Hydrogenation dynamics of Ru capped Y thin films

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ABSTRACT

The structural changes in Ru-coated Y films during hydrogenation were studied in this work. *In situ* XRD data were used to show that the Y to YH₂ transition requires significant hydrogen loading of the Y lattice. By comparing the XRD data with the *in situ* spectroscopic ellipsometry data, an effective medium model for the transition was obtained. This model describes the Y to YH₂ transition well. The YH₂ to YH₃ transition is also described by an effective medium model, however, with reduced accuracy around the midpoint of the transition. By comparing the YH₂ and YH₃ crystal sizes, we show that these deviations may be due to a surface plasmon resonance. The improved understanding of the ellipsometry measurements is important for optical hydrogen sensing applications.

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I. INTRODUCTION

When hydrogenation of thin layers of Y was studied for the first time, metal-insulator switching during the transition of YH₂ to YH₃ was discovered.¹ This optical change upon hydrogenation has found application in many fields, but with a particular emphasis on hydrogen sensing. Many Y-based sensors have been developed for hydrogen gas detection^{2–4} and the measurement of hydrogen diffusion in metals.⁵ These sensors have the advantage of using optical techniques to monitor the change in the hydrogen concentration. This avoids the necessity for electrical connections to the sensor and associated safety risks in the presence of oxygen-hydrogen mixtures.^{6,7}

A common feature of yttrium-based H-sensors is the presence of a Pd protective layer. In addition to protecting the yttrium from oxidation, the Pd coating adsorbs and dissociates molecular hydrogen, which is then released as atomic hydrogen into the Y film. It is possible to reach the YH₃ phase in a Pd/Y stack by varying the applied hydrogen pressure, though it dissociates back to a stable YH₂ phase when the hydrogen supply is switched off.⁸ This happens because (i) the YH₂ phase is thermodynamically more stable than YH₃⁹ and (ii) the desorption temperature of hydrogen from the Pd surface is close to room temperature.¹⁰ In a previous study, we demonstrated that a Ru protective layer, with a higher hydrogen desorption temperature, can stabilize YH₃ at lower applied hydrogen flux

and/or pressure. In order to exploit both the Y to YH₂ and YH₂ to YH₃ transitions for sensing hydrogen at lower pressures, it, therefore, can be an advantage to use Ru as a protective material. In addition, it is also desirable to study hydrogen diffusion through layers of other materials. In the case of a Ru protective cap layer, however, an atomic hydrogen source is needed to achieve hydrogenation of Y. Atomic H reduces native RuO₂ on the Ru surface, which would otherwise inhibit hydrogen diffusion. In this article, we analyzed the hydrogenation of a Y film, covered by a Ru layer, which is exposed to a flux of atomic hydrogen.

Ruthenium coated yttrium films are used to understand the optical properties of Y as a function of hydrogen loading, structural changes during the hydrogenation and dehydrogenation processes, and thermodynamics and kinetics of Y hydrogenation. In the previous work,¹⁰ it was shown that the YH₃-YH₂ transition is strongly influenced by the surface binding energy of hydrogen on the surface of the protective material on top of the Y film. The optical properties of the sensor may also be influenced by, for instance, the crystallinity of the different Y (hydride) phases and lattice expansion.

In most cases, the hydrogen concentration in a Y film is obtained by measuring its transparency.^{11,12} However, this requires a transparent substrate, reducing the optical contrast between the YH₃ film and the substrate near saturation. The lack of contrast between the film and its substrate complicates extracting the film's dielectric

constants, which leads to increased uncertainty in the hydrogen concentration. To resolve these difficulties, spectroscopic ellipsometry (SE) could be used, which is known to be highly sensitive to the optical properties of both dielectric and metallic films. Therefore, SE is an ideal candidate to increase the sensitivity to hydrogen diffusion for hydrogenation states up to YH_2 (where yttrium hydride is metallic), as well as to increase the accuracy of quantification during the YH_2 to YH_3 transition. Furthermore, by using a high-contrast substrate such as silicon, the optical properties of YH_3 near saturation are easier to obtain.

Though there are numerous works on Y hydrogenation,^{8,13–16} only a few of them used ellipsometry to monitor the process.^{8,16} To our knowledge, none of the published data include the dynamics of the phase transition, but instead focus on the beginning and end points of hydrogenation. For a sensor application, however, it is important to understand the structural changes in the Y film during the hydrogenation process and their impact on the ellipsometry signal.

One possible reason for the lack of dynamic ellipsometry data is that analysis is complicated by multiple processes occurring in parallel. It is difficult to obtain a realistic solution to the inverse problem without a reliable model containing film thicknesses and dielectric constants of the layers in the sample. To address this challenge, we combine *in situ* SE with *ex situ* and *in situ* X-ray diffraction (XRD), and *ex situ* X-ray reflectivity (XRR) to obtain a detailed picture of the film's structural changes. The combination of *in situ* and *ex situ* techniques allows data to be captured during hydrogen in-diffusion and during the phase transformations from Y to YH_2 and YH_2 to YH_3 .

