



	Experiment title: In-site study of the YH₂-YH_{3+x} transition during hydrogenation by GI-DAFS and HAXPES.	Experiment number: MA-2866
Beamline: BM25	Date of experiment: from: 29.06.16 to: 05.07.16	Date of report:
Shifts: 18	Local contact(s): RUBIO ZUAZO Juan	<i>Received at ESRF:</i>
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Report

The association and dissociation of metallic hydrides is of fundamental and technological interest. Hydrogenated metals are known to have markedly different physical and electro-optical properties. These include embrittlement and metal-to-insulator phase transitions. Metal hydrides have been proposed as a hydrogen storage solution and for switchable mirrors.

From in-house ellipsometry measurements we suspected the existence of a new insulating phase, YH_{3+x}, that forms when a thin Y layer is capped by Ru. The goal of the synchrotron measurements was to investigate the changes in structure and chemistry of the YH₂-YH_{3+x} transition *in situ* during hydrogenation to characterize the RuY-YH_x phase diagram.

The experiment was performed at experimental hutch 2 (EH2) on branch B of the HAXPES-XRD setup. To hydrogenate the films, a custom made H-radical source (HRS), consisting of a W filament and gas inlet placed 7 mm from each other, was installed on the vacuum chamber. The construction of the beamline allowed placing H-ion source approximately 45 mm from the sample surface.

In our application for beam time, we planned DAFS experiments to observe both short and long range order of the hydrogenation processes, unfortunately BM25 was unsuitable for this experiment because the photon energy cannot be varied continuously.

Accordingly to limitations of the beamline we have adjusted our experimental plan to measurements of XRD and Y HAXPES spectrum. We planned to measure continuously during hydrogenation, and, following successful hydrogenation, to dissociate the YH_x sample by increasing the sample temperature.

This experiment was inappropriate for the chamber for several reasons: the HAXPES detector could not be operated at the same pressure as the HRS. The HRS flow had to be reduced to keep the chamber pressure within limits for reasonable pump-down time. And, due to the positioning of the W filament, relative to the chamber windows, it was very difficult to set the filament temperature accurately. By operating within these limits, the

radical flux was insufficient to observe hydrogenation. In future a capillary cracker will be used, which can operate at low pressures while delivering a high and directed radical flux.

To overcome these limitations, it was decided to use a small vacuum chamber, placed on a single crystal diffraction goniometer. This chamber allowed for more rapid sample changes and greater pressure variation. Thus, the HRS could be operated at a more suitable flow rate. In this small vacuum chamber, we were able to detect the Y-YH₂-YH₃ transition in Ru capped Y films at the base pressure of $6 \cdot 10^{-6}$ mbar with hydrogen pressure of $5 \cdot 10^{-3}$ mbar. However, HAXPES was unavailable for this chamber, thus, the experimental results are limited to *in situ* XRD only.

Y films grow preferentially on a Si substrate in the (002) direction, parallel to the surface of the Si wafer. To measure the phase transition, the Θ - 2Θ X-ray diffraction measurement geometry was chosen. The phase diagrams were recorded in the 2θ range of 8° - 14° , which covers the Y (002), Y(100), YH₂ (111), and YH₃(002) Bragg peaks for 20 keV radiation.

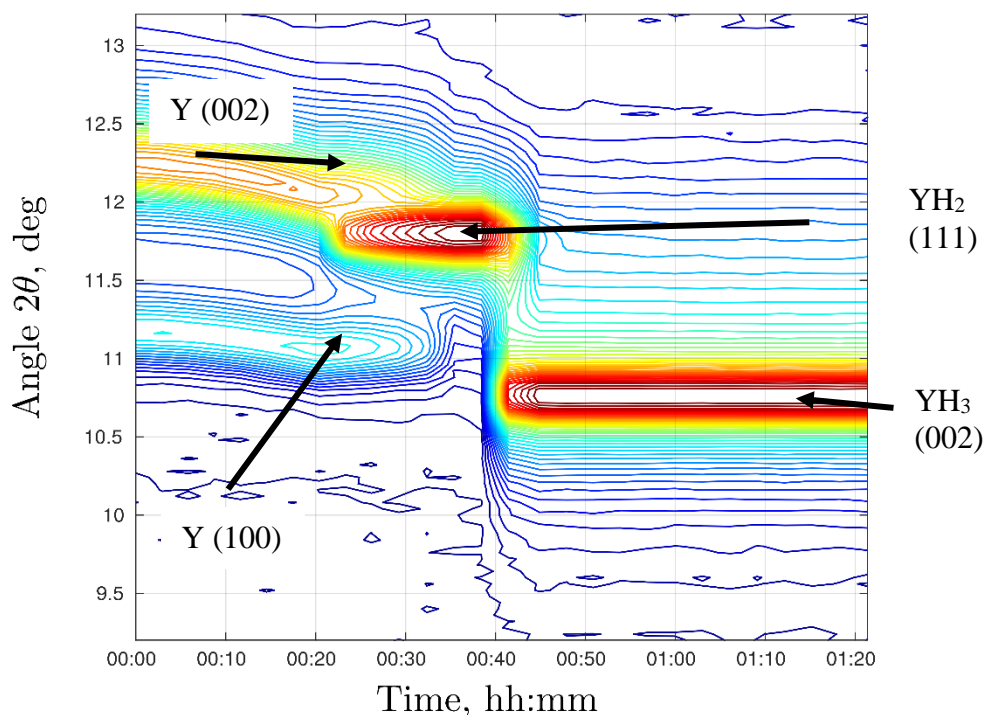


Fig. 1. Transition Y-YH₂-YH₃.

