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ARTICLE TYPE

Kinetics study on promising hydrogen storage properties of Mg-based thin films at room temperature

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Pd-Mg-Pd thin films with variable thickness of Mg layers were prepared. Their optical and electrical changes in both gasochromic and chemochromic processes were compared to investigate the kinetics of Mg-based thin films at room temperature. Hydrogen absorption and desorption kinetics of Pd-Mg-Pd thin films were strongly dependent on the thickness of the Mg layer. Especially, when the thickness lowered to 60 nm, MgH₂ layer formed immediately after exposing to H₂ at room temperature, while Mg layer rapidly generated during hydrogen desorption in ambient air. By means of optical and electrical resistance measurements, we found that the diffusion process contributed to hydrogen absorption and desorption was significant. The remarkable absorption and desorption kinetics at room temperature reported here suggested promising applications in Mg-based energy-efficient devices and hydrogen sensors.

Introduction

Among the diversity of storage materials, Mg is proposed as a competitive candidate because of its light-weight, low cost, and high capacity¹. To fulfill the requirements for their on-board application, however, several performance areas need significant improvement especially the kinetics and deposition temperature. These challenges are caused by the high thermodynamic stability (> 573 K) and sluggish kinetics². Approaches to address these issues consist of creating nano-composites and doping catalysts, resulting in enhanced kinetics and decreasing operation temperatures^{3,4}. It was demonstrated that reduction of the particle size could significantly improve the performance, confirmed by both the experiments and theoretical calculations^{5,6}. Decreasing the particle size has so far been achieved by means of milling and vapor-transport approaches⁷. To further enhance hydrogen storage performance, the influence of particle size on both absorption and desorption processes needs more clarification. However, techniques mentioned above were limited to the fabrication of Mg nano-composites with finely controlled size down to 80 nm.⁸

Meanwhile, more recent advancements in metal-hydride thin films gained particular interest to carry out such studies, since the composition, interface and crystallinity can be well tailored in nano-scales compared to other methods.^{9,10} Moreover, an approximate simplified model could be more easily established to study the in-depth mechanism¹¹. For thin films, we could study hydrogen absorption and desorption kinetics on the thickness dimension to explore the particle size effect¹². The desorption performance, especially at mild condition, was important for automotive applications. Recently, by means of elastic clamping and cooperation effect, Pd-Mg-Pd sandwich-structured film has exhibited enhanced kinetics at moderate conditions.¹³⁻¹⁵ It is thus

aiming at preparing Pd-Mg-Pd thin films with different thickness of Mg layers to investigate the size effect on hydrogen storage properties at mild condition.

In addition, rare-earth and Mg-based thin films are subject to extensive research since they possessed dramatic optical and electrical properties during hydrogen absorption and desorption, so called as switchable mirror.¹⁶⁻¹⁹ These novel and unique characteristics render Mg-based thin films interesting in applications such as hydrogen sensors, smart windows and solar absorbers.²⁰⁻²²

Herein, we investigate the thickness effect of Pd-Mg-Pd thin films on hydrogen storage performance at room temperature. Their structural, optical, electrical properties in both gasochromic and chemochromic processes have been studied. The hydrogen absorption and desorption mechanism were discussed by simulating the optical transmittance and electrical resistance.

Experimental Section

Preparation of Mg-based thin films

Pd-Mg-Pd thin films with variable Mg thickness were prepared by a custom designed direct current (DC) magnetron sputtering system with a background pressure of around 2×10^{-4} Pa. First, a 5 nm Pd layer was deposited onto Si (100) wafers, glass substrates by DC sputtering using a Pd (99.99%) target. The discharge power was 45 W and the argon (99.99%) pressure was 0.8 Pa. Then a 40 nm Mg layer was deposited on the Pd layer. The discharge power was 50 W and the argon pressure was 0.8 Pa. Finally, another 5 nm Pd layer was coated on top of the Mg layer by DC sputtering, which is necessary to protect Mg against oxidation and to promote hydrogen dissociation. Pd-Mg-Pd thin films with different thickness of Mg layer (60 nm, 80 nm, 100 nm) were prepared by the similar procedure. The deposition rates

of

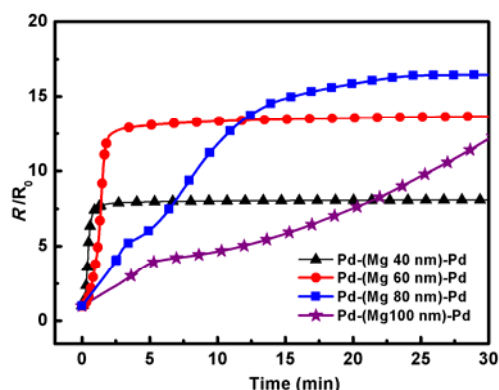


Fig.1 The relative resistance changes, R/R_0 , of Pd-Mg-Pd thin films with different thickness of Mg layers with respect to absorption time in 4×10^3 Pa H_2 at 298 K. R_0 is the initial resistance of the metallic film.

