Article ID: 1003－6326(2003)06－1401－04

Crystal structure and switchable optical properties of yttrium hydride films covered by palladium layer①

ZHANG Wen-kui(张文魁)[1], GAN Yong-ping(甘永平)[1], YANG Xiao-guang(杨晓光)[2], Huang Hui(黄 辉)[1], YU Li-yang(余厉阳)[2]

(1. Department of Applied Chemistry, Zhejiang University of Technology, Hangzhou 310032, China; 2. Institute of Materials and Chemical Engineering, Zhejiang University, Hangzhou 310027, China)

Abstract: The palladium/yttrium films were prepared using magnetron sputtering technique. The changes of crystal structure, morphology and optical properties of the films during the hydrogen absorption/desorption process were investigated. The results of SEM and AFM analysis show that yttrium films have columnar structure, and the Pd cover layers on the surface of the yttrium films are composed of nanometer-sized Pd particles, which contain a large amount of smaller crystalline grains. During the gas hydrogen absorption/desorption process, YH_3 and YH_2 hydrides form on the sites of Pd grains contacting with Y grains. Upon hydrogenation, YH_3 hydride forms and the switchable optical properties can be observed. The light transparency of the films increases with the increasing of hydrogen loading time and the light wavelength, and the absorption limitation occurs at λ= 400 nm. Upon dehydrogenation, YH_3 hydride dissociates into YH_2 hydride, and the maximum transparency occurs at λ= 689 nm.

Key words: palladium/yttrium films; morphology; switchable optical properties

CLC number: TG 146.4 **Document code:** A

1 INTRODUCTION

The rare-earth hydride films with switchable optical properties were firstly discovered by Huiberts et al[1-3] and have attracted more and more interest recently. Huiberts et al[1, 2] found that the films of YH_x and LaH_x exhibit remarkable reversible changes in their optical properties during hydrogenation/dehydrogenation process. By changing the hydrogen gas pressure or by electrochemical means, the films can be continuously and reversibly switched from a shiny mirror to a transparent window in a fraction of a second[3, 4]. The subsequent works[5-9] have disclosed that most of the rare-earth hydrides and their alloys hydrides, such as Gd-Mg[5, 6, 9], Y-Mg[3, 5-7], La-Mg[1-3, 8, 9], Sm-Mg[5, 6] and Lu-Mg[5, 6], etc., also exhibit the dramatic changes in the optical properties by changing the hydrogen content.

By electrochemical charging/discharging way[4, 10], the optical properties of the rare-earth films can be rapidly and conveniently achieved. So the rare-earth hydride films have shown the potential applications in the optical devices such as smart windows and optical shutters to active displays[2].

In this paper, the conventional magnetron sputtering technique was selected to prepare Pd/Y hydride films. Under low vacuum (10^{-3}－10^{-4} Pa), the yttrium films capped with a Pd layer of 5－20 nm were sputtered into ITO or glass substrate. The crystal structure, morphology and switchable optical properties were investigated as well.

2 EXPERIMENTAL

The Pd/Y thin films were deposited on glass substrates using magnetron-sputtering techniques. The chamber was first evacuated to 2.0×10^{-4} Pa, then filled with pure Ar up to 0.25 Pa. To ensure the adhesion of yttrium to glass, the glass was polished chemically. In order to reduce the air content in the chamber, the pre-deposition of yttrium was conducted. After pre-deposition, Y films were deposited subsequently on the polished glass for 5 min at 0.4 A and 500 V. After the deposition of yttrium films, palladium films were subsequently deposited for 30－60 s on the surfaces of yttrium films in the same deposition process. The Pd layer was generally about 5－20 nm, while the Y film was 100－200 nm thick.

The purity of palladium is 99.9% (manufactured by Institute of Yunnan Precious Metal), and 99% for yttrium (manufactured by Shanghai Yuelong Nonferrous Metals Co.).

