Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 5 (2010) 168–171

Procedia Engineering

www.elsevier.com/locate/procedia

Proc. Eurosensors XXIV, September 5-8, 2010, Linz, Austria

# Concentration Specific Detection of Hydrogen at Room Temperature using Palladium Nanoparticles-Nafion film

Sunil K. Arya[a], S. Krishnan[a], K. McGrath[b], F. Rinaldi[b], S. Bhansali[a*]

[a]*BioMEMS and Microsystems Laboratory, Department of Electrical Engineering, University of South Florida, Tampa, FL 33620*

[b]*QuantumSphere Inc., Santa Ana, CA 92705*

**Abstract**

$H_2$ sensing behaviour of Palladium nanoparticles (PdNP) mixed with nafion has been demonstrated as a function of $H_2$ concentration. PdNP (15 nm diameter) were mixed with nafion (5% solution) in varying concentrations and cast over interdigitated µ-electrodes (IDµE's). Measurements were carried out at room temperature and change in resistance of the PdNP-nafion film upon exposure to hydrogen was recorded. Resistance response studies revealed a unique concentration specific response, exhibiting a pulsed effect (above 1%) and a saturated response (upto 1%), for films cast with solution strength of 2.5 mg PdNPs in 10 µl nafion. The characteristic change in the sensing behaviour can be used to develop a sensor to determine the $H_2$ concentration level with high sensitivity and fast response.



*Keywords*: Hydrogen; Sensor; palladium nanoparticles; nafion; interdigitated µ-electrodes.

## 1. Introduction

Hydrogen is increasingly being accepted as potential mainstream energy sources for applications ranging from, fuel cells and propulsion systems to biomedical devices [1-3]. However threat of leaks continues to be major challenge in storage and distribution of hydrogen as increased concentration in the range of 4%–75% can result in an explosion [1, 4]. This potential hazard has been the key driver for the development of compact, reliable, low cost, low power consumption hydrogen sensors. Detection of hydrogen at room temperature at ambient temperature enables lower operational costs and significantly longer operational lifetimes. However, large response and recovery times have dogged the development of ambient temperature sensors. This paper presents a hydrogen sensor with high sensitivity, low detection limit, fast response and, short recovery time that is also specific and stable over long term.

Nanomaterials have high surface to volume ratio and better crystallinity. The ability to modulate their properties through size control has resulted in extensive use of such materials for sensing applications. Sensors made from these materials are smaller in size and exhibit superior sensitivity, real-time detection with low-power consumption [6]. For room temperature hydrogen sensing, Pd nanowire [7], Pd nanoparticles [8], polyaniline nanofibers [9], Metal oxide [3-5], carbon nanotubes [10, 11] etc., have been investigated as sensing materials. Among these, Pd based ambient temperature sensors show both a high sensitivity and selectivity towards hydrogen due to its large

* Corresponding author. Tel.: +1-813-974-3593; fax: +1-813-974-5250.
*E-mail address*: bhansali@usf.edu

1877-7058 
doi:10.1016/j.proeng.2010.09.074

sticking coefficient, low activation barrier to adsorption, high diffusion rate, and ability to catalyze dissociative adsorption and associative desorption of hydrogen [12]. However the high cost of Pd has been a concern for development of such sensors.

In this paper we report on our efforts to optimize the use of volume of Pd for ambient temperature sensing of hydrogen. Pd nanoparticles were supplied by Quantumsphere. These nanoparticles and the resulting cast films were characterized by Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) techniques, respectively. The films were exposed to hydrogen rich gases and the change in resistance upon exposure to different concentrations of hydrogen was measured and correlated to the gas concentration.

## 2. Materials and Methods

### *2.1. Measurement and apparatus*

TEM characterization was carried out using FEI Tecnai™ TEM. SEM pictures were taken using Hitachi S800 SEM. The sensor was tested for its response to hydrogen using conditions and procedure described earlier by Krishnan et al [13]. The gas sensing performance was studied by measuring the resistance change of the film on switching the gaseous environment from pure $N_2$ to $H_2$ enriched nitrogen in a cyclic manner at room temperature.