FIG. 1. Time evolution of the ellipsometric angle Ψ for a 70 nm Y film, coated with 3 nm of Ru, during exposure to atomic H [time axis is vertical for ease of comparison to subfigure (b)]. The five displayed wavelengths are evenly distributed over the detected spectrum. Five identical samples were exposed to hydrogen until the indicated times in graph (a). The *ex situ* XRD spectrum for each sample is shown in graph (b), starting with an unexposed sample (1) and finishing with a maximally saturated sample (5).

In this work, an ellipsometric model is developed for the entire Y hydrogenation process. Based on the XRD and XRR data, the optical signature of YH_2 and YH_3 formation was identified in the ellipsometry measurements. This allows for the construction of an accurate ellipsometric model for the transition from Y to YH_2 , and a qualitatively accurate model for the YH_2 to YH_3 transition. The combination of methods reveals insight into why the Y- YH_2 phase transition is delayed with respect to the start of hydrogen exposure. In addition, a possible local surface plasmon resonance in the YH_2 - YH_3 transition is revealed, which limits the accuracy of our present model to describe the YH_2 - YH_3 transition.

II. METHODS

To study Y hydrogenation, a series of samples were prepared using DC magnetron sputtering in a vacuum chamber with a base pressure of 10^{-8} mbar. Si (100) single crystal substrates of $15 \times 15 \text{ mm}^2$ size were coated with 70 nm of Y and 3 nm of Ru using Ru and Y targets with a purity of 99.95%. The surface roughness and sample structure were characterized by atomic force microscopy (AFM) (Bruker, Dimension Edge) and XRR (Malvern PANalytical Empyrean).

Hydrogenation of Y was monitored by *in situ* spectroscopic ellipsometry (Woollam M-2000XI) at an angle of incidence of about 75° and a spectral range of 240–1600 nm. Samples were exposed to atomic hydrogen in a vacuum chamber with a base pressure of 2×10^{-8} mbar. Hydrogen species were generated by passing 100 sccm of H_2 over a W filament heated to 2000 $^\circ\text{C}$, which was placed at 4 cm from the sample surface. The temperature of the filament was measured using an infrared temperature sensor (Raytek, RayMR1SCCF). The sample temperature was maintained below 40 $^\circ\text{C}$ with a water-cooled sample holder. The hydrogen flux increased the chamber pressure to 2×10^{-2} mbar during exposures. The flux to the sample surface was calculated to be $10^{18} \text{ at}/(\text{cm}^2/\text{s})$ after measuring the etch rate of a carbon layer (following the method of Braginsky *et al.*¹⁷). Atomic hydrogen exposure efficiently reduces the native oxide of the Ru cap of the Y film.¹⁸ Therefore, it is expected that the Ru oxide film is fully reduced during measurements of the hydrogenation of Y. Maximum hydrogenation was assumed to be achieved when the ellipsometric angles Ψ and Δ restabilized after a rapid and large change.

For the first set of ellipsometry measurements, exposure to atomic hydrogen was stopped at various moments during hydrogenation (28, 53, and 59 min). The exposed samples were removed from the vacuum, and XRD (Malvern PANalytical Empyrean) was used to obtain the crystalline structure of the yttrium/yttrium hydride layer. XRD measurements were performed in a θ -2 θ geometry using $\text{Cu-K}\alpha$ radiation (0.154 nm). Since the Ru capping layer stabilizes the YH_3 phase, it is possible to perform *ex situ* XRD on partially and fully saturated samples.

In situ XRD measurements during hydrogenation and dehydrogenation were performed using the BM 25 (SpLine) beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble. A small vacuum chamber (base pressure 6×10^{-6} mbar) was installed at the first focus point of branch B.¹⁹ XRD was performed using a photon energy of 20 keV. *In situ* measurements were made in a θ -2 θ

geometry, using a scan range that encompassed the Y (100), Y (002), YH₂ (111), and YH₃ (002) peaks. Each scan took approximately 3 min. Also, in-plane Grazing Incidence x-ray Diffraction (GIXRD) measurements with a fixed incident angle (higher than the critical angle) were performed in the same 2 θ range. Similar to the ellipsometry measurements, hydrogen exposures were performed by flowing molecular hydrogen past a W filament, placed 4 cm from the sample surface. To ensure that hydrogenation was slow compared to the scan time, the chamber pressure during exposure was limited to 5×10^{-3} mbar by reducing the hydrogen flow. The filament temperature was set to 1850 °C using a pyrometer (MAURER, KTR 1075-1-L). Dehydrogenation of YH₃ was achieved by switching off the hydrogen supply and heating the sample with a heater that was built into the sample holder.

