Accepted Manuscript

Investigation of nanocrystalline Gd films loaded with hydrogen

Petr Hruška, Jakub Čížek, Patrik Dobroň, Wolfgang Anwand, Arndt Mücklich,
Ryota Gemma, Stefan Wagner, Helmut Uchida, Astrid Pundt

PII: S0925-8388(14)03084-9
DOI: <http://dx.doi.org/10.1016/j.jallcom.2014.12.156>
Reference: JALCOM 32945

To appear in: *Journal of Alloys and Compounds*

Received Date: 10 August 2014
Revised Date: 14 November 2014
Accepted Date: 15 December 2014

Please cite this article as: P. Hruška, J. Čížek, P. Dobroň, W. Anwand, A. Mücklich, R. Gemma, S. Wagner, H. Uchida, A. Pundt, Investigation of nanocrystalline Gd films loaded with hydrogen, *Journal of Alloys and Compounds* (2014), doi: <http://dx.doi.org/10.1016/j.jallcom.2014.12.156>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Investigation of nanocrystalline Gd films loaded with hydrogen

Petr Hruška^{a,*}, Jakub Čížek^a, Patrik Dobroň^a, Wolfgang Anwand^b, Arndt Mücklich^c, Ryota Gemma^{e,d}, Stefan Wagner^e, Helmut Uchida^e, Astrid Pundt^e

^aCharles University in Prague, Faculty of Mathematics and Physics, Czech Republic

^bInstitute of Radiation Physics, Helmholtz-Zentrum Dresden-Rossendorf, Germany

^cInstitute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Germany

^dPhysical Sciences and Engineering Division, King Abdullah University of Science and Technology, Saudi Arabia

^eInstitute for Materials Physics, University of Göttingen, Germany

Abstract

The present work reports on microstructure studies of hydrogen-loaded nanocrystalline Gd films prepared by cold cathode beam sputtering on sapphire (11 $\bar{2}$ 0) substrates. The Gd films were electrochemically step-by-step charged with hydrogen and the structural development with increasing concentration of absorbed hydrogen was studied by transmission electron microscopy and in-situ X-ray diffraction using synchrotron radiation. The relaxation of hydrogen-induced stresses was examined by acoustic emission measurements. In the low concentration range absorbed hydrogen occupies preferentially vacancy-like defects at GBs typical for nanocrystalline films. With increasing hydrogen concentration hydrogen starts to occupy interstitial sites. At the solid solution limit the grains gradually transform into the β -phase (GdH₂). Finally at high hydrogen concentrations $x_H > 2.0$ H/Gd, the film structure becomes almost completely amorphous. Contrary to bulk Gd specimens, the formation of the γ -phase (GdH₃) was not observed in this work.

Keywords: gadolinium, hydrogen, defects, thin films

---

*Corresponding author

Email address: peta.hruska.1@gmail.com (Petr Hruška)

1. Introduction

The Gd-H system attracts attention of researchers because of its high absorption capacity and a negative enthalpy of solution for atomic hydrogen [1]. However, the knowledge about the Gd-H phase diagram is yet incomplete, especially at low temperatures. As the hydrogen concentration increases, bulk Gd undergoes the following phase sequence [2]: α (hcp, Gd) $\rightarrow$ β (fcc, GdH₂) $\rightarrow$ γ (hcp, GdH₃). At room temperature the hydrogen solubility in the α -phase is very low ($x_H < 0.01$ H/Gd). With increasing hydrogen concentration, the α -phase transforms into the β -phase and the transition is completed at $x_H \approx 1.9$ H/Gd. Further loading with hydrogen leads to the formation of the γ -phase starting from $x_H \approx 2.3$ H/Gd and being completed at $x_H \approx 2.8$ H/Gd.

