

Anodized aluminum oxide (AAO) based nanowells for hydrogen detection

Francisco Rumiche*^{a,b}, Hsien-Hau Wang^b, J. Ernesto Indacochea^a, Ming L. Wang^a
^a Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, IL, USA 60607;
^b Materials Science Division, Argonne National Laboratory, Argonne, IL, USA 60439;

ABSTRACT

A nanostructured sensing element based on anodic aluminum oxide (AAO) nanowells was fabricated and assessed for hydrogen gas sensing. AAO nanowells with an average diameter of 73 nm and depth proportional to the anodization time were immersed in a surfactant solution and coated with an 8 nm film of palladium nanoparticles. The electrical resistance change of the nanostructure with hydrogen gas exposure was used as the sensing parameter. The AAO nanowells-Pd nanostructures were characterized using atomic force microscopy (AFM), field-emission scanning electron microscopy (FESEM), and contact angle test. Hydrogen concentrations as low as 0.05 vol% (500 ppm) can be detected at room temperature. Response times as fast as 1.15 seconds were obtained. Compared to current devices and nanostructures in development, the AAO nanowell-Pd nanostructure is found to be considerably fast without compromising sensitivity and selectivity.

Keywords: Hydrogen sensing, anodic aluminum oxide, nanowell, palladium

1. INTRODUCTION

Detection and monitoring devices are essential components in the safe and efficient production, storage, and operation of the hydrogen infrastructure. A basic classification of hydrogen detectors comprises catalytic bead sensors, electrochemical sensors, resistive palladium alloys sensors, hydrogen field effect transistors and Schottky diodes, and semiconductor metal oxide sensors [1,2]. Although these technologies are suitable for many industrial applications, some of them are certainly not appropriate for fuel cells, household, biomedical, and transportation applications because of their size, high temperature operation, slow response, cost, and energy input. Therefore, to ensure safety, efficiency and reliability during operation, hydrogen sensors with good sensitivity, fast response, IC compatibility, ability to work at room temperature, low cost and low power consumption are required. The great surface activity, very small size, superior sensitivity and low-power consumption of nanostructures have recently attracted the attention of scientists to overcome the limitations of current hydrogen sensing devices [3-8]. Palladium is the most preferred active material for sensing devices due to its affinity with hydrogen. Hydrogen adsorbs and dissociates spontaneously in palladium and its alloys [9,10]. These phenomena induce changes in the electrical and optical properties of palladium forming the basis of operation for hydrogen sensors. In addition, it has been demonstrated that anodic aluminum oxide (AAO) provides an excellent substrate for hydrogen sensing not only because it provides a rough surface with large surface area for supporting palladium nanostructures but also because the surface is weakly conductive which facilitates the measuring of electrical properties variation [11,12].

In this paper, we focus on the AAO shallow region with an aspect ratio of less than 10 to produce an array of nanowells used as a substrate for thin films of palladium nanoparticles. We investigated three anodization conditions (2, 6 and 12 minutes) and their influence on hydrogen sensing at room temperature. Structural characterization of the nanostructures with use of atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) is presented.

*frumic1@uic.edu; phone 1 312 355-1451; fax 1 312 996-2426; www.uic.edu

Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2008,
edited by Masayoshi Tomizuka, Proc. of SPIE Vol. 6932, 693230, (2008)
0277-786X/08/\$18 · doi: 10.1117/12.776981

