

Optimizing magnesium thin films for optical switching applications: rules and recipes

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Abstract: While magnesium holds great potential as hydrogen storage material, interest has recently shifted to its use in optical switching applications. The hydrogen-induced phase transition from metallic magnesium to dielectric magnesium hydride is a promising candidate for switchable and active plasmonic systems. Most studies in the past have been performed on magnesium thin films and were directed to the investigation and optimization of hydrogen storage rather than to the optical properties. While these studies found a strong influence of the material morphology and crystallinity on the bulk and thin film properties, no in-depth study has revealed rules and recipes to tune and control the nanoscale morphology. Here, we demonstrate that the nanocrystallinity, that is, the crystallite size and morphology on the nanoscale, as well as the surface roughness of magnesium thin films in an optically switchable geometry, can be tuned and adjusted by a comprehensive set of evaporation parameters. The required film geometries, optical properties, and the applications at hand determine the deposition parameters and need to be chosen accordingly. Further, we find that the surface roughness changes drastically upon hydrogenation. Our results have an immediate impact on the understanding as well as the fabrication of optically active devices where magnesium is being used.

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1. Introduction

The optical properties of metals and dielectrics are strongly influenced by their material morphology. One prime example is magnesium (Mg). When depositing Mg using, e.g., thermal evaporation, the material is often highly nanocrystalline. Such a polycrystalline Mg film consists of many individual tens to hundreds of nanometer-sized crystals with a hexagonal shape [1,2]. The influence of this morphology on the optical properties is of great importance as Mg becomes increasingly attractive for optical switching [3–7]. This means that the optical properties can change upon external stimulus [8–13]. Here, metallic Mg changes to dielectric magnesium hydride (MgH₂) when exposed to hydrogen.

This phase transition has been used to realize and intensely study optically active systems [14–16]. Starting with simple switchable mirrors [17,18], Mg has gained significant interest in nanophotonics leading to several applications such as smart windows [19], switchable solar absorbers [20], or even optical hydrogen sensors [21]. Furthermore, in nanoplasmonics the reversible cyclability of the Mg-MgH₂ phase transition has recently been adapted for optically active and dynamic systems or devices [3,22]. Such systems include dynamic plasmonic color displays [23,24], dynamic holography [25], dynamic metasurfaces [26,27], or hydrogen-regulated chiral plasmonic systems [28].

For all the mentioned applications it is known that the nanocrystallinity and morphology of the evaporated Mg plays a crucial role for the optical switching (efficiency) during the hydrogenation or dehydrogenation process [29–31]. In more detail, the individual orientation of crystallites, the formation of grain boundaries between them, and their respective size and position is expected to define the hydride formation process as well as the hydrogen diffusion constants

[32-34]. As there is considerable struggle with the fabrication of high quality magnesium films with reproducible and stable optical switching performance, this work offers insight into the influence of the deposition parameters on morphology and optical properties as well as recipes and guidelines. We present a detailed investigation and comprehensive study of the impact of deposition parameters on the morphology of Mg thin films typically used for optical switching. They often contain additional catalytic layers made from palladium (Pd) and titanium (Ti). Using scanning electron microscopy (SEM) as well as atomic force microscopy (AFM), we analyze the Mg thin films and find that the deposition parameters, which include the deposition rate, film thickness, substrate temperature, and choice of substrate have a huge impact on the nanocrystallinity and morphology. These parameters can be used to tune the size of the Mg crystallites while simultaneously being able to change the surface roughness of the Mg thin films in a large range. During a hydrogenation process, besides a drastic change of the optical properties, the morphology of Mg changes strongly [15,32,35]. On the one hand, Mg thin films possess a highly crystalline morphology, usually with a large surface roughness [1]. On the other hand, they show up to 30% volume expansion when being hydrogenated to MgH₂ [36]. Consequently, Mg thin films exhibit significant topography as well as cracks after one or multiple hydrogenation and dehydrogenation cycles. Please note that the topography refers to the surface of the material whereas the morphology is more general and refers to the shape and structure of the material in total. Indeed, our studies reveal that, upon hydrogenation, the surface roughness shows a 2- to 3-fold increase in comparison to pristine Mg. Especially, during the first couple of minutes of a hydrogenation cycle the roughness shows a fast and strong increase. Furthermore, a detailed analysis of the optical performance shows that the efficiency of the optical switching of magnesium is greatly influenced by the material morphology.