The XRD analysis were carried out with a Rigaku D/max-ⅢB diffractometer, using CuK_α radiation in the 2θ range from 20° to 90° with a scan rate of 4(°)/min. The morphology of the rare earth films

① **Foundation item:** Project(59971046) supported by the National Natural Science Foundation of China

Received date: 2002－12－13; **Accepted date:** 2003－04－21

Correspondence: ZHANG Wen-kui, PhD, Professor; Tel: +86-571-88320394; E-mail: echem@zjut.edu.cn

was observed by ZAFM-Ⅱ atomic force microscopy (made by Zhejiang University). The scan time was 2 s, brightness threshold was 0.71, scan range was 2.0 μm × 2.0 μm, image size was 400 × 400 dots, and three-dimensional range was 1.0 μm × 1.0 μm. SEM analysis was carried out with AMRAY1840 scanning electron microscope.

For the test of optical properties, the Y/Pd films were set on a transparent vessel. Before hydrogenation, the vessel was evacuated and subsequently filled with pure hydrogen to 100 kPa.

3 RESULTS AND DISCUSSION

3.1 Crystal structure and morphology

Fig. 1 shows the XRD patterns of Y/Pd films deposited on polished glass substrate at different temperatures. The crystallinity of Pd layer is improved with the increase of the substrate temperature. Depending on the XRD patterns, the lattice spacing of the Pd layers and Y films is calculated and the results are presented in Table 1. The lattice spacing of Pd layers and Y films are also very close to the bulk value. However, the lattice spacing of yttrium films tends to increase with the substrate temperature.

The average crystalline grains of Pd layers are calculated using Scherer equation[11]. When the temperature of the glass substrates is 25, 100 and 150 ℃ respectively, the average crystalline grains of Pd layers are 2.3, 2.5 and 5.5 nm accordingly. It means the crystalline grains increase with the substrate temperature.

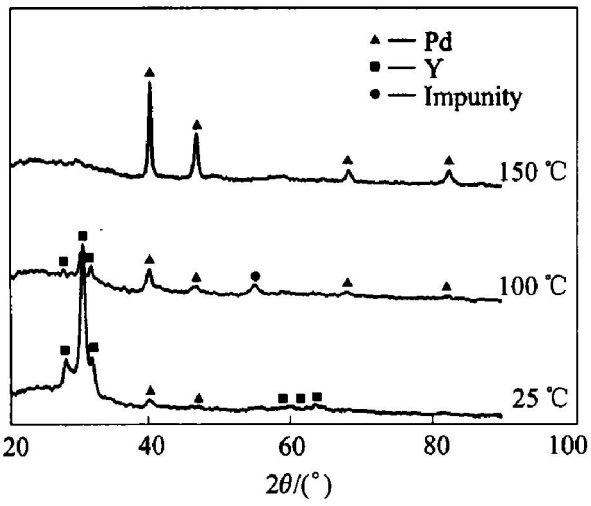

Fig. 1 XRD patterns of Y/Pd films deposited on glass substrate at different temperatures

Table 1 Lattice spacing of Pd layers and Y films deposited at different temperatures

Substrate temperature/ ℃	Lattice spacing of Pd layer/ (Å)	Lattice spacing of Y films/ (Å)
25	3.897	a= 3.666 c= 5.832
100	3.880	a= 3.694 c= 5.880
150	3.889	–

The SEM photograph of Y/Pd films deposited on glass substrate at 25 ℃ is shown in Fig. 2(a). Pd particles distribute dispersely on the surface of Y film, and there exists large amount of micro-holes (about 10 μm in size). According to the theory of the films deposition[12], the structure of the films is affected by the value of T_s/T_m (T_s is the temperature of substrate, T_m is the melting point of raw material). When $T_s/T_m < 0.3$, the as-deposited films show a columnar structure. The melting point of Y is 1 795 ℃, so the T_s/T_m is only 0.08 if the substrate temperature reaches 150 ℃. As shown in SEM photograph, the as-deposited Pd/Y films have the columnar structure. The AFM analysis discloses that the Pd top layer does not form a fully closed coating, and Pd crystalline grain with an average size of 200 – 300 nm are piled up each other with the clear boundary (Fig. 2(b)). Compared with the results calculated from Scherer equation, it means that the Pd particles are composed of smaller crystalline grains.

