Microstructural origin of the optical black state in Mg_2NiH_x thin films

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Abstract

Hydrogen absorption by a Pd capped thin Mg_2Ni film results in the nucleation of the Mg_2NiH_4 phase at the film/substrate interface and thus induces a self-organized two-layer system. This leads to the optical black state in Mg_2Ni thin films upon hydrogenation. This unusual hydrogenation behaviour is completely unexpected since the hydrogen enters through the top film surface. To explain the nucleation of Mg_2NiH_4 close to the substrate/film interface we performed scanning tunneling microscopy (STM) on as-prepared Mg_2Ni films with various thicknesses (20–150 nm). For films thinner than 50 nm, the film consists of small grains and clusters of small grains whereas on further growth the grain size increases and a columnar microstructure develops. We propose, therefore, that close to the substrate, the relatively porous structure of the film with small Mg_2Ni grains locally reduces the nucleation barrier for Mg_2NiH_4 formation.
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1. Introduction

Mg_2NiH_4 is an interesting example of a complex metal hydride switchable mirror and hydrogen storage material. Its hydrogenation properties may hold important clues for the optimization of the hydrogenation properties of complex metal hydrides in general. Thin films of Mg_2Ni capped with Pd react readily with hydrogen at H_2-pressures below 10^5 Pa at room temperature (RT). Their optical appearance changes from shiny metallic to transparent semiconducting upon hydrogen uptake. Besides shiny reflecting $Mg_2NiH_{0.3}$ and semiconducting transparent Mg_2NiH_4 [1,2], we discovered a third optical state in the visible [3] and near infrared [4], which is caused by an unusual hydrogen loading behavior of the thin films. This third optical state is characterized by a low reflection ($R < 25\%$) and zero transmission ($T < 0.01\%$) resulting in an anomalously high absorption of 75% in the visible wavelength regime. The black state originates from a self-organized double layering of the Mg_2Ni film upon hydrogen absorption [5,6]. After dissolving hydrogen homogeneously

in solid solution up to $Mg_2NiH_{0.3}$, Mg_2NiH_4 preferentially nucleates at the film/substrate interface as is clear from optical and ^{15}N-hydrogen depth profile measurements [5]. From these measurements it is evident that a 30–50 nm layer close to the film/substrate interface promotes the preferential nucleation of Mg_2NiH_4. Upon further hydrogenation, a single Mg_2NiH_4 layer is formed which grows towards the Pd caplayer until the whole film has transformed into a transparent semiconductor. No thermodynamic changes with respect to bulk data have been observed in the hydrogen absorption of Mg_2Ni. In particular, no additional plateau is found in the pressure-composition isotherms, which would have indicated the existence of an intermediate thermodynamic phase [5]. Furthermore no gradient in chemical composition is observed throughout the Mg_2Ni film as checked by Rutherford backscattering spectroscopy (RBS) and secondary ion mass spectroscopy (SIMS) measurements [7]. A microstructural origin of the unusual hydrogen uptake is then most likely. We perform in situ scanning tunneling microscopy (STM) measurements to investigate the microstructure of Mg_2Ni films with a thickness of 20–150 nm. The development of the morphology at every step of growth can be taken as a virtual depth profile of a Mg_2Ni thin film. Furthermore, to investigate the

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surface morphology on a larger scale, we perform atomic force microscopy (AFM) on Mg_2Ni films with a thickness ranging from 5 to 200 nm.

2. Experimental set-up

Preparation of Mg_2Ni samples at room temperature, takes place in an ultra high vacuum (UHV) system with a base pressure of $< 10^{-8}$ Pa by coevaporating Mg from a Knudsen cell (purity 99.98%) and Ni from an electron gun (purity 99.98%). For the STM measurements, the Mg_2Ni samples are prepared in the UHV chamber and transported in situ to the connected STM chamber, to protect them from oxidation. The samples with a typical thickness of 20–150 nm are deposited on a conducting oxidized Si substrate without a Pd caplayer. For ex situ AFM measurements, the samples of thickness of 5–200 nm are covered with 5–10 nm Pd to protect them from oxidation and to promote hydrogen dissociation/recombination and absorption.

