Observation of phase transitions in hydrogenated Yttrium films via normalized infrared emissivity

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ABSTRACT

The direct observation of a sequence of phase transitions during hydrogenation of Y thin films has been realized through the use of in situ isothermal infrared emissivity measurements. The formation of different phases, α-Y(H), YH 2 and YH 3, has been identified based on the observation of changes in the slope of the normalized IR emissivity vs. time curve during hydrogen loading. The presence of α-Y(H), YH 2 and YH 3 was confirmed by ex situ X-ray diffraction, transmission electron microscopy, and prompt gamma activation analysis. Transmission electron microscopy further demonstrated epitaxial orientation relationships between the Al 2 O 3 substrate, Ti buffer layer, the as-deposited Y film, as well as its hydrides. These results clearly demonstrate the power of IR emissivity imaging to monitor, in real time, the formation of hydride phases of both metallic and insulating character near the surface of a thin-film sample.

1. Introduction

In recent years normalized infrared (IR) emissivity imaging has been revealed to be a potent characterization tool for studying hydrogen storage in thin films [1,2]. In this measurement technique IR images of a thin film and of a hydrogen-inert reference material are recorded with an IR camera simultaneously during hydrogenation experiments. The thin film’s IR emission is then normalized by the IR emission from the reference material to give a normalized IR emissivity, which can be used to track changes in the thin film due to hydrogenation and minimize other effects, e.g., temperature variations.

The method is based on the electronic changes of a film as hydrogen is admitted (e.g., Fermi energy shifts to a region of lower density of states), which affects the strength of IR emission [3]. The often-occurring metal-to-insulator transitions present during the hydrogenation of metallic films results in an increase in the normalized IR emissivity of the sample. Already this approach has been validated for a number of Mg-based systems such as Mg–Ni and Mg–Ti [2,4]. Recently it was shown that normalized IR emissivity could also be used to monitor the formation of insulating phases in the Mg–Si system [1]. A complication of this technique is that it measures changes in the IR emission for the material located primarily within the first 400 nm of the film’s surface.

The goal of this paper is to demonstrate that this method can be applied to more complicated situations, for example to resolve the multiple phase transitions often present during hydrogen cycling of materials. The ability to monitor multiple phase transitions is vital as many complex hydrides, e.g., LiBH 4, Mg(RH 4) 2, and Li x BN 3 H 10 mixed with MgH 2 exhibit one or more phase transitions during hydrogen cycling [5–7]. Reference [8] contains a number of complex hydrides and their proposed reaction pathways, as calculated using first principles techniques.

Yttrium was chosen because it is known to have at least three hydride phases, a cubic β-phase with stoichiometry YH 2 , a hexagonal YH 3 phase (γ), and a high-pressure fcc YH 3 phase [9,10]. According to the Y–H phase diagram, there also exist two-phase regions in which α-Y, β and γ phases coexist [11]. The transition between the phases can be readily obtained at room temperature with rapid kinetics, which makes Y promising for switchable mirrors [12–15]. Visually, YH 2 has a shiny metallic finish, while YH 3 is transparent for most of the visible light spectrum. Although the β-phase is metallic in nature, it has been shown previously that there is a small maximum in the transmission of light in the red region (around 1.8 eV) [9,5]. The presence of the intermediate β-phase during the hydrogenation of Y films makes it ideal to test...
for the ability of normalized IR emissivity imaging to monitor both insulating and non-insulating phase transitions.

This article demonstrates that normalized IR emissivity imaging can be used to monitor, in situ, the formation of metallic and insulating hydrides during the hydrogenation of Y films. Confirmation of the presence of YH₂ and YH₃ is obtained through ex situ X-ray diffraction and transmission electron microscopy (TEM) of films at different stages of hydrogenation. TEM also shows that the transformation strain due to volume expansion during hydrogenation from YH₂ to YH₃ is accommodated by cracking in the film. Prompt gamma activation analysis (PGAA) was performed to determine the H/Y molar ratio during the later stages of hydrogenation.

2. Experimental procedure

2.1. Y film deposition and hydrogenation

The starting Y films were deposited in an UHV e-beam evaporation deposition system with a base pressure of better than 4 × 10⁻⁸ Pa (4 × 10⁻⁸ Torr). The system has two e-beam sources, each with 6 crucibles so that the deposition of the multilayer samples was accomplished without breaking vacuum. The films were deposited on a 5.1 cm diameter (0001) sapphire substrate, with all depositions being conducted at room temperature. The purity of all sources used in this study was better than 99.9%. First, a 100 nm Ti mirror/buffer layer was deposited at 0.1 nm/s directly on the sapphire to seed the growth of single crystal Y. Subsequently a 1.2 μm Y film was deposited at a rate of 0.4 nm/s. Finally, the film was capped with 5 nm of Pd to both prevent oxidation and dissociate H₂ gas. After deposition the substrate was cut into six 1 cm × 1 cm samples for hydrogenation and characterization.