### *2.2. Test chip fabrication and PdNP-nafion film deposition*

The IDμE chips were fabricated on an oxidized 4" silicon wafer using standard photolithography techniques. Cr/Au (200/2000 Å) layers were deposited using e-beam evaporation and were patterned through liftoff. IDμE with 5μm wide electrode fingers at a pitch of 10 μm were used for the experiments. PdNPs utilized in this research were manufactured by QuantumSphere through its patented vapor phase condensation process. To cast PdNP-nafion film, PdNPs were pre-cleaned using dilute HCl and water and dried. Pre-cleaned PdNPs (2 mg and 2.5 mg) were mixed with 10 μl of 5% nafion and dispensed on the IDμE chip and air dried. Additionally, thin Pd film (~5 nm) was also deposited on the IDμE structure to compare the $H_2$ response of the bulk and the particulate structure.

## 3. Results and discussion

### *3.1 Surface Morphology Analysis*

TEM and SEM were used to characterize PdNPs (Fig 1a) and PdNP-nafion film (Fig 1b). Fig 1a reveals the size of about 15 nm for PdNPs and network structure indicates the Van der waals interaction between the nanoparticles. Such interaction and agglomeration was found to be very high in PdNP-nafion film (Fig 1b).

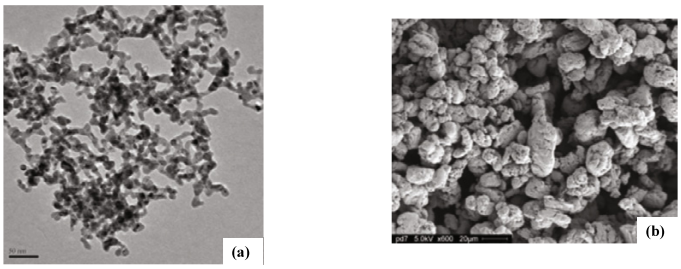


Fig 1. (a) TEM image of PdNPs and (b) SEM image of PdNP-nafion film.

### *3.2 Response studies*

Response studies were carried out on Blank IDμEs, nafion/IDμE, PdNP-nafion/IDμE, Pd/IDμE. Blank IDμEs and nafion coated IDμE (data not shown) do not show any change in resistance when exposed to $H_2$. Pd thin film (5 nm) coated IDμE exhibit the typical saturation profile and resistance increases with increasing concentration of $H_2$ gas (Fig 2a). For PdNP-nafion studies, films were prepared using 2 mg PdNP in 10 μl nafion and 2.5 mg PdNP in 10 μl nafion. Films in both cases were first exposed to $N_2$ gas for 1hr followed by pre-treatment with cyclic exposure of

$H_2$ and $N_2$ gas. Fig 2b shows the response of film having 2 mg PdNPs. It is clear from the fig that the PdNP-nafion film exhibits saturation effect, showing regular increase in resistance with increasing concentration of $H_2$ gas and, exhibits both fast response of 10 sec and quick recovery as compared to Pd thin film sensor. The increase in resistance can be attributed to the adsorption and diffusion of $H_2$ gas on Pd surface that results in an increased electron scattering and change of work function which affects the electron flow [12-14]. Further increase in resistance can be attributed to the diffusion of $H_2$ atoms into the Pd lattice to form the Pd-hydride which is less conductive than Pd. Fast response and recovery of the sensor is attributed to the particle size as the dissociation rate of H-molecules into H-atoms is believed to be dependent on the active surface area presented by Pd particles in the film.

