

## Defect studies of Mg films deposited on various substrates

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**Abstract.** In the present work the structure of Mg films deposited by RF magnetron sputtering was characterized using variable energy positron annihilation spectroscopy combined with scanning electron microscopy and X-ray diffraction. The effect of deposition parameters, namely temperature, type of substrate and deposition rate, on the microstructure was examined. All Mg films studied grow with the basal (0001) plane parallel with the substrate and exhibit only negligible in-plane stress. Films deposited at room temperature are characterized by nanocrystalline structure with high volume fraction of grain boundaries. and positrons are preferentially trapped in open volume defects present at grain boundaries. In these films positrons are trapped predominantly in open-volume defects present at grain boundaries. With increasing deposition temperature the mean grain size increases and the volume fraction of grain boundaries decreases. Hence, in Mg films prepared at elevated temperatures positrons are trapped mainly at misfit dislocations compensating different atomic spacing in the films and the substrate. Moreover, it was found that slow deposition rate leads to higher density of defects compared to fast deposition rate. By annealing of Mg film with thin 20 nm Pd overlayer at 300°C for 1 hour Pd layer is mixed with Mg film forming a Mg-Pd compound. The Mg-Pd phase likely contains structural open-volume defects which trap positrons.

### 1. Introduction

Magnesium hydride (MgH<sub>2</sub>) is an attractive material suitable for on-board hydrogen storage in mobile applications due to its safety, lightweight, low cost and in particular high hydrogen absorption capacity up to 7.6 wt. % [1]. However sluggish hydrogen sorption kinetics in MgH<sub>2</sub> is the major obstacle for its use in practical applications. Structure refinement down to nanoscale forms a dense network of grain boundaries which enable easier hydrogen distribution into grains and thus could remarkably speed up hydrogen sorption kinetics. The effect of microstructure on the hydrogen sorption kinetics can be investigated on thin films since samples with various microstructure from nanocrystalline to epitaxial can be relatively easily prepared by varying the parameters of the deposition. Structural studies of such Mg thin films are necessary as a first step of such investigation.

Variable energy positron annihilation spectroscopy (VEPAS) provides depth resolved information about defect structure in the studied material, hence it is a very useful tool for studies of the microstructure of thin Mg films [2-5].



## 2. Experimental

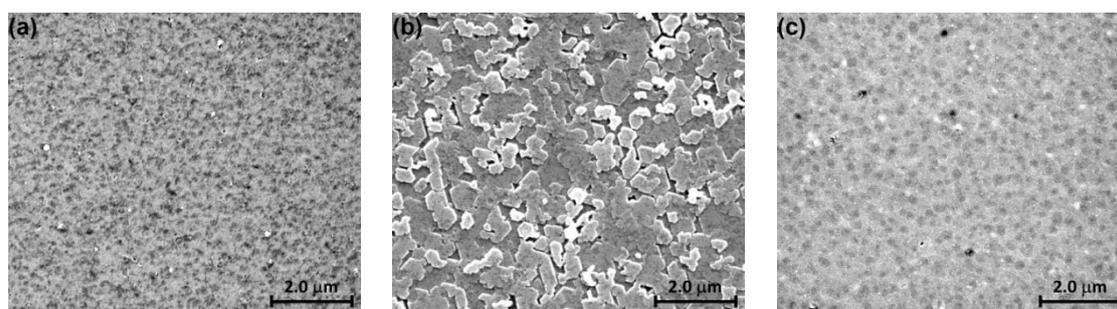
All Mg films were prepared in a vacuum chamber with pre-deposition pressure of  $\sim 10^{-4}$  Pa by RF (13.6 MHz) magnetron sputtering using an Ar atmosphere with a pressure of 3 Pa. Two different substrates were used: sapphire (0001) single crystal and amorphous fused silica (FS). Each film was immediately after deposition covered with 20 nm thick Pd over-layer in order to prevent oxidation of the Mg layer on the air and facilitating hydrogen absorption during electrochemical charging with hydrogen [6]. Four different deposition conditions were applied: (i) deposition at room temperature (RT), (ii) deposition on a substrate heated at 300°C, (iii) deposition at RT (including Pd cap) and subsequent annealing at 300°C for 1 h in the deposition chamber in Ar atmosphere with a pressure of 3 Pa and (iv) deposition at RT with slow deposition rate. Thicknesses of prepared films and deposition conditions are listed in Table 1.

Structural studies of Mg films were performed using FEI Quanta 200 scanning electron microscope (SEM). X-ray diffraction (XRD) measurements using Co  $K_{\alpha}$  wavelength of 0.179026 nm were performed in Bragg-Brentano symmetric geometry on a PANalytical X'Pert Pro diffractometer.