Mg and Pd were 0.26 nm s^{-1} and 0.33 nm s^{-1} , respectively. After deposition, the samples were hydrogenated at 4×10^3 Pa hydrogen (99.99%) at room temperature without any activation treatment. The dehydrogenation process was performed in dry air at different temperatures for tracing desorption mechanism. For the chemochromic process, hydrogenation was carried out with 0.06 M NaBH_4 in 1 M KOH at 298 K.

Characterizations of Mg-based thin films

The structures of the samples were studied by powder X-ray diffraction (XRD) (Rigaku D/max-200) using monochromated Cu $K\alpha$ radiation and θ - 2θ scan. The film thickness was determined by cross-section scanning electron microscopy (SEM) measurements (Hitachi S4800). Optical transmission measurements were performed with a Shimadzu UV-3100 spectrometer. The changes in resistance were recorded in a gas loading cell equipped with a four-probe resistance measurement, monitored by an Agilent 34401A multimeter.

Results and discussion

All the X-ray diffraction (XRD) patterns of the as-prepared Pd-Mg-Pd thin films with various thickness of Mg layers showed the presence of Mg (002) peak and Pd (111) peak. Upon exposure to 4×10^3 Pa H_2 at room temperature, the Mg (002) peak disappeared and the MgH_2 (110) peak occurred. By exposing these hydrogenated thin films to air at room temperature, not the Mg (002) peak but the Mg (101) peak were also observed, suggesting that the preferential orientation of (002) direction was weakened due to the reconstruction during hydrogenation and dehydrogenation.

The time-dependent electrical resistances of all the Pd-Mg-Pd thin films were compared during hydrogenation at room temperature. Upon hydrogen loading, changes in relative resistances, R/R_0 , of all the Pd-Mg-Pd thin films were compared in Fig. 1, where R_0 is the initial resistance of the metallic film. Among all, Pd-(Mg 40 nm)-Pd film switched fastest and quickly

approached saturated plateau in less than 5 min. The

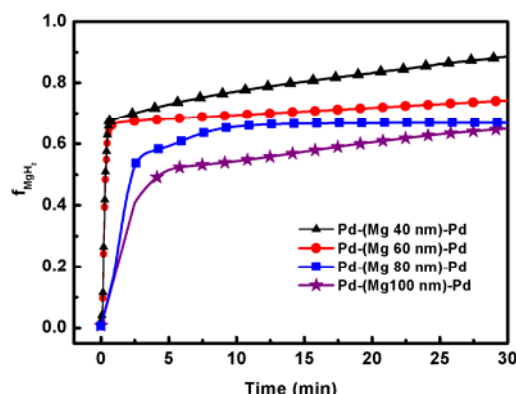


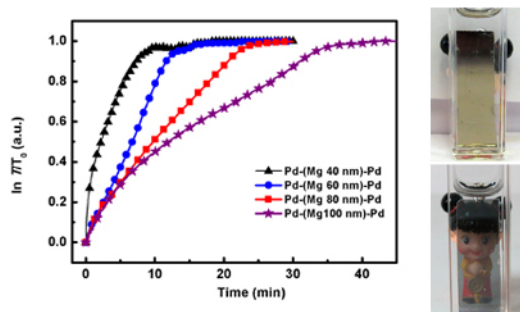
Fig.2 The volume fraction of MgH_2 in Pd-Mg-Pd thin films, f_{MgH_2} , with respect to the hydrogenation time under 4×10^3 Pa H_2 at 298 K.

