Control of YH_3 formation and stability via hydrogen surface adsorption and desorption

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Abstract

Yttrium is known to form two hydrides: YH_2, a metal, and YH_3, which is dielectric. However, the stability of YH_3 is not fully understood, especially in the context of thin films, where the yttrium layer must be coated to protect it from oxidation. In this work, we show that the stability of a YH_3 thin film depends on the capping layer material. Our investigation reveals that YH_3 appears to be stabilized by hydrogen that is adsorbed to the capping layer surface. This is evidenced by the YH_3-YH_2 transition temperature, which was found to be correlated with the desorption temperature of hydrogen from the surface. We posit that surface-adsorbed hydrogen prevents hydrogen from diffusing out of the thin film, which limits YH_3 dissociation to the solubility of hydrogen in the YH_2/YH_3 thin film.

Keywords: hydrogenation, atomic hydrogen, yttrium hydride, metal thin coatings, surface desorption

1. Introduction

The ability of rare-earth metals to form stable hydrides has found various applications in hydrogen storage, hydrogen sensing, and superconductivity. Yttrium is known to form di- and trihydrides, which was demonstrated in early works [1–4]. A pure bulk Y sample, exposed to ~1 bar of hydrogen and heated to 400˚C, reacts to form YH_2 [1]. YH_3 is formed once the temperature of YH_2 is lowered to 200˚C at a similar hydrogen pressure [2]. Further research showed that Y, in the form of a thin film (usually capped), does not powderize during hydrogenation, in contrast to bulk Y samples, allowing its electrical and optical properties to be extensively studied [5–9].

Later it was also found that a Y film, capped with a thin layer of Pd, simplifies the conditions needed for Y hydrogenation: hydride formation happens at lower hydrogen pressures and temperatures [7]. The role played by Pd is generally thought to be two-fold: (i) Pd dissociates H_2, providing a supply of reactive atomic hydrogen so that hydrogenation can proceed at room

temperature, and (ii) Pd protects Y from oxidation, allowing hydrogenation. Interestingly, Pd capped Y hydrides are reversible at room temperature. Once the H_2 supply is removed, the YH_3 phase dissociates at room temperature to form YH_2 and H_2 [10]. According to Huiberts et al. [7], YH_3 stability in bulk is due to the bulk phase having a lower enthalpy of formation than a thin film. Furthermore, due to the unique catalytic properties of Pd, Y hydrogenation with other capping materials has not been studied.

In this paper, we present an investigation of the dependence between the stability of YH_3 and the capping layer material. We propose that the observed (measured) dissociation temperature of YH_3 is more properly associated with the desorption temperature of hydrogen from the surface of the capping layer. In our model, the dissociation temperature of YH_3 is lower than room temperature, however, if the hydrogen cannot escape from the surface, hydrogen diffusion is blocked and, thereby, the YH_3 phase is stabilized. As a result, YH_3 dissociation only occurs at temperatures above the H_2 surface desorption temperature of the capping layer.

2. Experimental procedure

All samples were deposited using DC magnetron sputtering. Sputter deposition took place in a vacuum chamber with a base pressure of 10^{-8} mbar using Y, Ru, Pd, and Ta targets with a purity of 99.95%, and Ag and C targets with purities of 99.99% and 99.999% respectively. Silicon (100) wafers, precut 15×15 mm, were coated with 70 nm of Y and then covered with a capping layer of Ru, Pd, Ag or Ta. To protect the cap metal from oxidation, 5 nm of carbon was sputtered onto the Ta and Ag capped samples, which was later removed by hydrogen radicals during the hydrogenation experiment.

After deposition, the thickness, roughness, and crystallinity of the deposited layers were measured using X-ray reflectivity (XRR), atomic force microscopy (AFM) (Bruker, Dimension Edge), and X-ray diffraction (XRD) (Panalytical Empyrean). XRD and XRR were performed using Cu-Kα radiation with a wavelength of 0.154 nm. For XRD measurements, a parafocusing geometry was chosen with a 0.2 mm fixed divergence slit and a Ni filter for the incident beam, and a scanning line detector to obtain a higher diffracted intensity and an increased signal to noise ratio. A cross-sectional analysis of a Ru capped Y sample was provided by a High Resolution Transmission Electron Microscope (Philips CM300ST-FEG Transmission Electron Microscope, MESA+ Nanolab at University of Twente). TEM specimens were prepared by dimple grinding/polishing and argon ion etching [11].

