

# Pd Nanoparticles and Thin Films for Room Temperature Hydrogen Sensor

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**Abstract** We report the application of palladium nanoparticles and thin films for hydrogen sensor. Electrochemically grown palladium particles with spherical shapes deposited on Si substrate and sputter deposited Pd thin films were used to detect hydrogen at room temperature. Grain size dependence of H<sub>2</sub> sensing behavior has been discussed for both types of Pd films. The electrochemically grown Pd nanoparticles were observed to show better hydrogen sensing response than the sputtered palladium thin films. The demonstration of size dependent room temperature H<sub>2</sub> sensing paves the ways to fabricate the room temperature metallic and metal–metal oxide semiconductor sensor by tuning the size of metal catalyst in mixed systems. H<sub>2</sub> sensing by the Pd nanostructures is attributed to the chemical and electronic sensitization mechanisms.

**Keywords** Palladium · Hydrogen sensors

## Introduction

Current trend of research in hydrogen sensor technology is dedicated towards the development of room temperature sensors. Various types of sensors have been widely studied and used for sensing the oxidizing and reducing gases [1–5]. However, it has been a difficult task to detect the gases at room temperature even after adding the metal catalyst into the semiconductors. Recently, H<sub>2</sub> sensors have gained increased interest due to its application in many significant areas. Various methods have been reported for the development of H<sub>2</sub> sensors based on metal-oxide [4, 5], nanowires [6, 7], acoustic wave [8, 9], thin film metal and semiconductor [10, 11]. Most of the approaches utilize Pd as a catalyst, since Pd has great affinity towards H<sub>2</sub> absorption [12–14]. Pd undergoes a change in physical properties by adsorbing H<sub>2</sub>, which can be restored by removing H<sub>2</sub> gas from the ambient. Palladium based hydrogen sensors are based on the increase of electrical resistivity due to the increased electron scattering on hydrogen incorporation [15–18]. Penner et al. [19] have reported a novel mechanism of hydrogen gas detection using resistive palladium mesowire arrays that change their resistivity upon exposure to hydrogen virtually instantaneously. In an another very important work on hydrogen sensors Yushi et al. have fabricated and demonstrated the use of a single metallic nanowire as a hydrogen sensor with extremely high sensitivity [20].

In our recent work we have used Pd nanoparticles for synthesis of multiwall carbon nanotube for scanning probe microscopy application [21, 22]. In order to extend the application of chemically grown Pd nanoparticles we used these particles for hydrogen detection at room temperature. In this article we demonstrate the room temperature detection of hydrogen using Pd nanoparticles with different

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sizes. The hydrogen sensing results of electrochemically grown Pd are compared with the hydrogen sensing results obtained for the sputtered Pd thin films.

## Experimental Section

### Electrochemical Deposition of Pd Nanoparticles on Silicon Substrates

Palladium nanostructures were deposited on conductive Si (100) substrates (resistivity = 0.005  $\Omega$ -cm) through potentiostatic electrodeposition [21, 22]. An amount of the electrolyte, consists of Pd sulfate and sulfuric acid, was taken into an electrochemical cell for the growth of nanoparticles on silicon substrate at working electrode. Three-electrode configuration system was used for the growth of Pd nanostructures. Pt was used as counter electrode, Ag/AgCl as the reference electrode and silicon substrate as working electrode for electrochemical deposition of Pd on Si substrates. The Si substrates were cleaned using deionizer water, ethanol and additionally treated with HF solution for removing the native oxide layers just before the electrochemical growth. The three electrodes, with silicon substrate as working electrode, were dipped into the electrolyte solution and an appropriate bias was applied to the system. After the chosen deposition time the substrates were taken out of the solution and dried and tested for their hydrogen sensing response. Surface morphology of electrochemically grown Pd nanostructures was investigated extensively using the field emission scanning electron microscopy (FESEM). Crystallographic structure of the Pd nanostructure grown on silicon substrates was studied using glancing angle X-ray diffraction. Average grain size of electrochemically grown nanoparticles was estimated using X-ray diffraction data and given in our previous article [22].