hydrogenation rate was almost 18 times larger than that of Pd-(Mg 100 nm)-Pd film. During the initial hydrogenation process, MgH_2 grains nucleated as isolated islands in the metallic film. Thus, the resistance of the sample increased slowly. After the growth and combination of the hydride nuclei, a continuous insulator phase formed, leading to the rapid increase in resistance. At that time, the electronic property of the sample dramatically changed from a metallic state into an insulating state. At last, the resistance slightly increased and approached the saturation, since the insulating MgH_2 grains have already been the majority of the sample. In order to identify the absorption kinetics, the volume fractions of MgH_2 were calculated by fitting the resistance data, which was difficult to determine by gravimetric or volumetric methods in thin films. The Bruggeman effective medium approximation could be introduced to simulate the effective resistivity of Mg-MgH₂ system²³. Both the volume expansion caused by the transformation from Mg to MgH_2 and the alloying effect with Pd layers were included in our calculations¹⁵. The time evolution of MgH_2 volume fraction, f_{MgH_2} , in all the Pd-Mg-Pd films at 298 K is shown in Fig. 2. With the reducing thickness of the Mg layer, the hydrogen content increased significantly. In the first 60 s, the hydrogen content of Pd-(Mg 40 nm)-Pd increased to 0.7. While the hydrogen content of Pd-(Mg 100 nm)-Pd film reached 0.5 after 5 min and slowly approached 0.6 after 30 min. The hydrogen content of Pd-(Mg 40 nm)-Pd is 1.5 times larger than that of Pd-(Mg 100 nm)-Pd after 30 min. Variation trend in hydrogen contents seemed to be categorized in two types: When the thickness of the Mg layer is no larger than 60 nm, hydrogen contents sharply raised and approached saturation, suggesting the majority of Mg transformed from metallic state to semiconductor one. While the thickness of Mg layer is larger than 60 nm, changes in hydrogen content increased at the initial state. In the following diffusion process, the increasing rate slowed down and the progressively enlarged hydride layer finally formed. It could be explained that MgH_2 layer blocked the hydrogenation since the hydrogen diffusion rate is much smaller in the hydride layer than that of metallic part²⁴.

The optical switching process could also be accomplished with a NaBH_4 solution, so called as the chemochromic process²⁵. The thickness of Mg layers showed strong relationship on hydrogen

absorption rate not only during gasochromic but chemochromic

(a)



(b)

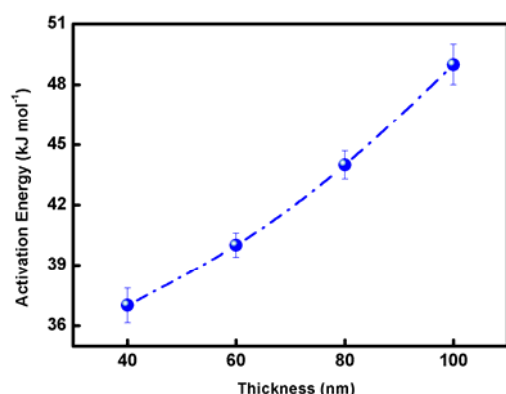


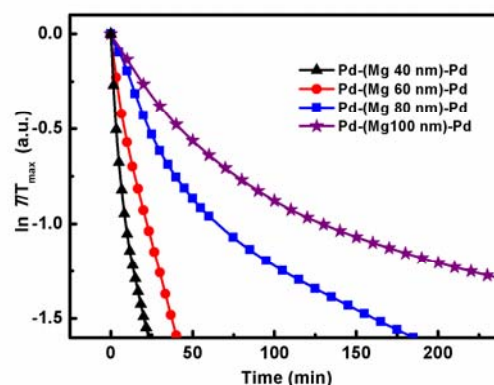
Fig.3 (a) Relative transmittance changes, $\ln T/T_0$, at 500 nm of all Pd-Mg-Pd thin films with respect to absorption time in a NaBH_4 solution. Top-right is the photograph of the as-prepared Pd-(Mg 60 nm)-Pd thin film. The cartoon was obstructed and the image of the camera was reflected on the mirror like film. Bottom-right is the photograph of the Pd-(Mg 60 nm)-Pd thin film after 20 min immersion in a NaBH_4 solution. The cartoon could be observed clearly through the transparent hydride film after the chemochromic process. (b) Hydrogen absorption flux of Pd-Mg-Pd thin films during the chemochromic process. The dashed line is a visual guide.

process. Chemical loading of Mg-based thin films was carried out by immersion in a NaBH_4 solution (0.06 M in 1 M KOH)²⁶. Pd catalyzed the hydrogen generation reactions from both the BH_4^- and water, leading to the hydrogen absorption process of the sample. *In situ* optical measurements were performed to monitor and compare the switching kinetics of Pd-Mg-Pd films during the chemochromic process. All the Pd-Mg-Pd thin films exhibited dramatic optical changes from initially a shiny metallic state to a transparent state in a NaBH_4 solution. Their reflectance decreased and the transmittance increased significantly, owing to hydrogenation.