The samples for ex situ studies were hydrogenated at 523 K under 0.4 MPa of UHP H₂ (99.999%) gas for times ranging from 4 min to 48 h. After hydrogenation the temperature was reduced first, followed by releasing the pressure to minimize the likelihood of unintentional dehydrogenation. Post-hydrogenation, the samples hydrogenated for times longer than 45 min were immediately studied by PGAA. During transportation the samples were kept in two plastic bags, with the inner bag containing the sample and the outer bag filled with dessicant, to minimize the interaction of the samples with the moisture from the air. After PGAA measurements the same samples were used for subsequent X-ray diffraction (XRD) and TEM analysis.

2.2. Characterization of the films

Although Y films have been shown to readily absorb hydrogen at room temperature, time resolved normalized IR emissivity imaging measurements were carried out at 523 K. The reasons for this were twofold. First, a large portion of the work on Y thin films has been conducted on polycrystalline films with thicknesses in the range of 100–200 nm. In such studies the large amount of grain boundaries coupled with the order of magnitude reduction in the film thickness allow for rapid hydrogenation. In this study the 1 μm films were found to be near epitaxial single crystals with few sub-grain boundaries and thus would hydrogenated much slower at room temperature. Secondly, measurements with IR cameras require a reference frame be taken at or near room temperature before acquisition is started, a larger differential between the reference frame and the measurement temperature gives better image contrast. The samples were hydrogenated in a chamber equipped with a sapphire window for IR emission observations [1]. Prior to the IR measurement the sample was held at temperature for 2 h in vacuum to try to ensure thermal equilibrium. Subsequently 0.40 MPa of hydrogen was introduced into the chamber. All other hydrogenations for supporting measurements were conducted under identical conditions.

The change in the IR emission of the sample was monitored as a function of time with an IR camera, the details of which can be found elsewhere [2]. The camera data acquisition system and signal gains were set to avoid emission saturation effects and collect raw images every 30 s. For these measurements data were taken every 30 s over a period of 10 h, the first 2 h of which were at temperature, but without hydrogen to remove the effects of camera drift during the measurement. Each image was analyzed post-measurement by an automated program that takes the average intensity over a user-defined area of the sample and normalizes it by the intensity over a user-defined area of an uncoated sapphire substrate. The normalized data is denoted normalized IR emissivity. Choosing a user-defined area allows one to avoid bad pixels in the camera and the clamps that hold the sample to the surface of the heater.

In the PGAA study, all samples hydrogenated for more than 45 min were analyzed by a high-resolution germanium spectrometry using a cold neutron beam. The neutron beam characteristics and the procedure for measuring the hydrogen content of thin films have been described in a previous publication [16]. Here the mass of a Y sample was determined by comparison of yttrium’s characteristic gamma count rate with that from a yttrium oxide standard. This allows the calculation of the hydrogen to yttrium ratio (H/Y) to monitor the hydrogenation of the films.

X-ray diffraction (XRD) studies were performed using a Bruker D8 micro-diffraction system with an area detector [17]. XRD data was taken in a conventional θ–2θ geometry over a 2θ range of 20–90° using a Cu Kα source.

Cross-sectional TEM specimens were prepared by the standard procedure of cutting, gluing, slicing, grinding, dimpling, and finally, a low-angle gentle ion milling and polishing (Gatan, Model 691 with a cold stage) at liquid-nitrogen temperatures. The microstructure of the films before and after hydrogenation was investigated by transmission electron microscope (TEM) JEM-3010/HR operated at 300 kV. In order to reduce the damage by electron beam irradiation, during TEM observation, the focusing operations were always carried out on the regions near the directly imaged parts.

3. Results and discussion

3.1. Normalized IR emissivity results

Fig. 1 shows the change of the normalized IR emissivity as a function of time for samples hydrogenated under 0.49 MPa hydrogen pressure at 523 K. Here, hydrogen has been added to the sample at 0 min, and the data before that is representative of the baseline. From this figure it is apparent that the normalized IR emissivity curve consists of two regions: an initial sigmoid shape that is interrupted by a faster increase in intensity and formation of another sigmoid shape. The start of the second sigmoid occurs at about 6–8 min into the measurement. After the second sigmoid, the change in the normalized IR emissivity saturates; after 45 min more than 95% of the change in normalized IR emissivity has occurred.