3. Experimental results

As shown by Lohstroh et al. nucleation of the hydrogen rich phase, Mg_2NiH_4, takes place in an approximately 30–50 nm thin layer close to the film/substrate interface [5,6]. Furthermore, the optical black state is observed in a broad compositional range (Mg_yNi, $y = 1.5$–6) [8] and for a variety of substrates (CaF_2, sapphire, quartz, glass covered with ITO (indium doped tin oxide)), hence the results of the growth studies of as-prepared Mg_2Ni thin films grown on oxidized Si are representative for the hydrogenation process as observed in Pd capped Mg_2Ni thin films. Therefore, we study the microstructure development during different stages of deposition of thin Mg_2Ni films. To obtain a three-dimensional image of a sample with a two-dimensional surface sensitive technique (see Fig. 1), we performed STM measurements on as-prepared Mg_2Ni samples with increasing thickness, 20, 50 and 150 nm, respectively, see Fig. 2a–f. This gives a representation of how the microstructure of the film develops with thickness. Here, we assume that the grown microstructure is stable and bulk diffusion is negligible. At a film thickness of approximately 20 nm (Fig. 2a and d) an island growth mode is observed with lateral grain sizes of 30–40 nm. These grains are homogenously dispersed over the substrate surface. On these islands the onset of a vague substructure of smaller grains can be seen. This island growth mode is an indication that the cohesive forces between the Mg–Ni clusters are larger than between the clusters and the substrate, which leads to an imperfect wetting of the substrate. Increasing the film thickness up to 50 nm (see Fig. 2b and e) results in a change of the microstructure. The original grain islands (from Fig. 2a and d) develop into pronounced clusters of grains. The typical diameter of the cluster is 50 nm and they are localized around the position of the original islands. The smaller
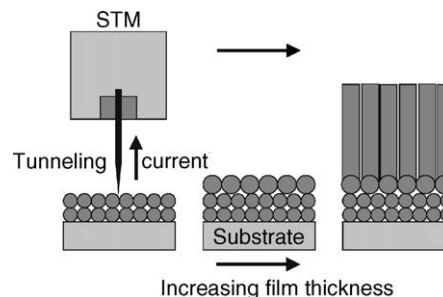

Fig. 1. Schematic representation of obtaining a three-dimensional image of a sample with a two-dimensional surface sensitive technique.

substructure grains constituting these clusters have a typical size of approximately 10 nm. As can be seen in Fig. 2b, the number of smaller grains and corresponding grain boundaries has increased tremendously. This implies that the microstructure close to the substrate has a very porous character with many grain boundaries and interfaces. The thickness of this porous layer is of the order of 30–50 nm which corresponds very well to the 30–50 nm layer close to the substrate, which was found to show a preferential nucleation of Mg_2NiH_4 and hence to be responsible for the optical black state. The most striking microstructure transition occurs on further deposition up to a thickness of 150 nm Mg_2Ni (see Fig. 2c and f). This leads to a rather complicated structure in which the initially grown islands develop into large clusters with a diameter of 100 nm. From the STM images these large grains (micro-crystals) appear to have a dense structure compared to the previous observed clusters of grains. In between these large structures the space is occupied with smaller grains having typical sizes of 10–30 nm. The development from small island growth (observed at a thickness of 20 nm) to large and dense grain development (at a thickness of 150 nm) is typical for a columnar growth mode.