2. Fabrication and sample design

For the fabrication of all thin films, we use thermal evaporation (Leybold Vacuum Univex 300). The tool can hold up to four evaporation boats simultaneously, which allows for the thermal evaporation of up to four different materials subsequently without breaking the vacuum. All thin film depositions in this work are carried out at a vacuum chamber pressure of $p < 1 * 10^{-6}$ mbar. Thickness and evaporation rate of the evaporated material are monitored with a quartz crystal microbalance. Additionally, a custom-made sample holder allows for heating of substrates during evaporation up to T_{sub} = 200°C. The temperature is set and controlled via a PID temperature controller (Thorlabs TC200-EC) in combination with a resistive heater (Thorlabs HT19R) and a platinum thermistor (Thorlabs TH100PT).

In the following, we vary a full set of deposition parameters and study their influence on the nanocrystallinity and morphology of Mg in a thin film layer geometry which can be used for hydrogen-regulated optical switching applications at room temperature and ambient pressures. For optical switching applications Mg is supported by other materials to facilitate hydrogenation [37–39]. Most commonly, these are thin palladium (Pd) and titanium (Ti) films. Here, Pd acts as a catalytic layer which is in contact with the actual hydrogen gas. Ti is added as a separation layer to prevent alloying between Pd and Mg [40]. For reflective optical applications, the largest optical contrast is obtained when Mg remains the uppermost material (phase transition from highly reflective Mg to highly absorptive and non-reflective MgH₂) and is not covered by any other material. Thus, we study the morphology of Mg thin films which are evaporated *on top* of the supporting Pd and Ti films. As shown below, hydrogenation of such a film geometry is then achieved with free-standing films with gas exposure from below (see Fig. 7–9).

3. Titanium as wetting layer

Besides its role as separation layer between Pd and Mg, Ti also acts as a wetting layer for Mg, as can be concluded from the results depicted in Fig. 1. We compare the surface topography

(AFM measurement) of a Mg thin film *without* (left column) and *with* the 5 nm Ti sub-layer (right column) on a silicon (Si) substrate. Both Mg films are evaporated with same evaporation parameters (thickness $d_{Mg} = 40$ nm, evaporation rate $ER_{Mg} = 6 \pm 0.4$ Å/s, $T_{sub} = RT$) within the experimental tolerances. The upper images in Fig. 1 depict the topography from normal view (2D) whereas the lower images depict a 3D tilted view of the Mg surface to give a better impression of the roughness. The difference in morphology between the two Mg thin films is significant. The Mg film without Ti sub-layer in the left column of Fig. 1 shows a very fine-structured surface with many small Mg nanocrystallites with different orientations. This causes the height variation (difference between highest and lowest height value) of the topography to lay within $\Delta h = 24$ nm with a surface roughness of RMS = 3.43 nm. In comparison, the Mg thin film is much smoother when adding the Ti sub-layer as observed from the images in the right column of Fig. 1. The Ti layer seems to aid the growth of larger Mg nanocrystallites. The topography is coarser but simultaneously smoother, leading to a surface roughness of RMS = 1.94 nm and a height variation which is only approximately half than that of the Mg film without Ti.



Fig. 1. Comparison of atomic force microscopy (AFM) topography of 40 nm magnesium thin films *without* (left column) and *with* a 5 nm titanium (Ti) sub-layer (right column). The Ti layer acts as a wetting layer for the Mg films. The top images show a normal view onto the surface. The scale bar is valid for both images. The bottom images show a tilted 3D view onto the surface. The substrate is atomically flat silicon. The field of view is always $1 \times 1 \ \mu\text{m}^2$. The thermal evaporation rates for Mg and Ti are $\text{ER}_{Mg} = 6 \pm 0.4 \ \text{Å/s}$ and $\text{ER}_{Ti} = 1 \pm 0.2 \ \text{Å/s}$, respectively.

4. Varying thickness

As our study is focused on Mg film geometries for such switching applications, catalytic and buffer layers are required. Thus, all following Mg sample geometries will contain a Ti *and* Pd sub-layer and we will determine the influence of four parameters, namely Mg layer thickness, Mg evaporation rate, sample temperature, and choice of substrate, onto the nanocrystallinity and morphology of Mg. Please note that we use throughout this work layer thicknesses and

Research Article

evaporation rates of $d_{Pd} = 10$ nm and $ER_{Pd} = 1 \pm 0.2$ Å/s for Pd and $d_{Ti} = 5$ nm and $ER_{Ti} = 1 \pm 0.2$ Å/s for Ti, respectively. It was shown by Renucci et al [41]. that the layer thickness has a huge impact on the morphology of Mg thin films. For switchable Mg films with Ti wetting and Pd catalytic layer, the dependency of the film thickness on the morphology is shown in the SEM images in Fig. 2.



