

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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.



	Experiment title: In-situ hydrogenation of thin films: finite size effects, kinetics, thermodynamics and defect generation	Experiment number: MA-1638
Beamline: BM20	Date of experiment: from: 08/12/2012 to: 12/12/2012	Date of report:
Shifts: 12	Local contact(s): Dr. Carsten Baehtz	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists):		
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Report:

Physical properties of nano-sized metal hydrogen systems strongly change with mechanical stress, evolving during hydrogen loading and phase transition. For very thin films this stress relaxation process is expected to be much less efficient [1,2] as systems will stay in the coherent state [1,3], hereby changing their thermodynamic properties and phase stabilities. To study the impact of coherency and mechanical stress contributions on the thermodynamics and kinetics of nano-sized systems, different metal-hydrogen thin film systems (M-H systems, M = Pd, Nb) are used as model systems at BM20. Epitaxial Niobium (8 nm and 33nm) and Palladium (100nm and 80 nm) thin films were charged and discharged electrochemically and with gaseous hydrogen. Accompanying changes of the out-of-plane lattice parameters and the generation of hydride phases were monitored on site by means of Bragg-Geometry. Measurement on ZnO were omitted because of the reduced number of awarded shifts (12 instead of 24).

For the NbH system, coherent (8nm) and semi-coherent (33nm) phase transition regimes were investigated by electrochemical charging. Experimental observation showed that samples wetted with electrolyte posses arbitrary transformation to the hydride phase under interaction with the X-Ray beam. Thereby, the electrolyte was removed from the film after each step-by-step loading to perform XRD scans. In **Fig. 1** the diffraction pattern evolution (Nb 110) of the α phase of the 33 nm film is shown as a function of hydrogen concentration for the first loading cycle. Precipitation of the hydride phase starts at an average hydrogen concentration of $c_a=0.21$ [H/Nb], reflected in the appearance of second hydride related peak, as marked in the graph. Therefore, in comparison to the bulk system with $c_a=0.06$ H/Nb, the solubility limit is strongly shifted to higher concentrations. This shift is mainly attributed to large in-plane mechanical stress [2]. Before the phase transformation starts, the α -phase Nb peak (110) moves to the lower reflection angles, exhibiting a strong out-of-plane lattice expansion of up to 1.8%. Additionally, thickness fringes are visible for the low concentration range, which reveal very smooth surface conditions. In the two phase region, the thickness fringes irreversibly disappear, reflecting on lattice deterioration during hydride precipitation: above a certain H concentration, initially coherent hydride precipitates loose their coherency with the surrounding α -matrix and become semi-coherent due to the emission of misfit dislocation [1,2,3].

In case of thinner films (8 nm) no separation between the hydride peak and α -phase peak has been found (see **Fig.2**). Only one broad peak moving forward to the lower angle range has been observed, revealing the conservation of coherency at hydride/ α - matrix interface. For this film thickness the thickness fringes are found to have a reversible behaviour in the loading/unloading experiment. In the transformation regime a destabilization of the hydride phase was observed, which fastly decomposed when the sample was exposed to atmosphere. This is attributed to the high internal mechanical stress and desorption supported by

the presence of oxygen. To reduce this effect, in future the H loading will be carried out from the gas phase only, where the hydrogens' chemical potential can be kept constant during the XRD measurements and oxygen contributions can be controlled more easily.

To study the properties of surface hydride formation with respect to the lateral stress contribution, epitaxial Pd-films films have been measured by use hydrogen gas loading in-situ XRD. The samples were prepared at 400°C and treated by Ar-ion bombardment to produce a ripples-like surface structure (periodic waves: 2nm height, 5nm width, 100nm length). Two samples were measured: 100 nm thick + ion-bombarded for 60 sec and 80 nm thick + ion-bombarded for 120 sec. The rippled film surface has a quasi-free volume, that can expand freely in all 3 dimensions - except for that region at the interface linked to the underlying compact film. It is, thereby, strongly reduced in lateral mechanical stress and hydride formation was expected to occur at a lower hydrogen pressure compared to conventional clamped films. This assumption is strongly supported by the conducted measurements, as shown in **Fig. 3**. As can be seen, first hydride precipitation in the initially 100 nm thick sample has been already found during the first loading step at about 49 mbar pressure. The small hydride peak stays unchanged up to 69mbar – supporting its interpretation as surface hydride forming in the ripples volumes. Only at pressures exceeding 69 mbar the complete clamped film starts to transform to the hydride phase. For the initially 80 nm thick sample this feature was not found (See **Fig.4**). Such a difference is attributed to the different film/substrate composite stress contribution [2]. However, the detailed origin of this effect is still under debate. Competing processes like ripple formation and film erosion complicate the situation here. Additional measurements at the home institution are ongoing to clarify the interpretation.