VEPAS measurements were performed using a magnetically guided variable energy positron beam "SPONSOR" [7] with slow positron energies varying from 30 eV to 35 keV. Energy spectra of annihilation gamma rays were measured by HPGe detectors having a relative efficiency of  $\sim 30\%$  and an energy resolution of 1.06(1) keV (FWHM at 511 keV). For each positron energy the Doppler broadening of annihilation profile was evaluated using the  $S$  parameter. The dependence of the  $S$  parameter on the positron energy was analyzed using the VEPFIT code [8].

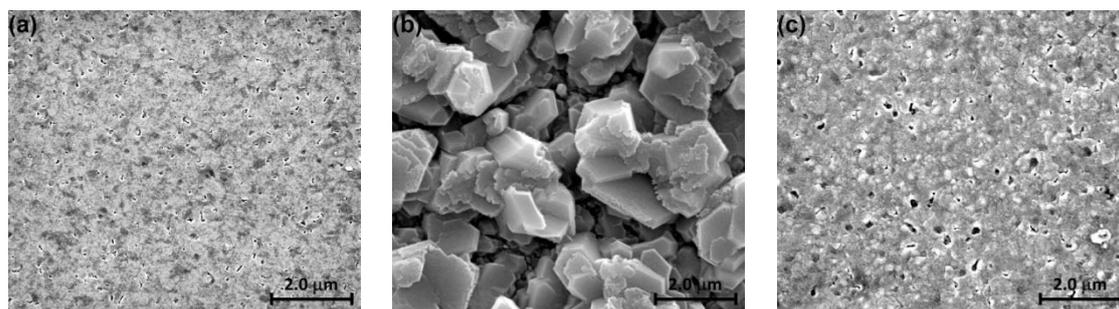
## 3. Results and discussion

Figures 1 and 2 show SEM micrographs of the Mg films deposited on sapphire and FS substrate respectively. Mg films exhibit nanocrystalline structure, the mean grain sizes were estimated by SEM and are listed in Table 1. The films deposited on amorphous FS substrate exhibit larger grains compared to the films deposited on crystalline sapphire substrate using the same deposition conditions. This is most probably connected with lattice misfit between the substrate and the Mg film which is more pronounced for the single crystalline sapphire substrate than for the amorphous FS substrate.



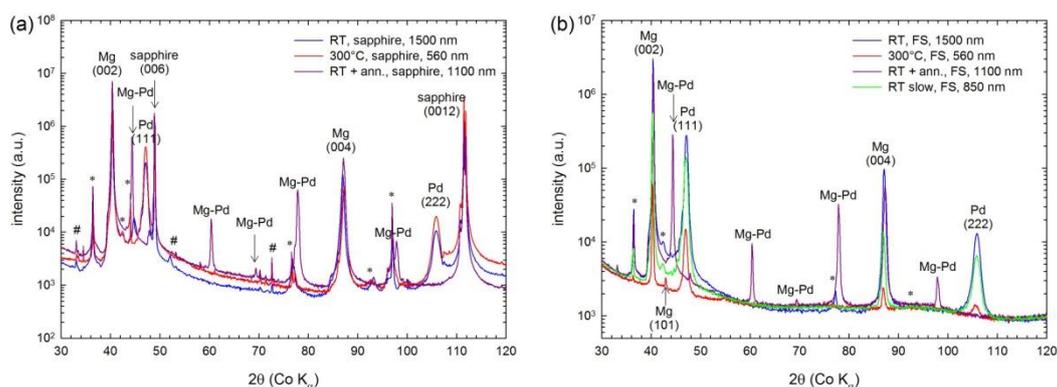
**Figure 1.** SEM micrographs of Mg films deposited on sapphire (0001) substrate at RT (a), at 300°C (b) and at RT and subsequently annealed at 300°C for 1 h (c).

According to the XRD measurements all Mg films are strongly textured independently on the type of substrate and the deposition condition. Mg films studied grew preferentially with the most densely populated basal plane (0001) parallel with the substrate, see Figure 3. The out-of-plane lattice parameter  $c$  measured in the Mg films differs from the tabular value of 0.52108 nm by less than 0.1%. This testifies to negligible in-plane stress in all Mg films studied. The lattice misfit between the film and the substrate is compensated by misfit dislocations. Microstrains induced by misfit dislocations lead to broadening of XRD profiles. Peak broadening is caused also by small crystallite sizes. These two sources of broadening of XRD profiles were separated by the Williamson-Hall method [9].



**Figure 2.** SEM micrographs of Mg films deposited on sapphire (0001) substrate at RT (a), at 300°C (b) and at RT and subsequently annealed at 300°C for 1 h (c).

The Mg films deposited on the sapphire substrate exhibit higher broadening of XRD peaks caused by microstrains due to higher density of misfit dislocations compared to the films deposited on the FS substrate. The microstrain and thereby also the density of misfit dislocations exhibit only moderate variations with the deposition conditions. These variations lie within the experimental uncertainties of XRD data.