3.2 Changes of crystal structure during hydrogen absorption/desorption process

Fig. 3 shows the XRD pattern for the Pd/Y

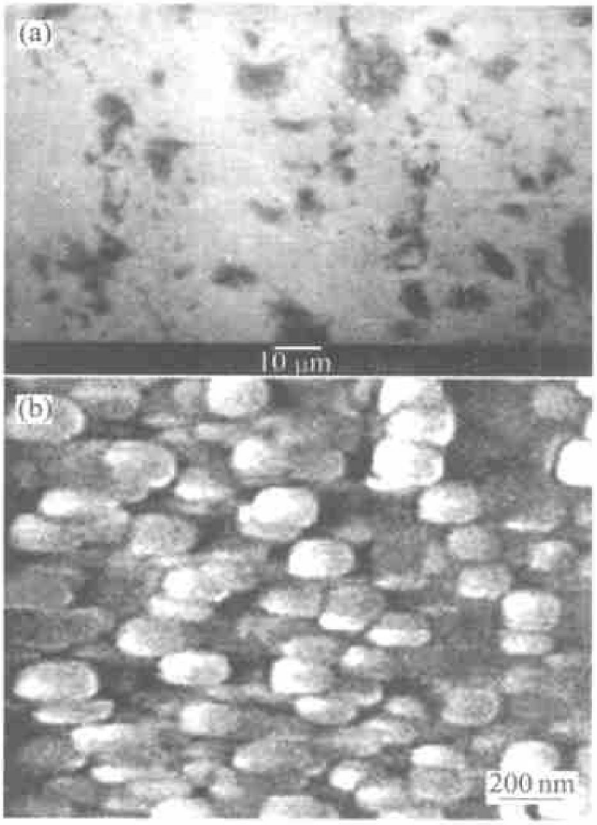

Fig. 2 SEM(a) and AFM(b) photographs of Y/Pd film deposited on glass substrate at 25 ℃

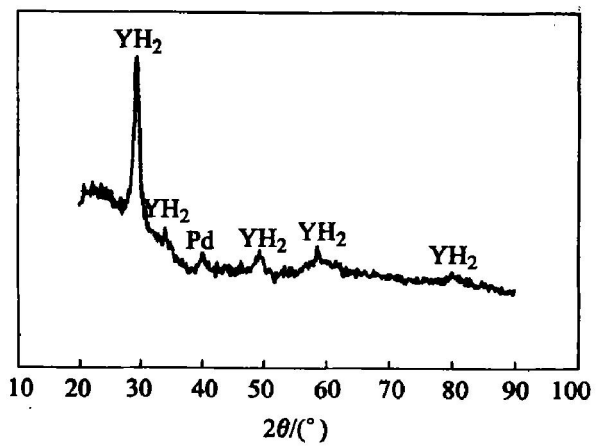

Fig. 3 XRD pattern for hydrogenation Pd/Y films (t= 25 ℃, p_{H_2}= 100 kPa)

films after hydrogenation. Upon hydrogenation, YH_2 hydride occurred in the films. Yttrium can react with hydrogenation to form the unstable trihydride YH_3, and YH_3 can dissociate to YH_2 in the air. Corresponding to the diffraction peak in XRD pattern, there only exists the peak of hydride due to the dissociation of YH_3 hydride. It is calculated that the sizes of YH_2 hydride and Pd is 5.248 Å and 3.897 Å, respectively.