Fig. 2. SEM micrographs of optically switchable Mg thin film surfaces showing the change of the nanocrystallinity and morphology for a varying Mg thickness d at constant evaporation rate ($\text{ER}_{\text{Mg}} = 7.5 \pm 0.5 \text{ Å/s}$). (a) depicts a surface of a 26 nm film with only very small crystallites forming a mostly uniform film. The size of the nanocrystallites increases for layer thickness d of (b) 50 nm, (c) 100 nm, (d) 150 nm, and (e) 200 nm. The Mg films are thermally evaporated on a silicon substrate with a 10 nm Pd- and 5 nm Ti-sub-layer. The scale bar is valid for all shown SEM micrographs.

They depict the surface of Mg films with different thicknesses but with same evaporation rate $ER_{Mg} = 7.5 \pm 0.5$ Å/s. All images are taken at the same magnification. Figure 2(a) shows that nanocrystalline Mg is already obtained for 26 nm thin films. Furthermore, we observe that the 26 nm film is not completely closed (see hole in the top part of the SEM image). By having a look at the SEM micrographs in Fig. 2(b)-(e) for film thicknesses of 50 nm, 100 nm, 150 nm, and 200 nm, we clearly see an increase of the size of the individual crystallites when increasing the layer thickness. The bulk of the film is composed of "film-crystallites" which are randomly oriented but form a closed film. In addition, one can find individual "surface-crystallites" which seem to form on top of the film surface and appear bright in the SEM micrographs. Mostly, these surface-crystallites show the typical full hexagonal shape of Mg with all six edges clearly visible. Additionally, both, film- and surface-crystallites grow very big in diameter. For example, the big surface-crystallite of the 200 nm thin film in Fig. 2(e) has a size of approximately 400 nm, which is twice the film thickness. We find that the surface-crystallites seem to be of random occurrence and are also randomly distributed as seen in the appendix Fig. 10. There is no "threshold" of the film thickness where the formation of these crystallites starts. One possible explanation for the growth of these surface-crystallites could be droplets on the film surface present during evaporation.

We use AFM to obtain a detailed view of the surface morphology and roughness. This is exemplarily shown in Fig. 3 with AFM measurements of the (a) 50 nm and (b) 200 nm Mg thin



Fig. 3. Tilted 3D view $(1 \times 1 \mu m^2)$ of optically switchable Mg thin films measured with an AFM. (a) 50 nm and (b) 200 nm Mg thickness, both evaporated with same evaporation rate $ER_{Mg} = 7.5 \pm 0.5$ Å/s. The sub-layers are the same for both samples (5 nm Ti and 10 nm Pd). One can clearly see the increase of nanocrystallite size and surface roughness for a thicker Mg film.

film (the same as the ones shown in Fig. 2(b) and (e), respectively). The images depict a 3D tilted view with a total field of view of $1 \times 1 \ \mu m^2$. The surface of the 50 nm Mg film in Fig. 3(a) shows only small crystallites and a small surface roughness with a height variation of $\Delta h = 20$ nm. In contrast, the 200 nm film in Fig. 3(b) comprises very large crystallites. One can clearly resolve the nanocrystallite edges and parts of their typical hexagonal shape. Additionally, we find many different orientations of crystallites and the film surface appears much rougher with a height variation of $\Delta h = 50$ nm. Such huge variations in morphology and crystallite size of the Mg films for different sub-layers (Fig. 1), varying layer thickness (Figs. 2 and 3), or similar will have a drastic influence on the optical performance and efficiency of potential optically active devices or applications. The roughness of the film or nanoparticles, i.e., the individual arrangement and size of film-consisting grains is important for the formation of the well-known blocking layer in the Mg film and thus can limit the diffusion coefficients or switching speeds [42], as we will discuss further below.

5. Varying evaporation rate

The second deposition parameter we investigate is a change in the evaporation rate of Mg while leaving the film thickness constant. We expect that there are several options how a change in the evaporation rate could influence the morphology and nanocrystallite size. A higher evaporation rate implies that more material is hitting the sample surface in the same period of time. On the one hand, this could lead to a higher local temperature of the "hot" material and substrate. Due to the higher mobility, the atoms have more time to arrange in a preferred order, namely for Mg a hexagonal shape. On the other hand, more material per second could give the atoms also less time to arrange in their preferred order, if we assume the substrate as an infinite heat reservoir. This would mean that there is no influence of the local temperature. Consequently, in this case a lower evaporation would assist the growth of larger crystallites. This would coincide with standard molecular-beam epitaxy (MBE) where an ultra-low evaporation rate is used to grow large crystalline material arrangements. However, for this possibility the vacuum pressure and thus remaining residual gases need to be taken into account, as the gases can cause a pinning of grain boundaries on the substrate and freshly deposited film [43]. Furthermore, more residual

