Transactions of the Materials Research Society of Japan 32[1] 171-175 (2007)

Effect of Annealing Temperature of Palladium Oxide Films on Gasochromic Performance

S. Yamamoto, K. Takano, A. Inouye* and M. Yoshikawa
Quantum Beam Science Directorate, JAEA, 1233 Watanuki, Takasaki, Gunma 370-1292
Fax: 81-27-346-9687, e-mail: yamamoto.shunya@jaea.go.jp
*School of Engineering, Tohoku University, 6-6 Aramaki Aoba-ku, Sendai 980-8579

The effect of annealing temperature of Pd films on the gasochromic performance for hydrogen gas has been investigated. The Pd films prepared using an rf magnetron sputtering on quartz glass and glassy carbon substrates were annealed at temperatures range from 300 to 900°C in air. The films are characterized by Rutherford backscattering spectrometry (RBS) and X-ray diffraction (XRD). The gasochromic performance of palladium oxide films coated with a 15 nm thickness Pd catalyst is examined by optical transmittance in hydrogen. The polycrystalline PdO film which is thermally oxidized at 600°C in air shows the superior gasochromic performance. The optical transmittance of the film is rapidly decreased down to 10 % within 2 minute exposures to 1 % H_2/Ar at room temperature. It is found that the gasochromic coloration of palladium oxide films for hydrogen is strongly influenced by annealing temperature.
Key words: palladium, palladium oxide, oxidation, hydrogen

1. INTRODUCTION

The fast detection of hydrogen leaks below the lower explosive limit (LEL) of 4% by volume ratio of hydrogen in air is an important technology. A great number of solid-state hydrogen gas sensors have been demonstrated [1]. Most of hydrogen sensors are based on electrical techniques of detection. However, a hydrogen sensor, which can safely detect hydrogen at room temperature, with a low cost and lightweight, is desirable. One accepted method for the detection of hydrogen is a fiber-optic sensing. The sensors based on fiber optics are very attractive owing to the remote sensing and the lack of sparking possibilities in explosive environments. Fiber-optic hydrogen sensors using Pd or Pd alloys thin films have been developed for the in hazardous atmospheres, such as the rocket engines use of liquid hydrogen as combustible [2], near the high radioactive waste repositories in an underground site [3]. Pd or Pd alloys thin layer is utilized for the selective hydrogen detection due to the change of optical transmittance or reflectance of Pd layer under hydrogen exposure [4-6]. Recently, the gasochromic materials, coloration by gases, have considerable promise as the optical hydrogen sensing films [7-9]. Palladium oxide films coated with noble metal (Pd, Pt, Au) catalysts were expected to have gasochromic coloration, since it is known to exhibit optical absorbance changes due to the reduction with hydrogen. To our knowledge the relation between the crystalline structure of palladium oxide and the gasochromic properties has not been investigated in detail. The formation of PdO occurs at 200°C when heating Pd in air. The oxidization of Pd is almost completed at 700°C and dissociation takes rapidly in the temperature range from 820 to 850°C [10]. However, the oxidization and dissociation temperatures of PdO depend on the Pd powder size [11]. Therefore, detailed characterization of annealed Pd films is required.

In this study, we investigate the effect of annealing temperature of Pd films on the gasochromic performance for hydrogen. The Pd films prepared using an rf magnetron sputtering were annealed at temperatures range from 300 to 900°C in air. The films were characterized by Rutherford backscattering spectroscopy (RBS) and X-ray diffraction (XRD). The gasochromic performance of palladium oxide films coated with Pd catalyst was examined by optical transmission in diluted hydrogen gas.

