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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Physical properties of matter change when the system dimension is reduced to the nano-size. Especially, nano-sized systems have different phase boundaries in phase diagrams and different mechanisms of phase precipitation. To study the impact of both microstructure and mechanical stress contributions on the thermodynamics of nano-sized systems, in the present test-series of experiments at BM 20 we investigated different metal-hydrogen thin film systems with different initial microstructures and film thicknesses in the range from 30 to 300 nm. Fibre textured, nanocrystalline and epitaxial Palladium thin films as well as fibre textured Magnesium thin films were stepwise electrochemical charged or dischared with hydrogen. The subsequent change of the out-of-plane lattice parameters and the occurrence of hydride phases were monitored in Bragg-Geometry. For successful measurements an inert gas atmosphre (Argon/N_2) and fast XRD measurements (approx. 1 min per scan) appeared mandatory.

Epitaxial as well as nanocrystalline Palladium films prepared at 673 K on sapphire (0001) substrates were shown to reveal initially very smooth surface conditions, as thickness fringes around the (111) Bragg-Peak appeared (Fig. 1). From the oscillation period of the fringes and their damping the films thickness T and the near surface lattice distortion (surface roughness σ) can be determined [1] (Parameters in Fig. 1 at $c_H = 0$: T = 85.02 nm, σ = 0.0025 nm) . Next to the out-of-plane expansion, during hydrogen charging and hydride formation the thickness fringes allow to monitor the films surface roughness evolution - a technique, that is conventionally only applicable in XRR geometry. The example of an 85 nm epitaxial Pd film on sapphire in Fig. 1 shows that the surface roughness increases with the precipitation of the hydride phase, suppressing the thickness fringes when the film is loaded up to a hydrogen concentration of $c_H = 0.13$ H/Pd. However, during subsequent discharging the thickness fringes reversibly return. Subsequent loading to $c_H = 0.45$ H/Pd, on the other hand, irreversibly changes the surface condidtions, as the thickness fringes do not return after a further unloading step. According to our interpretation this irreversible change in the surface roughness reflects on the lattice matching during hydride precipitation – initially coherent hydrides are formed, elastically straining the metal lattice, while above a certain hydrogen concentration the precipitates become incoherent by the emission of misfit dislocation. These dislocations cause irreversible steps on the films surface. Interestingly, this change is not coupled to the thin film phase boundary.

In Fig. 2 the lattice parameter evolution and the occurance of the hydride phase in 300 nm thick Pd films with different microstructures are shown. From the figure clear differences in the initial stress states of the films

and differences of their phase boundaries appear, approaching the bulk values with increasing epitaxy quality of the films. Furthermore, the initial slopes Δa/a of the lattice parameters in the solid solution region (α-phase) differ strongly (0.153 for nanocrystalline Pd, 0.104 for epitaxial Pd). This behaviour is in good agreement with calculations of the theoretically expected out-of-plane expansion of thin films that are clamped on elastically hard substrates. [2] The palladium film on silicon detached from the substrate in the two phase field. The accompanied strong reduction in mechanical stress resulted in a lattice relaxation, clearly visible in the continously increasing hydride (β-phase) lattice paramater.

Magnesium hydride is served as a promising candidate for hydrogen storage applications. However, Griessen et al. [3] state that it is not possible to completely hydride Mg thin films with more than 100 nm thickness due to the formation of a surface hydride blocking layer. In contrary, our test measurements at BM 20 revealed that hydride formation is possible for Mg-film thickness up to 188 nm, and that the thickness of the hydride layer can be tuned by proper loading condidtions. In Fig. 3 the appearance of the hydride peak in a 188 nm thick Mg film is shown. The hydrogen concentration at the onset of hydride peak visibilty strongly depends on the applied loading current.
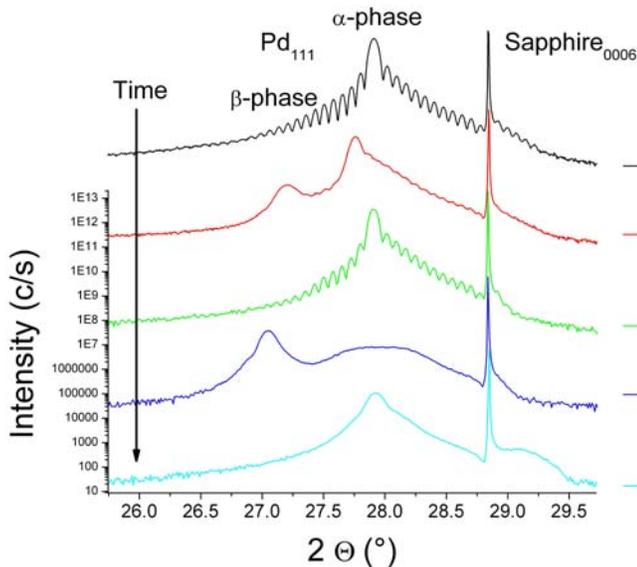