Absorbed hydrogen causes remarkable volume expansion of the Gd lattice. Contrary to bulk samples thin films are usually clamped to elastically hard substrates which prevent in-plane expansion of the film. Therefore, the expansion of hydrogen loaded films is highly anisotropic: the in-plane expansion is suppressed while the out-of-plane expansion is larger than in a corresponding bulk sample due to the Poisson effect [3]. As a consequence large in-plane bi-axial compressive stress appears in hydrogen loaded films [4]. It has been shown [5] that hydrogen-induced stresses strongly influence the thermodynamics of metal to hydride phase transitions. Moreover, it is also known that hydrogen strongly interacts with open volume lattice defects [5, 6]. Thus, the microstructure of the film influences the hydrogenation process, shifting phase boundaries and causing microstructural stress.

In the present study these effects were investigated by step-by-step hydrogen loading of nanocrystalline Gd films. The microstructure of the films was characterized by transmission electron microscopy (TEM) combined with *in-situ* X-ray diffraction (XRD). The relaxation of hydrogen induced stresses was examined by acoustic emission (AE) measurements.

2. Experimental details

Gd films with thickness of 1200 nm were deposited at room temperature on sapphire (11 $\bar{2}$ 0) substrates in an ultra-high vacuum (UHV) chamber with a base pressure of 10^{-10} mbar. Cold cathode beam sputtering was performed using argon gas with pressure of 2×10^{-4} mbar. The Gd films were covered with a 30 nm thick Pd over-layer in order to prevent oxidation and to facilitate hydrogen absorption into Gd.

The virgin films were step-by-step electrochemically charged with hydrogen using constant current pulses applied between a Pt counter electrode (anode) and the Gd film (cathode). Hydrogen charging was performed in a galvanic cell filled with 1 M KOH electrolyte. The current density was kept at 0.3 mA cm $^{-2}$. The hydrogen concentration in the samples x_H was calculated from the transported charge using the Faraday's Law:

$$x_H = \frac{ItV_m}{FV}, \quad (1)$$

where I is the loading current, t is the length of the loading pulse, V_m is the Gd molar volume, V is the volume of the loaded film and F is the Faradays constant.

In-situ XRD investigations of hydrogen-loaded films were performed at HASYLAB (DESY, Hamburg) using synchrotron radiation with a wavelength $\lambda = 0.499123$ Å. The XRD patterns were accumulated in the symmetrical Bragg-Brentano geometry.

TEM studies were carried out on a Phillips CM300SuperTWIN microscope operating at 300 kV. Thin foils for cross sectional TEM observations were produced using a Gatan precision ion polishing system (PIPS).

AE studies were performed *in-situ* during the hydrogen loading with a computer-controlled DAKEL-XEDO 3 AE system. A piezoelectric sensor MST8S (with a frequency band from 100 to 600 kHz) was attached to the back side of the substrate of the loaded film, while the front side with the Gd film was immersed in the electrolyte.

3. Results and discussion

A dark field TEM image (in cross-section) of the virgin Gd film is shown in Fig. 1a. The film consists of elongated column-like grains with the mean width of ≈ 50 nm. The electron diffraction pattern in the inset of the figure contains bright spots originating from the sapphire substrate and continuous rings from the Gd film. Uniform intensity distribution within the rings testifies to random lateral orientation of crystallites in the Gd film. Fig. 1b shows the XRD pattern for the virgin Gd film. One can see in the figure that the $(100)_\alpha$ reflection is the most pronounced while the $(002)_\alpha$ reflection is suppressed. It testifies that Gd crystallites grow predominantly with the $(10\bar{1}0)$ planes parallel with the substrate. The lateral orientation of crystallites is completely random. A shoulder visible on the right side of the $(100)_\alpha$ reflection most probably results from a weak $(111)_\beta$ reflection from the β -phase. Hence, the Gd film contains some β -phase precipitates already in the as-grown state due to hydrogen absorbed from the air. The reflections for the α and β -phase are shifted to lower diffraction angles compared to the positions for bulk Gd and GdH_2 indicated in Fig. 1b by dashed lines. This finding testifies that the virgin Gd film suffers from in-plane compressive stress leading to expanded out-of-plane lattice parameters. The compressive in-plane stress in the virgin Gd film is caused by several factors: (i) lattice misfit between the Gd layer and the sapphire substrate; (ii) low Ar pressure during sputtering which is known to induce compressive stress into films due to atomic peening processes [7]; out-of-plane lattice expansion of the α -phase caused by hydrogen absorbed from the air. Note that since the β -phase particles were observed in the virgin film the α -phase must be already saturated with hydrogen.

