Rapid response hydrogen sensor based on nanoporous Pd thin films

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ABSTRACT

Nanoporous structural palladium (Pd) thin films was achieved through DC sputtering technique and the following annealed process under vacuum condition, which could origin from the melting of ultrathin Pd film on Si substrates and surface tension effect. The results exhibits that the porous structures Pd films would transformed into dispersive Pd particles with the increase of annealing temperature. Contacts of hydrogen sensor based on the Pd nanoporous thin films were then established using platinum (Pt) electrodes. The continuous Pd thin film and dispersive Pd particles show slow or even no hydrogen (H_2) sensing response, while the response is rapid for the Pd film with nanoporous structures. The Pd film annealed at 300 °C showed first-rank hydrogen sensing property (with response time of ~30 s and recovery time of ~10 s), which exhibited linear relationship response to H_2 with concentration from 0.04 to 1.2 %. This sensing behavior would attributed to the electron scattering within nanoporous related to the dissociation of H_2 in Pd lattice. In addition, nanoporous Pd films also exhibited excellent selectivity against other reductive gases, such as CO, NH_3 , CH_3OH etc.

Keywords: palladium (Pd); nanoporous; thin films; hydrogen sensing

Introduction

Hydrogen (H_2) is one of the most important clean and renewable energy, while the production, storage, usage and transportation of H_2 gas are dangerous due to its highly combustible with a Lower Explosive Limit (LEL) of 4.65% at room temperature and pressure [1, 2]. Hence, the detection of H_2 leakage and monitoring H_2 concentration is extremely important [3, 4]. There are many fields concerns the producing and leakage of H_2 , such as coalmine, nuclear power plant, thermal power generation etc. Therefore, it is significant and necessary for hydrogen sensors with performance of high sensitivity, fast response, good selectivity and long-term stability. Moreover, most of the commercial semiconductor hydrogen sensor are still suffering from the slow response, poor selectivity at room temperature [5-7]. In contrast, noble metal-based hydrogen sensors, such as Pd, Pt or alloy exhibit excellent selectivity to H_2 owing to their high hydrogen solubility and diffusivity [8-10]. It's well known that Pd has great affinity towards H_2 absorption, and the lattice expansion of Pd is occurred and the resistivity increased after hydrogen atom diffused into the lattice of Pd thin film and form Pd-hydride [11-14]. However, Pd thin film sensor has very slow H_2 response rate for concentration below 2% at room temperature. In addition, the repeated absorption and desorption of hydrogen on Pd will lead to the well-known phenomenon of hydrogen embrittlement. It's reported that Pd nanostructures with specific morphologies can overcome the hydrogen embrittlement problems. For instance, Favier *et al.* have reported the hydrogen sensor based on electrodeposited Pd mesowire arrays. The lattice expansion reduced the nanogap between Pd mesowires,

which exhibited rapid reversible decrease in the resistance of the array when it was exposed to H₂ [15]. Josh *et al.* have demonstrated the hydrogen sensor based on Pd nanoparticle with spherical shapes deposited on Si substrate. The electro-chemically grown Pd nanoparticles show better hydrogen sensing response than the Pd thin films [16].

Although the sensors based on Pd nanowire or nanoparticle can reduce the hydrogen embrittlement phenomenon through release the stress and increase the response rate, the sensing properties is easy to be disturbed by the temperature-induced deformation of the sensing layers, which will limit the stability and accuracy of the sensors. Recently, porous structures with specific aspect ratios have raised active research for sensing H₂ or other inflammable gases. For example, Rani and Miyazaki *et al.* introduced a hydrogen gas sensor based on anodically oxidized nanoporous Nb₂O₅ and TiO₂ films [17, 18], the specific structure may be responsible for the improvement of sensing properties. Therefore, in this work, nanoporous Pd thin films fabricated by DC sputtering method and following heat treatment under vacuum conditions will be reported. The sensors with specific surface area exhibited rapid response to hydrogen gas with concentration of 100 ppm to 1.2 % in air at room temperature. The nanoporous structure can promote the release of stress induced by the lattice expansion during the sensing process.