Hydrogenation experiments were performed in a vacuum chamber with a base pressure of 1×10^{-7} mbar and a hydrogen pressure of 1.3×10^{-2} mbar. For all samples, a constant flow of hydrogen radicals was used. Hydrogen radicals were generated by flowing molecular hydrogen (108 sccm) past a W filament, placed about 5 cm from the sample surface, and heated to 2000˚C, as measured by an infrared temperature sensor (Raytek, RayMR1SCCF). Although Pd can dissociate molecular hydrogen, the H_2 splitting efficiency of a hot W filament is much higher, thus, hydrogenation

occurs faster in the latter case. The hydrogen radical flux was estimated from the etch rate of a carbon film to be 10^{18} at/cm^2/s [12]. The sample temperature was monitored using a K-type thermocouple, and maintained at 30-40°C by water cooling.

Hydrogenation of Y was monitored using *in situ* spectroscopic ellipsometry (Woollam M-2000XI) at an angle of incidence of 75° and a spectral range of 240-1600 nm. Exposure to H-radicals was stopped when the ellipsometric angles Ψ and Δ stabilized after a rapid change. The exposed samples were removed from the vacuum and tested with XRD, to characterize the hydride content.

Samples that formed a stable YH_3 phase after hydrogenation were heated in a nitrogen atmosphere on a hot stage of the Cu-K diffractometer and the dissociation temperature of YH_3 was measured. Heating was limited to temperatures below 350°C, as heating to higher temperatures initiated oxidation of the Y film. The temperature was increased in 10 degree steps, and at each step XRD spectra were measured until no change in diffraction pattern was observed. The temperature at which the (002) peak of YH_3 started to decrease was noted as YH_3 dissociation temperature.

3. Results and discussions

3.1. Pre-characterization

The thicknesses of the Y films and capping layers were determined using XRR. Typical values are shown in Table 1. Overall, Y thickness for all samples was 70 - 80 nm and the thickness of single caps was 3 - 4 nm. Note, that the protective carbon layer on the Ag cap is significantly thinner than the targeted thickness, which may indicate the intermixing of Ag and C. In the case of the Pd/Ru cap, the thickness of Ru has to be increased to prevent the direct contact between Y and Pd. It is also important to note that fitting XRR spectra for Pd/Ru sample was challenging, because Ru and Pd have low contrast for hard X-rays.

The XRD spectra of all samples only contain peaks associated with the Y film (and Si substrate), as the peak intensity of the thin capping layer is negligibly small in θ-2θ geometry. The Y peaks of all as-deposited samples appear to be the same, therefore, only the XRD spectra of a Ru capped Y film is shown in Figure 1. The vertical lines indicate tabulated Bragg peaks for powders. The peaks are shifted with respect to the tabulated values due to film stress. The small peak around 33˚ originates from the Si monocrystalline substrate. It is observed that Y, grown on crystalline Si, is poly- or nanocrystalline with (002) and (100) preferential growth directions. The minimal crystallite size was estimated using the Scherrer relation [13]:

$$d = (0.94\,\lambda)/(w\,cos\theta),$$

where *w* is the full width at the half maximum of the XRD peak, λ – the radiation wavelength, and θ – the diffraction angle. The calculated Y crystallite size (in the direction normal to the sample surface) was estimated to be no less than 15 nm.

The surface of a typical sample is fairly smooth, as can be concluded from an AFM scan (Figure 2), with root mean square roughness of 0.6 nm.