### Sputtering Deposition of Pd Thin Films

Palladium thin films were prepared by DC-magnetron sputtering system on oxidized silicon substrate with SiO<sub>2</sub> layer thickness of 100 nm on Si. The Pd films were utilized, as-grown, to detect hydrogen at room temperature. A custom built DC-magnetron sputtering system was utilized to deposit the nanocrystalline palladium thin films. Deposition process was carried out at a vacuum of 10<sup>-6</sup> Torr. A 99.95% pure Pd metal was used as the target material. The distance between the target and substrates was kept at 10 cm and the substrate was rotated at a uniform rate during the deposition. The chamber was pumped down using a cryopump and ultra high pure argon was introduced into the chamber through a mass flow controller. Pre-sputtering was carried

out for 5 min to etch away any dirt present in the target and then the metal was deposited on the substrate. A regulated DC power source with a constant input power of 60 W was used to deposit thin film nanocrystalline Pd. Pd films were deposited at pressures varying from 22 to 120 m Torr. In sputtered Pd films it was observed that on increasing the deposition pressure from 22 to 120 m Torr the average grain size varied from 10 to 30 nm. XRD and atomic force microscopy (AFM) was used to study structure and morphology of the films.

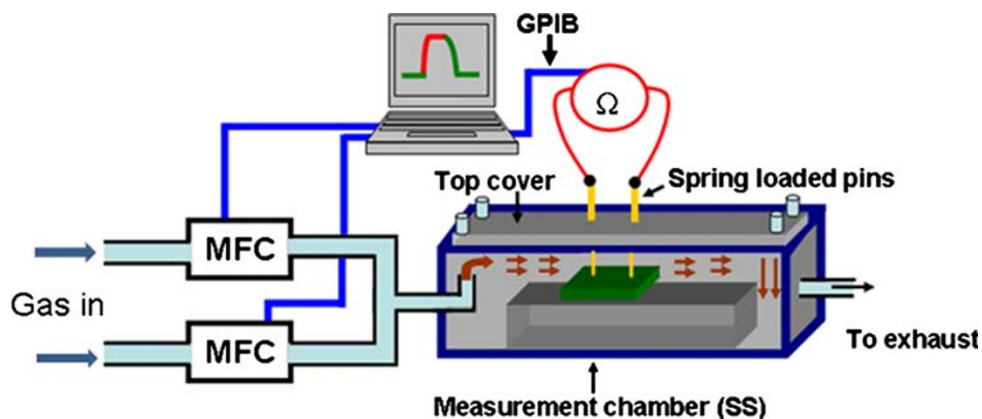
### Hydrogen Sensor Characterization

Hydrogen sensing performance of Pd thin film (via sputtering deposition) and Pd nanoparticles (via electrochemical deposition) was evaluated by using a custom built sensor test chamber. Resistance of the Pd films deposited on Si substrates was measured in presence of nitrogen (reference gas) and hydrogen (target gas) by using a two-probe configuration at room temperature with the help of a multimeter (Keithley Instruments Inc., Model 2400 SMU), and a gas controller (MKS Inc., Type 247 controller), as shown in Fig. 1. Ultra high purity H<sub>2</sub> and N<sub>2</sub> (reference gas) were fed on the test chamber and exhausted safely on the opposite side. The test chamber is attached to the control system forming the test bed. Resistance of the sensor was measured by selecting any two electrodes exhibiting excellent ohmic contact. The sensor cell is connected to the gas inlet line that comes from the mass flow controllers. A Keithley model 2400 multimeter attached to a computer via a GPIB cable is used to acquire the resistance data using National Instruments LabView software. LabView is also used to control the mass flow controllers and record the gas concentration.