This microstructure is in good agreement with transmission electron microscopy (TEM) and secondary electron microscopy (SEM) cross-section measurements. Here we found that Mg_2Ni films display a vertical columnar structure with an increase of disorder and grain boundaries close to the film/substrate interface [7]. To obtain the surface morphology on a larger scale, we performed ex situ AFM measurements. AFM micrographs on Mg_2Ni films capped with Pd, with thickness of 5 and 200 nm are shown in Fig. 3a–f, respectively. The 5 nm thick Pd layer will be present in the form of 5 nm Pd grains at the film surface and due to the limited resolution of the AFM these grains cannot be observed. The AFM micrographs display exactly the same features as the STM measurements. The 5-nm thick film, Fig. 3a–c shows an island growth that consists of equally dispersed small grains of 30 nm diameter. When the thickness of the film is increased to 200 nm, Fig. 3d–f, the grains grow to 100 nm and show the same characteristics as in Fig. 2c and f. However, the smaller grains surrounding the large grains as previous seen in Fig. 2c and f, cannot be seen, due to the limited resolution.
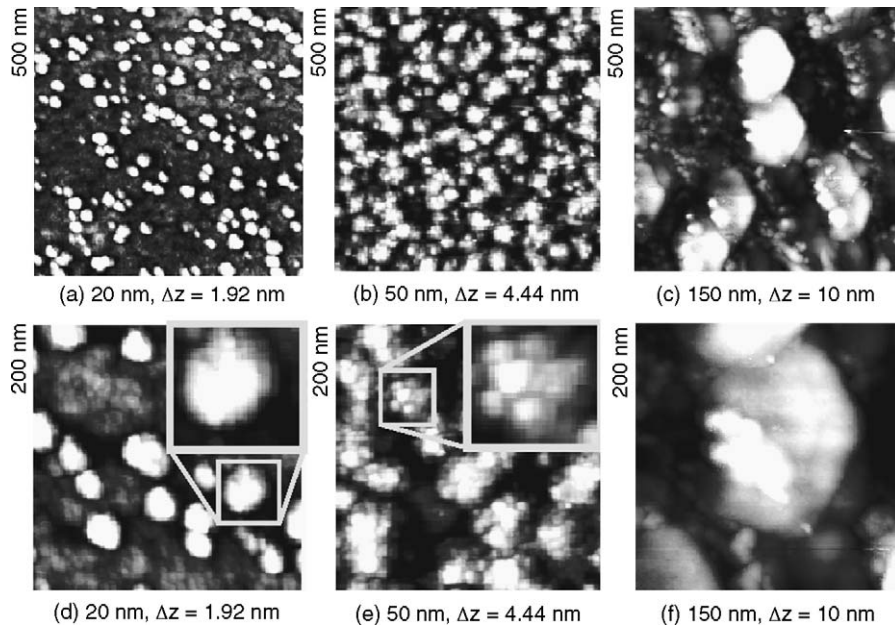
Fig. 2. STM micrographs of in situ grown thin Mg_2Ni films with thicknesses 20, 50 and 150 nm. Panels (a–c) depict a scan range of 500 nm while panels (d–f) show a 200 nm × 200 nm area of the same samples. The maximum height difference from low (dark color) to high (white) is given by Δz. For a thickness of 20 nm (a and d) the islands are equally dispersed and at $d = 50$ nm (b and e) clusters of small grains are observed. At $d = 150$ nm (c and f) the films have a columnar structure.
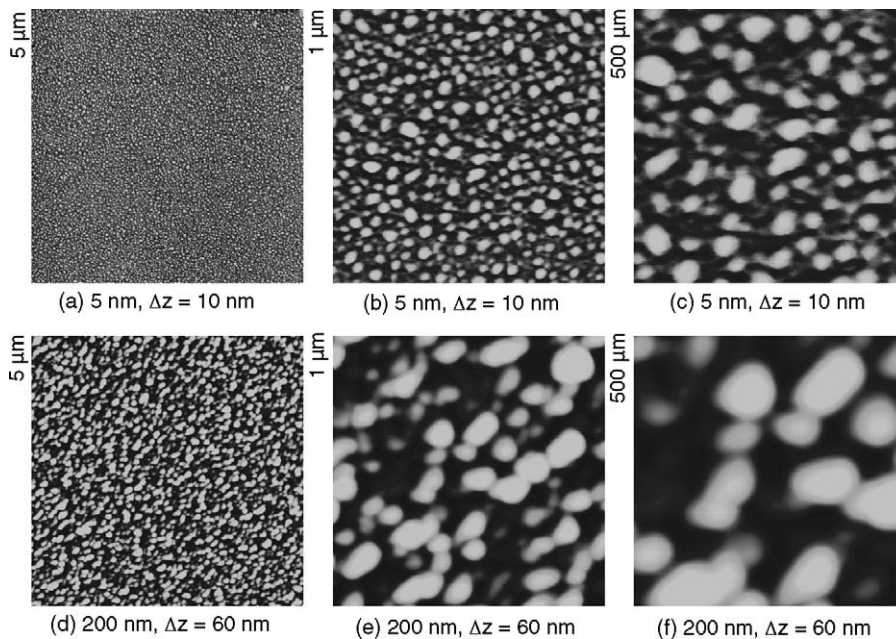

Fig. 3. AFM micrographs of Pd capped Mg_2Ni films of $d = 5$ and 200 nm thickness for different scan sizes and height scale Δz. At a thickness of 5 nm the film consists of finely dispersed small grains while at $d = 200$ nm large grains of 100 nm diameter are observed, which are the tops of the columns.