gases, especially oxygen, can cause a higher Mg oxidation. For a detailed analysis we evaporate Mg thin films with a constant thickness of $d_{Mg} = 200 \text{ nm}$ again on silicon substrates with the aforementioned sub-layers. The SEM micrographs of the Mg film surface are shown in Fig. 4 for evaporation rates ER_{Mg} of (a) $1 \pm 0.5 \text{ Å/s}$, (b) $2 \pm 0.5 \text{ Å/s}$, (c) $4 \pm 0.5 \text{ Å/s}$, (d) $6 \pm 0.5 \text{ Å/s}$, (e) $7.5 \pm 0.5 \text{ Å/s}$. So far, we find no significant difference between the nanocrystallite size or topography appearance for the different evaporation rates. However, AFM studies reveal a drastic change of the surface roughness for different evaporation rates, as we will discuss and try to explain in the context of the possibilities mentioned above in the following.



Fig. 4. SEM micrographs of optically switchable Mg thin films showing the change of the nanocrystallinity and morphology for different evaporation rates ER at constant layer thickness ($d_{Mg} = 200 \text{ nm}$). The evaporation rate is changed in the following steps: (a) 1 ± 0.5 Å/s, (b) 2 ± 0.5 Å/s, (c) 4 ± 0.5 Å/s, (d) 6 ± 0.5 Å/s, (e) 7.5 ± 0.5 Å/s. There appears to be no significant difference in the nanocrystallinity and morphology for different evaporation rates. The Mg films are thermally evaporated on a silicon substrate with a 10 nm Pd- and 5 nm Ti-sub-layer. The scale bar is valid for all shown SEM images.

6. Surface roughness comparison

From AFM measurements we can calculate the surface roughness (RMS) and compare the RMS values of Mg thin films deposited with different parameters. The change in surface roughness for a varying thickness (constant evaporation rate) is depicted in Fig. 5(a), whereas the surface roughness for a varying evaporation rate (constant thickness) is depicted in Fig. 5(b). For each data point we evaporate separate Mg films with same respective deposition parameters on three individual samples. For each sample, we take two subsequent AFM scans at different positions to obtain an average of six individual RMS values for each data point shown in Fig. 5. The vertical error bars represent the standard deviation from this averaging, whereas the horizontal error bars in b represent the usually high fluctuation in the evaporation rate during evaporation. For the varying thickness in Fig. 5(a) we find a large *increase* of the surface roughness for an increase in film thickness, as it is already expected from the 3D view AFM measurements in Fig. 3. As explained, the evaporation rate is kept constant at ER_{Mg} = 7.5 ± 0.5 Å/s. The RMS value of RMS = 5.31 nm for a thickness of d_{Mg} = 26 nm. Overall, we find a negative exponential

dependence of the surface roughness on the Mg film thickness. From Fig. 5(b) we find a large linear *decrease* of the surface roughness when increasing the evaporation rate of Mg while leaving the film thickness constant at $d_{Mg} = 200$ nm. Here, the RMS values change from RMS = 8.52 nm for an evaporation rate of $ER_{Mg} = 1 \pm 0.5$ Å/s to less than half (RMS = 3.89 nm) for an evaporation rate of $ER_{Mg} = 16 \pm 0.5$ Å/s. At first sight this finding of a decrease in roughness for an increase in evaporation rate seems to be counterintuitive as for most other materials the dependence is exactly opposite. For example, aluminum thin films show a constant increase of the surface roughness for higher evaporation rates [44,45].



Fig. 5. RMS (surface roughness) in dependence of two different thermal evaporation parameters: (a) varying layer thickness d of the Mg layer at constant $ER_{Mg} = 7.5 \pm 0.5$ Å/s, (b) varying evaporation rate ER at constant $d_{Mg} = 200$ nm. Two AFM scans for three samples each with same parameters were used for each thickness and evaporation rate, meaning an average of six measurements per thickness value d and evaporation rate value ER. The vertical error bars represent the standard deviation from averaging the individual RMS values. The horizontal error bar in (b) represents the fluctuation of the evaporation rate during evaporation, which is usually on the order of $\Delta ER = \pm 0.5$ Å/s. The Mg films are thermally evaporated on a silicon substrate with a 10 nm Pd- and 5 nm Ti-sub-layer.

