Nanometer-scale Hydrogen ‘Portals’ for Control of Magnesium Hydride Formation

Chia-Jung Chung,¹ Chinmay Nivargi,¹ and Bruce Clemens¹

¹Department of Materials Science and Engineering,
Stanford University, Stanford, California 94305, USA
1. EXPERIMENTAL DETAILS

Sputtering of Epitaxial Mg Films In order to grow epitaxial Mg films, the cleanliness of the substrates are crucial to form the crystallographic registry between the film and the substrate. Single crystal sapphire substrates with (0001) orientation were used in this study[2, 3]. Substrates were first cleaned with a soak in acetone for 3 minutes and then blown dry with nitrogen. Another soak in methanol for 3 minutes was used to remove the residue left by acetone. After drying with the same procedure, substrates were soaked in an etch containing ammonium hydroxide, hydrogen peroxide (50% solution), deionized water in the volumetric ratio of 1:1:5, respectively, for 3 minutes. After this, the substrates were rinsed thoroughly with deionized water and blown dry completely with dry nitrogen. Substrates were loaded to the load lock of the deposition chamber as soon as the cleaning procedure was completed. The base pressure of the main chamber was $\sim 5 \times 10^{-9}$ torr before deposition of Mg films. In order to remove any surface contamination/oxide of the Mg target, pre-sputtering at argon pressure of 1.3 mTorr for 10 minutes was performed. After pre-sputtering, Mg films were deposited on the substrate with deposition rate of 1.11 Å/sec.

Sputtering of Pd Nanoparticles After deposition of Mg films, argon gas pressure was decreased to $3.7 \times 10^{-5}$ torr to pre-sputter Pd target for 5 minutes. After pre-sputtering, Ar and He flow rates 71.6 and 20.6 sccm, respectively, were used to deposit Pd nanoparticles on as-grown Mg films[4]. The main chamber pressure was $4.2 \times 10^{-4}$ torr and the deposition rate of Pd nanoparticles was $\sim 0.09$ Å/sec during deposition. The SEM image of the Pd nanoparticles filtered at 5 nm distributing uniformly on the Si substrate is shown in Fig. S1.

X-Ray Diffraction for Structural Characterization X-ray diffraction measurements were done using a PANalytical X’Pert Pro diffractometer equipped with a 4-circle goniometer using Cu K-alpha radiation. X-ray mirror incident beam optics along with parallel plate collimator diffracted beam optics were chosen to give a high-intensity, line-focused beam with reasonable resolution. A symmetric ($\theta$-2$\theta$) scan, which kept the orientation of the scattering vector parallel to the sample normal but changed only its magnitude, was used to obtain information about the overall structure and preference for out-of-plane texture in the samples. To determine the presence of in-plane orientation induced by epitaxial alignment
Supplementary Figure S1. SEM image of produced Pd nanoparticles. The image shows uniform particle size distribution of Pd nanoparticles selected at 5 nm.

with the substrate, we performed $\phi$ scans, where the scattering vector was moved away from the sample normal direction by tilting the sample to allow diffraction from planes that were at known angles away from the out-of-plane direction (we examined the Al$_2$O$_3$ (202) peaks and the Mg (101) peaks). In-plane alignment could then be determined by rotating about the sample normal through the angle $\phi$.

Optical Transmission Measurement Pictures in Fig. S2 show the significant optical property change before and after hydrogenation. Hydrogenation experiments in this paper were all performed under pure hydrogen pressure of 700 torr at room temperature. The optical measurement setup consisted of a high power LED at wavelength 635 nm, a hydrogenation chamber, a photodiode, and a digital multimeter. The hydrogenation chamber had two kodial glass viewports that allowed LED light to enter and leave the chamber. More information can be found in reference [5].
Supplementary Figure S2. Schematic of the optical transmission measurement setup and photographs of samples before and after hydrogenation.

2. GROWTH LAWS FOR TWO-DIMENSIONAL GROWTH

The schematic below shows two-dimensional growth of the hydride nuclei in the nanoporous geometry. Balancing the flux of the hydrogen at the growth interface to the hydrogen incorporated in the hydride in time $dt$ for mass conservation, we find:

$$Q \, dt = c_H (2\pi rh) \, dr$$

where $Q$ is the flux of the H atoms arriving at the growth interface in time $dt$, $c_H$ is the concentration of hydrogen in the hydride, $h$ is the film thickness and $r$ is the radius of the hydride region. The H atom flux $Q$ is limited by the number of atoms arriving at the Pd nanoparticle-Mg film interface or by diffusion through the growing nucleus itself. In the flux limited case, the flux $Q$ is constant, leading on integration to the expression:

$$r = \sqrt{\frac{Qt}{2\pi c_H h}}$$

giving a growth law of $r \sim t^{1/2}$. For a diffusion limited growth, the flux $Q$ is given by $J_D A$, where $J_D$ is the diffusive flux, given by Fick’s first law of diffusion as:

$$J_D = -D_H \nabla c = D_H \frac{\Delta c_H}{r}$$

where $\Delta c$ is the difference in concentration of H across the hydride radius. The area is again the area at the growth interface $A = (2\pi rh)$. This, on integration leads to:

$$r = \sqrt{\frac{2D_H \Delta ct}{c_H}}$$
As can be seen, both the limiting cases give a \( r \sim t^{1/2} \) behavior for the growth law.