Experimental

Materials synthesis and characterization

Nanoporous Pd films were fabricated through DC magnetron sputtering process on

SiO₂/Si-(100) substrate and followed by heat treatment under vacuum condition. The substrates were ultrasonic cleaned in baths of acetone, methanol, and de-ionized water, respectively. Firstly, the deposition chamber evacuated to 6.4×10^{-4} Pa. Then the Pd thin films were deposited on substrate at ~1 Pa with DC input power of 70 W for 1 s. After that, Pd thin films were *in-situ* annealed in the vacuum chamber for 1 h at 200 °C, 250 °C, 300 °C, 350 °C and 400 °C, respectively. The phase structures of the samples were identified by X-ray diffraction (XRD, Bruke D8 Advanced) with CuK α radiation ($\lambda=1.54184$ Å). The surface morphology of the thin films was characterized by atomic force microscopy (AFM, Veeco Nanoscope VIII) and scanning electron microscopy (SEM, JEOL 7100F).

Sensor fabrication and measurement

The hydrogen sensors were fabricated by depositing the Pd thin films onto pre-patterned Pt electrodes. The hydrogen sensing properties of the sensor were tested by using a homemade gas-sensing testing system. The resistance of the sensors were monitored by digital source meter (Keithley 2400) with source voltage of 1.5 V. After the sensor was located at the center of the test chamber, a certain volume of H₂ and dry air were introduced into the mix chamber through the mass flow controller. After the testing chamber was evacuated to 50 Pa, the pre-mixed testing gas in the mixing chamber was introduced into the test chamber for the measurement of hydrogen response. For the measurement of recovery process, dry air was introduced into the chamber to sweep the hydrogen gas and monitor the resistance variation of the sensors.

Results and Discussions

Fig. 1 shows XRD patterns of the as-deposited Pd thin films after annealed under vacuum conditions at different temperatures. The diffraction peaks (2θ) located at $\sim 40^\circ$ were corresponding to (111) plane of cubic structure Pd (JCPDS Card No. 65-6174). The full width at half maximum (FWHM) were reduced, and the average grain sizes of the samples were increased from 5.7 to 14.6 nm with increasing annealing temperatures according to the Scherer formula.

Fig. 2 shows the corresponding AFM 2D topography of the samples annealed at different temperatures. The root-mean-squared (RMS) roughness of the samples were measured to be 0.412, 0.459, 0.739, 2.11 and 11.2 nm, respectively. When the annealing temperature is 200 °C, Pd films with smooth surface were obtained besides several dispersed particles on Si substrate (as shown in Fig.2a). As the annealing temperature increased to 250 °C, Pd films tends to crackles due to the mismatch between metal Pd and Si substrate (Fig.2b). As the temperature reach up to 300 °C, Pd films with nanoporous structure are formed, as shown in Fig.2c. While as the annealing temperature over 350 °C, Pd nanoparticles with various size distributions were appeared, which may related to the melting and Ostwald ripening process of tiny Pd particles at higher temperatures (Fig.2d-2e). We consider that the competition between metal surface melting effect and surface tension effect under various temperatures should be responsible for the formation of porous Pd films. In case of the annealing temperature is lower than 350 °C, the partial melting is dominate, the melting of Pd will lead to in-plane shrink and tend to form the porous structures, as

shown in Fig.2f. While as the annealing temperature is higher than 400 °C, the acceleration of Ostwald ripening process and grain growth is dominate, which may lead to the dispersed isolate Pd particles on substrate.