Proc. of SPIE Vol. 6932 693230-1

2. EXPERIMENTAL DETAILS

AAO nanowells were fabricated using a two-step anodization process [13,14]. Annealed aluminum foil 0.01 in. thick, 99% purity, was used as the base material. The samples were anodized for 4 hours in 0.3 M oxalic acid solution at 3 °C applying 40 V. A uniform pattern on the aluminum surface was revealed after immersing the samples in an acid bath at 70 °C that removed the alumina layer. AAO nanowells developed uniformly after a second anodization using the same parameters as those used in the first step, except the time. Three anodization times were selected for this study, 2, 6 and 12 minutes. In order to enhance surface hydrophobicity, all AAO nanowell samples were immersed in a 1mM dichloromethyl-octylsilane in toluene solution for 24 hours; then rinsed in a 50% toluene/50% ethanol solution and dried at 110 °C for 1 hour. The effectiveness of the surfactant solution was evaluated by measuring the contact angle of a deionized water droplet on the surface of the samples before and after immersion. Contact angle measurements were performed using a First Ten Amstrongs FTÅ 125 dynamic contact angle analyzer with an APPR b/w camera. Then, an 8 nm thin film of palladium nanoparticles was deposited on top of the nanowells by thermal evaporation using a BOC Edwards Auto 306 vacuum coating system. The last step in the fabrication of the nanostructured element was the attachment of two pieces of thin copper wires at the ends with two conductive carbon paste electrodes, with the help of an optical microscope. FESEM was conducted with a Hitachi S-4700-II instrument with an accelerating voltage of 10 KV. AFM was performed using a Nano Scope® IV multimode scanning probe microscope system. Figure 1 is a schematic illustrating the nanostructured sensing element.

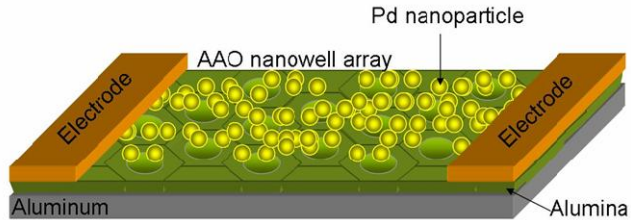


Fig. 1. Schematic of the AAO nanowell-Pd nanostructure

The hydrogen sensing element was mounted onto standard four-probe holders acting as a two-probe experimental stage with copper wires soldered to two of the four-probe electrical contacts. A schematic of the experimental setup used for the hydrogen sensing measurements is shown in Figure 2. The sample was sealed inside a small test chamber with a gas inlet and outlet. The gas flow through the test chamber was controlled via a MKS type 247 mass flow controller. The sample stage was connected to a Keithley 2001 digital multimeter via a BNC connector to monitor the changes in the electrical resistance with exposure to different levels of hydrogen gas. The gas cycle consisted in flowing first pure argon, followed by a fixed hydrogen/argon ratio, and then pure argon again. The tests were conducted at room temperature. At least three cycles were performed for each sample at each hydrogen concentration. Resistance measurements were conducted at hydrogen concentrations between 0.05% (500 ppm) and 1% (10000 ppm). All data acquisitions were carried out with a LabView software program through a GPIB interface card.

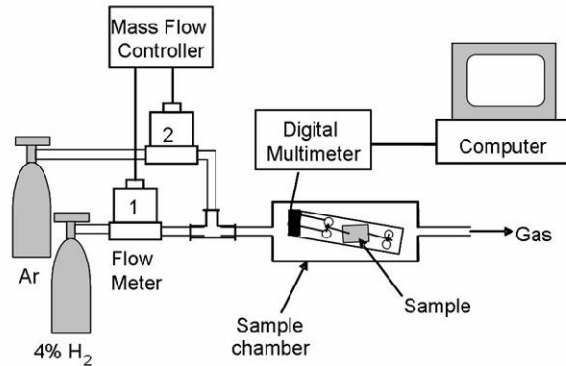


Fig. 2. Schematic of hydrogen sensing experimental setup.

3. RESULTS AND DISCUSSION

3.1 AAO nanowell and nanostructure characterization

Figure 3 shows the AFM images of the AAO nanowells anodized for 2, 6, and 12 minutes. A highly ordered structure composed of nanopores with the same diameter arranged in a two-dimensional hexagonal closed packed pattern is observed. Each pore, about 70 nm in diameter, is surrounded by six bumps of approximately 30 nm in diameter. The pore depth was observed to increase with increasing anodization time as seen in the 3D images. The highly ordered structure is the result of the two anodization steps. The first anodization produces initially a disordered AAO membrane because of the high initial pore density ($\sim 10^{10}$ - 10^{12} cm⁻²) and potential nucleation sites remaining on the surface after the electropolishing stage [15]. Ordering of the pore arrangement increases with the anodizing time after the steady state growth of the porous structure is established [13,14]. Stripping off the porous alumina produced during the first anodization leaves a textured surface composed of a highly ordered dimple array. During the second anodization each dimple will initialize a new pore resulting in a final highly ordered nanowell array.

