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## Technical Communication

# In-situ infrared imaging methodology for measuring heterogeneous growth process of a hydride phase

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### ABSTRACT

In the paper we report on a new methodology, which allows measuring in-situ heterogeneous growth rates of hydride phase in films during metal-hydride phase transformation. This optical method is based on infrared imaging of a wedge-shaped thin film during hydrogen loading. In the paper the method is demonstrated for  $\text{Mg}_{98.4}\text{Ti}_{1.6}$  wedge-shaped thin film and main conclusions are supported by results of transmission electron microscopy. The methodology combined with the structural characterizations verified fast formation of  $\text{MgH}_2$  layer on top followed by drastically slower growth of the  $\text{MgH}_2$  phase. The initial averaged growth rate of the  $\text{MgH}_2$  phase was estimated as  $\sim 1.3$  nm/s, and as  $\sim 0.03$  nm/s subsequently.

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## 1. Introduction

Development of hydrogen storage materials with fast absorption/desorption cycle is essential for the advances in hydrogen fuel-based economy, especially for the transportation sector [1–4]. Rapid progress in finding suitable materials can occur only with understandings and control of the thermodynamics and kinetics of hydrogenation. Conventionally, thermodynamics and kinetics of hydrogenation are evaluated as an average value of a whole sample through traditional Sievert-type measurements, with an assumption of homogenous phase transformation [5–15]. However in most cases the transformation to a hydride phase is a heterogeneous process starting at surfaces [16,17]. Thus establishing a methodology

which enables one to monitor heterogeneous growth process of a hydride phase is of importance to obtain advanced understandings of the thermodynamics and kinetics of hydrogenation in hydrogen storage materials.

Infrared (IR) imaging is a sensitive technique for detecting formation of a hydride phase in thin films with a varied parameter such as composition [18–24] on a single chip. If we select thin film's thickness as a varied parameter instead of composition, times required for complete hydrogenation of various thicknesses reflecting the heterogeneous growth process of a hydride phase will be collected at single experiment. Therefore in this paper, we propose a methodology based on the in-situ IR imaging of a wedge-shaped thin film having continuous thickness gradient.

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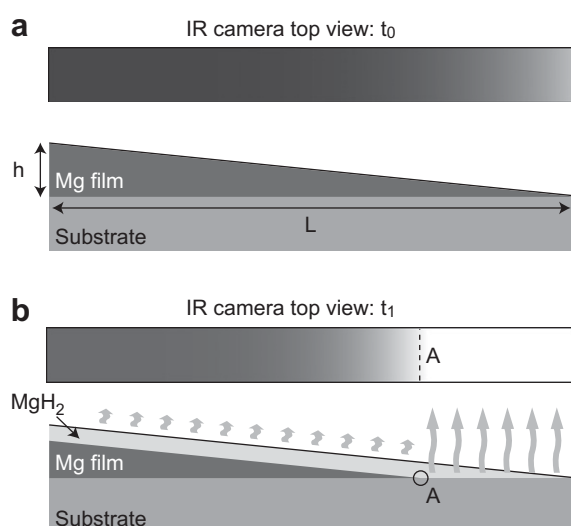
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The methodology relies on the high emissivity of a substrate and optical transparency of a hydride phase. The concept of the methodology is explained with the help of schematic drawings in Fig. 1. A wedge-shaped metallic thin film with a very small height-to-length ratio ( $h/L = 5 \times 10^{-5}$ ) is deposited on an IR emissive substrate. The metallic thin film blocks IR radiation from the substrate. Thus the as-deposited thin film may come to be dark in the IR camera top view [Fig. 1(a)]. When hydrogenation starts, a layer of hydride phase may form on top of the thin film and grows toward the substrate. The thinner part of the thin film will be readily and completely hydrogenated, becoming insulating and optically transparent to the strong IR radiation from the substrate [Fig. 1(b)] [25]. Accordingly, the IR camera will see the bright region up to the intersection point A, up to where the thin film is completely hydrogenated. The bright region will continuously extend with the growth of the hydride phase. Movement of the boundary between dark and bright regions is thus directly related to increase of the completely hydrogenated thickness of the thin film. It should be noted that the thickness gradient of the wedge-shaped thin film helps optical monitoring of the nm-scale growth process of the hydride phase; for  $h/L = 5 \times 10^{-5}$ ,  $\Delta L = 2 \times 10^4 \Delta h$ , where  $\Delta L$  is the measured change in the position A in Fig. 1(b) and  $\Delta h$  the hydride layer thickness.