Fig. 1 The XRD patterns of Pd thin films after heat treatment under vacuum condition at different temperatures. (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C

Fig.2 The AFM 2D topography (a~e) of Pd thin films after heat treatment at different temperatures and its growth process scheme (f). (a) 200 °C; (b) 250 °C; (c) 300 °C; (d) 350 °C; (e) 400 °C

Fig. 3 (a) The schematic diagram of nanoporous Pd film sensors; (b) the room-temperature response to 1.2 % hydrogen gas of Pd films annealed at different temperatures; (c) The sensitivity, response and recovery time of nanoporous Pd film sensors.

The schematic diagram of hydrogen sensor based on nanoporous Pd thin films is shown in Fig.3a. The interspacing between two Pt electrodes is about 5 mm. Fig. 3b and 3c show the room-temperature response curves to the same hydrogen concentration (1.2 %) in air of the sensors based on Pd thin films annealed at various temperatures. As shown in Fig. 3b, the initial resistance of all sensors is very small, which increases rapidly after contacting hydrogen molecule, and the resistance quickly recovered to the initial states when evacuated hydrogen environment. In order to systematically evaluate the sensing performance, the sensitivity factor (S) of the sensors was defined as $S = (R - R_0)/R_0$, where R and R_0 represents the resistance of the sensors in testing gas and pure air, respectively. Furthermore, the response time was defined as the time from the initial state to 90 % of saturation resistance. Fig. 3c shows the variation of sensitivity ($S_{\max}$) and response/recovery time of Pd films annealed under various temperatures. As shown, the sensitivity of Pd films increased gradually with increasing the annealing temperatures, which could relate to the variation of

microstructure in Pd film as increasing the temperatures. Pd is well known for its ability to absorb high amounts of hydrogen. The metal palladium undergoes a structural change with the absorption of hydrogen into the metal. When the metal Pd is exposed to hydrogen atmosphere, hydrogen molecules are adsorbed on the surface of the metal and dissociated into hydrogen atoms, which will fill the octahedral sites and form α -phase of the Pd hydride in this absorption process. Then the hydrogen atoms diffuse into the lattice space. With the continuation of H absorption, a new phase of $\alpha + \beta$ coexistence is formed, which lead to lattice expansion and structural transformation. The phase transition will add to the scattering of the electrons in the crystal lattice and alters the electrical resistance of Pd [19-23]. We consider that the dissociated hydrogen atom, which needs longer diffusion to saturate for continuous films due to the small gap between the Pd particles. Moreover, nanoporous structures have larger specific surface area, which facilitate more H_2 dissociated into atomic hydrogen, and diffusion reached saturation in a short period. The increased resistance of the sensing layer can attributed to the increased electron scattering by the hydrogen atoms [24,25]. Moreover, the response time of the sensors obtained at 200 to 350 °C is lower than 10 s, which is faster than continuous Pd films and dispersive Pd particles in existing work [26,27]. While the response time of the sensors increased to ~ 60 s greatly when the annealing temperature increased to 400 °C. Similar phenomenon is observed for the recovery time. This may be due to the much higher grain size of the sample annealed at 400 °C, which could slow down the diffusion of hydrogen atom into/out of the Pd grain.

Fig. 4 shows the detailed H_2 response to the concentration of 0.04 ~ 1.6 % in air of nanoporous Pd films annealed at 300 °C, which exhibited relatively optimized performance than the others ones (higher sensitivity and faster response/recovery process). As shown in Fig. 4b, the sensitivity

exhibited linear correlation with the hydrogen concentration ranging from 0.04 to 1.2 %. When the hydrogen concentration increased to 1.6 %, the sensitivity increased slightly, which could be attributed to the saturation of hydrogen adsorbed in the Pd layer. Furthermore, the response time was also increased as the concentration enhanced from 0.04 to 1.2 %. However, the response time was decreased when the hydrogen response was saturated as the concentration reaching up to 1.6 %. Fig. 4c shows five testing cycles of the sensor towards hydrogen concentration of 1.6 % in air. The response curves exhibited good repeatability and recovery performance at room temperature. Moreover, the sensor also shows great selectivity to hydrogen compare to other reductive gases such as NH_3 , acetone, ethanol, methanol and CO , which can be attributed to the great affinity of Pd towards hydrogen atoms [28,29]. The good repeatability and selectivity as well as fast room-temperature linear response provide great potential of the nanoporous Pd thin films in the hydrogen sensing fields.