2. EXPERIMENTAL

Palladium oxide films are prepared by thermal oxidation of polycrystalline Pd films. The Pd films were annealed at temperatures range from 300 to 900°C in air using an electric furnace. Pd films were prepared using an rf magnetron sputtering from a Pd (purity 99.9%) target in an argon. The films were deposited on mirror-polished quartz substrates (10 × 10 × 0.5 mm^3) at room temperature. The deposition chamber equipped with an rf magnetron sputter source was pumped down to a base pressure of about 5×10^{-4} Pa using a turbo-molecular pump. The sputtering gas of the argon (purity 99.999%) was made to flow into the deposition chamber through a mass-flow meter to obtain the required argon pressure under the pumping conditions. The gas pressure was measured by an absolute pressure gauge (Baratron 626, MKS). During the

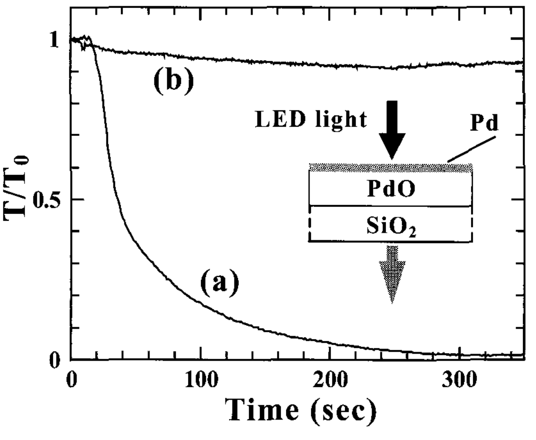

Fig. 1 Optical response of the coloration for the PdO films in 1 % H_2/Ar. (a) with Pd catalyst, and (b) without Pd catalyst.

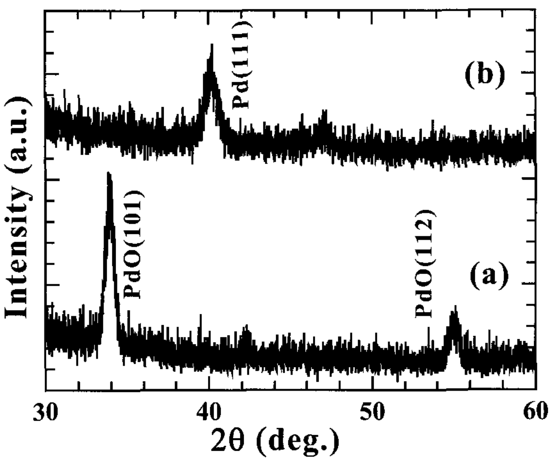

Fig. 2 XRD patterns of PdO film with Pd catalyst, (a) before, and (b) after exposed in 1 % H_2/Ar.

deposition, the pressure of argon gas was maintained at 150 mPa and the rf power was kept at 50 W. The Pd target to substrate distance was approximately equal to 100 mm. The Pd catalyst with a 15 nm thickness was coated by sputtering at room temperature before the evaluation of gasochromic performance. For the gasochromic coloration measurements, the transmittance of the samples was measured using a spectrometer (USB2000, Ocean Optics) with a fiber optics at a wavelength of 645 nm from a light-emitting diode (LED). To confirm the detection of hydrogen less than LEL, the samples were exposed in 1 % H_2/Ar flow of 100 sccm. The optical detection area in the films was 1 mm in diameter. The crystalline structure of palladium oxide films was determined by the XRD using a high-resolution diffractometer (X'Pert-MRD, PANalytical). The X-ray source was operated at 40 kV and 30 mA for Cu-Kα radiations. The composition of palladium films was determined by the RBS. A 3 MV single-stage-accelerator at JAEA/Takasaki was used for the RBS measurements with 2.0 MeV $^4He^+$ particles. The backscattered particles were detected at 165° with respect to the incident beam direction by a surface barrier detector. The thickness of the films was determined with a surface profiler (DEKTAK3ST, Veeco). The surface morphology of the films was examined using an AFM (SPA400, SII).