Bright field HRTEM images are shown in Figure 3. The image shows that a thin amorphous intermixing layer is formed on the Ru/Y interface (visible by its brighter contrast compared to pure Ru, image 1). At the Y/Si interface, a 4 nm thick amorphous interface layer is formed (image 2). Its formation was probably induced by the reaction of Y with O that was contained in the native Si oxide layer, since Y oxide has a low enthalpy of formation. The orientation of the Y crystallites confirms the XRD findings, but the measured d-spacing of 3.06 Å indicates that the Y film is fully oxidized in the process of TEM specimen transfer and preparation.

3.2.Results

Samples were exposed to hydrogen radicals until no further change in ellipsometric angles Ψ and Δ were observed. Figure 4 shows the time evolution of the ellipsometric angle Ψ at a wavelength of 791 nm during hydrogenation for samples with different capping layers. Depending on the sample, the following features are observed. For Ta and Ag capped samples, Ψ first increases as the carbon layer is removed by H*. Likewise, for samples with Ru and Pd top surfaces, the first Ψ changes (a decrease in this case) are due to the removal of the native oxide layer. After the removal of the protective coating, H may diffuse through the capping layer to reach the Y film and the formation of YH_2 starts, which may then be followed by the formation of YH_3. The transitions for Ru and Ta caps show similar dynamics, while almost no change in Ψ for samples with a Ag cap could be detected after a long exposure to H* (see Figure 4).

After no change in the SE signal was registered, which suggests that the Y film is saturated with hydrogen, samples were transferred to the Cu-K diffractometer and their XRD spectra were measured under ambient conditions (Figure 5). The diffraction patterns for both the Ru and Ta capped samples contain diffraction peaks of both a dominant YH_3 (002) phase, and a weak YH_2 (111) phase. On the other hand, the samples with Pd and Pd/Ru caps have a strong YH_2 peak along with some traces of a YH_3 (002) peak. The sample with Ag cap remains unchanged (comparing to before exposure, Figure 1) except of the shoulder of the Y (002) peak, which may indicate that a minor amount of YH_2 is formed.

The growth of the YH_3 crystallite size for Ru capped samples was investigated in more detail. According the Scherrer equation, the YH_3 crystallite size was 33.2 nm, which is more than twice the deposited Y film crystallite size. This change in crystallite size is not due to lattice expansion after incorporating hydrogen, as the increase of the unit cell volume due to hydrogenation is only 12%. The increase in unit cell volume, however, closely matches XRR measurements, which show that the thickness of the Y film increases by 15% after hydrogenation. The growth of the crystallites is, thus, much larger than the film thickness growth, which evidences that hydrogenation leads to ordering of crystallites. Notably, the same rearrangement of crystallites in

the Y film is observed for all types of samples where saturation to YH_2 or YH_3 phase was possible. This suggests that crystallite ordering already happens during the Y-YH_2 transition.

The YH_3 dissociation temperature was measured by heating the samples and measuring the changes in the XRD pattern. It was observed that YH_3 in Ru capped samples dissociated at 423 K, while, for Ta, the YH_3 dissociation temperature was above the maximum that could be achieved in our experimental apparatus. For Ag and Pd capped samples, YH_3 was not stable at room temperature, which was the minimum our setup was capable of. The intensity of the YH_2 (111) and YH_3 (002) peaks as a function of temperature is shown in Figure 6 for the case of a Ru cap. The hydrogen desorption temperature for the Ru surface [14] is close to the dissociation temperature of YH_3 that we obtained, while the desorption temperature for Ta is much higher than the temperature limit of the setup (see Table 2).

4. Summary and Conclusions

In this work, we studied the hydrogenation of thin Y films, coated with different materials. In the case of a Ag capping layer, no significant hydrogenation was observed. This may be due to the high desorption rate of hydrogen from the Ag surface at room temperature. For other samples the stable Y hydride phase was analyzed. For both Pd and Pd/Ru caps, the thermodynamically favorable YH_2 phase was formed, while a stable YH_3 phase was obtained for the cases of Ru and Ta caps. The samples with a YH_3 phase that was stable at room temperature were heated in an N_2 atmosphere to measure the temperature of YH_3 dissociation. The dissociation temperature for the Ru/YH_3 sample was 423 K, while the dissociation of YH_3 was not reached for the Ta capped sample due to the limited maximum temperature of the experimental setup (T_{max} = 623 K). We note that the measured dissociation temperature for Ru/YH_3 is close to the reported temperature of hydrogen desorption from a Ru surface. We also noted that the desorption of hydrogen from Ta is reported to occur at 775 K, [15] which is higher than the experimental setup allowed.