We attribute this to the fact that many materials usually show an amorphous surface with no nanocrystallites on or in the film after deposition. In such films, the individual arrangement of the amorphous grains has almost no influence on the surface roughness itself. Rather, the size of the grains is decisive for the roughness of the film, which in amorphous films can be tuned via the evaporation rate. In contrast, our magnesium thin films consist of large nanocrystallites and thus behave fundamentally different. Here, the size of the nanocrystallites and the individual orientation as well as arrangement of the nanocrystallites greatly influences and defines the surface roughness of the film. One typical Mg nanocrystallite sticking out of a film when its c-axis is aligned parallel to the film surface causes a higher surface roughness in comparison to a perpendicular alignment. Whereas the crystallite size can be tuned via the film thickness, it seems to be possible to vary this crystallite orientation via the evaporation rate. We suspect the following to contribute to this observed phenomenon:

Firstly, residual gases such as water vapor or oxygen in the evaporation chamber can adsorb on the freshly deposited film and pin grain boundaries [43]. Especially for reactive metals, such as Mg, a lower evaporation rate causes more contact of the material with these residual gases resulting, e.g., in a higher oxidation of the material. This can lead to a higher grain boundary density in Mg films while the crystallite size remains constant (see crystallite size discussion in Fig. 4). Consequently, the growth direction and orientation of the nanocrystallites needs to

change so that the c-axis of the crystallites is aligned parallel to the substrate plane. The film becomes rougher.

Secondly, we must consider the effect of dewetting due to substrate heating during evaporation. Dewetting can occur well below the melting point of a material and thus needs to be considered especially during thermal evaporation [46]. The radiant heat from long deposition times at low evaporation rates results in a higher substrate temperature than from short deposition times at high evaporation rates [47]. Consequently, a higher evaporation rate results in a smoother film as it can help to prevent dewetting of the Mg nanocrystallites and a re-orientation [48].

7. Varying substrate temperature

Next, we will study and discuss in the following the influence of the substrate temperature T_{sub} during evaporation on the morphology and nanocrystallinity of the Mg thin films. Mg is a sublimating metal, meaning it is evaporating under vacuum conditions already at temperatures far below its melting point. When we choose T_{sub} too high, Mg seems to evaporate again from the substrate and we will not be able to deposit any material. We find that this is happening at substrate temperatures of $T_{sub} = 140^{\circ}$ C. At this temperature we find that almost no Mg is left on the substrate after evaporation. As a limit temperature we find $T_{sub} = 90^{\circ}$ C. Please note that the temperature T_{sub} is measured via a temperature probe, which is placed inside the sample holder close to the surface where the samples are placed (see appendix Fig. 11 in the Supporting Information for a picture of the substrate temperature during evaporation onto the nanocrystallinity is depicted in Fig. 6 where SEM micrographs illustrate the surface of three 200 nm Mg thin films deposited with different substrate temperatures T_{sub} . All Mg films are deposited at a similar evaporation rate of ER_{Mg} = 7.5 ± 0.5 Å/s on a silicon substrate with Pd and Ti sub-layers.

Figure 6(a) depicts a Mg thin film top surface when the substrate was not heated at all $(T_{sub} = RT)$. We find that for an increase of the substrate temperature to $T_{sub} = 90^{\circ}C$ (see Fig. 6(b)) the crystallite size is increased. We obtain surface-crystallites with a diameter of up to 600 nm. This is most likely related to the mobility of the Mg atoms on the sample surface which is increased when we increase the sample temperature. Therefore, the Mg atoms have more time to arrange in the preferred order and the hexagonal nanocrystallites become larger. Figures 6(c) and (d) depict SEM micrographs of a Mg thin film deposited on a substrate heated to $T_{sub} = 120^{\circ}C$. (d) is taken with a lower magnification and presents a zoom-out view of (c). One can clearly see that the film aggregates and becomes porous which causes many gaps and holes. The typical hexagonally shaped nanocrystallites are almost completely lost and the film appears mo re amorphous. Furthermore, film thickness measurements with a stylus profiler show that the evaporated film measures a thickness of d measured = 312 nm and not the total thickness as expected and measured by the crystal balance monitor of $d_{Crystal Balance} = 215$ nm (= 10 nm Pd + 5 nm Ti + 200 nm Mg). As the crystal monitor basically measures the weight of the evaporated film, we expect dewetting to be the reason for the apparent discrepancy. The film swells, aggregates, and becomes porous, thus increasing in actual thickness, as has been reported for silver and other materials [48,49]. In contrast, the films in Fig. 6(a) and (b) match the expectation almost exactly.