III. RESULTS

A. Ellipsometry and *ex situ* XRD

The typical time evolution of the ellipsometric angle Ψ for a Ru/Y sample is shown in Fig. 1(a). The ellipsometry data are compared to the XRD data obtained from a set of identical samples that were partially exposed. This comparison is used to determine the intermediate states of Y hydrogenation. The exposure times indicated by the lines marked 1 through 5 correspond to the times when the exposure to hydrogen of the different samples in the set was interrupted. The as-deposited sample corresponds to state 1, and state 5 is the maximally hydrogenated sample. The XRD spectra show that the observed changes in Ψ are indeed caused by the formation of YH₂ and YH₃ [Fig. 1(b)]. The fully hydrogenated sample still has a small fraction of the YH₂ phase [subplot 5 of Fig. 1(b), note the logarithmic scale], which was observed in prior research.²⁰ The integrated intensity of the YH₂ (111) peak for a maximally hydrogenated sample is only 7% of the maximum integrated intensity of the YH₂ (111) and YH₃ (002) peaks, which corresponds to YH_{2.9}. This estimate is somewhat higher than the values reported elsewhere, possibly due to the stabilizing effect of the Ru layer.¹⁰ Once formed, the YH₃ phase stays stable under the Ru cap at the room temperature. Note that the location of the Y peaks of the as-deposited sample is shifted, which is a result of the film stress.

B. *In situ* XRD

In order to understand the formation and dissociation of the YH₃ phase, Ru-capped samples were investigated *in situ* with XRD at SpLine, ESRF. The evolution of the X-ray diffraction pattern during hydrogenation [Fig. 2(a)] and dehydrogenation [Fig. 2(b)] was recorded. Hydrogenation is started by switching the W filament on. Due to vicinity to the W filament, the sample was also heated to about 340 K during hydrogenation, which is indicated below the 2 θ plot of Fig. 2(a). Regardless of the different temperatures and hydrogen pressures, the Y hydrogenation recorded with *in situ* XRD [Fig. 2(a)] and SE [Fig. 1(a)] have similar trends in 2 θ peaks shifts and SE angle evolution, respectively. The *ex situ* XRD measurements show that there is some remaining YH₂ at the end of the transition [Fig. 1(b), subplot 5], while a complete transition to YH₃ is seen in the *in situ* experiment. The difference in end

hydrogenation states is caused by some release of hydrogen during transportation of samples in air from the H exposure chamber to the diffractometer.

Following saturation, the temperature was gradually increased from 300 K until dehydrogenation started, which corresponded to a temperature of 410 K [see Fig. 2(b)]. As discussed previously,¹⁰ this temperature is an activation temperature for the desorption of hydrogen from the Ru surface. Note that the phase transition from YH₂ to YH₃ occurs faster than the reverse transition {5 min for hydrogenation [Fig. 2(a)], compared to 20 min for dehydrogenation [Fig. 2(b)]}, even when the temperature is above the threshold temperature. A similar slower speed of dehydrogenation compared to hydrogenation has been observed in Pd-capped Y systems and was attributed to stress in the film and the kinetics of structure transformations.¹⁵ However, for Ru-capped Y films, the lower rate of hydrogenation is not only due to film stress but also due to the higher surface desorption temperature of hydrogen from ruthenium.^{10,21}

As hydrogenation begins, the lattice slowly expands, but there is no evidence of YH₂ formation. This is clearly visible in Fig. 2(a) where from 0 to 20 min the Y (002) XRD peak shifts from 12.26° to 12.05°. Such a shift is significantly larger than expected from thermal expansion (heating by 40 K would result in a 2 θ shift of 0.005°), and is most likely caused by the presence of interstitial hydrogen expanding the Y lattice. Thus, crystalline YH₂ formation takes place after the Y lattice is at least partially loaded with hydrogen. However, the enthalpy of formation for YH₂ is negative and the applied hydrogen pressure and flux of atomic H are sufficient to be above the plateau pressure for saturating the Y film to YH₃ in equilibrium conditions, implying that YH₂ should form continuously.

It is likely, however, that the formation of isolated YH₂ in a Y crystal structure is energetically unfavorable due to the increase in the surface energy of both Y and YH₂ at the interface formed between the two. On the other hand, the energy in the film increases due to the strain imposed by lattice expansion. Hence, the transition from Y to YH₂ only begins when the increase in energy due to the elastic strain exceeds the increase in energy due to the interface formed between Y and YH₂. The strain energy of the Y lattice is used to estimate a pseudoactivation energy for the formation of the Y/YH₂ interface. The elastic energy equals $U = \frac{1}{2} E \left(\frac{\Delta d}{d} \right)^2$, where E is Young's modulus, $E = 63.5$ GPa,²² d is the initial lattice constant of Y, and Δd is the difference in the Y lattice constants between the beginning of exposure and before the YH₂ formation. A calculation yields an elastic energy of 2.1 eV/at. along the (002) diffraction plane. This implies 2.1 eV for the interface formation between Y and YH₂.