The formation (or lack of formation) of YH_3, depending on the cap layer provides reasonable evidence that the observed dissociation temperature of YH_3 is actually controlled by desorption of hydrogen from the capping layer surface. This evidence is strengthened by the observation that Pd-capped Ru/Y does not have a stable YH_3 phase at room temperature. If the direct interaction between the YH_x phase and the cap-layer were the (de-)stabilizing factor, then Ru should stabilize YH_3 even when the Ru is capped with Pd. On the other hand, if YH_3 thin films are unstable at (or below) room temperature, then a stable YH_3 phase should not be observed in any of the samples.

During YH_3 dissociation, hydrogen will leave the thin film via diffusion from the surface. At equilibrium, the flux of hydrogen exiting the thin film will balance hydrogen production via dissociation. However, if hydrogen binds to the capping layer surface, the net flux will drop to zero. In this case, YH_3 dissociation will form an equilibrium with the hydrogen dissolved (or trapped) in the surrounding material (YH_x and capping material). The small volume of dissolved

hydrogen in the capping material and the low solubility of hydrogen in YH_x imply that the majority of hydrogen must remain bound to Y to form YH_3. As a result, we conclude that the apparent stability or instability of YH_3 is, in case of thin films, governed by the surface desorption temperature of the capping layer.

Note

Declarations of interest: none.

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Figures

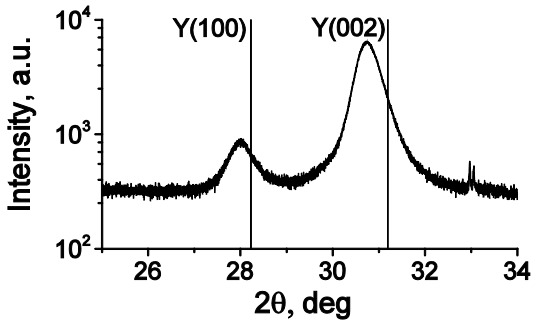

Figure 1. XRD spectra of a typical as-deposited sample of 70 nm Y capped with 3 nm Ru.

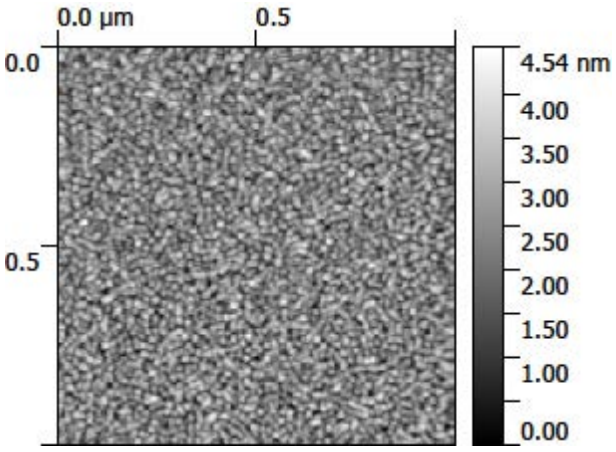

Figure 2. AFM picture of the surface of a 3 nm Ru/70nm Y sample.