The development of XRD patterns with increasing hydrogen concentration in the Gd film is shown in Fig. 2. Obviously with increasing hydrogen concentration the α -phase keeps transforming into the β -phase which is reflected by diminishing of the $(100)_\alpha$ reflection and rising of the $(111)_\beta$ reflection. Similarly the $(101)_\alpha$ reflection gradually decreases while the $(002)_\beta$ reflection grows. At

Figure 1: Virgin Gd film: (a) dark field TEM image. The inset shows the electron diffraction pattern. The orientation where the dark filed image was taken is indicated by a circle. (b) XRD pattern; dashed lines show the positions of reflections for bulk Gd.

hydrogen concentration $x_H \approx 1.6$ H/Gd the film is completely transformed into the β -phase. This concentration is lower than $x_H \approx 1.9$ H/Gd where the α to β transition is completed in bulk Gd [2]. Hence, the two-phase co-existence region is narrowed in the film. Narrowing of the two-phase field has been often observed in nanocrystalline materials and has been attributed to the high volume fraction of grain boundaries (GBs), which exhibit disordered structure [5]. Hydrogen firstly fill low energy sites at GBs and subsequently also the interstitial sites inside grains. Contrary to grains, GB regions are not transformed into the hydride phase at high hydrogen concentrations. These processes lead to narrowing of the two-phase field. Preferential hydrogenation of GBs was confirmed by positron annihilation spectroscopy [8, 9]. Precipitation of the hydride phase in the grain interiors takes place only when GBs are saturated with hydrogen. The onset of the α to β transition is, therefore, shifted to higher hydrogen concentration, not shown here. Since the hydride phase is not formed at GBs due to their distorted structure the total volume transformed into the hydride phase is lower than in a perfect single crystal [5]. As a consequence the phase transition to the hydride phase is finished at lower hydrogen concentration than in a coarse grained bulk sample [5].

Fig. 3a shows the development of the lattice parameters for the α and β -

Figure 2: Development of XRD patterns for a Gd thin film during hydrogen loading.

phase determined from fitting of the XRD patterns. The relative intensities of the $(100)_\alpha$ and $(111)_\beta$ reflection are plotted in the lower panel of Fig. 3a. The lattice parameters a for both the α -phase and the β -phase are larger than for bulk samples. This is due to the compressive in-plane stress of the virgin film and further increasing during hydrogen loading. The lattice parameter c for the α -phase is less influenced by the compressive stress and remains close to the bulk value. One can see in Fig. 3a that during the α to β -phase transition the lattice parameters remain approximately constant. This testifies to incoherent precipitation of the β -phase precipitates in the α -phase matrix [10]. Similar behaviour can be observed in bulk samples.

However, contrary to bulk Gd samples [11] further hydrogen loading of the Gd film at hydrogen concentration above 2.3 H/Gd did not lead to the appearance of the γ -phase reflections. It only causes broadening of the β -phase peaks. Hence, in the nanocrystalline Gd film the γ -phase was not formed even by hydrogen loading for a long time period corresponding to nominal hydrogen concentration of 3.0 H/Gd. It should be, however, noted that the actual hydrogen concentration in the Gd film is lower than 3.0 H/Gd due to hydrogen entering the Pd cap and due to hydrogen loss by formation of H_2 bubbles which

Figure 3: (a) Upper panel: dependence of the lattice parameters for the hcp α -phase and the fcc β -phase on the hydrogen concentration. Vertical lines show the lattice parameters for bulk Gd and GdH_2 ; lower panel: development of relative intensities of the $(100)_\alpha$ and $(111)_\beta$ reflections; (b) cumulative number of AE events recorded during hydrogenation of the Gd film.

were noticed during such prolonged hydrogen loading.