Fig. 3a illustrates the time-dependent transmittance changes, $\ln (T/T_0)$, at 500 nm after immersing in a NaBH_4 solution, where T_0 is the initial transmittance. Pd-(Mg 40 nm)-Pd film showed the fastest response. It took less than 10 min to switch from opaque state to transparent one and achieve complete hydrogenation. The hydrogenation rate increased with the reducing thickness of Mg layers. The absorption rate of Pd-(Mg 40 nm)-Pd film is about 4 times larger than that of Pd-(Mg 100 nm)-Pd film. To further

compare the kinetics during chemochromic process, the

(a)



(b)

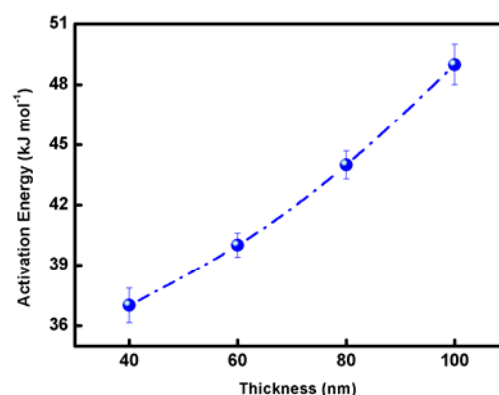


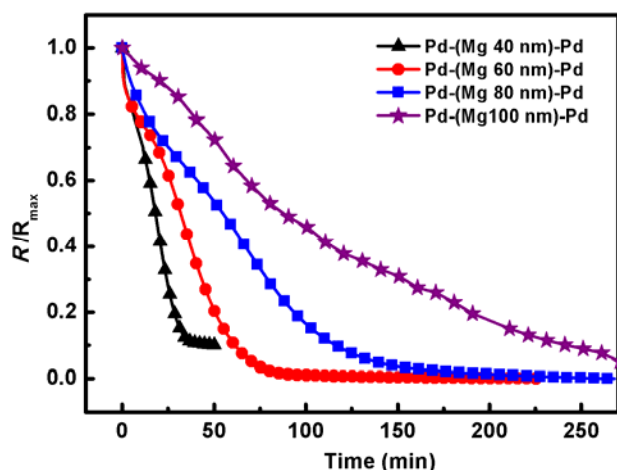
Fig.4 (a) Relative transmittance changes, $\ln T/T_{\max}$, at 500 nm of all the hydride films with respect to desorption time in air at 298 K. (b) The relationship of activation energies and the thickness of Mg layers during the hydrogen desorption process in air. The dashed line is a visual guide.

absorption flux was estimated according to the slope of initial absorption curve¹². The initial hydrogen absorption flux also increased with decreasing thickness of the Mg layer, shown in Fig.3b. The thinner Mg layers showed the higher hydrogen absorption flux during chemochromic process.

An obvious gap on kinetics between thin films with different thickness of Mg layers was observed in the desorption process. The thickness effect on hydrogen desorption performances in ambient air was studied by optical and electrical characterization. Fig. 4a shows the variation in transmittance, $\ln (T/T_{\max})$, at 500 nm of all the Pd-Mg-Pd thin films during dehydrogenation in air at room temperature. Only after 30 min, Pd-(Mg 40 nm)-Pd thin film completely dehydrogenated in air at room temperature. With the increasing thickness of Mg layers, the entire hydrogenation processes cost extended time. The dehydrogenation rate of Pd-(Mg 40 nm)-Pd is at least 10 times larger than that of Pd-(Mg 100 nm)-Pd. The desorption kinetics in air can be investigated by calculating the activation energy. The dehydrogenation processes of all Pd-Mg-Pd thin films were monitored at different temperatures in air. Assuming that it was completely dehydrogenated when the transmittance saturated as a function of

time, it was then possible to determine the desorption rates from

(a)



(b)