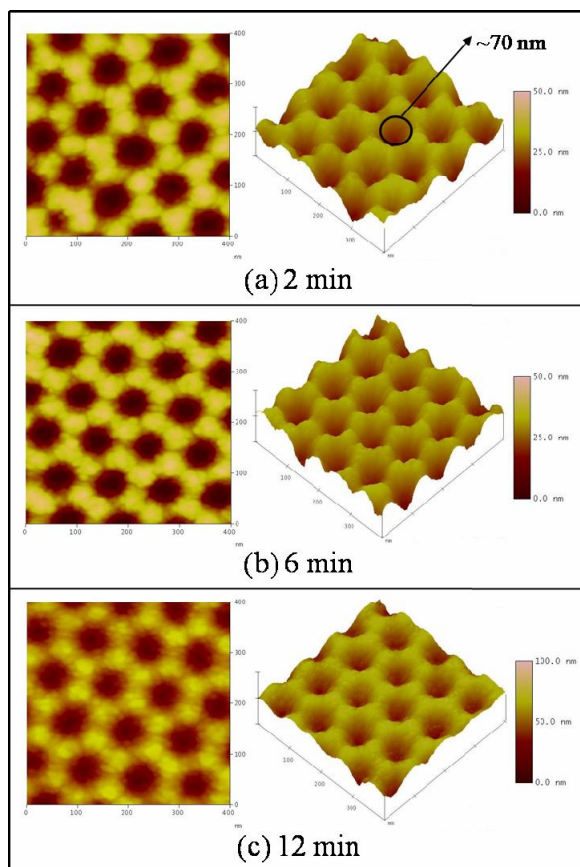


Fig. 3. AFM images of the AAO nanowells for different anodization times.

Before the palladium deposition the AAO nanowells were chemically treated to modify the surface wettability. Figure 4 shows the profile of a water droplet on the AAO nanowells surface before and after immersion in a 1mM dichloromethyl-octylsilane solution for 24 hours. It is observed that the contact angle, defined as the angle between the AAO nanowells surface and the tangent to the water droplet, increased after immersion. This indicates that the AAO surface has been covered by the low-surface-energy silane and therefore possesses a relatively hydrophobic surface. As the anodization time increases the effect of the silane on the contact angle decreases.

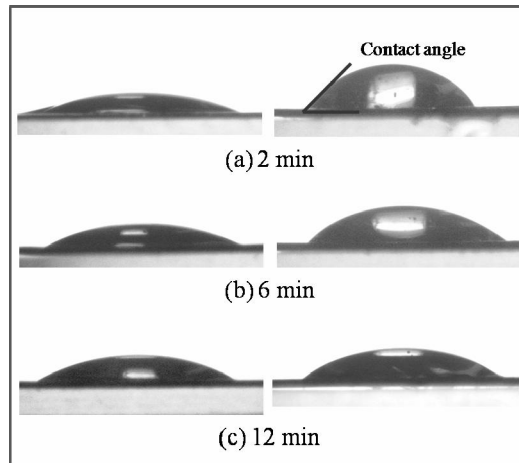


Fig. 4. Water droplet profile on the AAO nanowells surface before (left side) and after (right side) immersion in surfactant solution for different anodization times.

Figure 5 shows the AFM images of the nanostructured elements composed of AAO nanowells anodized for 2 and 12 minutes, treated with the surfactant solution, and coated with an 8 nm thin film of palladium nanoparticles. A reduction in the pore diameter is observed from about 70 nm (Figure 3) to 60 nm (Figure 5). This is attributed to the conformable and tight adherence of the palladium film to the pore surface, such that the topological surface details of the AAO membrane are easily observed.

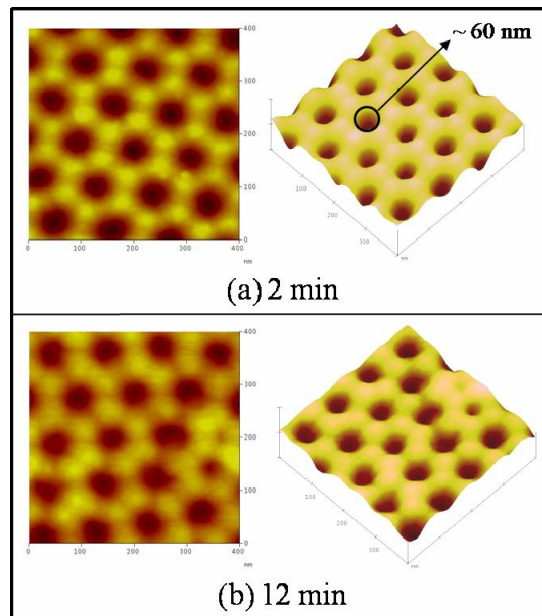


Fig. 5. AFM images of the AAO nanowells for two anodization times and coated with Pd nanoparticle film.

