magnetron sputtering. A Pd thin cap layer was added to promote hydrogen dissociation and to prevent magnesium oxidation. Depositions were done in a custom built r.f.-magnetron sputtering system (13.56 MHz) equipped with 3 independent 2” sources and a r.f.-biased sample holder. The magnetron sputtering sources were positioned at a ~30° inclination to the substrate normal and a target-to-substrate (center to center) distance of 12 cm. The sample holder, on the ceiling of the vacuum chamber, was rotated at 5 r.p.m. in order to assure a deposition uniformity better than 5%. Chromium, magnesium and palladium layers were deposited, in sequence, onto silicon wafers and fused silica sheets. The natural oxide on the Si wafers was removed by dipping in concentrate HF. These samples were then rinsed in deionized water and stored in isopropanol. Silica sheets were washed with a detergent, rinsed with deionized water and ultrasonically cleaned in trichloroethylene, acetone and isopropanol. Once in the sputtering chamber, the substrates were sputter cleaned at 20 W for 20 min in order to remove any residual surface contamination (in these conditions we measured a 10nm-thick sputtered layer for silica).

The Cr layer was sputtered at first onto the bare substrates in order to assure a good adhesion of the Mg layer. Targets materials were 2” diameter Cr (99.9 %), Mg (99.95%) and Pd (99.99 %) disks. Sputtering was performed in pure Ar (99.9995 %) at a pressure of 4x10⁻³ mbar. The base pressure was better than 10⁻⁶ mbar. Before starting the depositions, sources were conditioned for 15 min. at the operating conditions. Depositions were performed at room temperature. Powers delivered to the sputtering sources were 50 W, 20W and 10 W for Cr, Mg and Pd, respectively. Sputtering times were 50 s, 3300 s and 700 s for Cr, Mg and Pd, respectively.

The elemental composition of the films was measured by Rutherford backscattering spectroscopy (RBS) using a 2 MeV ⁴He⁺ beam at Laboratori Nazionali INFN of Legnaro (Padova). X-ray diffraction (GIXRD) patterns were recorded in grazing incidence (with typical incidence angle $\omega = 0.8^\circ$) and parallel beam geometry with a Panalytical X’Pert Pro MRD diffractometer equipped with a parabolic mirror in front of a CuKα X-ray source. For in-situ desorption measurements a heatable specimen holder (Anton Paar DHS 900 hot stage) has been used. Structural and compositional characterization was performed with a field-emission gun FEI TECNAI F20 (S)TEM transmission electron microscope equipped with an EDAX energy-dispersive X-ray spectrometer (EDS).

RESULTS AND DISCUSSION

The RBS spectrum for a sample with the silicon substrate is reported in figure 1. Dots correspond to the experimental spectrum, while the continuous line is a spectrum synthesized with the RUMP code [5].

FIG. 1: RBS spectrum of the Pd-capped Mg thin film
The peak at channel 457 corresponds to particles scattered from the Pd layer, that at channel 360 corresponds to particles scattered from the Cr layer, and signals at channels 276 and 268 originate from Mg and the Si substrate, respectively. The very good fit of the synthesized spectrum to the experimental one was obtained considering a multilayer structure of pure Si/Cr/Mg/Pd with elemental amounts of $20 \times 10^{15}$ Cr/cm$^2$, $800 \times 10^{15}$ Mg/cm$^2$, and $55 \times 10^{15}$ Pd/cm$^2$.

To better investigate the structure of the layers and of their interfaces, transmission electron microscopy (TEM) analysis has been performed on the as-deposited sample. Figure 2 shows the resulting cross-sectional bright-field TEM image: the different layers can be clearly distinguished. TEM compositional analysis with energy dispersive X-ray spectrometry (EDS) confirmed the composition of the different layers as deduced by RBS analysis. The total film thickness is about 230 nm with a high degree of roughness at the surface. The stack is composed of 5 nm of Cr, 180 nm Mg and 10 nm Pd on top. The remaining 30-40 nm are a mixed intermetallic Mg-Pd layer at the interface between the Mg and Pd layers. In particular, the diffraction contrast in the central Mg layer indicates the typical columnar growth of the Mg grains with a texturing in the direction perpendicular to the substrate surface. This level of texturing can be relevant during hydrogen sorption processes as a preferential diffusional path.

The as-deposited samples underwent different cycles of H$_2$ absorption-desorption to investigate the structural effect on the thin film. Typical loading conditions were: T=100°C at a pure hydrogen pressure of 1 bar for 4 hours. Desorption was monitored with GIXRD both in-situ to follow the kinetics of desorption and to estimate an activation energy for the process and ex-situ to check the evolution of the nanostructure as a function of the number of subsequent sorption cycles.

Figure 3 shows the GIXRD diffraction patterns for the as-deposited, hydrogen-loaded and desorbed samples. In the as-deposited sample the columnar growth of the Mg film is evident from the intensity distribution of the P63/mmc hexagonal phase peaks, indicating a strong texturing perpendicular to the substrate. In Fig. 3a the reflections of the polycrystalline Pd cap layer are also indicated. The main effect of hydrogenation is shown in figure 3b by the formation of the magnesium hydride phase (the tetragonal one being dominating). Upon a single cycle of desorption in air at 100°C for 4 hours the GIXRD pattern in fig. 3c shows the loss of Mg texture with an intensity distribution among the hcp reflections more similar to a really polycrystalline sample with randomly oriented nanograins.

![FIG.2: TEM image of the as deposited sample on silicon substrate](image)

![FIG.3: XRD spectra of the as deposited (a), hydrogen loaded (b) and desorbed samples (c). (Arrow:Mg, |: Pd, *:orthorhombic MgH$_2$, x:tetragonal MgH$_2$). The substrate in this case is glass.](image)