125 The cumulative number of AE events detected in the Gd film during hydrogen loading is plotted in Fig. 3b. A considerable number of AE events was detected already inside the $\alpha + \beta$ two-phase field and a further increase in the number of AE events was observed after loading to higher hydrogen concentrations ($x_H > 1.6$ H/Gd). The occurrence of AE events testifies to collective movement of dislocations and gives clear evidence that hydrogen-induced stress evolving during the α to β transition is partially released by plastic deformation [12] either by extrinsic dislocation loops emitted by growing β -phase precipitates [13, 14] or by glide of dislocation segments originating from misfit dislocations at the film/substrate interface [15]. The latter mechanism is likely
130 operating also at higher hydrogen concentrations ($x_H > 1.6$ H/Gd) in the film transformed completely into the β -phase.

135 The microstructure of the hydrogen loaded film was examined by TEM. While the film loaded within the $\alpha + \beta$ two-phase field ($x_H < 1.6$ H/Gd) exhibits column-like structure with α and β phase crystallites (not shown here) the film's microstructure has markedly changed by loading to high hydrogen concentrations ($x_H > 2.3$ H/Gd). Fig. 4 shows the microstructure of the Gd
140

film after prolonged hydrogen loading up to nominal $x_H = 3.0$ H/Gd. The microstructure of the region close to the sapphire substrate and the sub-surface region is shown in Fig. 4a and 4b, respectively. One can see in Fig. 4a that
 145 a foam-like defected structure was formed in the region close to the substrate. The electron diffraction pattern confirms that the structure of the film is fully amorphous there. The subsurface region in Fig. 4b exhibits small crystallites embedded in the amorphous matrix. Hence, prolonged hydrogen loading leads to the amorphization of the nanocrystalline Gd film.

Figure 4: Bright field TEM micrographs of the Gd film nominal loaded with hydrogen up to $x_H = 3.0$ H/Gd: (a) the region close to the sapphire substrate; (b) sub-surface region. Electron diffraction patterns are shown in the insets.

150 The absence of the γ -phase in the Gd film might be associated with its nanocrystalline structure since the formation of the γ -phase in nanoscopic crystallites may be energetically unfavorable. Another possibility is that the compressive in-plane stress in the film hinders the phase transition into the γ -phase. The important role of stress in the film is supported by the finding that amor-
 155 phization of the film is more pronounced in the deep region close to the surface where the in-plane stress is more pronounced than in the more relaxed sub-surface region. To clarify which of the two factors plays the dominant role in the suppression of the γ -phase formation in the nanocrystalline Gd film additional studies are required. These studies should include investigations of
 160 epitaxial Gd films which exhibit in-plane stress but do not have nanocrystalline

structure and Gd films deposited on soft substrates which exhibit nanocrystalline structure but a strongly reduced in-plane stress. Recently the formation of the γ -phase has been reported in epitaxial Gd films prepared by electron beam evaporation [16, 17]. Although information about the stress in these films is not
 165 available it indicates that the nanocrystalline structure might be the more important factor. Note that similar effect as in Gd films may occur also in Y films. While formation of YH₃ is well documented in epitaxial [18, 19] and polycrystalline [20] Y films it was not reported for nanocrystalline Y films. Moreover, the phase transition from YH₂ to YH₃ was found to produce porosity in the Y
 170 film [21].

4. Conclusions

The development of the microstructure of hydrogen loaded Gd films was studied by *in-situ* XRD combined with TEM. The virgin Gd film consists of column-like nanocrystalline grains and exhibits compressive in-plane stress.
 175 Traces of the β -phase were observed already in the virgin film. With increasing hydrogen concentration the film gradually transforms into the β -phase. The region of the $\alpha + \beta$ phase co-existence was found to be narrower than in a bulk Gd. *In-situ* AE studies revealed that hydrogen-induced stress is relaxed partially by plastic deformation of the film during the α to β phase transition and also when
 180 the film was completely transformed into the β -phase. Contrary to bulk Gd the γ -phase was not formed in the nanocrystalline Gd film. Prolonged loading up to nominal hydrogen concentration of 3.0 H/Gd leads to the amorphization of the film structure.