3. RESULS AND DISCUSSION

The gasochromic performance of palladium oxide films was examined by optical transmittance in 1 % H_2/Ar atmosphere at room temperature. Figure 1 shows optical response curves of gasochromic coloration for the palladium oxide films with 32 nm thicknesses annealed at 600°C, (a) coated with Pd catalyst, and (b) without Pd catalyst, respectively. The transmittance T at a wavelength of 645 nm was measured as a function of exposure time of hydrogen. T_0 is the transmittance at the beginning of the measurements. The normalized transmittance T/T_0 of the film with Pd catalyst is rapidly decreased down to 0.1 within 2 minute. In this case, the change of brown palladium oxide film on quartz glass to metal color was easily identified by the naked eye. On the contrary, the T/T_0 of the film without Pd catalyst shows a monotonic decrease. The result indicates that the Pd catalyst on palladium oxide film causes gasochromic coloration for hydrogen at room temperature.

The crystalline structure of palladium oxide films before and after expose in hydrogen was determined by the XRD in standard θ-2θ geometry. For the sample preparation, A Pd film with 90 nm thickness on a quartz glass substrate was annealed at 600°C in air for 1h and then coated Pd of 15 nm thickness as catalyst at room temperature. Figure 2 shows the XRD patterns of a palladium oxide film (a) before and (b) after exposed in 1 % H_2/Ar at room temperature, respectively. One can recognize that the crystalline structure of the film changes from PdO to Pd in 1 % H_2/Ar. It is indicated that the gasochromic coloration of palladium oxide films is due to the reduction with hydrogen gas.

To examine the effect of annealing temperature of Pd films on the gasochromic performance, polycrystalline Pd films with 32 nm thickness were annealed at temperatures range from 300 to 900°C in air for 1h. The annealed films were coated with Pd catalyst for the examination of gasochromic performance. The dependence of gasochromic performance on annealing temperature of polycrystalline Pd films is shown in Fig 3. The normalized transmittance T/T_0 of the films on quartz substrates was taken after exposure 20 min in 1 % H_2/Ar. The T/T_0 of the films is decreased with increasing annealing temperatures and comes to a minimum at 600°C. This result indicates that the palladium oxide film with superior gasochromic performance for hydrogen was obtained by annealing at 600°C in air.

To characterize the crystalline structure of

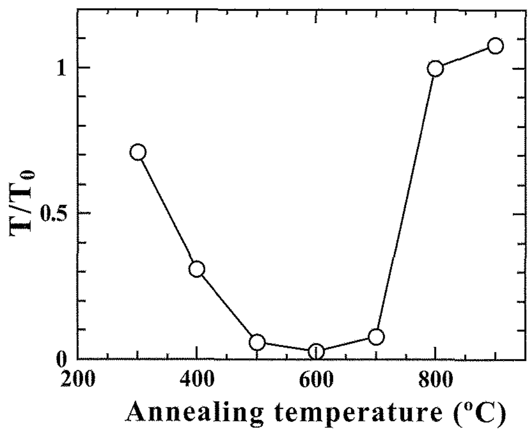

Fig. 3 The dependence of gasochromic performance on annealing temperature of polycrystalline Pd films. The normalized transmittance T/T_0 of the films on quartz substrates was taken after exposure 20 min in 1 % H_2/Ar.

annealed Pd films, the XRD measurements were performed in θ-2θ geometry. Polycrystalline Pd films with 90 nm thickness on quartz glass substrates were annealed at 600 and 900°C in air for 1h. Figure 4 shows the XRD patterns of the films annealed at different temperatures (a) as-deposited, (b) 600 °C, and (c) 900 °C, respectively. The figure shows that the as-deposited film with polycrystalline Pd structure and then become completely oxidized film with polycrystalline PdO structure at 600 °C. The characteristic peaks of the XRD patterns of the film annealed at 600 °C can be attributed to a PdO phase as referred to the JCPDS 43-1024 file. Furthermore, the XRD pattern of the film annealed at 900 °C shows formation of another crystalline structure similar to the as-deposited polycrystalline Pd structure. It can be seen that the thermal decomposition of PdO occurs at temperature higher than 800 °C [10, 11].