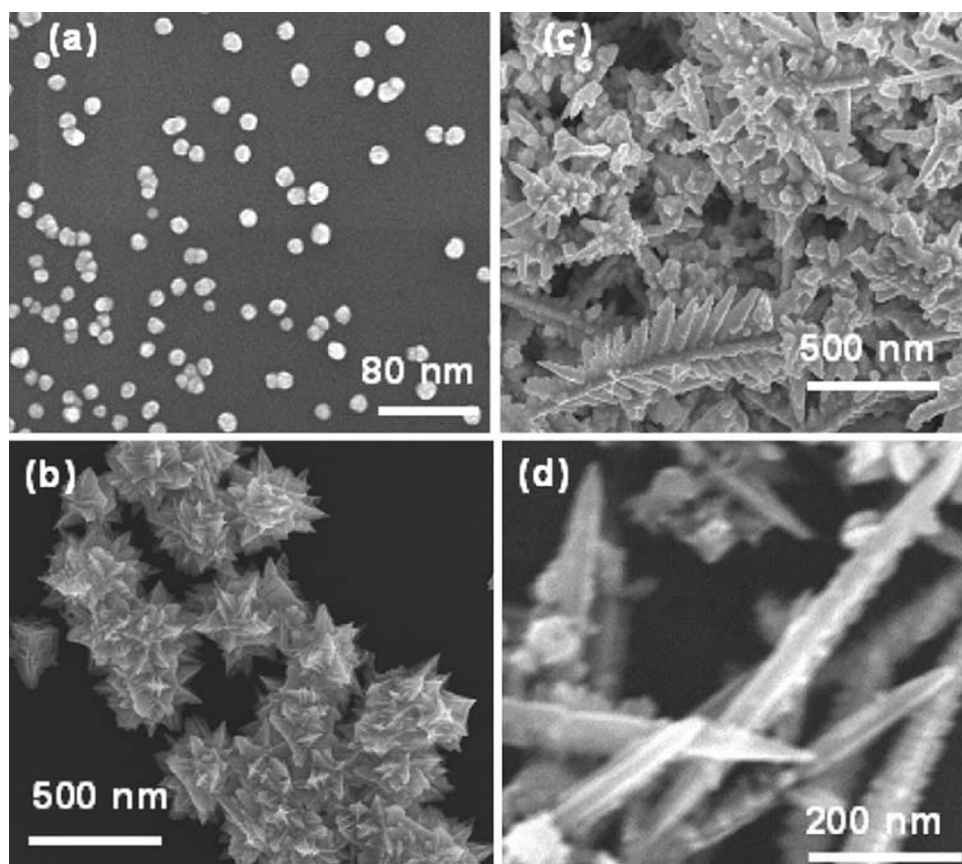
## Results and Discussion

Mechanism of electrochemical growth for the Pd nanoparticles has been studied using the voltammetry techniques and discussed in detail in our previous work [22]. In the electrochemical deposition, transfer of electrons from one electrode to another occurs. This transfer creates a current with its magnitude giving information about the substance. Figure 2 shows the morphology of some selected samples, for showing the variation in size and shape with growth parameters. Figure 2a shows spherical shaped nanoparticles grown at a voltage of -0.1 V applied to the working electrode by using the electrolyte solution which is mixture of Pd sulfate (0.04 mol/L) and sulfuric acid. Figure 2 b, c, and d for the nanoparticles grown at -1.0, -2.0 and -3.0 V, respectively. We have discussed the variation of shapes of Pd nanoparticles in our previous

**Fig. 1** Experimental set-up for hydrogen sensor measurements

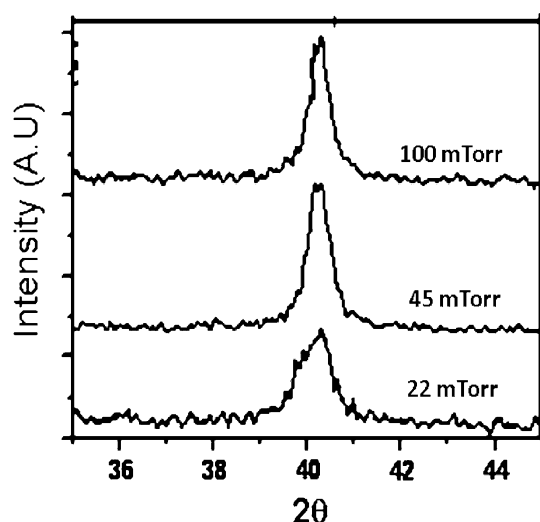


**Fig. 2** SEM micrographs for Pd nanoparticles grown at voltage of  $-0.1$  V (a),  $-1.0$  V (b),  $-2.0$  V (c) and  $-3.0$  V (d) respectively applied to the working electrode using the electrolyte solution which is mixture of Pd sulfate (0.04 m/L) and sulfuric acid



