Structural studies of thin Mg films

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Abstract. In the present work variable energy positron annihilation spectroscopy (VEPAS) was employed for investigation of defects in Mg films. VEPAS characterization was combined with scanning electron microscopy and X-ray diffraction in order to determine grain size and texture respectively. The aim of this study was to examine the effect of deposition temperature and various substrates on structure and defects in Mg films prepared by RF magnetron sputtering. SEM observations revealed that films deposited on sapphire (0001) substrate exhibit always smaller grains than films deposited on amorphous fused silica and silicon (100) substrates, which have comparable grain size. Defect studies by VEPAS showed that positrons in Mg films studied are trapped at misfit dislocations and at vacancy-like defects in grain boundaries. Moreover, the films deposited on a substrate heated at 300°C exhibit lower concentration of defects and larger grain size compared to the films deposited at room temperature. Subsequent annealing at 300°C for 1 h of the films deposited at room temperature causes a slight decrease of defect density due to coarsening of grains.

1. Introduction
Magnesium hydride (MgH₂) is an attractive material suitable for on-board hydrogen storage in mobile applications due to its safety and high hydrogen absorption capacity up to 7.6 wt. %[1]. However slow sorption rate in the MgH₂ is the major obstacle for its use in practical applications. Structure refinement down to nanoscale could remarkably speed up the hydrogen sorption kinetics since a high volume fraction of grain boundaries provides a network for easier hydrogen distribution into grains. The effect of microstructure on the hydrogen sorption kinetics can be investigated on thin films since samples with nanocrystalline to epitaxial structure can be relatively easily prepared by varying the deposition conditions. Obviously structure characterization of Mg thin films is necessary as a first step of this investigation.

Variable energy positron annihilation spectroscopy (VEPAS) provides information about defect structure in various depths in the studied material, hence it is a very useful tool for studies of the microstructure of Mg thin films [2, 3, 4, 5].

2. Experimental
A set of 4 different Mg films was prepared by RF (13.6 MHz) magnetron sputtering with a deposition rate of 1.5 - 2.1 nm/s and using a pressure of 3 Pa (Ar atmosphere): (i) films
with thickness of $\sim 1 \mu m$ deposited at room temperature (RT), (ii) thin films ($\sim 100$ nm) deposited at RT, (iii) thin films ($\sim 100$ nm) deposited on a substrate heated at 300°C and thin films ($\sim 100$ nm) deposited at RT and then annealed in UHV deposition chamber at 300°C for 1 h. Subsequently 20 nm thick Pd cap was deposited on each film. The Pd cap prevents oxidation of the films on the air and facilitates hydrogen absorption during electrochemical charging [6]. Three different substrates were used: sapphire (0001), silicon (100) and amorphous fused silica. Structural studies of Mg films were performed using FEI Quanta 200 SEM.

VEPAS measurements were performed using magnetically guided variable energy positron beam "SPONSOR" [7] with slow positrons of energies from 27 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 $(1.06 \pm 0.01)\%$ (FWHM at 511 keV). 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

Fig. 1 shows SEM micrographs of the thin Mg films deposited on fused silica. The mean grain sizes estimated by SEM are listed in Table 1. The film deposited at 300°C (Fig. 1a) exhibits the largest grains with the mean grain size of $\sim 253(6)$ nm. The mean grain size of the film deposited at RT is $\sim 71(2)$ nm (Fig. 1b), subsequent annealing of the film at 300°C led to increase of the mean grain size up to $\sim 89(6)$ nm (Fig. 1c). The thicker film (thickness $\sim 1 \mu m$) deposited at RT on fused silica exhibits the mean grain size of $\sim 375(6)$ nm as determined by SEM. The increase of the mean grain size with the thickness of the film is likely due to the fact that the first generation crystallites attached directly to the substrate are smaller in size than the next generations growing on the top the previous generation. The films deposited on Si substrate exhibit comparable grain sizes as those on fused silica, but films deposited on sapphire are characterized by lower grain sizes as a rule, see Table 1.

![Figure 1. SEM micrographs of thin Mg films ($\sim 100$ nm) on fused silica deposited at 300°C (a), at RT (b) and at RT and subsequently annealed at 300°C for 1 h (c).](image)

XRD revealed that Mg films are always strongly textured independently on the type of substrate, the deposition temperature or the thickness. The XRD patterns measured in the Bragg-Brentano geometry contains Mg(0002), Mg(0004), Pd(111) and Pd(222) peaks only, i.e. Mg films grew with preferred orientation of the most densely populated basal plane (0001) parallel to the surface of the substrate while Pd layer grew on the top of Mg film with (111) plane parallel with the surface.

The dependences of the $S$ parameter on the energy of incident positrons for Mg films deposited on sapphire and fused silica substrate are plotted in Fig. 2a and 2b, respectively. The $S(E)$ curves for the bare substrates are plotted in the figure as well. In addition, the $S(E)$ curve for a bulk Mg sample annealed (250°C) in UHV chamber and covered by 20 nm Pd over-layer prior
Figure 2. Dependence of the $S$ parameter on positron energy for Mg films deposited on sapphire (a) and fused silica substrate (b). The $S(E)$ curves for the bare substrates and annealed (250°C) bulk Mg reference are plotted in the figure as well. All data were fitted by VEPFIT code (solid lines). Insets show zoomed low energy parts of the $S(E)$ curves for thinner films ($\sim 100$ nm).

to its removal from the chamber to prevent oxidation is shown in Fig. 2 for comparison. The mean positron diffusion length $L_+ = (195 \pm 8)$ nm obtained from fitting the $S$ vs $E$ values for the annealed bulk Mg agrees well with the value reported in Ref. [3].