Fig. 4 shows the surface morphology for the hydrogenated Pd/Y films. After hydrogenation, a large amount of micrometer-sized particles occur in the surface of Pd/Y films. AES and XRD analyses disclose that these particles are YH_2 hydride containing large amount Pd element. Yttrium is easy to be oxidized in atmosphere but difficult to form

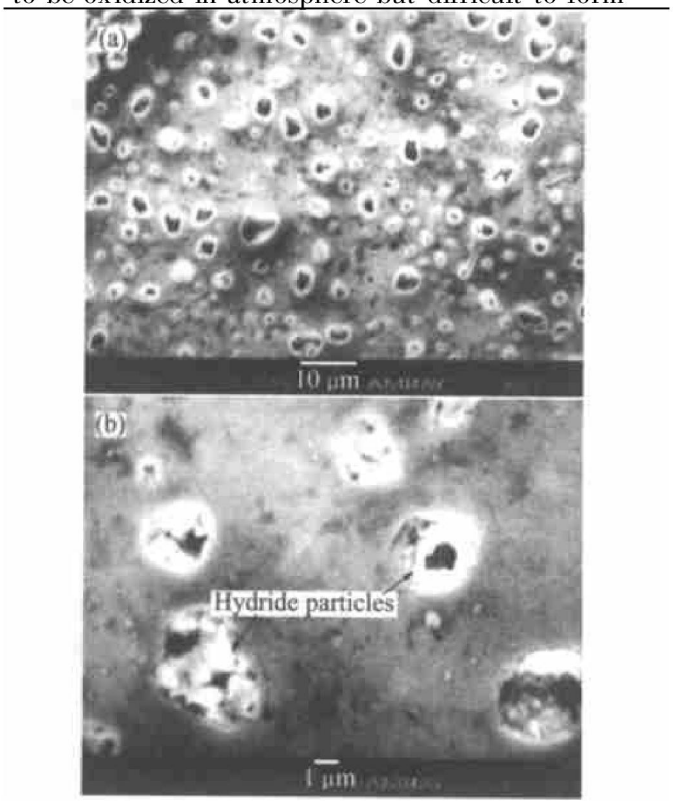

Fig. 4 SEM photographs of the hydrogenated Pd/Y films

hydride in low pressure of hydrogen at low temperature, and the hydrogen absorption only occurs slowly in the higher temperature. However, in the presence of hydrogen catalysts such as Pd element, the following chemical reaction can take place in the lower temperature:

$$H_2 + Pd \rightarrow 2H(Pd) \quad (2)$$

$$2H + Y \rightarrow YH_2 \xrightarrow{+H} YH_3 \quad (3)$$

The formed YH_3 hydride can dissociate into YH_2 hydride in the air:

$$2YH_3 \xrightarrow{\text{dissociation}} 2YH_2 + H_2 \quad (4)$$

Because the Pd crystallines distribute dispersely on the surface of yttrium films(Fig. 2), the hydrogen molecule contacting with Pd grains can be dissociated into hydrogen atom which can be absorbed by yttrium to form hydride. The slow diffusion rates of hydrogen atom in films at room temperature result in the local hydrogenation, i.e., the yttrium hydride is difficult to form on the site without contacting with Pd grains. The local micro-crack occurs in the films due to the volume expansion when yttrium absorbs hydrogen to form hydride (Fig. 4).

3.3 Changes of optical properties during hydrogenation

The as-prepared Pd/Y films like a shiny metallic mirror. Upon hydrogen absorbing, the yttrium film changes into a transparent yellowish sample. The changes of the optical properties for Pd/Y films during gas hydrogen absorption/desorption process are measured, and the results are shown in Figs. 5 and 6. With the increasing of the hydrogenation time, the optical transparency of the Pd/Y films increase gradually up to 1.5(Fig. 5(a)). According to the results of Huiberts et al[2], this indicates the formation of YH_3 hydride. Fig. 5(b) shows the optical curve for YH_3 hydride at different light wavelength. As shown in Fig. 5(b), the optical transparency of the Pd/Y hydride films increases with the increase of light wavelength. The films are transparent when the wavelength is in the range of 400 – 860 nm, if the light wavelength < 400 nm, the transparency of the films is approximated to zero. This phenomenon is associated with the band gap. The previous results disclosed that yttrium trihydride has an optical gap of 2.8 eV[11], corresponding to 400 nm light wavelength.