The results of measurements performed on the cross-sectional AFM images for both plain AAO nanowells and AAO nanowell-Pd nanostructure are presented in Figure 6. These results are plotted as a function of anodization time. It is seen that the diameter of the AAO nanowells remains practically constant and independent of anodization time. This is consistent with what is reported in the literature, that is, the AAO pore diameter depends only on electrolyte chemistry and anodizing voltage and not on the anodization time [11-15]. In our investigation all samples were anodized in a single

electrolyte (0.3 M oxalic acid solution) and at an applied voltage of 40 V. The average pore diameter of the AAO nanowell was found to be about 73 nm. The average pore diameter for the Pd coated nanostructure specimens was 64 nm. Furthermore, it can be observed in Figure 6 that the nanowell depth of the plain AAO nanowell increases with anodization time. This is consistent with the AAO pore growth mechanism reported by Li et al. [15]. Our results show that the pore depth increases with anodization time, for two and four minutes, but then it remains constant for longer anodization times. This is attributed to the depth resolution of the AFM. Due to its very limited penetration into the pore, the AFM is not suitable to measure the depth for the nanowells with anodization times longer than 4 minutes.

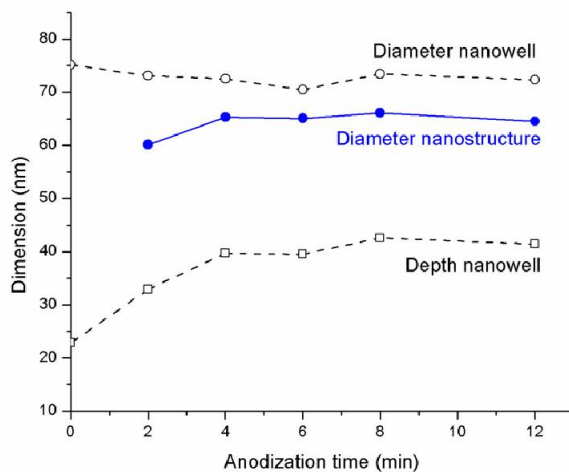


Fig. 6. Diameter and depth of plain AAO nanowells and AAO-nanowell nanostructure as a function of anodization time.

Figure 7 shows the FESEM micrographs of the nanostructure with the AAO nanowells anodized for 12 minutes. Figure 7(a) shows the domain structure, characterized by domain boundaries, and point defects, which are pointed out by small white arrows in the photograph; some areas of misfit on the regular arrangement of the nanowells that resemble dislocations are also observed. Figure 7(b) shows the arrangement of the nanowells within a domain, it is observed that these pores are highly ordered and aligned. The mean nanostructure pore diameter and pore to pore distance for this nanostructure are approximately 60 nm and 110 nm respectively. Similar images were observed for the samples anodized for 2 and 6 minutes.

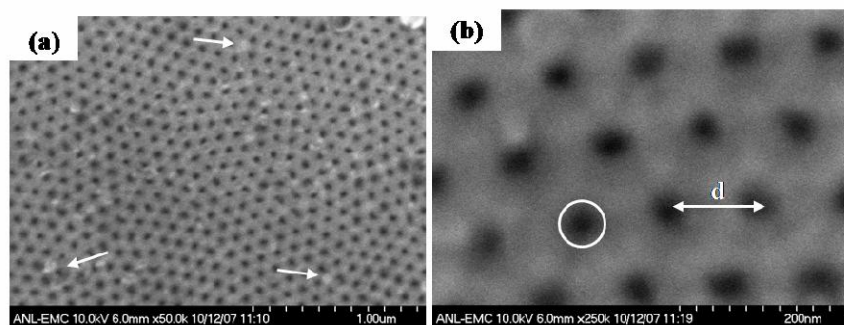


Fig. 7. FESEM image of the AAO nanowell- Pd nanostructure anodized for 12 min.