3. GROWTH LAW WITH OXIDE ENCROACHMENT

The above treatment can be modified to incorporate the oxide encroachment as shown in the schematic, by considering interface flux limited and diffusion limited growth of the oxide, constricting the nanoportal. This time, balancing the flux of oxygen arriving at the growth interface of the nanoportal in time \( dt \) to the amount incorporated in a growing shell for mass conservation:

\[
Q' dt = -c_H (2\pi (r_0 - x)) \, dx
\]

where \( x \) is the thickness of the oxide shell as shown in the schematic and \( r_0 \) is the initial radius of the open nanoportal. \( Q' \) is then limited either by the flux of oxygen at the edge of the Pd nanoparticle itself (flux limited) or by diffusion through the already grown oxide shell.

**Interface Limited Oxide Encroachment**

In the former case, \( Q' \) is constant, and hence integration of equation (1) leads to the area of the nanoportal as a function of time being:

\[
r_{np} = r_0 - x = \sqrt{r_0^2 - \frac{Q't}{\pi c_H}}
\]

Hence:

\[
A_{np} = \pi (r_0^2 - vt)
\]

where \( v = \frac{Q'}{\pi c_H} \) is similar to a growth velocity term for the portal size. It can be seen that the portal pinches off at time \( t_p \) obtained as:

\[
t_p = \frac{r_0^2}{v}
\]

This area dependence in equation (2) can then be substituted into the differential equation for the patch radius from the paper to obtain:

\[
j_H \left(\pi \left(r_0^2 - vt\right)\right) \, dt = c_H (2\pi r h) \, dr
\]
which on integration leads to:

\[ r = \sqrt{\frac{j_H}{c_{\text{H}}} \left( r_0^2 t - \frac{vt^2}{2} \right)} \]  

(4)

Thus we have a relatively simple expression for the radius and area of the hydride patches as a function of time. As can be seen, the radius of the patch is sensitive to the initial radius \( r_0 \) of the nanoportal.

To account for the constant ‘leak’ flux through defects in the MgO layer, a constant flux term \( Q_F \) was included along with the flux through the nanoportal on the left hand side of equation (3), before performing the integration.

**Diffusion Limited Oxide Encroachment**

In the diffusion limited case, the flux \( Q' = J_{\text{diff}}l_{\text{shell}} \). The flux \( J_{\text{diff}} \) can be expressed using Fick’s first law as:

\[ J_{\text{diff}} = \frac{D_O \Delta c}{x} \]

where \( D_O \) encapsulates the diffusion coefficient for oxygen through the hydride under the nanoportal and \( \Delta c \) is the concentration difference across the grown oxide shell. The circumference of the shell through which the oxygen diffuses is \( l_{\text{shell}} = 2\pi(r_0 - x) \). Putting this together in equation (1), we get:

\[ \left( \frac{D_O \Delta c}{x} \right) \left( 2\pi(r_0 - x) \right) = -c_{\text{H}} \left( 2\pi(r_0 - x) \right) \, dx \]

This leads to a simple expression for the nanoportal radius as a function of time:

\[ r_{np} = r_0 - x = r_0 - \sqrt{\frac{2D\Delta ct}{c_{\text{H}}}} \]

and hence:

\[ A_{np} = \pi(r_0 - x)^2 = \pi \left( r_0 - v\sqrt{t} \right)^2 \]  

(5)

where again \( v = \sqrt{\frac{2D\Delta c}{c_{\text{H}}}} \) is similar to a growth velocity term for the portal size. It can be seen that the portal pinches off at time \( t_p \) obtained as:

\[ t_p = \left( \frac{r_0}{v} \right)^2 \]
This area dependence in equation (5) can then be substituted into the differential equation for the patch radius from the paper to obtain:

\[ j_H \left( \pi \left( r_0 - v \sqrt{t} \right)^2 \right) dt = c_H (2\pi rh) \, dr \]  

(6)

which on integration leads to

\[ r = \sqrt{\frac{j_H}{c_H h} \left( r_0^2 \sqrt{t} - \frac{4r_0vt\sqrt{t}}{3} + \frac{v^2t^2}{2} \right)} \]  

(7)

Again, a relatively simple expression is obtained for the hydride patch size, which is different from that for the interface limited case from (4).

4. TRANSFORMATION KINETICS

We begin with the equation for the fraction of the area transformed derived in the paper:

\[ f = 1 - \exp \left( -\frac{A_e(t)}{A_0} \right) \]  

(8)

with \( A_e(t) \) given by:

\[ A_e(t) = A_0 \int_0^t I(\tau) A_r(t - \tau) \, d\tau \]  

(9)

The nucleation rate \( I(\tau) \) is expressed as:

\[ I(\tau) = \frac{N_0}{\tau_N} e^{-t/\tau_N} \]  

(10)

Combining the above equations, we get:

\[ f = 1 - \exp \left( -\int_0^t \left( \frac{N_0}{\tau_N} e^{-t/\tau_N} \right) A_r(t - \tau) \, d\tau \right) \]  

(11)

with \( A_r(t - \tau) \) defined by power law growth or the specific growth laws discussed above in equations (4) and (7). This was the equation used to fit the optical transmission data for transformation kinetics.

REFERENCES