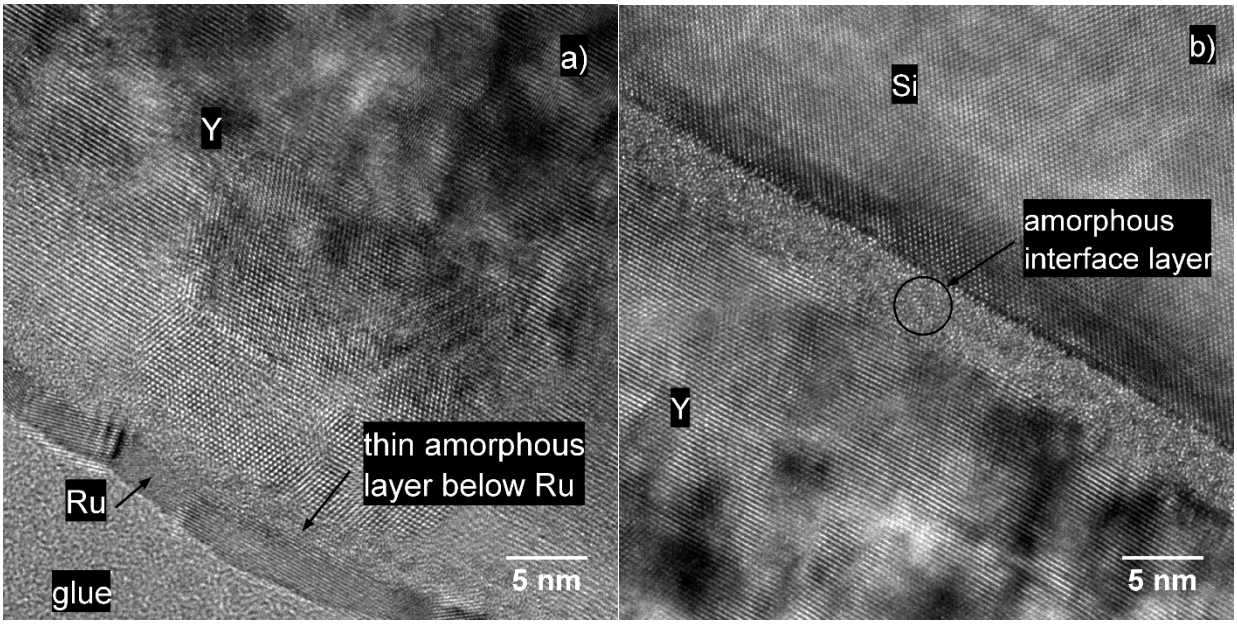

Figure 3. HRTEM of 3Ru/70Y: a) Ru/Y interface, b) Y/Si interface

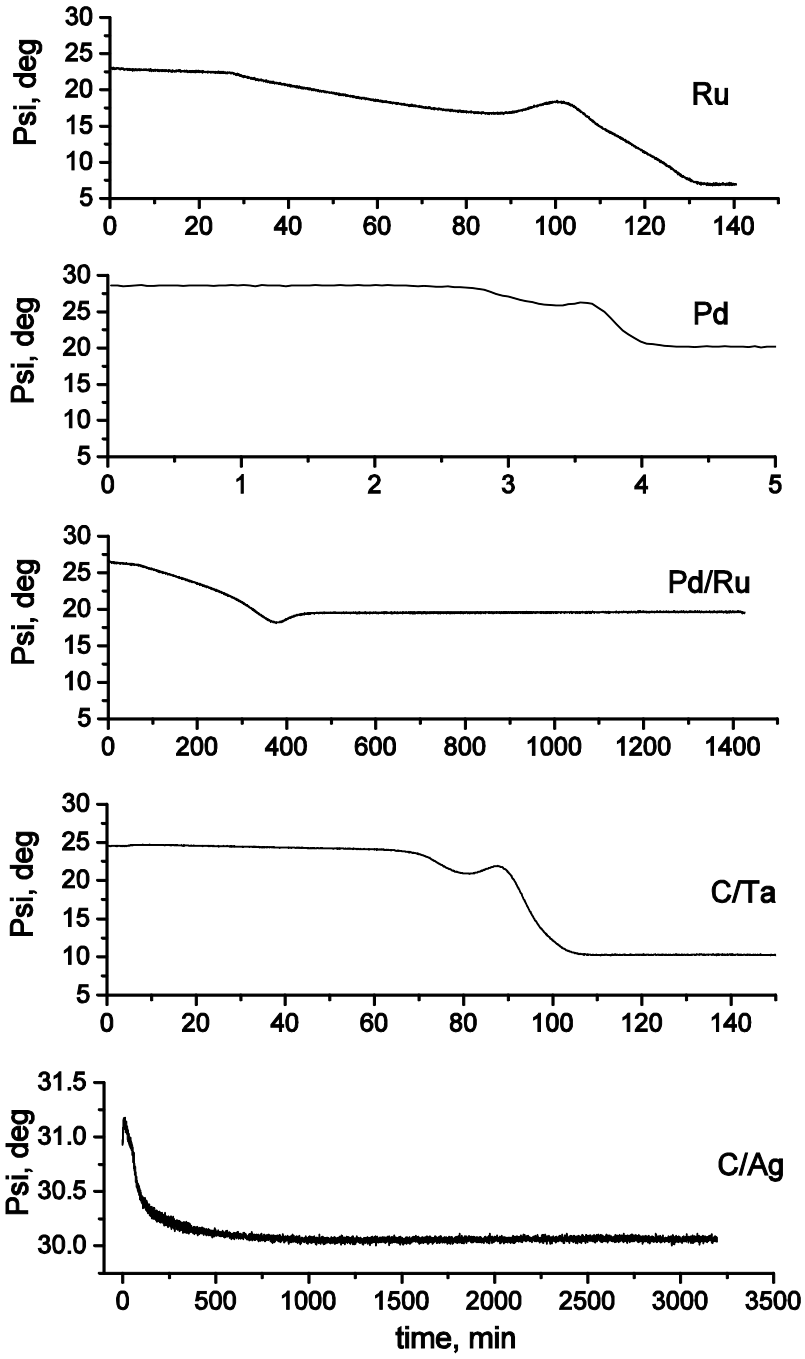

Figure 4. Time evolution of ellipsometric angle Ψ for all samples at a wavelength of 791 nm during exposure to hydrogen radicals. The name of the capping material is indicated on each graph (note that the large difference in Ψ -axis scale for Ag capped sample). The W filament was switched on at time 0 and remained on till the end of the measurements shown on the figure.