3.2 Hydrogen sensing performance

The hydrogen sensing properties were measured by exposing the nanostructure to various hydrogen concentrations: 1%, 0.5%, 0.3%, 0.2%, 0.1% and 0.05%, using argon as the carrier gas. Each sample was exposed to the gas cycle described above; the exposure to argon gas first was done to obtain a baseline reading. Figure 8 shows the dynamic response at room temperature of two nanostructures with nanowells anodized for 2 and 12 minutes. It is observed that both

nanostructured elements detect hydrogen gas for all the concentrations tested. The resistance increases promptly as the carrier gas is charged with hydrogen and the nanostructure makes contact with it; the baseline resistance reading corresponds to the flow of Ar gas, prior and after the hydrogen/argon gas mixture flow. It is evident that the sensor response is more significant at higher hydrogen concentrations, yet a good resolution is still achieved at the lowest hydrogen concentration of 0.05% (500 ppm).

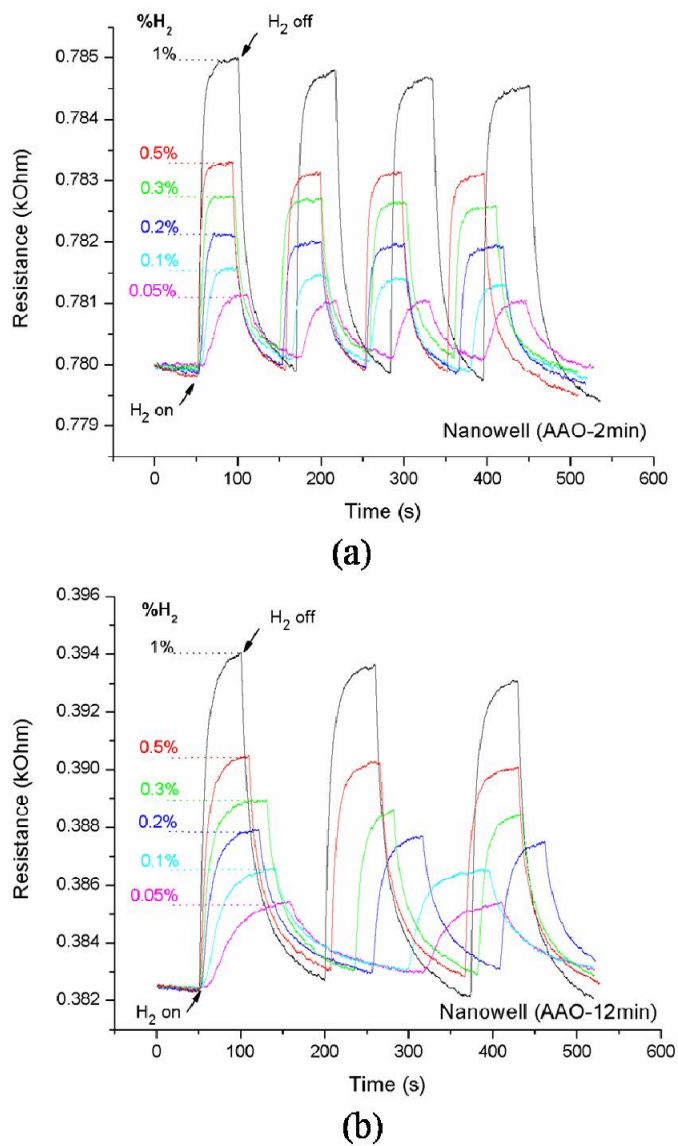


Fig. 8. Hydrogen sensing curves for the AAO nanowell-Pd nanostructure. The anodization times were (a) 2 minutes and (b) 12 minutes.

The increase in the electrical resistance of both systems as they become in contact with hydrogen is attributed to the formation of a hydride phase which obviously would have higher resistivity. When palladium is exposed to hydrogen gas, the H_2 molecules dissociate into hydrogen atoms which in turn will diffuse into the palladium lattice and react with Pd atoms to form palladium hydride (PdH_x). During PdH_x formation the lattice maintains the pure palladium FCC structure. However, stresses in the lattice are induced due to the hydrogen atoms located in the interstitial octahedral

sites [10]. Furthermore, intrinsic defects in nano-scaled palladium films can create hydrogen enrichment areas that will favor the formation of high resistivity PdH_x phase [16]. The superposition of the hydrogen-induced lattice stresses, favored PdH_x formation, and changes in the electronic structure of the palladium [17] results in an increase in the resistance of the whole structure. As observed in Figure 8, the higher the hydrogen concentration the higher the variation in resistance. Furthermore, a complete and relatively fast recovery due to the hydrogen desorption was observed for all the samples when they were exposed back to argon. Similar curves were obtained for the nanostructure anodized for 6 minutes.