Fig. 6. SEM micrographs of the surface of 200 nm optically switchable Mg thin films deposited at different substrate temperatures (a) $T_{sub} = RT$, (b) $T_{sub} = 90^{\circ}C$, and (c,d) $T_{sub} = 120^{\circ}C$. (d) shows a zoom-out view of (c). The Mg films are thermally evaporated ($ER_{Mg} = 7.5 \pm 0.5 \text{ Å/s}$) on a silicon substrate with a 10 nm Pd- and 5 nm Ti-sub-layer. The heating from RT to 90°C causes an increase in nanocrystallite size. When heating to 120°C, holes and gaps are arising leading to a thicker film. While we measure almost exactly the expected thickness of 215 nm (10 nm Pd + 5 nm Ti + 200 nm Mg) for the films in (a) ($d_{measured} = 211 \text{ nm}$) and (b) ($d_{measured} = 216 \text{ nm}$), the film heated to $T_{sub} = 120^{\circ}C$ in (c,d) possesses a film thickness of $d_{measured} = 312 \text{ nm}$.

8. Varying substrate

As a last important deposition parameter, we discuss the influence of the choice of substrate on the morphology of Mg. We have recently demonstrated the *in-situ* investigation of the hydrogenation process of Mg thin films with scattering-type Scanning Near-field Optical Microscopy (s-SNOM) [32]. Here, we evaporated Mg thin films with Pd and Ti sub-layers on a gold grid (Substratek TEM membranes) with a pre-coated 2-3 nm Pd film to obtain free-standing films. This allowed for a diffusion of hydrogen from below into the Mg film while the top surface could be raster-scanned with the s-SNOM tip. The same concept is adapted below to measure *in-situ* the surface roughness with an AFM. Consequently, Fig. 7 shows SEM micrographs of Mg thin films when we replace the Si substrate with the gold grid substrate. (a) and (b) depict a 50 nm and 200 nm Mg thin film deposited on Si, whereas (c) and (d) illustrate Mg films with same thicknesses on a gold grid substrate. We clearly see that the nanocrystallite size and morphology is conserved and behaves very similar on both substrates. We obtain identical sizes of film- as well as surface-crystallites. This underlines that the Ti separation and wetting layer dominates the morphology and nanocrystallinity of Mg, rather than the choice of substrate.



Fig. 7. Comparison of the nanocrystallinity of optically switchable Mg thin films evaporated on different substrates with 10 nm Pd and 5 nm Ti sub-layer. (a) 50 nm Mg on silicon, (b) 200 nm Mg on silicon, (c) 50 nm Mg on gold grid, (d) 200 nm Mg on gold grid. The films on the gold grids are free-standing and allow for further *in-situ* investigations of the surface roughness upon hydrogen exposure from below. The scale bar is valid for all SEM images.

9. In-situ hydrogenation

As a final step, we use the free-standing Mg thin films on the gold grid substrate to study the surface roughness as well as their optical performance *in-situ* during hydrogenation.

9.1. Surface roughness

For the surface roughness, we use Mg thin films with a thickness of $d_{Mg} = 50$ nm to allow a fast vertical hydrogen diffusion. The evaporation rate is $\text{ER}_{Mg} = 4.5 \pm 0.5$ Å/s. Again, the Mg films are supported by 10 nm Pd and 5 nm Ti layers. As shown in the results in Fig. 8, we measure the time-evolution of the surface roughness for two samples which have been fabricated with identical parameters within experimental tolerances. In both cases the measurement procedure is the same and works as follows. The Mg films are mounted on a home-built gas flow-cell to allow hydrogen (H_2) access from below. First, we take an AFM scan $(1 \times 1 \,\mu m^2)$ of the pristine Mg film while the film is exposed to pure nitrogen (N_2) . Subsequently, when the scan is finished, we add 2% of H_2 in N_2 to allow for the hydrogenation of Mg for a time t. This is followed by flushing with pure N_2 again to keep the Mg/MgH₂ film in a constant state. This prevents hydrogen desorption and we take a subsequent further AFM scan. We repeat this procedure for each data point shown in Fig. 8(a) and (b) until the surface roughness saturates. We find that the surface roughness increases strongly during such a full hydrogenation process. For both samples, we obtain a twoto three-fold increase of the RMS when the films switch from Mg to MgH_2 . Especially, during the first 5 min and 4 min (light orange marked areas), the surface roughness of the Mg film in Fig. 8(a) and (b), respectively, changes strongly within a short period of time. We expect this is due to Mg below the surface switching to hydride and expanding in volume fast. This causes a



Fig. 8. Development of the surface roughness RMS of an optically switchable Mg thin film upon hydrogenation (2% H₂ in N₂). Metallic Mg changes to dielectric MgH₂ causing a up to 30% volume expansion and an increase of the RMS. (a) and (b) show the measurement on two samples which have been fabricated with identical parameters within the experimental tolerances (Mg evaporation parameters: $ER_{Mg} = 4.5 \pm 0.5$ Å/s, $d_{Mg} = 50$ nm, Ti and Pd sub-layers). They show a slightly different behavior of the surface roughness for longer hydrogen exposure. For both, during the first 5 min and 4 min (orange marked areas), respectively, the surface roughness changes very fast with the highest slope.