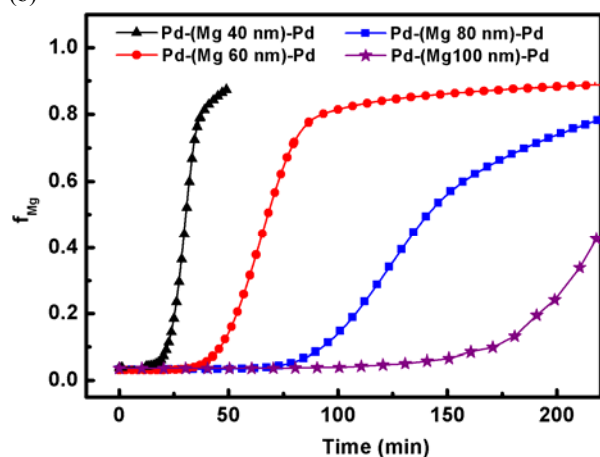


Fig.5 (a) The relative resistance changes of all the hydride films during dehydrogenation in air at 298 K. $R_{\max}$ is the initial resistance of hydride film. (b) The time-dependent volume fractions of Mg, f_{Mg} , of all the hydride films during dehydrogenation in air at 298 K.

the slopes of the curves¹⁵. We applied, $\ln(T/T_{\max})$, the logarithm of the optical transmittance data to simulate the reacted fraction, based on the Lambert-Beer's law and the Johnson-Mehl-Avrami theory^{27, 28}. Activation energies were finally deduced from the temperature dependent desorption rates, according to the Arrhenius law¹¹. The relationship between activation energies and thickness of Mg layers is shown in Fig 4b. The activation energy lowered to 37 kJ mol⁻¹ when the thickness of Mg layer decreased to 40 nm. Comparable to the Ni-catalyzed Mg powders, the smaller activation energy was attributed to the thin film structure and the Pd catalyst layer²⁹. The overall activation energy of hydrogen desorption reduced with the decreasing thickness of Mg layers. The improved H₂ desorption properties in thinner films can be attributed to the shorter diffusion path for H atoms.

To further understand the hydrogen desorption kinetics in ambient air, relative changes in resistance were compared in Fig.

5. Pd-(Mg 40 nm)-Pd showed the largest desorption rate in air at room temperature, almost 10 times larger than that of Pd-(Mg 100 nm)-Pd, similar as the above transmittance data. To in-depth investigate the desorption mechanism, the time-dependent volume fraction, f_{Mg} , is calculated by fitting the resistance data. It could be deduced that few Mg nuclei initially generated in hydride films and then Mg nuclei grew and joined together. The latter is the rate-determination process of hydrogen desorption in ambient air, strongly dependent on the thickness of the Mg layer.

Conclusion

In summary, the thickness effect on hydrogen storage properties during gasochromic and chemochromic processes were compared in Pd-Mg-Pd thin films. Pd-(Mg 40 nm)-Pd exhibited the best absorption and desorption kinetics. Both hydrogenation and dehydrogenation rate apparently increased when the Mg layer was thinner than 60 nm. The improved H₂ absorption and desorption properties in thinner films can be attributed to the shorter diffusion path for H atoms. The thickness-performance relationship provided a new avenue for other hydrides. For all the thin films, H₂ absorption and desorption can be accomplished at room temperature, there with meeting the target for automotive applications of Mg. These films could become the material of choice for a variety of sensing and storage applications.

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Notes and references

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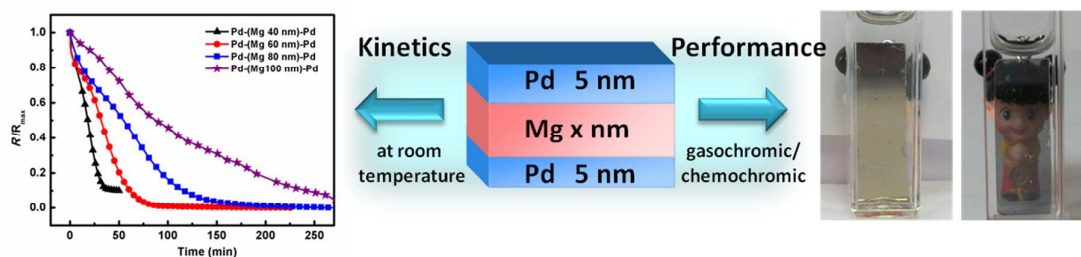
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Kinetics study on promising hydrogen storage properties of Mg-based thin films at room temperature

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The thickness effect on hydrogen absorption and desorption kinetics at mild condition were investigated in Mg-based thin films.