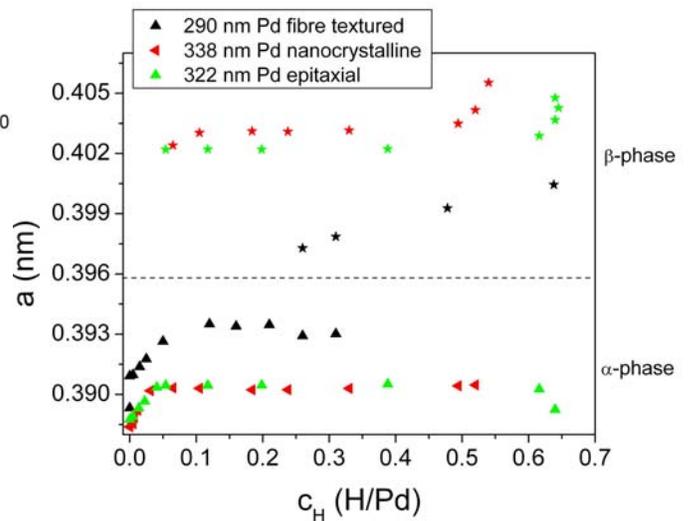Fig. 1: Thickness Fringes and phase evlution of 85 nm epitaxial PdH_c on sapphire.

Fig. 2: Lattice parameter and phase evolution of PdH_c thin films with different microstructures.

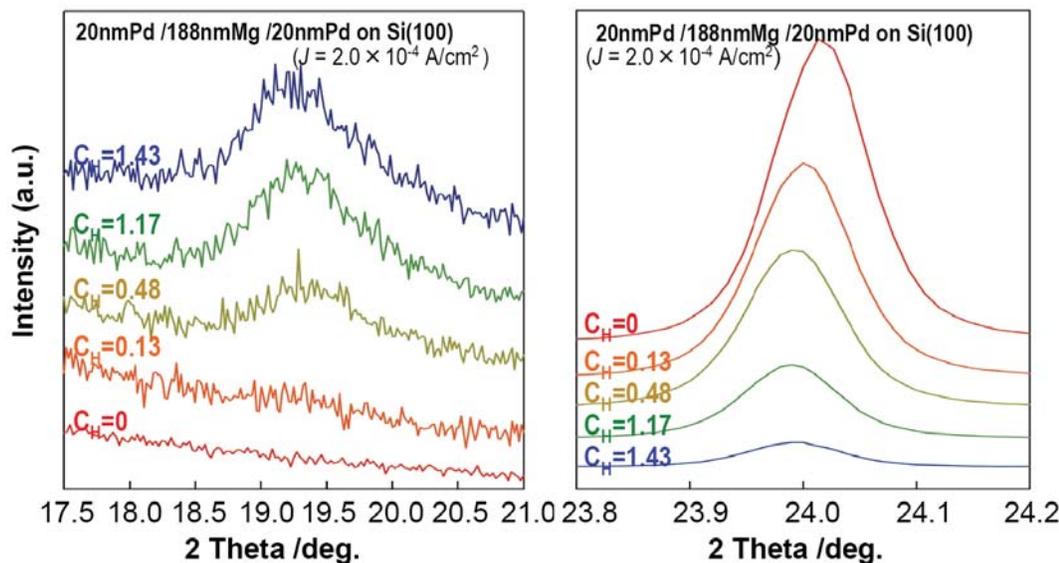Fig. 3: Hydride formation in a 188 nm Mg thin film. Left side: MgH_2-peak, right side: α-peak.

[1] Zolotoyabko, E.: J. Appl. Cryst. (1998), 31, 241.
[2] Pundt, A: Annu. Rev. Mat. Res. (2006), 36, 555.
[3] Baldi, A. et al., Appl. Phys. Lett.(2005), 95, 071903.