strong and fast buckling and deformation of the film on its surface pushing individual crystallites up (and down) while also leading to a strong and fast increase of the surface roughness. The surface roughness of both films saturates after 8 and 24 minutes with values of approximately RMS = 8.5 nm and RMS = 7 nm, respectively. We expect the small difference between the saturation time to lie with the fluctuations of the Mg deposition. As shown, the film morphology is strongly dependent on the deposition parameters. However, the hydrogenation properties of Mg thin films seem to depend even more on these deposition parameters (especially film thickness and substrate conditions). A small difference between sample preparation parameters (including sample and surface contamination) of nominally identical Mg thin films could consequently lead to small differences in the pristine morphology (please note the same pristine surface roughness of sample 1 and 2 of RMS = 2.8 - 3.0 nm) but to larger differences in the hydrogenation process such as in the shown change of the surface roughness. Furthermore, the shown RMS values are extracted from *in-situ* AFM measurements of an area of only $1 \times 1 \ \mu m^2$. It is known that the surface of such thin Mg films does not hydrogenate completely and different areas contain more hydride than others after saturation [32]. Thus, it strongly matters in our comparison of nominally identical films where we take the actual AFM measurement on the respective sample, as we could end up with a more or less hydrogenated film in our measurement area after saturation. This would cause also different time constants for the saturation of the RMS values.

9.2. Optical performance

To study the optical performance of the Mg thin films during hydrogenation, we use the same sample geometry, namely Mg films deposited onto a gold grid with Pd and Ti sub-layers. In this sample geometry it is thus possible to allow a gas flow from below via the Pd side and measure the optical properties (reflectance) of only the Mg layer without a notable influence of Ti or Pd.

The results are displayed in Fig. 9. We compare the optical performance of two Mg films with a thickness of 50 nm (left column) and 200 nm (right column). Figure 9(a) and (b) depict the spectral dependence of the normalized reflectance of the pristine (blue) and the hydrogenated 50 nm and 200 nm Mg film, respectively. The respective hydrogenation times until saturation are \sim 720 s and \sim 18310 s at an H₂ concentration of 5% in N₂. The reflectance spectra are normalized to the maximum value of the respective spectrum of the pristine film (blue curves). This allows for a relative comparison of the reflectance change of the two different Mg films. We find that the spectral appearance of both films is very similar in their pristine states. Both show high reflectance for smaller wavelengths whereas a minimum is obtained in the range around $\lambda = 700$ nm. However, the reflectance spectra of the hydrogenated films differ strongly. The 50 nm film in Fig. 9(a) shows an overall flattening of the spectrum over the entire wavelength range as well as a drastic decrease in overall reflectance. In contrast to the 50 nm film, the hydrogenated 200 nm film in Fig. 9(b) exhibits very similar spectral signatures as in its pristine state. Furthermore, the overall change in reflectance is rather small. This can be explained by the different optical appearance of the films as depicted in the optical microscope images in Fig. 9(c)-(f). In the pristine state, both films (panel c and e) have, as expected for Mg, a grey/silver appearance. However, in the hydrogenated state in panels d and e, we find that the 50 nm film becomes black and has thus almost completely switched to dielectric MgH_2 , whereas the 200 nm film lacks this black appearance. In fact, the free-standing 200 nm film develops substantial deformation. This can be explained by Mg below the pristine surface which hydrogenates and expands in volume. A blocking layer forms deep inside the film due to the blocking effect hampering further hydrogenation of the film. It is well-known that favorable absorption of hydrogen only takes place in Mg films with thicknesses below 100 nm further explaining the better optical performance of the 50 nm film [30]. As we have seen in Fig. 3, the two films in Fig. 9 differ also strongly in their morphology and surface roughness, as the film-crystallites of the 200 nm film are much larger in size compared to the 50 nm film. We expect these large crystallites to be the main reason for the early formation of the blocking layer inside the film. Additionally, these crystallites will cause the blocking layer to be strongly adapted to the morphology of the material and thus very inhomogeneous. This might allow for some crystallites at the surface to hydrogenate, however, on a longer timescale with low diffusion coefficients. In brief, the spectral change in reflectance of the 200 nm film in Fig. 9(b) is mostly due to a change of the overall topography and not due to a change in the optical material properties or a phase change from Mg to MgH₂ at the surface.