Since the enthalpy of YH₂ formation is -2.25 eV/at. H,²³ the phase transition proceeds rapidly once the energy stored in the lattice is sufficient to initiate the transition. The enthalpy of YH₃ formation is only slightly lower at -2.54 eV/at.²³ The formation of the YH₃ phase is twice as fast as for YH₂ with no evidence of lattice expansion: it only takes about 6 min, compared to 12 min for the Y to YH₂ transition (not including the time of Y lattice expansion). This can be expected when both transitions are limited by H flux diffusing through Ru (since half of hydrogen is required for the YH₂ to YH₃ transition in comparison to Y to YH₂). Hence, it can be concluded that diffusion through Y, YH₂, and YH₃ is not a rate-limiting step.

FIG. 2. Time evolution of *in situ* XRD spectra for a 70 nm Y film, coated with 3 nm of Ru, during hydrogenation (a) and dehydrogenation (b). Horizontal lines indicate the tabulated diffraction angles for a Y powder. The lower subplots show the sample temperature during (de)hydrogenation.

It should also be noted that XRD measurements are only sensitive to the presence of crystalline phases. Hence, from XRD alone we cannot exclude the formation of intermediate amorphous YH₂ and YH₃ phases. Ellipsometry is sensitive to the formation of amorphous phases, because the optical properties of amorphous materials are different from the crystalline polymorphs of the same chemical composition. We discuss the possibility of the existence of amorphous YH₂ and YH₃ phases in Sec. III C.

To better understand the growth and decay of the crystallites in the film, θ - 2θ XRD measurements were complemented with in-plane 2θ Grazing Incidence x-ray Diffraction (GIXRD), the combination of which allowed probing the atomic planes in two orthogonal directions: in-plane and normal to the sample surface. To obtain the crystallite size, the XRD peaks were fitted with a pseudo-Voigt function. The extracted parameters, such as the peak position and FWHM, are plotted as a function of time in Figs. 3(a) and 3(b). Since the crystallites in (a) and (b) are probed in perpendicular directions, YH₃ peaks that are produced by mutually perpendicular atomic planes, (002) and (100), are observed. It should be noted that, due to the (111) preferred orientation (normal to the sample surface) of the YH₂ phase, the YH₂ peak is not present in the in-plane GIXRD measurement. Both θ - 2θ (a) and GIXRD (b) measurements confirm that the lattice expands in the (002) direction to a greater extent [see Figs. 3(a) and 3(b)], which is in line with earlier neutron scattering experiments.^{24,25} Using the Scherrer equation,²⁶ the crystal sizes were calculated from the FWHM values and are shown in Figs. 3(c) and 3(d). The average crystal size rapidly increases after the transition from Y to a hydride phase.

The XRD data reveal several necessary elements required for an ellipsometry model. The hydrogen loading before the YH₂ transition will cause a minor modification in the Y optical properties. The lack of YH₂ lattice expansion indicates that no significant hydrogen loading is required for the YH₃ transition. However, it is known that the optical properties of the Y-H system strongly

change with the hydrogenation state between YH_{1.9} and YH_{2.1}. Thereby, we take the YH_{1.9} state as end point of the Y-YH₂ transition as observed by XRD and verify that the ellipsometry spectra can be fitted with literature data of the dielectric function of YH_{1.9}, as will be further detailed in Sec. III C. We will still refer to this phase as YH₂ for simplicity.

C. Ellipsometry modeling

Let us now focus on the interpretation of the ellipsometry data obtained during hydrogenation. Figure 4 shows the time evolution of the ellipsometric angles for the Ru capped Y film during atomic H loading. When considering the entire hydrogenation process, we take into account only two processes that lead to a change of the reflectance, namely, the removal of native ruthenium oxide²⁷ and the formation of yttrium hydrides. The large optical contrast between Y, YH₂, and YH₃ dominates the reflectance change and, once the Y to YH₂ transitions begin, we attribute all changes in the reflectance solely to transformations of the yttrium (hydride) layer. However, due to ruthenium oxide removal and Y lattice expansion, small changes of reflectance (first 30 min in Fig. 4) happen before YH₂ starts to form. Since ellipsometry is most sensitive to the topmost layer of metal-coated samples, even small changes on the surface of a Ru cap will affect the reflectance. Therefore, the initial removal of RuO₂ should not be neglected. The observed Y lattice expansion is assumed to have a smaller impact on the reflectance and, therefore, is not taken into account by the model. To successfully model the hydrogenation of Y, we divide the process into three ranges (Fig. 4). The thicknesses of Ru and Y layers were obtained from XRR to be 3 and 68 nm, respectively, and assumed constant throughout first two ranges. The Y thickness was set as a free parameter for the YH₂ to YH₃ transition (the 3rd range). When representing a layer as a mixture of phases/materials in each range, an effective medium