Considering the results of gasochromic performance of annealed Pd films as shown in Fig. 3, it can be seen that the change of gasochromic performance is coincident with the change of palladium oxide phase. It was clarified that appropriate gasochromic performance is obtained in the PdO phase. The composition of the palladium oxide films with different annealing temperatures was examined by the RBS. For determination the O/Pd atomic ratio of palladium oxide, the Pd films were deposited on a carbon substrate to obtain the isolated peaks from each element in the backscattering spectrum. The depth profile of palladium and oxygen components in annealed films was also evaluated. Polycrystalline Pd films with 64 nm thickness were annealed at temperatures range from 200 to 600°C in air for 1h. Figure 5 shows the O/Pd atomic ratio of the annealed films with different annealing temperatures. The figure shows the Pd

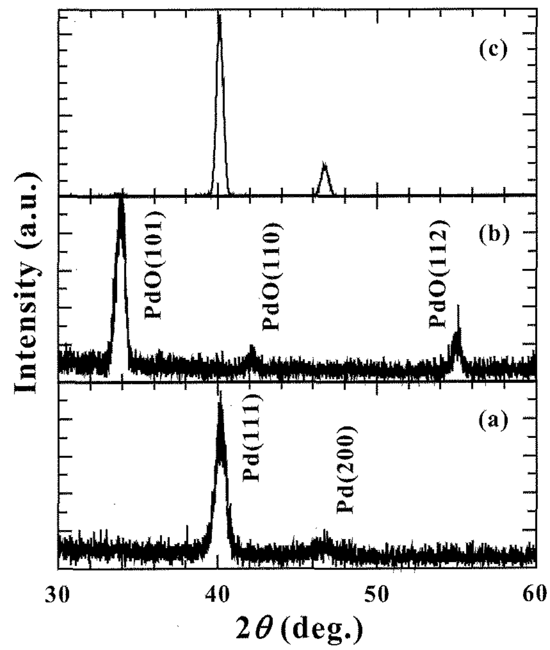

Fig. 4 XRD patterns of Pd films annealed at different temperatures, (a) as-deposited, (b) 600 °C, (c) 900 °C, respectively.

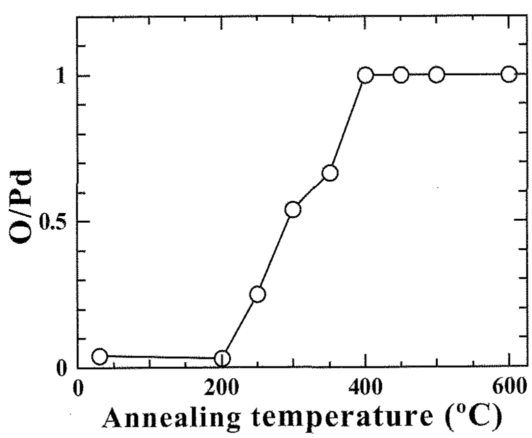

Fig. 5 O/Pd atomic ratio of the films with different annealing temperatures. The O/Pd was determined by the RBS.

phase remains up to at 200 °C and begins to oxidize at around 250 °C and then becomes completely oxidized at 450 °C. However, the films annealed at temperatures from 250 to 450°C, thermal oxidization were observed in the surface region. The oxidation of the film in the whole region was confirmed at 500 °C by the RBS. The results of XRD and RBS for the annealed films confirm the formation of PdO phase completed at 600 °C in air.