Fig. 6(a) shows the change curve of optical transparency at λ= 689 nm of Pd/Y films during dehydrogenation. As the time of exposure on the air increases, the transparency of the films decreases gradually. After 3 500 s, the decrease rate tends to be a constant, indicating that YH_3 hydride is unstable in the air. The final product is YH_2 hydride. Compared with Fig. 5(a), the transparency

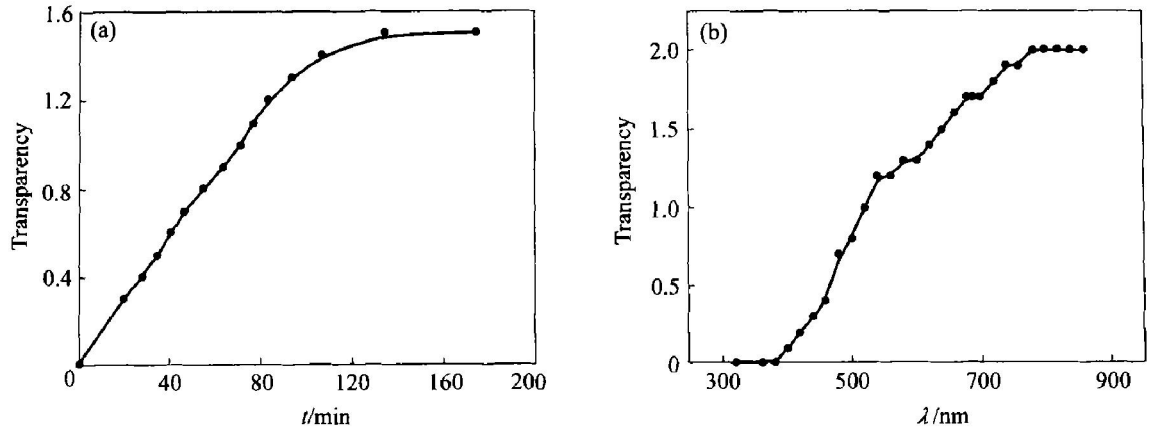

Fig. 5 Change of optical transparency of Pd/Y films during hydrogenation(a) (λ= 689 nm) and optical transparency curves for YH_3 hydride at different light wavelength(b)