FIG. 3. Time evolution of XRD peak positions for a 70 nm Y film, coated with 3 nm of Ru, during hydrogenation in θ - 2θ (a) and in the in-plane grazing incidence geometry (b). The time evolution of the crystallite size, calculated from the peak width, is shown in (c) and (d). The time of hydrogenation is different due to the different hydrogen pressures: [(a) and (c)] 3×10^{-3} mbar and [(b) and (d)] 1.6×10^{-2} mbar.

approximation (EMA) is used in a Bruggeman analysis mode. Optical constants for RuO_2 , Y, and YH_2 were obtained from prior studies.^{28,29} Van Ghogh *et al.*²⁸ have published optical constants for YH_3 . But due to the lack of contrast between YH_3 and the glass substrate in Van Ghogh's experiment, the dielectric constants (even when including a non-zero fraction of YH_2) could not reproduce the SE measurements in this work. Indeed, the variation in maximum hydrogenation between different published results makes it difficult to obtain a reliable optical model for YH_3 . Hence, we chose not to use published optical models for YH_3 .

The effective optical constants for Ru and YH_3 were obtained from b-spline fits. It is known that RuO_2 is reduced under atomic hydrogen flux²⁷ and we assume that range I in Fig. 4 corresponds mainly to RuO_2 reduction. Thus, the end of range I corresponds to a metallic Ru layer.

A b-spline fit to the ellipsometry spectrum, using the model shown in the first row of Table I, yields effective optical constants for Ru. These constants, and the thickness of the Ru layer, are not changed for the remainder of the modeling procedure. After the optical constants for Ru are obtained, the optical constants for YH_3

are obtained by performing the same fitting procedure at the end of the hydrogenation procedure. In this case, we use the model from the second row of Table I. The best fit is obtained for a YH_3 thickness of 78 nm, which is consistent with the calculated volumetric lattice expansion of 12%.¹⁰ To investigate the reliability of the obtained dielectric function, the b-spline dielectric function for YH_3 was then parametrized using the sum of two Tauc-Lorentz oscillators (see Fig. 5). The Tauc-Lorentz oscillator is given by³⁰

$$\epsilon_2 = \begin{cases} \frac{AE_0 B(E-E_g)^2}{(E^2-E_g^2)^2 + B^2 E^2} \cdot \frac{1}{E}, & \text{where } E > E_g, \\ 0, & \text{where } E \leq E_g, \end{cases} \quad (1)$$

$$\epsilon_1 = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \epsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi, \quad (2)$$

where ϵ_1 and ϵ_2 are real and imaginary parts of a dielectric function, respectively, A is the oscillator amplitude, B is the broadening

FIG. 4. Ellipsometric angles Ψ (a) and Δ (b) for a 70 nm Y film, coated with 3 nm of Ru, during hydrogenation. The whole hydrogenation process is divided into three ranges: I—reduction of ruthenium oxide, II—the transition from Y to YH_2 , and III—transition from YH_2 to YH_3 . The fit of the Ru optical constants is done at the time labeled with A. Time B corresponds to the point when the dielectric constants of the YH_3 phase are extracted from the fit (see the text for further explanation). A schematic of the layered model used for fitting within each range is shown above the corresponding range.

term of the peak, E_0 is the peak central energy of the oscillator, E_g is the bandgap, and E is the photon energy (all parameters are in electron volt). P denotes the Cauchy principal value of the integral (over the photon energy). Parameterizing the b-spline yields a

TABLE I. Sources of the optical constants of all materials used in the fitting procedure.

Material	Source/model
Ru	b-spline fit of Ru dielectric constants at point A (see Fig. 4)
YH_3	b-spline fit of YH_3 optical constants at point B in Fig. 4
Y	Ref. 28
YH_2	Ref. 28, dielectric function for $\text{YH}_{1.9}$
RuO_2	Ref. 29

bandgap of 2.5 eV, which is consistent with values reported elsewhere.⁸

With optical models for the individual components in place, the ellipsometry data are analyzed using EMA models for the full temporal range. The schematics of the layered models and fitting procedures are summarized in Fig. 4. In range I, where ruthenium oxide is removed, an EMA model of RuO_2 and voids is used. In range II, where the Y to YH_2 phase transition takes place, an EMA of Y and YH_2 is used. And, finally, in range III, an EMA of YH_2 and YH_3 is used. In the first two ranges, only one parameter is fit: the ratio of the two relevant constituents (see Table II). The angle offset (the offset of the incident angle) and the thickness of the YH_2/YH_3 film are also set as free parameters in the III range. The thickness of the film is expected to expand during the phase transition, so must be fit, while the angle of incidence is allowed to vary to account for the thermal expansion of the mounting system.

FIG. 5. Parametrized Tauc-Lorentz dielectric function for YH₃, extracted from a b-spline fit to the data (see Table I).