Fig. 4 The room-temperature hydrogen response of nanoporous Pd film sensors annealed at 300 °C.

(a) The transient response to various concentration of H₂ in air; (b) The H₂ concentration-dependent response time and sensitivity; (c) repeatability; (d) selectivity.

Conclusions

The nanoporous Pd thin films were fabricated by DC sputtering and annealing process. With increasing of annealed temperature, the crystallization degree enhanced and the grain sizes increased, while the surface density of Pd decreased. The hydrogen sensors based on the Pd nanoporous films exhibited fast and reversible room-temperature hydrogen sensing performance with response time lower than 30 s. The increasing of annealing temperature may lead to the increase of sensitivity and recovery time. The sample after annealed at 300 °C showed optimized sensing property, which exhibited linear response to hydrogen with concentration from 0.04 to 1.2 %. The sensing behavior can attributed to the electron scattering induced by the dissolved hydrogen in the Pd lattice. The Pd nanoporous thin films also exhibited great selectivity against other reductive gases. Therefore, nanoporous Pd films provide a fast response sensing structure for hydrogen leakage at room temperature.

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REFERENCES

- [1] Hübert T, Boon-Brett L, Palmisano V, Bader MA. Developments in gas sensor technology for hydrogen safety. *Int J Hydrogen Energy* 2014;39:20474-83.
- [2] Choi KJ, Jang HW. One-Dimensional Oxide Nanostructures as Gas-Sensing Materials: Review and Issues. *Sensors* 2010;10:4083-99.
- [3] Gu H, Wang Z, Hu Y. Hydrogen gas sensors based on semiconductor oxide nanostructures. *Sensors* 2012;12:5517-50.
- [4] Buttner WJ, Post MB, Burgess R, Rivkin C. An overview of hydrogen safety sensors and requirements. *Int J Hydrogen Energy* 2011;36:2462-70.
- [5] Huang J, Wan Q. Gas Sensors Based on Semiconducting Metal Oxide One-Dimensional Nanostructures. *Sensors* 2009;9:9903-24.
- [6] Varghese OK, Gong D, Paulose M, Ong KG, Grimes CA. Hydrogen sensing using titania nanotubes. *Sens Actuators B* 2003;93:338-44.
- [7] Wang Z, Hu Y, Wang W, Zhang X, Wang B, Tian H, et al. Fast and highly-sensitive hydrogen sensing of Nb₂O₅ nanowires at room temperature. *Int J Hydrogen Energy* 2012;37:4526-32.
- [8] Kumar MK, Rao MSR, Ramaprabhu S. Structural, morphological and hydrogen sensing studies on pulsed laser deposited nanostructured palladium thin films. *J Phys D: Appl Phys* 2006;39:2791-5.
- [9] Kim B-J, Kim J-S. Hydrogen sensor using the Pd film supported on anodic aluminum oxide. *Intern J Hydrogen Energy* 2014;39:16500-5.
- [10] Zeng XQ, Latimer ML, Xiao ZL, Panuganti S, Welp U, Kwok WK, et al. Hydrogen gas sensing with networks of ultrasmall palladium nanowires formed on filtration membranes. *Nano Lett* 2011;11:262-8.