Figure 1 shows the evolution of the X-ray diffraction pattern during the hydrogenation of Y. During the transition from Y to YH₂, the expansion of the Y lattice can be seen—probably due to hydrogen solvation in the Y lattice. However, at some critical H concentration, the Y rapidly hydrogenates to form YH₂, as evidenced by the rapid appearance of the (111) peak of YH₂ bcc. When the entire Y film has hydrogenated to the YH₂ phase, a smooth transition to YH₃ is observed. In this case, there is no evident expansion of the YH₂ lattice, indicating that there is very little interstitial H in the sample during this time period. As YH₂ and YH₃ phases have bcc and hcp crystal lattice, respectively, the phase transition is observed as a gradual weakening and disappearance of the YH₂ (111) peak while the YH₃ (002) peak grows (Fig. 1). Note that after the transition to YH₃ is complete, the lattice does not appear to expand, indicating that, even after hydrogenation, very little hydrogen penetrates the YH₃ lattice, which is inconsistent with our optical observations. In both cases, a careful analysis of the sensitivity and possible systematic errors is required to draw reliable conclusions. It should be mentioned that the sample was heated by HRS during measurements, and even with nitrogen gas cooling, the equilibrium temperature was about 330 K, which is significantly higher than used for the optical experiments performed in our laboratory.

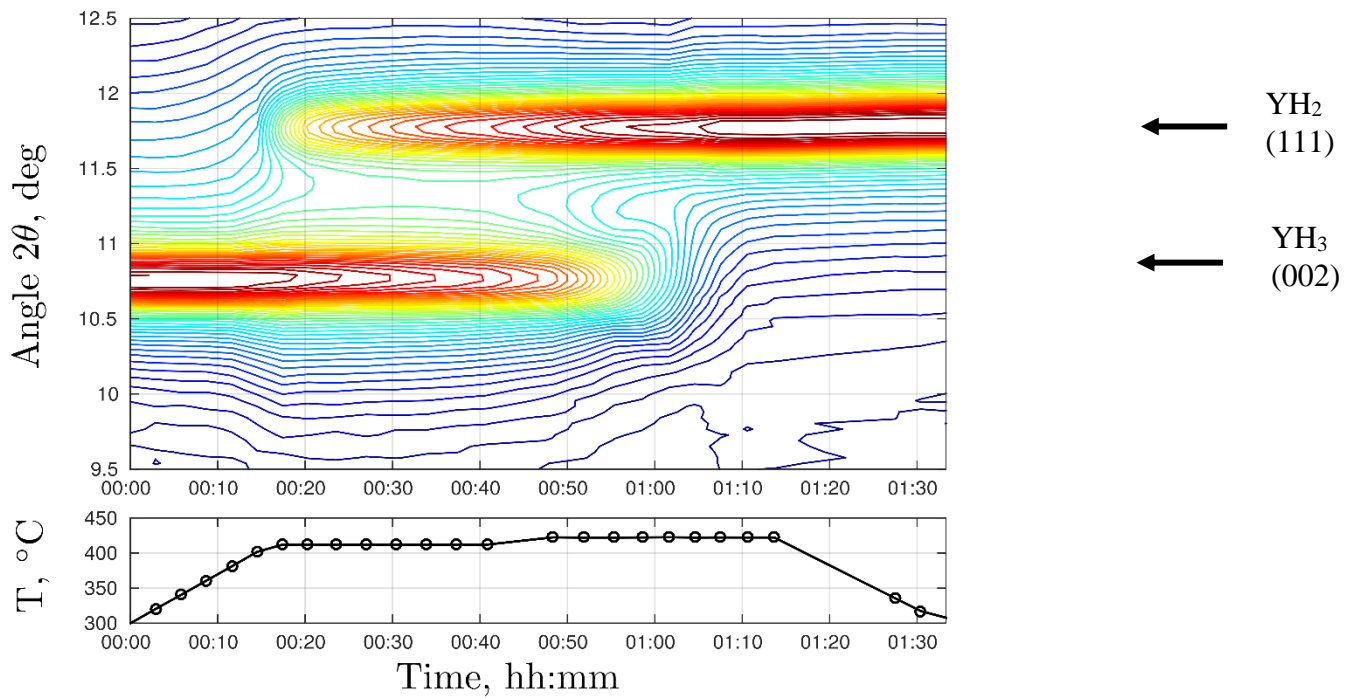


Fig. 2. De-hydrogenation process YH_3 - YH_2 .

The dissociation of YH_3 to YH_2 was studied under the elevated temperatures. As shown on Fig. 2, at the temperatures close to the threshold (400 K), the YH_3 and YH_2 phases coexist at some equilibrium ratio. The threshold temperature of YH_3 - YH_2 transition was found to be 410 K. According to previous research, YH_3 phase exists only as long as there is sufficient pressure of H radicals¹. In contrast to this experimental finding, the theoretical prediction for the decomposition temperature (Chem. Rev. 2004, 104, 1283 – 1315) is 623 K. Furthermore, experimentally, pure YH_3 is never observed, instead a fraction of $\text{YH}_{\leq 2.9}$ is found. Our results differ in that the experimentally observed dissociation temperature is higher than previously observed, and we obtain a pure YH_3 phase. Both observations require further study.