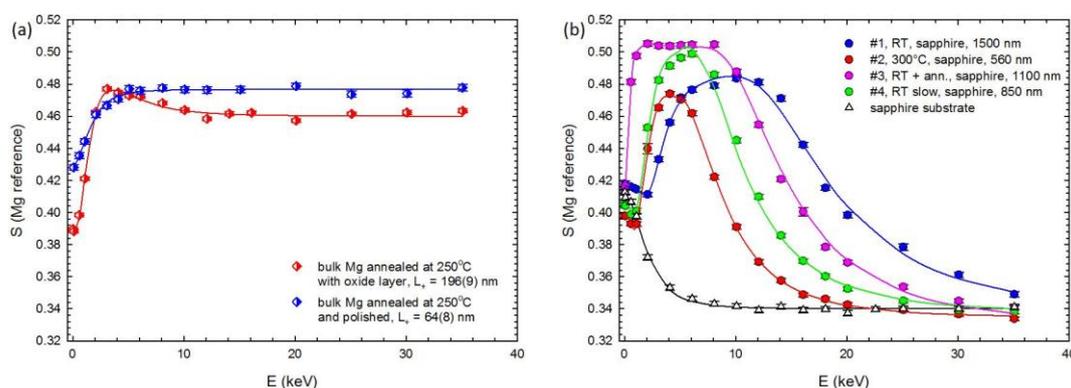
**Figure 3.** XRD patterns of Mg films deposited on sapphire (a) and FS (b). Symbols "\*" and "#" stand for Co  $K_{\beta}$  reflections and Co lamp artifacts, respectively.

One can see in Figure 3 that annealing of the Mg film with Pd cap at 300°C for 1 h in Ar atmosphere with a pressure of 3 Pa led to disappearance of the both Pd(111) and Pd(222) peaks and five new peaks of an unknown Mg-Pd phase appear. We were not able to identify the Mg-Pd phase formed in the films by comparison with records existing in crystallographical databases. Most probably a metastable phase was formed due to short annealing time, low annealing temperature and an anisotropy of the film. As a rough model we considered a simple hexagonal structure consisting of alternating basal planes filled with Mg and Pd atoms. The  $c$ -lattice parameter of such structure is 0.475 nm, i.e. the distance between the Mg and the Pd planes ( $c/2$ ) is close to the inter-planar distance of (111) planes in fcc Pd lattice (0.225 nm) and the inter-planar distance of (0002) planes in hcp Mg (0.261 nm). Hence thermally activated diffusion of Pd atoms into Mg layer forms a Pd sublattice. Such structure explains the XRD reflections observed at 44.6°, 68.8° and 97.8° corresponding to (0002), (0003) and (0004) planes, respectively. More precise structure modeling is needed to explain also the the two remaining reflections observed in the spectra.

The dependences of the  $S$  parameter on the energy  $E$  of incident positrons for two reference bulk Mg samples are plotted in Figure 4a. The red  $S(E)$  curve corresponds to a bulk Mg sample annealed at 250°C for 1 h in silicon oil bath. The maximum at  $\sim 3$  keV is due to positron annihilations in a thin oxide layer formed on the Mg surface during annealing. The sample exhibit a single component

positron lifetime spectrum with lifetime 223(1) ps which agrees well with the Mg bulk lifetime obtained from ab-initio theoretical calculations [10]. The mean positron diffusion length  $L_+ = 195(8)$  nm obtained from fitting of the  $S(E)$  curve agrees well with the value reported in Ref. [3]. This testifies the annealed bulk Mg contains very low density of defects and virtually all positrons are annihilated in the free state. The blue  $S(E)$  curve in Figure 4a shows data for a bulk Mg sample annealed in a UHV chamber at 250°C and covered by 20 nm Pd over-layer prior to its removal from the chamber to prevent oxidation. The Pd layer was subsequently removed by polishing, hence the oxide layer was not formed, but polishing induced dislocations into the sample, which led to the shortening of the positron diffusion length down to  $L_+ = 64(8)$  nm.

The dependences of the  $S$  parameter on the positron energy for the Mg films deposited on sapphire substrate are shown in Figure 4b, the data for the bare sapphire substrate are plotted in the figure as well. The  $S(E)$  curves for Mg films exhibit firstly a drop of  $S$  due to positron annihilations in Pd cap, except of the Mg film #3 (deposited at RT and annealed at 300°C) where Mg-Pd phase was formed. With increasing energy positrons penetrate into the Mg layer and the  $S$  parameter increases. Due to the different thicknesses of Mg films and varying positron diffusion lengths the  $S$  parameter approaches maximum at different energies. The maxima of the  $S$  parameter curves are always higher than the bulk  $S$  parameter for the annealed bulk Mg. This testifies that Mg films contain defects which trap positrons. When energy of incident positrons is further increased positrons become to penetrate into the sapphire substrate leading to a decrease of  $S$  which gradually approaches the bulk  $S$  parameter for the bare sapphire substrate.