4. Discussion

We investigated the development of the microstructure of a Mg_2Ni film from the surface morphology at consecutive stages of growth. Close to the substrate, a 30–50 nm thick sub-layer of small grains and agglomeration of grains into clusters is observed. This porous structure contains numerous grain boundaries and grain interfaces. Upon further deposi-

tion, some of the initially grown clusters show a pronounced grain growth and a columnar microstructure develops, forming the second sub-layer. We conclude that 200 nm Mg_2Ni thin film is divided roughly into two layers, each layer having a different microstructure. The generally accepted reason for columnar formation is geometrical shadowing, in which some parts of the film do not receive atoms from the incident beam with the result that some earlier formed grains will dis-

appear or will be incorporated by others. On the other hand, the grains that receive most of the incident atoms will develop into columnar structures [14–16]. In our case the samples are prepared by co-deposition from two opposite Ni and Mg sources which are tilted at an angle of by 30°, making geometrical shadowing possible. The microstructure of the Mg_2Ni samples agrees quite well with the microstructure predicted by temperature zone models. Temperature zone models and columnar growth models [14–16] divide the growth modes of thin films and the obtained microstructures into several zones, depending on the ratio between the actual deposition temperature at the substrate and the melting temperature of the deposited material, respectively. The Mg_2Ni films, deposited at RT, are characterized by an intermediate behaviour, in which a sublayer of small grains precedes columnar growth.

As mentioned in Section 1, we do not have a chemical gradient in our samples, thus the specific microstructure of the films must be responsible for the preferred nucleation of Mg_2NiH_4 close to the substrate interface. As is known from experiments on powder and bulk samples, hydrogen absorption kinetics is very sensitive to crystalline imperfections in the form of defects, chemical inhomogeneity and stress development during hydrogenation [9,10]. Alloys consisting of nanocrystalline and/or amorphous phases show an improved hydrogen absorption and desorption kinetics at the same hydrogenation temperature, H_2-pressure and sample composition compared to those with a more crystalline structure [11–13]. We conclude similarly that the small grains in the vicinity to the substrate easily transform into the hydride phase. The activation energy for nucleation of the hydride phase is presumably smaller for the small grains than for the large columns. Furthermore, one of the reasons for the improved kinetics in the small-grained layer can be the 32 vol.% expansion of Mg_2Ni upon hydrogenation. This expansion is more easily in this porous layer than in the densely packed columnar structures. Another reason is that the hydrogen does not have to diffuse through an already formed thick hydride layer [17]. Therefore, for the unusual hydrogenation of Mg_2Ni thin films, we propose the following model: while the metal alloy composition is uniform throughout the film thickness, we find that the grain size of the as-deposited films at the interface is extremely small as compared to the ensuing columnar growth behavior. The vertical grain boundaries of the columns allow a fast and efficient diffusion of hydrogen from the Pd-covered surface to the substrate, whereas the very small grain size close to the substrate results in a preferred hydride nucleation, prior to the rest of the film. Hence, the observed optical black state is presumably a direct consequence of the growth related microstructure of this thin film.

5. Conclusion

Using an AFM/STM investigation of as-deposited Mg_2Ni thin films at subsequent stages of growth we investigatedthe development of the microstructure of these films. We find that the initial growth is characterized by an island growth mode, which develops into a very porous structure consisting of small grains and a high density of grain boundaries. This sub-layer has a thickness of 30–50 nm. Further deposition results in an extensive grain growth and is the onset of a columnar structure. We conclude that the unusual hydrogen absorption in Mg_2Ni thin films is a result of this specific microstructure. The hydrogen dissociated and absorbed at the Pd topside of the sample can easily diffuse along the vertical boundaries of the columns to the substrate side. Due to the small grains and the large number of interfaces in the initial 30–50 nm the hydrogenation kinetics are improved and a preferred nucleation of Mg_2NiH_4 close to the film/substrate interface takes place. The more dense packed columnar structure has less favorable kinetics and will be hydrided slower. This double layer formation is the origin of the optical black state. Hence, it appears that the particular microstructure of Mg_2Ni lies at the origin of this peculiar optical phenomenon.

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