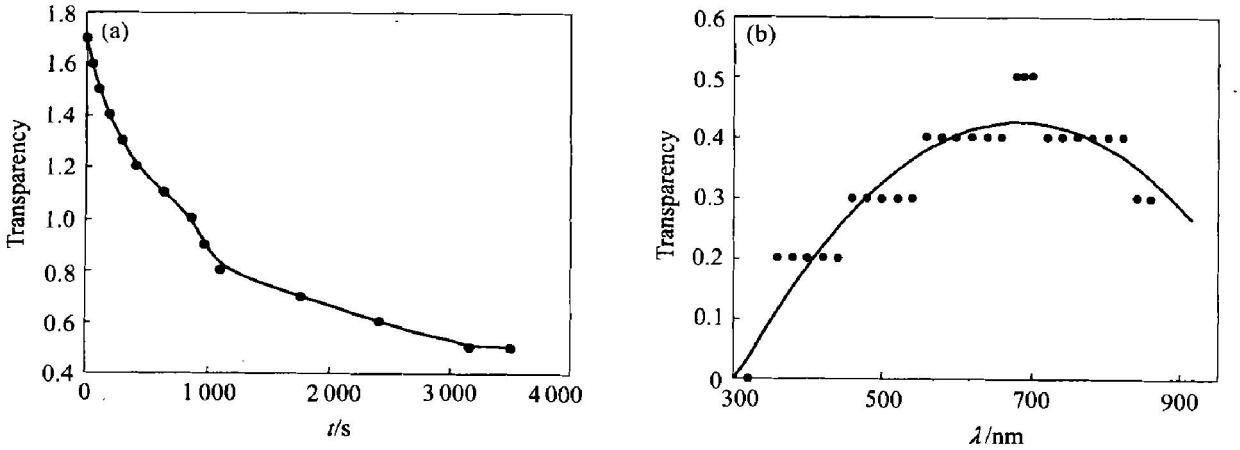

Fig. 6 Change of optical transparency of Pd/Y films during dehydrogenation(a) (λ= 689 nm) and optical transparency curves for YH_2 hydride at different light wavelength(b)
(Temperature is 25 ℃, $p(H_2)$= 100 kPa)

change rates of the films have remarked difference. Only small amount of YH_3 hydride transferred to YH_3 hydride, so the transparency of Pd/Y films show an obvious decrease. In the reverse process, the transparency increase only after a large amount of YH_2 hydride has been transferred to YH_3 hydride. Fig. 6(b) shows the optical transparency curves for YH_2 hydride at different light wavelength. There exists a parabolic relationship between the optical transparency and the light wavelength. The maxim transparency occurs at around λ= 689 nm, i.e., the so-called "red transparent windows" proposed by van der Sluis et al[5].

REFERENCES

[1] Huiberts J N, Rector J H, Wijngaarden R J, et al. Synthesis of yttrium trihydride films for ex-situ measurements [J]. J Alloys Comp, 1996, 239: 158-171.

[2] Huiberts J N, Griessen R, Rector J H, et al. Yttrium and lanthanum hydride films with switchable optical properties[J]. Nature, 1996, 231: 380-383.

[3] Griessen R, Huiberts J N, Kremers M, et al. Yttrium and lanthanum hydride films with switchable optical properties[J]. Journal of Alloys and Compounds, 1997, (253-254): 44-50.

[4] Notten P H L, Kremers M, Griessen R. Optical switching of Y hydride thin film electrodes[J]. J Electrochem Soc, 1996, 143(10): 3348-3353.

[5] van der Sluis P, Ouwerkerk M, Duine P A. Optical switches based on magnesium lanthanide alloy hydrides [J]. Appl Phys Lett, 1997, 70: 3356-3358.

[6] van der Sluis P. Optical switches of gadolinium-magnesium multilayers[J]. Appl Phys Lett, 1998, 73: 1826-1828.

[7] Nagengast D G, Gogh A, Kooij E S. Contrast enhancement of rare-earth switchable mirrors through microscopic shutter effect[J]. Appl Phys Lett, 1999, 75: 2050-2052.

[8] Rottkay K, Rubin M, Duine P A. Refractive index changes of Pd-coated magnesium lanthanide switchable mirrors upon hydrogen insertion[J]. Journal of Applied Physics, 1999, 85(1): 408-413.

[9] Janner A M, Sluis P, Mercier V. Cycling durability of switchable mirrors[J]. Electrochimica Acta, 2001, 46: 2173-2178.

[10] Matveeva T, Parkhutik V. Kinetics of the electrochemical loading of hydrogen into thin yttrium films covered by palladium[J]. J Electrochem Soc, 2002, 149(10): D148-D153.

[11] YANG Bang-chao, WANG Wen-shen. Thin Films Physics and Technology [M]. Xi'an: University of Electronic Sci & Tech Press, 1994. (in Chinese)

[12] Zhang Li-de. Preparation and Application Technology of Superfine Particles [M]. Beijing: Chinese Petroleum Chemical Engineering Press, 2001. (in Chinese)

(Edited by HE Xue-feng)