- [11] Kiefer T, Villanueva LG, Fargier F, Favier F, Brugger J. Fast and robust hydrogen sensors based on discontinuous palladium films on polyimide, fabricated on a wafer scale. *Nanotechnology* 2010;21:505501.
- [12] Rashid T-R, Phan D-T, Chung G-S. A flexible hydrogen sensor based on Pd nanoparticles decorated ZnO nanorods grown on polyimide tape. *Sensors & Actuators B: Chem* 2013;185:777-84.
- [13] Joshi RK, Krishnan S, Yoshimura M, Kumar A. Pd Nanoparticles and Thin Films for Room Temperature Hydrogen Sensor. *Nanoscale Res Lett* 2009;4:1191-6.
- [14] Lo C, Tan S-W, Wei C-Y, Tsai J-H, Lour W-S. Sensing properties of resistive-type hydrogen sensors with a Pd-SiO₂ thin-film mixture. *Intern J Hydrogen Energy*. 2013;38:313-8.
- [15] Favier F, Walter EC, Zach MP, Benter T, Penner RM. Hydrogen sensors and switches from electrodeposited palladium mesowire arrays. *Science* 2001;293:2227-31.
- [16] Joshi RK, Krishnan S, Yoshimura M, Kumar A. Pd Nanoparticles and Thin Films for Room Temperature Hydrogen Sensor. *Nanoscale Res Lett* 2009;4:1191-6.
- [17] R.A. Rani, A.S. Zoolfakar, J.Z. Ou, et al. Nanoporous Nb₂O₅ hydrogen gas sensor. *Sensors & Actuators B* 2013;176:149-56.
- [18] H. Miyazaki, T. Hyodo, Y. Shimizu, M. Egashira. Hydrogen-sensing properties of anodically oxidized TiO₂ film sensors. *Sensors and Actuators B* 2005;108:467-72.
- [19] Cheng Y-T, Li Y, Lisi D, Wang W. Preparation and characterization of Pd/Ni thin films for hydrogen sensing. *Sensors & Actuators B* 1996;30:11-6.
- [20] Wu F, Morris J. The effects of hydrogen absorption on the electrical conduction in discontinuous palladium films. *Thin Solid Films* 1994;246:17-23.

- [21] Xu T, Zach M, Xiao Z, Rosenmann D, Welp U, Kwok W, et al. Self-assembled monolayer-enhanced hydrogen sensing with ultrathin palladium films. *Appl Phys Lett* 2005;86:203104.
- [22] H. Frieske, E. Wicke. Magnetic susceptibility and equilibrium diagram of PdH_n. *Berichte der Bunsengesellschaft für Physikalische Chemie* 77 (1973) 48–52.
- [23] Y.K. Gautam, A.K. Chawla, A. Saif, R.D. Khan, R. Agrawal, Chandra. Hydrogen absorption and optical properties of Pd/Mg thin films prepared by DC magnetron sputtering. *International Journal of Hydrogen Energy* 37 (2012) 3772–3778.
- [24] M. Khanuja, D. Varandani, B.R. Mehta, Pulse like hydrogen sensing response in Pd nanoparticle layers, *Applied Physics Letters* 91 (2007) 253121–253123.
- [25] C. Christofides, A. Mandelis, Solid-state sensors for trace hydrogen gas detection, *J. Appl. Phys.* 68 (6) (1990) R1–R30.
- [26] J. RaviPrakash, et al. Hydrogen sensors: Role of palladium thin film morphology. *Sensors and Actuators B: Chemical*. 2007. 120(2): p. 439-446.
- [27] Yogendra K. Gautam, Ravish Jain. Studies on hydrogen sensing properties of nanostructured Pd and Pd/Mg thin films prepared by pulsed laser deposition. *Sensors and Actuators B: Chemical*. 176 (2013) 453–459
- [28] Aruna I, Mehta B, Malhotra L. Faster H recovery in Pd nanoparticle layer based Gd switchable mirrors: Size-induced geometric and electronic effects. *Appl Phys Lett* 2005;87:103101.
- [29] Kumar P, Malhotra L. Effect of current density on thermodynamic properties of nanocrystalline palladium capped samarium hydride thin film switchable mirrors. *J Nanomater* 2007;2007:52083.