It should be pointed out that the regions of small slope in normalized IR emissivity correspond to regions where little to no changes in the phase composition of the samples occurs. This is in contrast to a pressure composition isotherm (PCT) plot where the plateau region is where the phases change most rapidly. The most likely source of the two sigmoid is a multi-phase transition of Y, first to a mixture of Y(H) and YH₂, second to a mixture of YH₂ and YH₃, and finally the film approaches a single phase YH₃. To provide evidence of this reaction path “snap shot” studies of the hydrogenation process were monitored with XRD and TEM on separate samples hydrogenated for different times.

3.2. Microstructural characterization during hydrogenation

3.2.1. Y → YH₂ transition

Fig. 2 shows X-ray diffraction scans taken from an as-deposited sample and samples hydrogenated at 523 K for 4 min, 10 min,
After 4 min of hydrogenation, just after the initial slope of the normalized IR emissivity decreases, the film’s XRD pattern consists primarily of the (1 1 1) peak of YH$_2$ and a smaller peak located at 30.75° 2-theta. The second peak fits reasonably well to (0 0 0 2) of the α-Y(H) solution solid with about 20 at% H (2-θ of 30.75° compared to 30.88° calculated extrapolating the results of Khatamian et al.), which is close to solubility limit of the α-Y(H) phase [19]. A similar XRD pattern is measured after 10 min of hydrogenation, thus suggesting that the film still consists of a mixture of YH$_2$ and α-Y(H) phases, with YH$_2$ being the majority phase. The 10 min point roughly corresponds with the beginning of the second sigmoid in the IR curve; where YH$_2$ has begun to form. The lack of evidence for YH$_3$ in the X-ray diffraction is likely related to the formation of a thin layer of YH$_3$ near the surface, which is not of sufficient volume fraction to be measured by XRD, but is picked up by the extremely surface sensitive IR emission.

TEM of the 10 min sample (Fig. 4(a)) shows no evidence of α-Y(H) phase suggesting that it is a minority phase possibly limited to regions where clamps were used to fix the substrate to the heater. There is also no observed diffraction from YH$_3$. For reasons that will be explained later YH$_3$ is not directly observable via TEM, and must be identified by forensic microscopy. Instead, what is seen is that the film has completely transformed into a single phase YH$_2$, which has grown with the epitaxial relationship (1 1 1)$_{Y(H)}$//(0 0 0 1)$_{Ti}$. Therefore after 10 min of hydrogenation the film has completed the transformation to YH$_2$, and the formation of YH$_3$ has likely begun at the surface.

3.2.2. YH$_2$ → YH$_3$ transition

After 45 min of hydrogenation (after the change in normalized IR emissivity has saturated) XRD reveals two peaks corresponding to (0 0 0 2) YH$_3$ and (1 1 1) YH$_2$, indicating the transformation is approximately 50% complete. Additionally, PGAA of this sample shows a H/Y ratio of approximately 2.69 ± 0.19, meaning the transformation from YH$_2$ to YH$_3$ is 69 ± 19% completed.

The peak positions of YH$_2$ and YH$_3$ in the 45 min sample differ from their positions after 10 min and 24 h, respectively. The differences in the observed lattice parameters can be understood.
as follows: \( \text{YH}_3 \) is difficult to form stoichiometrically, requiring pressures in excess of 4 GPa, and is normally denoted \( \text{YH}_3 \) for this reason [20]. However, changes in the optical properties of the film, associated with the formation the structure for \( \text{YH}_2 \), begin for hydrogen contents above 2.75 at%. Therefore the shift of the \( \text{YH}_2 \) peak to lower angles after 24 h of hydrogenation is attributed to the \( \text{YH}_2 \) approaching stoichiometry [20]. In the case of \( \text{YH}_2 \), TEM observation reveals ordering reflections, which are speculated to be responsible for the increase in the overall hydrogen concentration to \( \text{YH}_2 \) before the formation of \( \text{YH}_2 \) begins. The over-stoichiometric \( \text{YH}_2 \) is known to have a smaller lattice parameter than is found in stoichiometry, thus the (1 1 1) peak is located at a slightly larger 2θ [21]. Precipitation of \( \text{YH}_2 \) in \( \text{YH}_3 \) may relieve the \( \text{YH}_2 \) from the excess H to a two-phase equilibrium, thus returning the phase to \( \text{YH}_2 \) with a larger lattice parameter.

While the 45 min sample exhibits a combination of \( \text{YH}_3 \) and \( \text{YH}_2 \) peaks in XRD, according to electron diffraction the TEM sample consists mostly of the \( \text{YH}_2 \) phase. Instead, the 45 min sample exhibits a markedly different morphology from the 10 min sample (Fig. 4(b)). Imaging reveals significant disruption of the film’s continuity in the form of pancake-like pores. The pores are elongated in the direction parallel to the substrate surface along the (1 1 1) plane of \( \text{YH}_2 \).