Figure 6(a) shows the results of fitting the entire hydrogenation process in the manner described above. More detail regarding ellipsometry measurements and fitting results is provided in the [supplementary material](#). In range I, the fraction of voids in RuO₂, which represents the fraction of pinholes in the oxide, rapidly increases when the W filament is switched on and stays constant thereafter. A void fraction of 100%, which corresponds to an oxide-free surface, was never reached, similar to the data from Ugur *et al.*¹⁸ However, an XPS study on the reduction of RuO₂ by atomic hydrogen showed that nearly complete reduction can be achieved.³¹ This probably implies that the model does not fully describe the RuO₂ reduction process. We speculate that this may be partially caused by substoichiometry of the initial RuO₂ film. In addition, simultaneously with the reduction of RuO₂, the expansion of the Y lattice starts, which was omitted in the model used here. Nevertheless, the model consistently shows that the void fraction in RuO₂ increases rapidly after atomic hydrogen is supplied, suggesting that oxide reduction happens much faster than H permeation through the Ru capping layer. Previous research on Ru-capped thin films indicates that the surface roughness of Ru layers does not

TABLE II. The free parameters of each model that were used for fitting ellipsometric data (see Fig. 4).

Fit range	Free parameters
I	Fraction of voids in the RuO ₂ layer
II	Fraction of Y in YH ₂
III	Fraction of YH ₃ in the YH ₂ mixture; Angle offset; layer thickness

FIG. 6. The fitted fractions (a) and mean square error (d) of the fit as a function of time: range I—fraction of voids in RuO₂ layer, range II—fraction of Y in YH₂ phase, and range III—fraction of YH₃ in YH₂. The angle offset (b) and the YH₃ thickness (c) were also fit parameters in range III.

increase due to atomic hydrogen exposure.³¹ Therefore, we do not consider porosity of the Ru layer in our model.

The hydrogenation trend in range II and range III agrees well with the observations from *in situ* XRD (Fig. 2). The time of YH₂ phase formation (the border of ranges II and III in Fig. 4) was reliably determined from the fitting of ranges II and III. Since range II excludes the sudden change in optical properties between hydrogenation states YH_{1,9} and YH_{2,1}, a smooth concentration change in range II is obtained. Thus, we conclude that the model, in general, shows the degree of hydrogenation relatively well. The fit of YH₂ to YH₃ transition was improved to some extent by setting the angle offset and the thickness of YH_x as free parameters [Figs. 6(b) and 6(c)]. However, the high mean square error in the range III [Fig. 6(d)] suggests that the optical properties of the film are not well described by the model over the entire phase transition.

It is clear from the XRD data that there may be some YH₂ still present at saturation, which might introduce some minor additional error. However, including YH₂ at 7%–10% concentration in the construction of the optical model does not improve the fit. Therefore, it is most likely that a physical process has not been included in the model. It should be noted that an initial bad fit in range III [Fig. 6(d)] may be due to the change of optical properties between YH_{1,9} and YH_{2,1}, which was not accounted for in the ellipsometric model.

Wang *et al.*¹³ have shown that reconstruction of bcc YH₂ into hcp YH₃ creates voids in the film due to shrinkage of the crystal lattice in the plane perpendicular to the c-axis of the YH₃ lattice.

However, adding voids as a third constituent to the YH_2 - YH_3 mixture did not improve the fit. Another possibility is the presence of amorphous material. It is possible that there is an unknown fraction of amorphous YH_2 or YH_3 in the sample during the phase transition, but the end point is highly crystalline. For the case of the YH_2 to YH_3 phase transition, we attempted to include a third material in the EMA model (with optical properties obtained from a b-spline fit at the point where the MSE was maximum). However, this was not observed to improve the fit substantially. Although not conclusive, the failure to obtain an improved fit suggests that it is unlikely that a significant amorphous phase forms.

The formation of a metal-dielectric nanostructure is known to modify the optical properties of thin films in ways that are not well described by common effective medium theories.³² Mie theory describes how the growth of isolated nanocrystals may give rise to plasmonic effects that make an EMA model invalid.^{33,34} When comparing the time at which the maxima in the MSE occur [Fig. 6(d)] with the mean crystal size estimation of YH_2 and YH_3 by XRD [Fig. 3(c)], it is observed that peaks in the MSE correspond to small isolated YH_3 crystallites in a YH_2 matrix (in the beginning of range III) and, later, to isolated YH_2 crystals in YH_3 . Mie scattering theory calculations³⁴ of YH_2 spheres, embedded in a YH_3 matrix, reveal that YH_2 has a local surface plasmon resonance at 450 nm (see Fig. 7). This resonance may become significant during YH_3 formation at two points during the transition. The resonance may be excited near the beginning of the transition, when small crystallites of YH_3 are isolated in YH_2 . Near the end of the transition, when there are isolated crystallites of YH_2 in a YH_3 matrix, the resonance may also be excited. In between these two points, the increased connectivity between isolated crystallites will broaden the surface plasmon resonance peak and reduce its influence. Although neither the crystal growth data nor the MSE provides direct evidence for a surface plasmon resonance, the combined data of Figs. 3 and 6 support its existence and effect on the ellipsometry spectrum.