Fig 2c reveals the resistive response of PdNP-nafion film having 2.5 mg PdNP in 10 µl nafion. In this case a similar saturation effect was observed up to a 1% $H_2$ exposure where the electrical resistance increases and subsequently saturates as the $H_2$ feed is switched on. However, above 1% Hydrogen concentration, a pulse effect was observed where the sensor on exposure to $H_2$ gas exhibits an initial increase in resistance followed by sharp decrease. Both the saturation effect below 1% $H_2$and pulse effect over 1% $H_2$ were found to be stable and reproducible over a number of $H_2$ on–off cycles. The ability to exhibit both saturation and a pulse effect on the same chip can be explained by the combination of an electronic effect (EE) and a geometric effect (GE). Where EE is responsible for an increase in resistance while GE results in a decrease in resistance. A combination of both gives rise to the observed pulse effect [12]. The occurrence of such a pulse effect on increasing the concentration of PdNPs from 2 mg to 2.5 mg can be attributed to a denser packing of PdNPs in the film which also results in a decrease in average layer thickness of nafion around PdNPs. As this film is exposed to $H_2$ gas, the resulting $H_2$ adsorption with its initial increase in resistance, also gives rise to PdNP particle size expansion, promoted further by the formation of PdH. For exposures greater than 1% $H_2$ concentrations, the PdNP expansion is large enough to cause sufficient reduction in inter-particle gap and it can be attributed to the inter-particle electron barrier, resulting in a significant decrease in resistance. The absence of a pulse effect at lower $H_2$ concentrations is related to a small or negligible change in the nanoparticle dimensions, and thus an insignificant change in the average inter-particle gap [12]. As the $H_2$ concentration increases more particles make contact which results in a decreasing resistance response. The response time was found to be around 10 sec in all PdNP-nafion films.

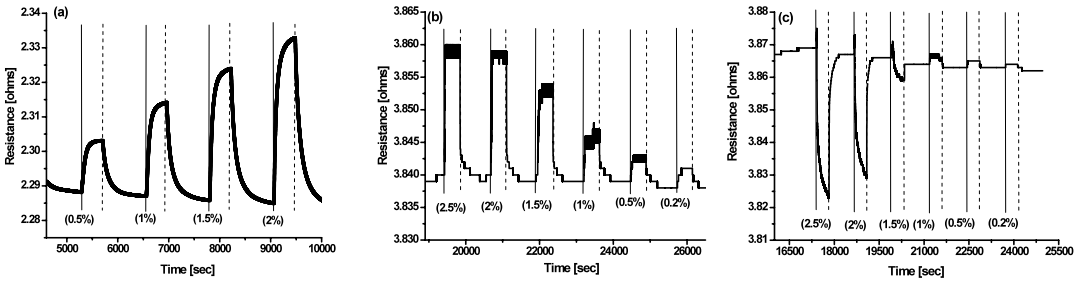


Fig 2. Resistive response of (a) 5nm thin Pd film on IDµE, (b) PdNP-nafion film with 2 mg PdNP and (c) PdNP-nafion film with 2.5 mg PdNP for various $H_2$ concentrations. Solid and dashed lines represent H2 'on' and 'off' states, respectively

*3.3 Selectivity, life time and reproducibility over a number of hydrogen on–off cycles.*

A PdNP-nafion film with 2.5 mg of PdNPs was studied for selectivity against $CO_2$ gas under similar conditions (Fig 3a). From fig 3a it is clear that the film does not show any pulse effect for $CO_2$ and is selective for $H_2$ and thus can be used selectively for hydrogen sensing at room temperature. To verify durability, the same film was exposed to $H_2$ gas over many pulses, over a period of 6 months and was found to respond as when initially tested. To verify repeatable response behaviour of these films, both the Pd-nafion film with 2 mg PdNP (Fig 3b) and the 2.5 mg PdNP (Fig 3c) film were exposed many $H_2$ gas (2.5%) pulses, over a long period of time. From the above Figures it is clear that these films are stable and exhibit repeatable response behaviour.