The surface morphology of annealed Pd film was observed by the AFM. The Pd films with 64 nm thickness on quartz glass substrate were annealed at temperatures range from 200 to

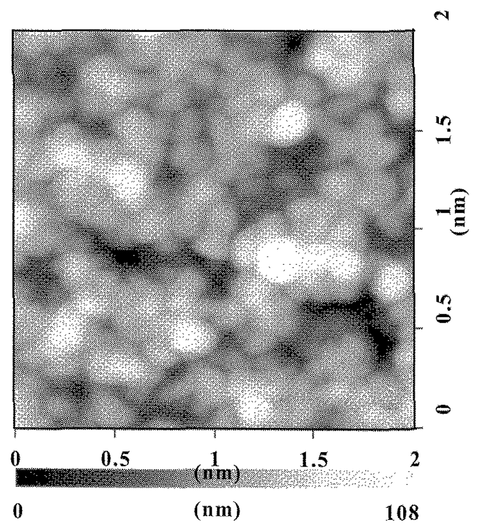

Fig. 6 AFM (2 μm × 2 μm) image of the PdO film prepared by annealing at 600 °C in air for 1h.

600°C in air for 1h. Figure 6 shows the AFM (2 μm × 2 μm) image of the PdO film prepared by annealing at 600 °C in air. The surface of the film shows coarse grains with about 300 nm in diameter. These coarse grains on the film surface were observed at annealing temperature higher than 450 °C. It suggests that the coarse grains are formed due to the oxidization of Pd. It is considered that the formation of coarse grains provides a large specific surface area, which leads to a strong adsorption ability for gases.

4. CONCLUSIONS

We investigated the effect of annealing temperature of polycrystalline Pd films on the gasochromic performance for hydrogen gas. The Pd films prepared by an rf magnetron sputtering were annealed at temperatures range from 300 to 900°C in air. Palladium oxide film with PdO phase shows the appropriate gasochromic performance for hydrogen. The PdO films with superior gasochromic performance for 1 % H_2/Ar were obtained by annealing at 600°C in air for 1h. The results of XRD and RBS indicate that the gasochromic coloration of PdO films is due to the reduction with hydrogen gas. The results should lead to an optimization of preparation conditions to provide the gasochromic films used for the optical hydrogen sensors.

ACKNOWLEDGMENT

This work was partly supported by a Grant-in-Aid for Scientific Research(C) from the Japan Society for the Promotion of Science (No. 17560625)

REFERENCES

[1] C. Christofides, A. Mandelis, *J. Appl. Phys.*, **68**, R1-R30 (1990).
[2] X. Bévenot, A. Trouillet, C. Veillas, H. Gagnaire, M. Clément, *Sensors and Actuators B*, **67**, 57-67 (2000).
[3] M. Aleixandrea, P. Correderab, M.L. Hernanzb, J. Gutierrez-Monreala, *Sensors and Actuators B*, **107**, 113-120 (2005).
[4] P. Fedtke, M. Wienecke, M.-C. Bunescu, M. Pietrzak, K. Deistung, E. Borchardt, *Sensors and Actuators B*, **100**, 151–157 (2004).
[5] Z. Zhao, M.A. Carpenter, H. Xia, D. Welch, *Sensors and Actuators B*, **113** 532-538 (2006).
[6] D. Zalvidea, A. Díez, J.L. Cruz, M.V. Andrés, *Sensors and Actuators B*, **114** 268-274 (2006).
[7] Yong-su Oh, J. Hamagami, Y. Watanabe and M. Takata, *Sensors and Actuators B*, **13-14**, 547-548 (1993).
[8] C. Salinga, H. Weis, M. Wuttig, *Thin Solid Films*, **414**, 275–282 (2002).
[9] V. Vitry, F. Renaux, R. Gouttebaron, J.-P. Dauchot, M. Hecq, *Thin Solid Films*, **502**, 265-269 (2006).
[10] G. Bayer, H.G. Wiedemann, *Thermochimica Acta*, **11**, 79-88 (1975).
[11] S. Penner, D. Wang, B. Jenewein, H. Gabasch, B. Klötzer, A. Knop-Gericke, R. Schlögl, and K. Hayek, *J. Chem. Phys.*, **125**, 0947031-0947038 (2006).

(Received December 10, 2006;Accepted January 31, 2007)