Sensitivity and response time were used to evaluate and compare the hydrogen sensing performance of the nanostructured sensors. Sensitivity is defined by the formula:

$$S = \frac{(R_s - R_o)}{R_o} \times 100\% \quad (1)$$

where, R_s is the resistance value after exposure to a specific hydrogen concentration and R_o is the average baseline obtained in argon gas only. The response time is defined as the time to reach the 36.8% (e⁻¹) of the total change in resistance upon exposure to hydrogen. Figure 9 shows the sensitivity as a function of the square root of hydrogen concentration for the nanostructures anodized for 2, 6, and 12 minutes. A linear relationship can be observed when plotting sensitivity versus the square root of hydrogen concentration. Obviously the greater the hydrogen concentration in the gas, the greater the sensitivity; in addition, sensitivity increases as the anodization time to fabricate the AAO nanowells increases. The Pd-nanostructure anodized for 12 minutes has the highest sensitivity at all concentrations; a maximum sensitivity value of 3% was obtained at 1% hydrogen concentration. Higher sensitivity in the sample anodized for 12 minutes may be due to the deeper pores that create not only larger surface area but also more favorable sites for the adsorption to occur.

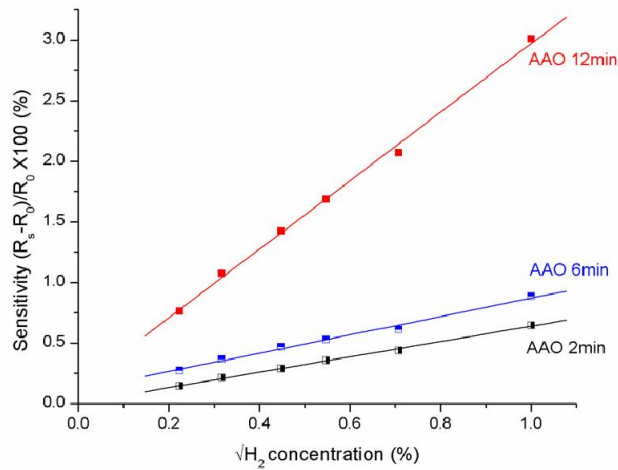


Figure 9. Sensitivity versus square root of hydrogen concentration.

The response time as function of hydrogen concentration for all three samples is shown in Figure 10. The response time diminishes with increasing concentrations of hydrogen gas for all anodization times, until a concentration of about 0.5% is reached and then it appears to level off. The sample anodized for 6 minutes had the fastest response time for hydrogen concentrations greater than 0.2%, followed by the sample anodized for only 2 minutes; it was observed, however, that for hydrogen levels less than 0.2% both the 2 and 6 minute anodized Pd-nanostructure assemblies showed similar response time. The fastest response time was 1.15 sec for a concentration of 1% hydrogen corresponding to the 6 minute anodization. The sample anodized for 12 minutes, however, had the slowest response time for all hydrogen concentrations; the longer response times for this particular specimen are likely caused by the larger surface area and numerous active points compared to the other two samples. It must be noted that even for very low levels of hydrogen gas (less than 0.2%) the response times are still modestly short, but still comparable or faster than those reported by other investigations [3-8].