**Figure 4.** The dependences of the  $S$  parameter on the energy  $E$  of incident positrons for two reference bulk Mg samples (a) and Mg films deposited on sapphire substrate (b). Solid lines are model curves calculated by VEPFIT.

The  $S(E)$  curves for Mg films were fitted by VEPFIT assuming 3 layers: (i) Pd cap with thickness of 20 nm, (ii) Mg film with thickness given in Table 1 and (iii) semi-infinite sapphire substrate. In case of the film #3 (deposited at RT and annealed at 300°C) the layer (i) was omitted since Pd diffused into the Mg layer and formed Mg-Pd phase. The model curves calculated by VEPFIT are plotted in Figure 4 by solid lines and are in a good agreement with the experimental points. Each layer is characterized by its positron diffusion length  $L_+$  and the  $S$  parameter. In order to reduce the number of fitting parameters  $L_+$  and  $S$  for the substrates were fixed at the values obtained for the bare substrates. All Mg films studied exhibit shorter  $L_+$  and higher  $S$  than the annealed bulk Mg. It testifies that the Mg films contain open-volume defects which trap positrons. These defects are vacancy-like defects located in a vicinity of grain boundaries and misfit dislocations. According to pulsed low-energy positron beam measurement [4] vacancies and vacancy clusters may be present inside of the grains as well.

Compared to the film deposited at RT the deposition at elevated temperature 300°C leads to coarser grain structure, see Figure 1, i.e. the fraction of grain boundaries and therefore defects which are able to trap positrons is lowered. This leads to the increase of the positron diffusion length and the decrease

of the  $S$  parameter in the Mg layer. On the base of XRD data we suppose the density of misfit dislocations remains approximately unchanged.

sample	thickness	dep. conditions	substrate	$L_+$	$S$	grain size
#1	1540 nm	RT	sap.	45(2) nm	0.4878(4)	210(6) nm
#1	1540 nm	RT	FS	46(1) nm	0.4843(4)	282(7) nm
#2	560 nm	300°C	sap.	50(5) nm	0.4718(7)	400 (10) nm
#2	560 nm	300°C	FS	n.a.	n.a.	740(30) nm
#3	1100 nm	RT + ann.	sap.	1(5) nm	0.5030(4)	259(9) nm
#3	1100 nm	RT + ann.	FS	n.a.	n.a.	289(7) nm
#4	850 nm	RT slow	sap.	1(3) nm	0.5067(5)	n.a.
#4	850 nm	RT slow	FS	n.a.	n.a.	229(6) nm
–	–	ann.	bulk Mg ann.	196(9) nm	0.4634(5)	–
–	–	ann. + pol.	bulk Mg pol.	64(8) nm	0.4767(8)	–
–	–	–	sap. substr.	46(5) nm	0.3400(2)	–
–	–	–	FS substr.	24(1) nm	0.4367(3)	–

The annealing of the Mg film with Pd cap (sample #3) leads to slightly larger mean grain size and thereby to lower fraction of grain boundaries. However one can clearly see in Figure 4b and Table 1 that the film contains significantly higher amount of defects compared to the films deposited at RT and 300°C. Most likely migration of Pd atoms introduced open-volume lattice defects into the film. However further structural investigations of the Mg-Pd phase are necessary to identify these defects.

At the slow deposition rate Mg atoms have more time to find an equilibrium site compared to the films deposited by fast deposition rate. Thus the interaction between the growing film and the substrate becomes more important. This leads to higher density of defects reflected by the highest value of the  $S$  parameter and the shortest positron diffusion length among all the Mg films studied.

The film deposited on sapphire substrate at RT exhibits higher value of the  $S$  parameter than the film deposited on FS under the same conditions. This is in accordance with the author's previous study [5] of the Mg films with thickness ~100 nm.

#### 4. Conclusions

A set of Mg films deposited under various conditions on sapphire and fused silica substrates was prepared by RF magnetron sputtering. The films exhibit nanocrystalline structure, (0001) texture and a negligible in-plane stress. Defect studies by positron annihilation spectroscopy revealed that positrons in the Mg films are trapped in vacancy-like defects at grain boundaries and at misfit dislocations. Film deposited at 300°C exhibits larger grains and lower concentration of defects than film deposited at RT due to reduced volume fraction of grain boundaries. Annealing of the film covered with Pd at 300°C for 1 h leads to formation of Mg-Pd phase and induces large amount of open-volume defects into the film. Film deposited with slow deposition rate contains highest amount of defects due to the stronger sensitivity to the lattice misfit between the film and the substrate.

#### Acknowledgement

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