FIG. 7. The scattering cross section of a single isolated YH_2 sphere in a YH_3 medium, calculated from the Mie scattering theory.³⁴

IV. CONCLUSIONS

In this work, the structural changes of Ru-coated Y films during hydrogenation are characterized. An ellipsometric model was developed to quantify the ratio of hydride phases YH_2 and YH_3 in a Y film, from which the absorbed amount of hydrogen can be determined. The proposed model encompasses the entire hydrogenation process, which, in combination with other structure analysis, allowed a consistent study of hydride formation. The results suggest that RuO_2 is reduced to Ru by atomic hydrogen in the first seconds, well before any phase transformation occurs. We show that the delayed onset of the Y to YH_2 transition is not due to the lack of hydrogen in the Y lattice. Instead, the lattice first loads with hydrogen, followed by a rapid phase transition. We speculate that the delayed onset is because the Y- YH_2 interface energy is rather large at approximately 2.1 eV.

Once the transition begins, it is described well by an effective medium approximation using pre-existing optical models for Y and YH_2 . The time of YH_2 formation was reliably determined from the model, which is an important step for sensor development. The hydrogenation time can be used to estimate the hydrogen flux through the capping layer.

To describe the YH_2 to YH_3 transition, we obtained an optical model for the YH_3 phase, with parameters, such as the bandgap, that are broadly in agreement with previous models. In this case, however, the transition deviates from an EMA model. These deviations occur at stages in the transition when isolated crystallites are present, for which calculations show a significant plasmonic resonance. This can be interesting for future applications of active plasmonics with a tunable size of the YH_2 crystallites. For highly accurate hydrogen sensors, a model that includes plasmonic effects may be necessary. For that, additional experiments for isolating the plasmonic effect are desirable.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for spectral ellipsometry data and its fit with the EMA models at chosen time points.

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REFERENCES

- ¹J. N. Huiberts *et al.*, "Yttrium and lanthanum hydride films with switchable optical properties," *Nature* **380**, 231–234 (1996).
- ²N. Strohfeldt *et al.*, "Yttrium hydride nanoantennas for active plasmonics," *Nano Lett.* **14**, 1140–1147 (2014).