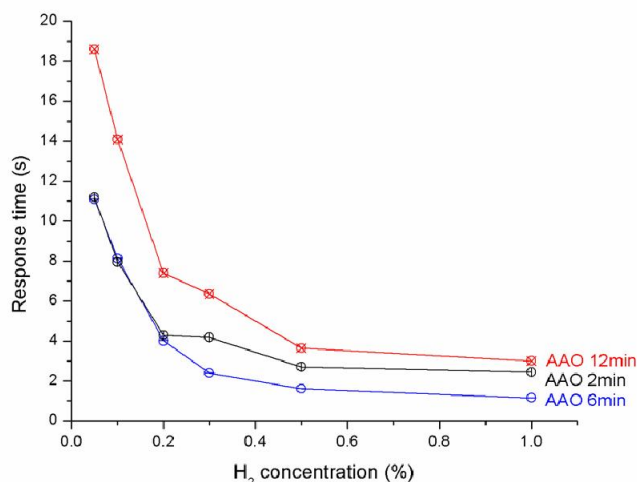


Figure 10. Response time versus hydrogen concentration.

4. CONCLUSIONS

1. A hydrogen sensing nanostructure system with superior response time characteristics based on AAO nanowells has been successfully fabricated.
2. A detection limit as low as 0.05% (500 ppm) at room temperature has been demonstrated.
3. Sensitivity and response time were found to be affected by the anodization time.
4. Compared to current sensors and nanostructure devices in development, AAO based nanowells coated with palladium nanoparticles film exhibit fast response times without compromising sensitivity and selectivity.

REFERENCES

- [1] Aroutiounian V.M., "Hydrogen detectors", *International Scientific Journal for Alternative Energy and Ecology* 3 (23), 21-31, (2005).
- [2] Aroutiounian V.M., "Metal oxide hydrogen, oxygen, and carbon monoxide sensors for hydrogen setups and cells", *International Journal of Hydrogen Energy* 32, 9, 1145-1158, (2007).
- [3] Mubeen S., Zhang T., Yoo B., Deshusses M., Myung N., "Palladium nanoparticles decorated single-walled carbon nanotube hydrogen sensor", *Journal of Physical Chemistry C*, (2007).
- [4] Ding D., Chen Z., Rajaputra S., Singh V., "Hydrogen sensors based on aligned nanotubes in an anodic aluminum oxide template with palladium as a top electrode", *Sensors and Actuators B* 124, 1, 12-17, (2007).
- [5] Shimizu Y., Hyodo T., Egashira M., "H₂ sensing performance of anodically oxidized TiO₂ thin films equipped with Pd electrode", *Sensors and Actuators B* 121, 219-230, (2007).
- [6] Wang M., Feng Y., "Palladium-silver thin film for hydrogen sensing", *Sensors and Actuators B* 123, 1, 101-106, (2007).
- [7] Kartopu G., Habouti S., Es-Souni M., "Synthesis of palladium nanowire arrays with controlled diameter and length", *Materials Chemistry and Physics*, in press, (2007).
- [8] Tien L.C., Norton D.P., Gila B.P., Pearton S.J., Wang H., Kang B.S., Ren F., "Detection of hydrogen with SnO₂-coated ZnO nanorods", *Applied Surface Science* 253, 4748-4752, (2007).
- [9] Smith D.P., *Hydrogen in metals*, The University of Chicago Press, (1948).
- [10] Lewis F.A., *Palladium Hydrogen System*, Academic Press, London, New York, (1967).

- [11] Elam J.W., Xiong G., Han C.Y., Wang H.H., Birrell J.P., Welp U., Hryn J.N., Pellin M.J., Baumann T.F., Poco J.F., Satcher Jr. J.H., "Atomic layer deposition for the conformal coating of nanoporous materials", *Journal of Nanomaterials*, ID 64501, 1-5, (2006).
- [12] Elam J.W., Zinovev A., Han C.Y., Wang H.H., Welp U., Hryn J.N., Pellin M.J., "Atomic layer deposition of palladium films on Al₂O₃ surfaces", *Thin Solid Films* 515, 1664-1673, (2006).
- [13] Masuda H., Fukuda K., *Science* 268, 1466, (1995).
- [14] Masuda H., Satoh M., "Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask", *Japanese Journal of Applied Physics* 35, 126-129, (1996).
- [15] Li F., Zhang L., Metzger R., "On the growth of highly ordered pores in anodized aluminum oxide", *Chem. Mater.* 10, 2470-2480, (1998).
- [16] Pundt A., "Hydrogen in nano-sized metals", *Advanced Engineering Materials* 6, No 1-2, 11-21, (2004).
- [17] Nowicka E., "Correlation between surface and bulk phenomena in the process of thin palladium hydride and titanium hydride film formation", *Vacuum* 48, No.3, 199-202, (1997).