## 2. Experimental

In order to test the proposed methodology, we prepared an  $\text{Mg}_{98.4}\text{Ti}_{1.6}$  thin film with thickness gradient from 0 nm to approximately 500 nm on 1 cm-long (0001)  $\text{Al}_2\text{O}_3$  single-crystal substrates. An Mg-Ti binary system is selected for its promising fast hydrogen reaction kinetics [26,27]. The thin film was



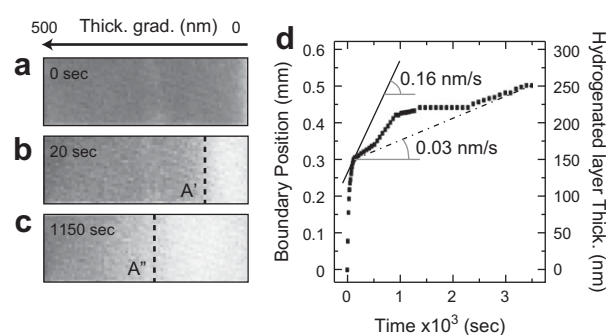
**Fig. 1** – Cross-sectional schematics of a wedge-shaped thin film capped with a very thin Pd layer on an IR emissive substrate and its expected IR camera top view (a) before and (b) after hydrogenation. Strong IR radiation from the substrate is indicated by arrows. The point A separates fully hydrogenated region on its right side from partially hydrogenated region on its left side.

electron-beam deposited at room temperature and capped with a 5 nm-thick Pd layer to prevent oxidization and facilitate fast dissociation of hydrogen molecules [28–31]. Composition was verified by energy dispersive spectroscopy. The heterogeneous growth process of a hydride phase in a  $\text{Mg}_{98.4}\text{Ti}_{1.6}$  thin film was monitored using the IR imaging where the IR images were collected every 10 s while the thin film was hydrogenated at 373 K and 0.3 MPa hydrogen gas pressure for 1 h (see details on the IR camera in ref. [19]). Before hydrogen gas was introduced into the reaction chamber, the sample was stabilized for 2 h in vacuum at 373 K. After one hour hydrogenation, the sample was then cooled down to room temperature without removing the hydrogen gas pressure. The hydrogenated thin film was prepared for cross-sectional transmission electron microscopy (TEM) by a water-free polishing procedure and ion milling with a cold stage to prevent hydrogen desorption from the thin film.

## 3. Results and discussion

Representative IR images at different times of hydrogenation are shown in Fig. 2 (a)–(c). Before hydrogenation has started, the dark IR image shows almost no contrast [Fig. 2(a)]. On the other hand, as expected in Fig. 1(b), the thinner part of the thin film changes from dark to bright and the bright region extends toward the thicker part of the thin film during the hydrogenation [Fig. 2(b) and 2(c)].

Fig. 2(d) shows a plot of approximate boundary positions determined from hundreds of IR images [the position A in Fig. 1(b)] as a function of hydrogenation time. Because the boundary position directly indicates completely hydrogenated thickness of the thin film within each hydrogenation time, nonlinear movement of the boundary position is attributed to the heterogeneous growth process of the  $\text{MgH}_2$  hydride phase. This verifies the methodology's capability to monitor the heterogeneous growth process of a hydride phase. By looking at such nonlinear movement of the boundary position, we can



**Fig. 2** – Selected IR images of the  $\text{Mg}_{98.4}\text{Ti}_{1.6}$  film hydrogenated for (a) 0 s, (b) 20 s, and (c) 1150 s. Dashed lines indicate the approximate boundary position (the point A in Fig. 1) separating the fully hydrogenated bright region from partially hydrogenated dark region. (d) A plot of approximate boundary positions (right-axis) and corresponding completely hydrogenated film thicknesses (left-axis) as a function of the hydrogenation time. A thin line and a chain line represent tangent.

achieve important information for hydrogen storage materials, e.g., the thickness of the Mg-based thin film should be less than 150 nm (corresponding boundary position is  $\sim 0.3$  mm) for fast hydrogenation within  $\sim 120$  s. The slowing down of the growth rate to  $\sim 0.03$  nm/s after the Mg(Ti)H<sub>2</sub> layer reached 150 nm thickness can be explained by the well-known blocking effect of the continuous hydride layer on hydrogen diffusion to feed the growth [32–34].

In addition, provided that the MgH<sub>2</sub> layer grows toward the substrate in an Mg<sub>98.4</sub>Ti<sub>1.6</sub> thin film as shown in Fig. 1(b), instantaneous and average growth rate of the MgH<sub>2</sub> layer can be calculated, which are difficult to obtain by traditional measurement methods. The former can be calculated from slope of a tangent at each data point, e.g., 0.16 nm/s at  $\sim 120$  s (corresponding to  $\sim 150$  nm-thick MgH<sub>2</sub> layer). Then, the latter can be calculated from slope of the line connecting two data points as shown in Fig. 2(d), e.g.,  $\sim 0.03$  nm/s between  $\sim 120$  s and  $\sim 3600$  s (corresponding to 150 nm to 250 nm-thick MgH<sub>2</sub> layer).