The $S(E)$ curves for Mg films exhibit firstly a drop of $S$ due to positron annihilations in Pd cap. With increasing energy positrons penetrate into the Mg layer and the $S$ parameter increases. In the Mg films with thickness of $\sim 1.5$ µm the $S$ parameter becomes approximately constant in the range 8 - 12 keV (see Fig. 2) indicating that practically all positrons are annihilated inside the Mg film. The $S$ parameter for the Mg films is higher than the $S$ parameter measured in the well annealed bulk Mg. It indicates that Mg films contain defects which trap positrons. At higher energies ($E > 12$ keV) positrons implanted into the Mg film become to penetrate into the substrate leading to a decrease of $S$ which gradually approaches the bulk $S$ parameter for the bare substrate. The $S(E)$ curves for the thinner films ($\sim 100$ nm) exhibit similar behavior but the decrease of $S$ starts at lower energies because of lower thickness of the Mg layer.

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 of $\sim 1.5$ µm or $\sim 100$ nm and (iii) substrate. The model curves calculated by VEPFIT are plotted in Fig. 2 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. The positron diffusion length and the $S$ parameter obtained for the Mg films are listed in Table 1. 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 misfit dislocations necessary for accommodation of the lattice mismatch between the film and the substrate and open volume point defects (vacancies and vacancy clusters) located at grain boundaries which were identified by a pulsed low-energy positron beam [4].

The insets in Fig. 2 show detail of the low energy parts of $S(E)$ curves for the thinner Mg films ($\sim 100$ nm). The $S(E)$ curves for the films deposited at RT and the films deposited at RT and subsequently annealed at 300°C are almost the same, but in the films deposited at 300°C the rise of $S$ has considerably lower slope indicating longer positron diffusion length. Indeed from inspection of Table 1 one can conclude that films deposited at 300°C exhibit higher $L_+$ than the films deposited at RT. This is in agreement with SEM observations which revealed that films
Table 1. Results of fitting of the $S(E)$ curves for Mg films, bulk Mg and bare substrates by the VEPFIT code and the mean grain size determined by SEM; n.a. = not analyzed.

| thickness (nm) | $T_{dep}$ | $T_{ann}$ | substrate            | $L_+$ (nm) | $S$   | grain size (nm) |
|---------------|----------|----------|---------------------|------------|-------|-----------------|
| 1540          | RT       | –        | sapphire            | 45(2)      | 0.4878(4) | 77(2)           |
| 1540          | RT       | –        | fused silica        | 46(1)      | 0.4843(4) | 375(6)          |
| 1540          | RT       | –        | silicon             | n.a.       | n.a.    | 325(8)          |
| 156           | 300$^\circ$C | –        | sapphire            | 60(5)      | 0.483(2) | 133(4)          |
| 156           | 300$^\circ$C | –        | fused silica        | 77(7)      | 0.480(2) | 253(6)          |
| 156           | 300$^\circ$C | –        | silicon             | n.a.       | n.a.    | 195(7)          |
| 121           | RT       | –        | sapphire            | 35(4)      | 0.485(2) | 59(2)           |
| 121           | RT       | –        | fused silica        | 39(5)      | 0.478(2) | 71(2)           |
| 121           | RT       | –        | silicon             | n.a.       | n.a.    | 77(3)           |
| 123           | RT       | 300$^\circ$C | sapphire | 50(5)      | 0.483(2) | 81(3)          |
| 123           | RT       | 300$^\circ$C | fused silica       | 52(6)      | 0.482(2) | 89(3)          |
| 123           | RT       | 300$^\circ$C | silicon          | n.a.       | n.a.    | 92(2)           |
| –             | –        | 250$^\circ$C | bulk Mg | 196(9)      | 0.4634(5) | –              |
| –             | –        | –         | sapphire subst.    | 46(5)      | 0.3400(2) | –              |
| –             | –        | –         | fused silica subst.| 24(1)      | 0.4367(3) | –              |

Deposited at 300$^\circ$C are characterized by larger grains leading to reduced volume fraction of grain boundaries containing open volume defects. The fitted parameters for the films deposited at RT are very similar taking into account the experimental uncertainties. But as a common trend it can be noticed that post-growth annealing at 300$^\circ$C led to a slight increase of $L_+$ which is again likely connected with grain growth which decreases the density of defects at grain boundaries.

4. Conclusions
A set of Mg films deposited under various conditions on 3 different substrates was prepared by RF magnetron sputtering. The films exhibit (0001) texture and the mean grain size increases with the thickness of the film. Defect studies by positron annihilation spectroscopy revealed that positrons in the Mg films are trapped at misfit dislocations and in vacancy-like defects at grain boundaries. Films deposited at 300$^\circ$C exhibit larger grains and lower concentration of defects than films deposited at RT due to reduced volume fraction of grain boundaries.

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