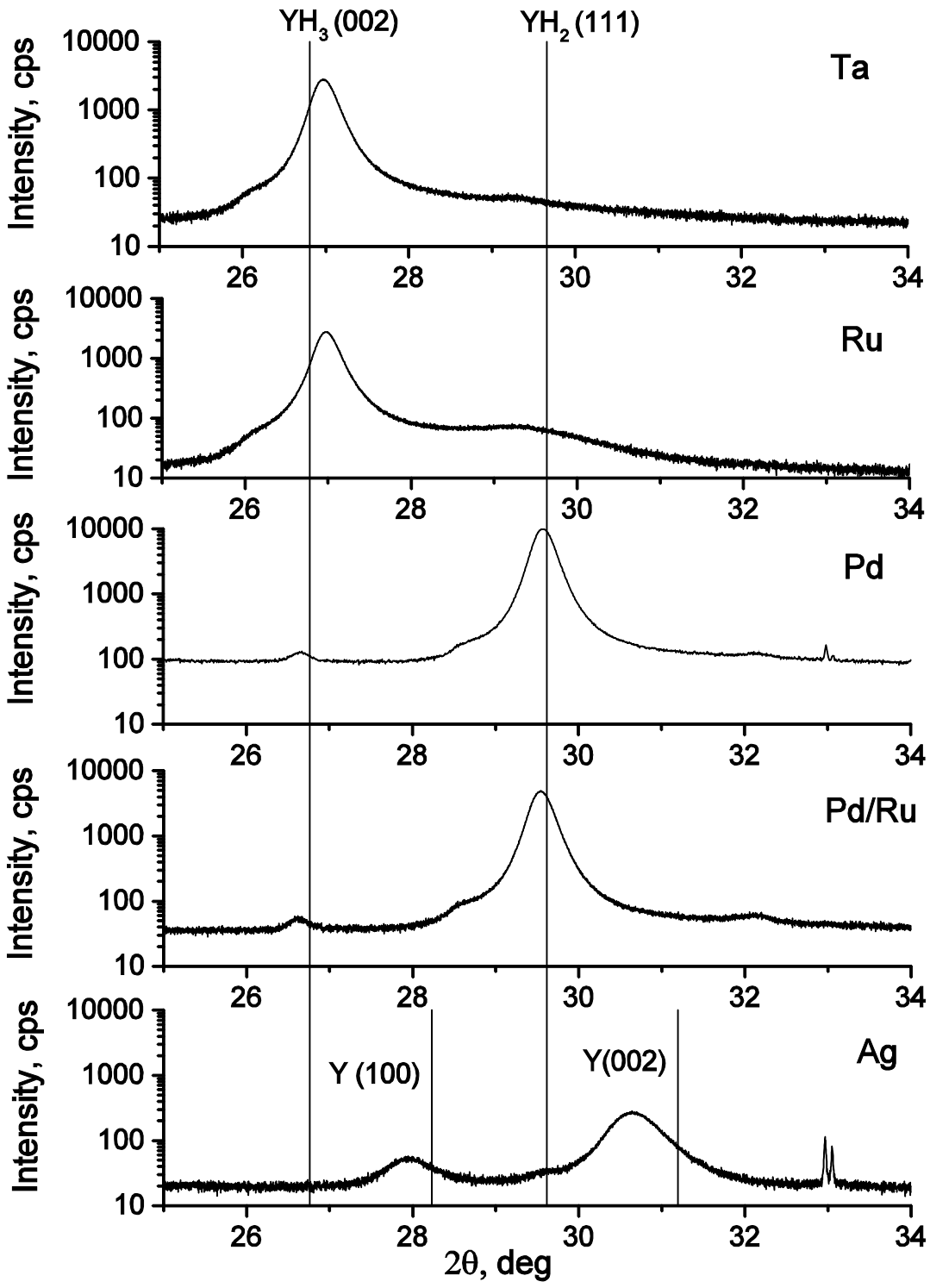

Figure 5. XRD spectra of hydrogenated samples with different capping layers. The lines indicate the tabulated peaks for powders.

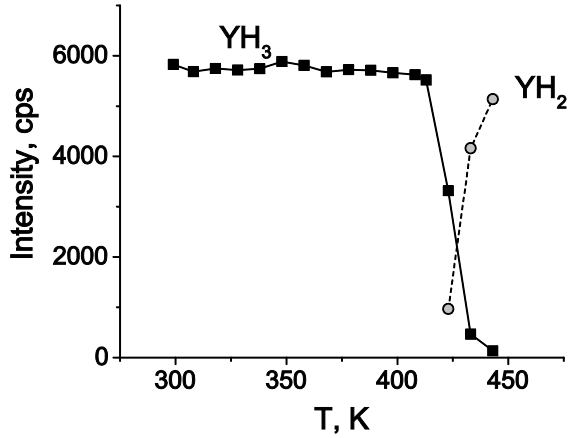

Figure 6. Intensity of the diffraction peak (002) of YH_3 and (111) of YH_2 for a Ru/Y sample versus the temperature.

Tables

Table 1. Thicknesses (in nm) of Y and capping layers for all sample types.

Caps / Thicknesses	Ta	Ru	Pd/Ru	Pd	Ag
Y	73.6	72.4	79.7	72.3	70.2
Cap	3.8	2.9	4.4/5.4	4	3.4
Carbon layer	5	-	-	-	3.6

Table 2. Desorption temperatures of hydrogen for capping materials and dominant yttrium hydride phase of the corresponding hydrogenated sample

	Ta	**Ru**	**Pd/Ru**	**Pd**	**Ag**
YH_x of saturated sample	YH_3	YH_3	YH_2		No hydride
Hydrogen desorption temperature of topmost capping layer, K	775[1]	410[2]	293 (weakly bounded H)[3]		160[4]

[1] Ref. [15]

[2] Ref. [14]

[3] Ref. [16]

[4] Ref. [17]