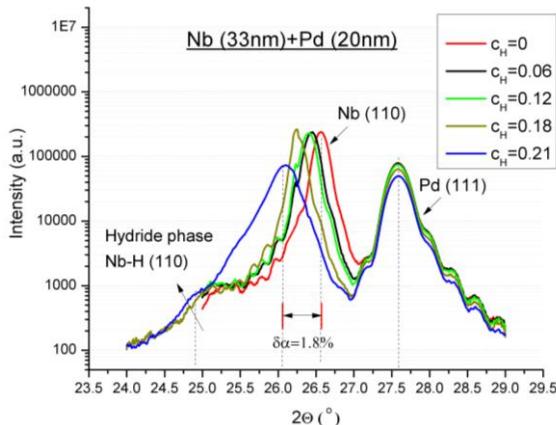


Fig. 1 XRD patterns for NbH (110): 33 nm thick film, incoherent phase transition regime, precipitation of second hydride related peak is visible. Volume fractions of α and β phase can be considered separately.

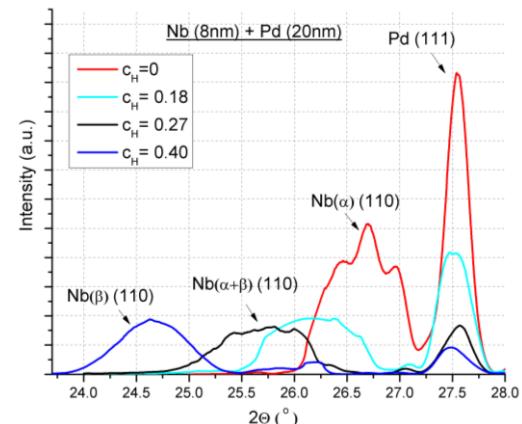


Fig. 2 XRD patterns for NbH (110): 8 nm film, coherent phase transition regime, only one broad peak is visible. Kind of lattice parameter distribution in the two-phase region (no peak separation)

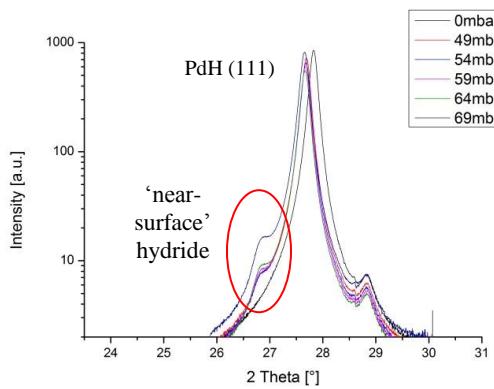


Fig.3 XRD patterns for 100 nm PdH (111) film Ar-ion bombarded for 60 sec: early 'near surface hydride' precipitation is found.

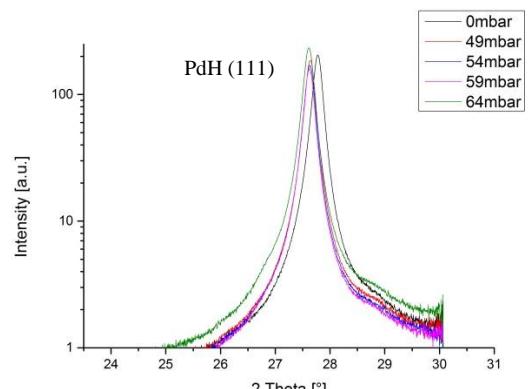


Fig.4 XRD patterns for 80 nm PdH (111) Ar-ion bombarded for 120 sec: no surface hydride precipitation is found.

1. K. Nörthemann, A. Pundt, Appl. Phys. Rev. B **78**, (2008) 014105-1.
2. A. Pundt, R. Kirchheim, Annual Review Materials research **36** (2006) 555-608 (Review).
3. S. Wagner, H.T.Uchida, V. Burlaka et al., Scripta mater. **64** (2011) 978.