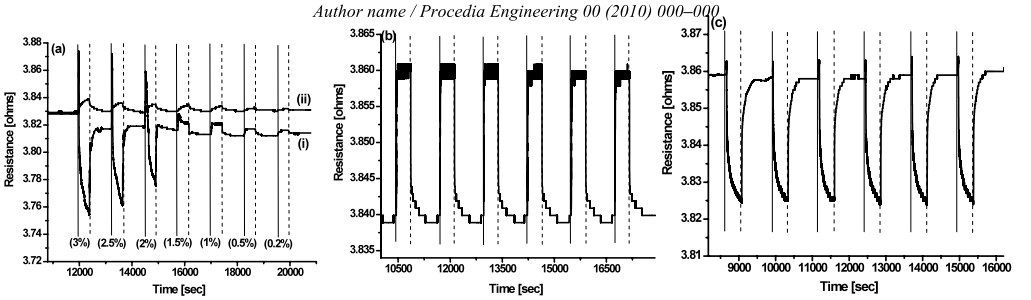


Fig 3. Resistive response of PdNP-nafion film (a) with 2.5 mg PdNP for various concentrations of (i) $H_2$ and (ii) $CO_2$, (b) with 2 mg PdNP and (c) 2.5 mg PdNP for 2.5% concentration of $H_2$ gas. Solid and dashed lines represent target gas 'on' and 'off' states, respectively

## 4. Conclusion

A sensitive and concentration dependant hydrogen sensor using PdNP-nafion film over IDμE has been fabricated. The concentration of PdNP in film was tailored to sense $H_2$ in real time. Results reveal response time of 10 sec for PdNP-nafion films. In addition, two different types of sensing behaviours were observed when an higher concentration of PdNP was used. Sensing properties for the film were found to be stable even when used for more than 6 months of continuous sensing. Thus the as prepared PdNP-nafion film enables a simple, stable and economic way to detect $H_2$ in real time.

## Acknowledgments

Nanoparticles for this research were provided by QSI. The authors would also like to thank BiTT seed award that Supported Dr. Arya. The microfabrication of the devices was supported by NSF CMMI award 0700659.

## References

[1] Korotcenkov G, Han SD, Stetter JR. Review of electrochemical hydrogen sensors. *Chem Rev* 2009;**109**:1402–33.

[2] Mubeen S, Zhang T, Yoo B, Deshusses MA, Myung NV. Palladium nanoparticles decorated single-walled carbon nanotube hydrogen sensor. *J Phys Chem C* 2007;**111:**6321-27.

[3] Huang FC, Chen YY, Wu TT. A room temperature surface acoustic wave hydrogen sensor with Pt coated ZnO nanorods. *Nanotech* 2009;**20**: 065501.

[4] Arakelyan VM, Martirosyan KS, Galstyan VE, Shahnazaryan GE, Aroutiounian VM. Room temperature gas sensor based on porous silicon/metal oxide structure. *phys stat sol (c)* 2007;**4:**2059–62

[5] Deshpande S, Karakoti A, Londe G, Cho HJ, Seal S. Room temperature hydrogen detection using 1-D nanostructured tin oxide sensor. *J Nanosci Nanotechnol* 2007;**7**:1–4.

[6] Gouma PP. *Nanomaterials for chemical sensors and biotechnology*. Pan Stanford Publishing Pte. Ltd; 2009.

[7] Im Y, Lee C, Vasquez RP, Bangar MA, Myung NV, Menke EJ, et al. Investigation of a single Pd nanowire for use as a hydrogen sensor. *Small* 2006;**2**:356-8.

[8] 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.

[9] Virji S, Kaner RB, Weiller BH. Hydrogen sensors based on conductivity changes in polyaniline nanofibers. *J. Phys. Chem. B* 2006;**110**:22266-70

[10] Schlecht U, Balasubramanian K, Burghard M, Kern K. Electrochemically decorated carbon nanotubes for hydrogen sensing. *App Sur Sci* 2007;**253**:8394–7.

[11] Oakley JS, Wang HT, Kang BS, Wu Z, Ren F, Rinzler AG, et al. Carbon nanotube films for room temperature hydrogen sensing. *Nanotech* 2005;**16**:2218–21.

[12] Khanuja M, Kala S, Mehta BR, Kruis FE. Concentration-specific hydrogen sensing behavior in monosized Pd nanoparticles layers. *Nanotech* 2009;**20**: 015502.

[13] Krishnan S, Sekhar PK, Joshi R, Bhansali S. Nanocrystalline palladium thin films for hydrogen sensor application. *Sens Lett* 2009;**7**:1–7.

[14] Sun Y, Wang HH. High-performance, flexible hydrogen sensors that use carbon nanotubes decorated with palladium nanoparticles *Adv Mater* 2007;**19**:2818-23.