Acknowledgments

185 This work was supported by the Czech Science Foundation (project P108-12-G043).

References

References

- [1] G.E. Sturdy, R.N.R. Mulford, J. Am. Chem. Soc. 78 (1956) 1083.
- 190 [2] F.B. Manchester (Ed.), ASM International Materials Park, 2000, p. 58.
- [3] Q.M. Yang, G. Schmitz, S. Fhler, H.U. Krebs, R. Kirchheim, Phys. Rev. B 54 (1996) 9131.
- [4] U. Laudahn, A. Pundt, M. Bicker, U.V. Hlsen, U. Geyer, T. Wagner, R. Kirchheim, J. Alloys Comp. 293295 (1999) 490.
- 195 [5] A. Pundt, R. Kirchheim, Annu. Rev. Mater. Res. 36 (2006) 555.
- [6] R. Kirchheim, Prog. Mat. Sci. 32 (1988) 261.
- [7] A. Debelle, G. Abadias, A. Michel, C. Jaouen, Appl. Phys. Lett. 84 (2004) 5034.
- [8] J. Čížek, I. Procházka, G. Brauer, W. Anwand, A. Mücklich, R. Kirchheim, A. Pundt, C. Bähitz, M. Knapp, Appl. Surf. Sci. 252 (2006) 3237.
- 200 [9] J. Čížek, I. Procházka, M. Vlach, N. Žaludová, S. Daniš, G. Brauer, W. Anwand, A. Mücklich, R. Gemma, R. Kirchheim, A. Pundt, Appl. Surf. Sci. 255 (2008) 251.
- [10] S. Wagner, H. Uchida, V. Burlaka, M. Vlach, M. Vlček, F. Lukáč, J. Čížek, C. Baehtz, A. Bell, A. Pundt, Scripta Mat. 64 (2011) 978.
- 205 [11] M. Ellner, H. Reule, E.J. Mittemeijer, J. Alloys Comp. 309 (2000) 127.
- [12] R. Gemma, P. Dobroň, J. Čížek, A. Pundt, Acta Mater. 67 (2014) 3042.
- [13] T. Schober, Scr. Metall. 7 (1973) 1119.
- [14] B.J. Makenas, H.K. Birnbaum, Acta Metall. 28 (1980) 979.
- 210 [15] W. D. Nix, Metall. Trans. A. 20 (1989) 2217.

- [16] A. Miniotas, P. Nordblad, M. Andersson, B. Hjörvarsson, *Europhys. Lett.* 58 (2002) 442.
- [17] H. Hirama, M. Hayakawa, T. Okoshi, M. Sakai, K. Higuchi, A. Kitajima, A. Oshima, S. Hasegawa, *J. Cryst. Growth* 378 (2013) 356.
- 215 [18] K. Wang, J.R. Hattnick-Simpers, L.A. Bendersky, *Acta Mater.* 58 (2010) 2585.
- [19] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijnaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, *Nature* 380 (1996) 231.
- [20] S.J. van der Molen, J.W.J. Kerssemakers, J.H. Rector, N.J. Koeman, B. 220 Dam, R. Griessen, *J. Appl. Phys.* 86 (1999) 6107.
- [21] J.R. Hattnick-Simpers, K. Wang, L. Cao, C. Chiu, E. Heilweil, R.G. Downing, L.A. Bendersky, *J. Alloys Comp.* 490 (2010) 42.

- Microstructure development of hydrogenated nanocrystalline Gd films was studied
- The virgin film contains already traces of the β -phase (GdH₂)
- With increasing hydrogen concentration Gd gradually transforms into the beta-phase
- The region of $\alpha+\beta$ phase coexistence is narrower compared to bulk Gd
- The γ -phase (GdH₃) is not formed
- Prolonged hydrogen loading leads to amorphization of the film structure