The almost complete absence of the \( \text{YH}_2 \) phase (Fig. 4(b)) in the TEM sample is believed to be due to instability of the \( \text{YH}_2 \) phase at the low base pressure of the TEM column (~1.3 × 10^{-5} Pa), which results in reverse \( \text{YH}_3 \rightarrow \text{YH}_2 \) transformation in the thin regions of electron transparency [22]. The observed porosity can be speculated as resulting from cracking during \( \text{YH}_2 \) to \( \text{YH}_3 \) hydrogenation to accommodate the large volume change. A more detailed microstructural work in a future publication will attempt to clarify these observations [23].

It should be noted that the film exhibits cracks through only approximately 600 nm of its thickness, indicating that the transformation to \( \text{YH}_3 \) is incomplete, but that it has begun near the film’s surface and is continuing toward film/substrate interface. This indicates that the saturation of the change in the intensity of the IR emissivity is most likely related to the finite escape depth of the IR light being emitted by the \( \text{YH}_3 \).

Finally, after 24 h the hydrogenation has been completed and XRD shows only the presence of \( \text{YH}_3 \), PGAA confirms that after 24 h the H/Y ratio is 3. TEM observation of this sample shows that the entire thickness of the film now contains the pores associated with the growth of \( \text{YH}_2 \). Again, the entire film transformed back to \( \text{YH}_2 \) during TEM imaging, but transient diffraction patterns for \( \text{YH}_2 \) were observed if a previously un-imaged region was probed in diffraction mode. The spots, however, vanished too rapidly to be properly captured.

### 4. Discussion

Since \( \text{YH}_2 \) is metallic a significant change in the normalized IR emissivity during its formation was not expected but was nevertheless observed [12]. The two-step change in the normalized IR emissivity curve as a function of hydrogenation time observed is quite similar to what was reported by Kremers et al. for galvanostatic loading of an Y films [10]. Both methods report slope changes to the quantity being used to report the hydrogen content, IR emission intensity in this study and electrode potential in the previous work. In Kremers’s work the hydrogen content of the film was directly calculated using the integrated charge flow and geometrical considerations, and was then compared with the electrode potential. Here the hydrogen to yttrium ratio was directly evaluated via PGAA, however the error bars inherent to thin-film measurements by neutron techniques (generally ± 7%) are substantial enough to prevent accurate determination of the precise hydrogen content of the sample, especially for subtle changes in composition (i.e. \( \text{YH}_2 \rightarrow \text{YH}_3 \)). The large error is related to the very low mass of hydrogen present in the samples (tens of micrograms).

From the results of X-ray diffraction of samples hydrogenated for 4 and 10 min it is clear that the Y film continuously transforms to \( \text{YH}_2 \), either by propagation of a hydride layer from the top of the film, or by formation and growth of \( \text{YH}_2 \) grains throughout the film. After 10 min of hydrogenation TEM shows for some regions of the films only the presence of \( \text{YH}_2 \) throughout the thickness of the film. The initial sigmoid in normalized IR emissivity is therefore attributed to formation of metallic \( \text{YH}_2 \).

The ability of IR emissivity imaging measurements to track this change can be partially explained by the work of Kremers et al. who reported previously that the optical transmission of \( \text{YH}_2 \) shows a small maximum near \( x = 2 \) from 1.6 to 2 eV, which is within of our IR camera’s spectral range [10]. Any change of the optical properties of a material in the near IR region will be picked up by our camera, and this change in transmission is likely partially responsible for our ability to measure the initial change from Y to \( \text{YH}_2 \). Once the Y has completely transformed to \( \text{YH}_2 \), the film begins the transformation to the insulating \( \text{YH}_3 \), in part near the surface of the film, which results in a second more pronounced increase to the normalized emissivity.

### 5. Conclusions

In conclusion IR emissivity has been used to directly measure the multiple phase transitions associated with Y hydrogenation. XRD and TEM studies were used to show that the initial change in the normalized IR emissivity is attributable to the formation of \( \text{YH}_2 \) at
the surface of the film. TEM studies of the films reveal a special ori-
entational relationship between the substrate, the Ti buffer layer,
and the Y film that allow the film to be grown and change phases
epitaxially. It was also revealed that the Y to YH$_x$ phase transfor-
mation results in the formation of porosity of the film along (1 1 1)
planes. The ability for normalized IR emissivity to measure metal-
to-metal transitions in addition to metal-to-insulator transitions
renders it a versatile measurement technique for the hydrogen
storage properties of a large variety of materials.

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