- ³P. Ngene *et al.*, “Seeing hydrogen in colors: Low-cost and highly sensitive Eye readable hydrogen detectors,” *Adv. Funct. Mater.* **24**, 2374–2382 (2014).
- ⁴F. J. A. A. den Broeder *et al.*, “Visualization of hydrogen migration in solids using switchable mirrors,” *Nature* **394**, 656–658 (1998).
- ⁵A. Remhof *et al.*, “Switchable mirrors for visualization and control of hydrogen diffusion in transition metals,” *Phys. Rev. B: Condens. Matter Mater. Phys.* **66**, 020101 (2002).
- ⁶M. A. Butler, “Fiber optic sensor for hydrogen concentrations near the explosive limit,” *J. Electrochem. Soc.* **138**, L46 (1991).
- ⁷T. Radeva *et al.*, “Highly sensitive and selective visual hydrogen detectors based on Y_xMg_{1-x} thin films,” *Sens. Actuators B Chem.* **203**, 745–751 (2014).
- ⁸A. T. M. van Gogh *et al.*, “Structural, electrical, and optical properties of $La_{1-x}Y_xH_x$ switchable mirrors,” *Phys. Rev. B: Condens. Matter Mater. Phys.* **63**, 195105 (2001).
- ⁹L. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, “The thermodynamics of the yttrium-hydrogen system,” *J. Phys. Chem.* **69**, 2510–2515 (1965).
- ¹⁰O. Soroka, J. M. Sturm, R. W. E. van de Kruijs, C. J. Lee, and F. Bijkerk, “Control of YH_3 formation and stability via hydrogen surface adsorption and desorption,” *Appl. Surf. Sci.* **455**, 70–74 (2018).
- ¹¹M. W. Lee and W. P. Shin, “Optical properties of the γ -phase yttrium trihydride $YH_{3-\delta}$,” *J. Appl. Phys.* **86**, 6798–6802 (1999).
- ¹²S. J. Van Der Molen *et al.*, “Hydriding kinetics of Pd capped YH_x switchable mirrors,” *J. Appl. Phys.* **86**, 6107–6119 (1999).
- ¹³K. Wang, J. R. Hatrick-Simpers, and L. A. Bendersky, “Phase transformation in an yttrium-hydrogen system studied by TEM,” *Acta Mater.* **58**, 2585–2597 (2010).
- ¹⁴M. W. Lee, C. Y. Kuo, H. C. Lin, and H. C. Wang, “Variations of the infrared transmission properties with the metal-insulator transition in thin films of the yttrium-hydride system,” *J. Appl. Phys.* **89**, 6135–6138 (2001).
- ¹⁵E. S. Kooij, A. T. M. Van Gogh, D. G. Nagengast, N. J. Koeman, and R. Griessen, “Hysteresis and the single-phase metal-insulator transition in switchable YH_x films,” *Phys. Rev. B: Condens. Matter Mater. Phys.* **62**, 10088–10100 (2000).
- ¹⁶D. J. Santjojo, T. Aizawa, and S. Muraishi, “Ellipsometric characterization on multi-layered thin film systems during hydrogenation,” *Mater. Trans.* **48**, 1380–1386 (2007).
- ¹⁷O. V. Braginsky *et al.*, “Removal of amorphous C and Sn on Mo:Si multilayer mirror surface in hydrogen plasma and afterglow,” *J. Appl. Phys.* **111**, 093304 (2012).
- ¹⁸D. Ugur, A. J. Storm, R. Verberk, J. C. Brouwer, and W. G. Sloof, “Kinetics of reduction of a $RuO_2(110)$ film on $Ru(0001)$ by atomic hydrogen,” *Microelectron. Eng.* **110**, 60–65 (2013).
- ¹⁹J. Rubio-Zuazo *et al.*, “The multipurpose X-ray diffraction end-station of the BM25B-SpLine synchrotron beamline at the ESRF,” *Nucl. Instrum. Methods Phys. Res. Sect. A* **716**, 23–28 (2013).
- ²⁰J. N. Huiberts *et al.*, “Synthesis of yttrium trihydride films for ex-situ measurements,” *J. Alloys Compd.* **239**, 158–171 (1996).
- ²¹K. L. Kostov, W. Widdra, and D. Menzel, “Hydrogen on $Ru(001)$ revisited: Vibrational structure, adsorption states, and lateral coupling,” *Surf. Sci.* **560**, 130–144 (2004).
- ²²K. A. Gschneidner, “Physical properties of the rare earth metals,” *Bull. Alloy Phase Diagrams* **11**, 216–224 (1990).
- ²³V. V. Akhachinskij, “Enthalpy of formation of $YH_{1.994}$ and $YH_{2.792}$,” in *Proceedings of an International Symposium on Thermodynamics of Nuclear Materials* (International Atomic Energy Agency, 1980), Vol. II.
- ²⁴D. Khatamian, C. Stassis, and B. J. Beaudry, “Location of deuterium in α -yttrium,” *Phys. Rev. B* **23**, 624–627 (1981).
- ²⁵I. S. Anderson, J. J. Rush, T. Udovic, and J. M. Rowe, “Hydrogen pairing and anisotropic potential for hydrogen isotopes in yttrium,” *Phys. Rev. Lett.* **57**, 2822–2825 (1986).
- ²⁶J. I. Langford and A. J. C. Wilson, “Scherrer after sixty years: A survey and some New results in the determination of crystallite size,” *J. Appl. Crystallogr.* **11**, 102–113 (1978).
- ²⁷H. Oizumi, A. Izumi, K. Motai, I. Nishiyama, and A. Namiki, “Atomic hydrogen cleaning of surface Ru oxide formed by extreme ultraviolet irradiation of Ru -capped multilayer mirrors in H_2O ambience,” *Jpn. J. Appl. Phys., Part 2* **46**, L633–L635 (2007).
- ²⁸A. T. M. van Gogh, “Probing the metal-insulator transition in rare-earth based switchable mirrors,” Ph.D. thesis (Vrije Universiteit, 2001).
- ²⁹P. Hones, T. Gerfin, and M. Grätzel, “Spectroscopic ellipsometry of RuO_2 films prepared by metalorganic chemical vapor deposition,” *Appl. Phys. Lett.* **67**, 3078 (1995).
- ³⁰G. E. Jellison and F. A. Modine, “Parameterization of the optical functions of amorphous materials in the interband region,” *Appl. Phys. Lett.* **69**, 371–373 (1996).
- ³¹I. Nishiyama *et al.*, “Reduction of oxide layer on Ru surface by atomic-hydrogen treatment,” *J. Vac. Sci. Technol. B* **23**, 3129 (2005).
- ³²B. A. Belyaev and V. V. Tyurnev, “Electrodynamic calculation of effective electromagnetic parameters of a dielectric medium with metallic nanoparticles of a given size,” *J. Exp. Theor. Phys.* **127**, 608–619 (2018).
- ³³X. Fan, W. Zheng, and D. J. Singh, “Light scattering and surface plasmons on small spherical particles,” *Light: Sci. Appl.* **3**, e179 (2014).
- ³⁴C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley-Interscience, 1998).