Nevertheless, the buckling of the film in Fig. 9(f) still gives information about the hydrogenation of material inside the film and thus allows us to study the influence of Mg thickness and thus morphology on the temporal behavior of the switching process. We show in Fig. 9(g) and h the temporal change of the normalized reflectance at $\lambda = 700$ nm during hydrogenation and dehydrogenation of the 50 nm and 200 nm film, respectively. As expected from Figs. 9(a) and (b), the change in reflectance of the 50 nm film is much larger in comparison to the 200 nm film. Furthermore, we find that the time to saturate the hydrogenation is much faster for the 50 nm film (~700 s versus >10000 s). This can be explained again with the blocking effect as well as the higher hydrogen diffusion coefficients for thinner Mg films [30]. In contrast, the dehydrogenation of the 50 nm with 20% oxygen (O₂) in N₂ takes almost twice as long as the dehydrogenation of the 200 nm film (~5700 s versus ~2700 s).



Fig. 9. Optical performance of Mg thin films with different morphology. The left and right column show the performance of a 50 nm and 200 nm Mg film with Pd and Ti sublayers, respectively. Both films are thermally evaporated on a gold grid to produce free-standing films where hydrogen exposure is possible from below while the reflectance of only the Mg film can be measured from above. (a) and (b) display the respective spectrally resolved normalized reflectance of the pristine Mg films (blue curves) and MgH₂ films after saturation (red curve) of hydrogenation (5% H₂ in N₂). The curves are normalized to the maximum of the pristine film. (c,d) and (e,f) show the optical microscope images (taken in reflection) of the respective free-standing Mg film (including surrounding grid) in the pristine state (blue frame) and after hydrogenation (red frame). Scale bar is 20 µm. (g) and (h) depict the respective time-dependency of the normalized reflectance at $\lambda = 700$ nm during hydrogenation with 5% H₂ in N₂ (red shaded area) and 20% O₂ in N₂ (blue shaded area).

10. Conclusion

In conclusion, we have studied in this work the influence of a comprehensive set of deposition parameters on the nanocrystallinity and morphology of magnesium thin films in a geometry used for optical switching applications. We have shown that film thickness, evaporation rate, as well as the substrate temperature allowed to tune and adjust the material properties. For a change in the Mg film thickness we observed a huge increase in the nanocrystallite size as well as surface roughness, whereas the evaporation rate seemed to have little influence on the nanocrystallite size but caused a strong decrease in surface roughness. During hydrogenation this surface roughness changed drastically and showed an up to three-fold increase, dominated by a fast increase during the first couple of minutes. Furthermore, we showed that the optical switching performance, e.g., switching times or optical contrast, of magnesium is greatly influenced by the material morphology. Our work is highly important for any switchable optical applications where Mg as phase-change material is being used. It will enable to tune and optimize the Mg morphology for active optical applications and devices but also for hydrogen storage. Our work will allow others to choose and adjust their deposition parameters with respect to their desired material morphology, topography, or optical performance necessary in potential applications or devices. For example, some applications might require a very smooth Mg surface, where we would suggest to use a thinner film fabricated at a high evaporation rate. In contrast, other applications might require a highly crystalline and rough surface with large nanocrystallites, where we thus would recommend a thicker film fabricated at a low evaporation rate. Furthermore, the presented results will allow others to analyze their fabricated optical structures and understand as well as overcome potential instabilities such as degradation problems during hydrogen-regulated switching. Lastly, several optical phenomena, such as nonlinear optical effects can be influenced strongly by the material composition and morphology. Here, we believe that our results will be a direct guide and will help to understand such phenomena in much more detail.

Appendix



Fig. 10. Low magnification SEM micrographs of the same magnesium (Mg) thin films shown in Fig. 2 in the main manuscript. The films consist of film-crystallites. Additionally, we find surface-crystallites with mostly the whole typical hexagonal shape of the Mg crystal lattice visible. We vary the Mg thickness d at constant evaporation rate ($ER_{Mg} = 7.5 \pm 0.5$ Å/s). (a) depicts a surface of a 26 nm films with only very small crystallites forming a mostly uniform film. The size of the nanocrystallites increases for layer thickness d of (b) 50 nm, (c) 100 nm, (d) 150 nm, and (e) 200 nm. The Mg films are thermally evaporated on a silicon substrate with a 10 nm Pd- and 5 nm Ti-sub-layer. The scale bar is valid for all shown SEM micrographs.



Fig. 11. Sample holder for substrates which can be heated to allow for changing the substrate temperature T_{sub} during material deposition via thermal evaporation. The sample is placed above the temperature probe to allow for a small discrepancy between measured and actual substrate temperature. The holder is made from copper to obtain good thermal conductivity. Thermal isolation is achieved by adding TECAPEEK.

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Disclosures

The authors declare no conflicts of interest.

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