TEM characterizations were conducted to verify the assumption that hydride layer forms on top of the thin film and grows toward the substrate. Fig. 3(a) shows a bright field TEM image of the Mg<sub>98.4</sub>Ti<sub>1.6</sub> thin film hydrogenated for 1 h and cross-sectioned at 500 nm thickness. The microstructure of the thin film consists of columnar grains, which were identified by selected area electron diffraction (SAED) as Mg<sub>98.4</sub>Ti<sub>1.6</sub> grown with [0001] texture normal to the Al<sub>2</sub>O<sub>3</sub> substrate [Fig. 3(b) and 3(c)]. The preferred Al<sub>2</sub>O<sub>3</sub>[0001]||Mg[0001](11–20) orientation relationship was reported for similar columnar structures of Mg films [35,36]. In an upper part of the film, below the thin Pd layer, there is a  $\sim 120$ – $150$  nm-thick layer exhibiting a uniform contrast that is clearly distinguishable from the strong diffraction contrast of the columnar grains. The layer was identified by SAED and dark field imaging as consisting of small grains of the Mg(Ti)H<sub>2</sub> phase. The grains are random but with preferred (110)<sub>MgH<sub>2</sub></sub>//(0002)<sub>Mg</sub> orientation [Fig. 3(b)] [17]. In addition, pockets of MgH<sub>2</sub> were found along the columnar grain boundaries. Similar a  $\sim 120$ – $150$  nm-thick layer of MgH<sub>2</sub> was also

observed in other TEM samples of the Mg<sub>98.4</sub>Ti<sub>1.6</sub> thin films cross-sectioned at different thicknesses. Therefore, the TEM result agrees with the assumption that hydride layer forms on top of the thin film and grows toward the substrate.

#### 4. Conclusions

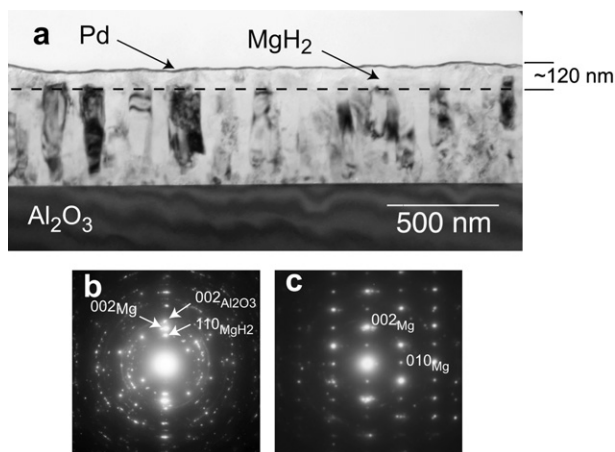
In summary, a methodology based on the in-situ IR imaging of a wedge-shaped thin film having continuous thickness gradient was established to study heterogeneous growth process of a hydride phase of solid-state hydrogen storage materials. The small angle ( $5 \times 10^{-5}$  rad) of the wedge-shaped thin films enabled optical monitoring of the nm-scale growth process of the hydride phase. For the Mg<sub>98.4</sub>Ti<sub>1.6</sub> thin film, where a hydride layer formed on top of the thin film and grew toward the substrate, the methodology enabled in-situ evaluation of; 1) completely hydrogenated thickness of the thin film within each hydrogenation time, 2) instantaneous growth rate of a hydride layer at each hydrogenation time, and 3) average growth rate of a hydride layer between two hydrogenation times. The information obtained by the established methodology is not limited to thin films, e.g., the film thickness for initial fast-hydrogenation provides a guideline for the design of powder grain size of hydrogen storage materials to be hydrogenated within a reasonable time. The results of the paper suggest that for fast hydrogenation of Mg(Ti) powders [37–39], the size of particulates should be less than 300 nm, twice the thickness of the Mg<sub>98.4</sub>Ti<sub>1.6</sub> thin film hydrogenated within  $\sim 120$  s.

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**Fig. 3 – (a) A cross-sectional bright field TEM image of the Mg<sub>98.4</sub>Ti<sub>1.6</sub> film after 1 h hydrogenation showing a layer of MgH<sub>2</sub> below Pd layer. (b) Selected area electron diffraction patterns taken from the entire film plus the substrate and (c) only from upper part of the film.**

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