Watching In Situ the Hydrogen Diffusion Dynamics in Magnesium on the Nanoscale

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Abstract: We present a method to image the phase transition from metallic magnesium to dielectric magnesium hydride on the nanometer scale in-situ. This allows to understand and improve the intrinsically limited diffusion kinetics and switching speeds.

Metal to insulator phase transition materials are currently of very high interest as they show large potential for, e.g., switchable optical systems [1-3]. In such dynamic systems, the nanoscale switching mechanism is clearly of utmost importance, yet, so far, the details are not well understood. In this study, we present a method to image the phase transition from metallic magnesium (Mg) to dielectric magnesium hydride (MgH$_2$) on the nanometer scale in an in-situ environment. It allows us to perform in-situ scattering-type scanning near-field optical microscopy on the Mg surface while hydrogen is absorbed [4,5].

![Schematic drawing of the principle for in situ s-SNOM](image)

Fig. 1. Schematic drawing of the principle for in situ s-SNOM. We use free-standing thin films realized by thermally evaporating 10 nm Pd, 5 nm Ti, and 50 nm Mg on a Pd-Au membrane. This allows hydrogenation from below. The metalized AFM tip of the s-SNOM setup is scanning the top surface to investigate the local optical properties, while the Mg thin film is absorbing hydrogen. In addition, a characteristic IR phonon of MgH$_2$ enables chemically specific imaging. The Mg layer is in contact with air, causing oxidization. However, the very thin MgO layer is transparent for imaging at the frequency of the MgH$_2$ phonon and is barely influencing our s-SNOM measurements.

The main idea of our method is sketched in Fig. 1. We use gold grids precoated with a 2 to 3 nm palladium (Pd) thin film. Subsequently, we thermally evaporate 10 nm Pd, 5 nm titanium (Ti), and 50 nm Mg thin films. The Pd acts as a catalytic layer, splitting the hydrogen molecules and enabling the diffusion into the Mg film. Ti is used to prevent alloying of Mg and Pd, which would cause the formation of a hydrogen diffusion barrier. Mounting the grids into a homebuilt gas cell, hydrogen gas can access the free-standing thin films from below, while the top Mg surface is accessible for the s-SNOM measurements. Scanning the tip of the s-SNOM over the exposed Mg surface, we can observe and investigate in situ the time dynamics of the hydride formation and the diffusion of hydrogen into the film with nanometer resolution.

Additionally, we perform nanoFTIR spectroscopy and identify a phonon resonance across the phase transition which is used as local sensing method to track the progression of the hydrogenation front. The resonance causes a very high material contrast between Mg and MgH$_2$ in 2D near-field scattering phase images, as depicted in Fig. 2. The images show a 50 nm Mg film in its (a) pristine state, (b) after 10 min, and (c) after 30 min of hydrogen exposure.
Fig. 2. **Nanoscale imaging of the diffusion of hydrogen in a 50 nm Mg thin film.** 1x1 µm$^2$ 2D s-SNOM measurements of the near-field scattering phase show a large phase contrast between Mg and MgH$_2$. A grain boundary map extracted from mechanical phase measurements is plotted on the scattering phase images to investigate the diffusion mechanism in detail. The Mg film is shown (a) in its pristine state, (b) after 10 min and (c) after 30 min of exposure to 2% hydrogen gas diluted in nitrogen.

The simultaneously measured mechanical phase is used to extract the exact geometry and position of the grain boundaries between individual nanocrystallites of the polycrystalline films. In order to aid the data interpretation, they are plotted as a black mask on top of the scattering phase images in Fig. 2. This allows us to precisely track the progression of the hydride phase formation.

Our results reveal that the phase transition is nucleated at grain boundaries. From these sites, the hydrogenation front progresses into the adjoining nanocrystallites. Most interestingly, the hydrogenation seems to saturate before the entire film is hydrogenated, leaving areas of metallic Mg within the dielectric MgH$_2$. By evaluating the hydrogen loading dynamics of individual nanocrystallites, we are able to determine the “intrinsic” limiting diffusion speed of hydrogen in Mg and show that we reach loading times of single crystallites of less than one minute.

Our results constitute an important step forward in the understanding of the hydrogen loading and unloading process in Mg and are expected to help improving the hydrogen diffusion kinetics. This is necessary to further enhance the switching speeds of active optical and plasmonic systems. In addition, our method is applicable for investigations on several other gas-in-metal systems, where the gas causes a sufficient change in the optical properties of the pristine metal. Especially for hydrogen storage, hydrogen generation, and electrochemical applications, the influence of, e.g., grain boundaries in a huge diversity of material systems is of large interest.

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