article [22]. Average grain size of the spherical shaped Pd nanoparticles can be varied by changing the deposition time. Deposition time was selected as 7, 14 and 21 min. In order to maintain the same film thickness the dilution of the electrolyte solution was changed whereas the applied voltage was kept constant. Dilution and deposition time was optimized to get the Pd nanoparticle films of nearly same thickness for hydrogen sensor application. The dilution of the Pd sulfate solution was selected as 0.040, 0.027, and 0.020 mol/L for the deposition time of 7, 14 and 21 min respectively to obtain homogeneous films of 150 nm on silicon substrates. Film

continuity and ohmic contact was checked by measuring their resistance prior to the gas sensor measurement. Variation of average grain size for the sputter deposited films was achieved by growing the films with different pressure condition in the range 22–120 m Torr. Figure 3 shows the typical X-ray diffraction patterns (XRD) for the sputtered Pd thin films. Film thickness of 150 nm was same for sputtered thin films used for hydrogen sensing. Grain size in the films was observed to increase with increasing the pressure. The average grain size values as estimated using the full width at half maximum of the XRD pattern are given in Table 1. Figure 4 shows



**Fig. 3** X-ray diffraction patterns for the sputtered Pd thin films

**Table 1** Variation of average grain size with pressure during film deposition by sputtering

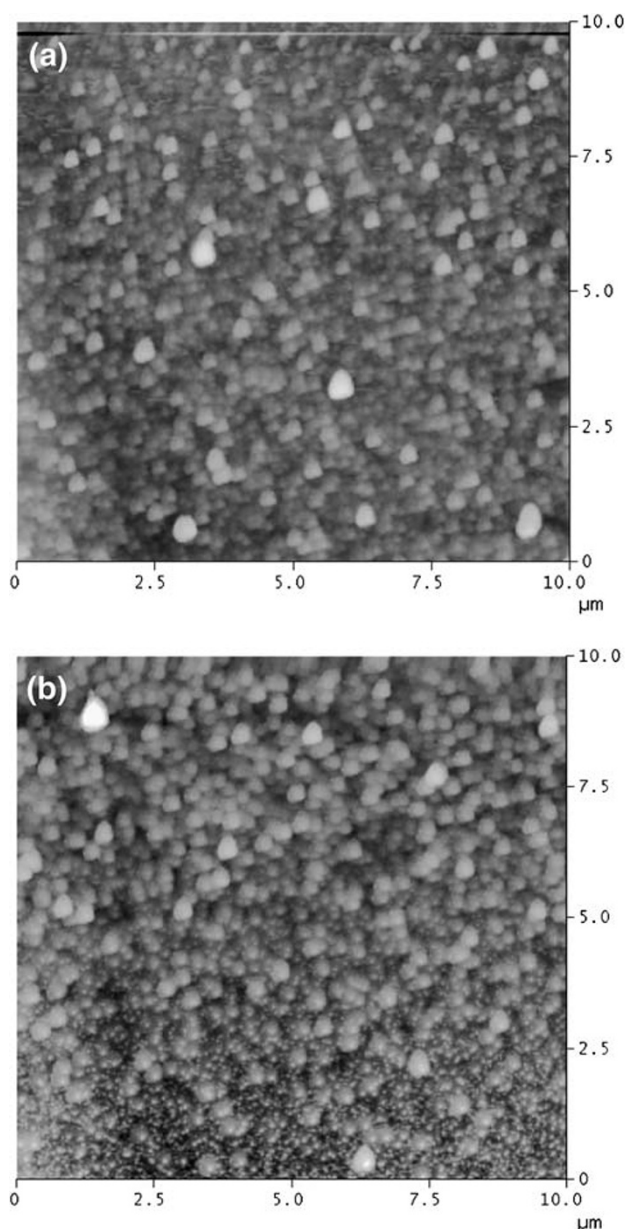
Deposition pressure (m Torr)	Average grain size (nm)
22	11
45	15
75	18
100	25
120	30

the surface morphology of the sputtered Pd films studied by using atomic force microscopy.

The gas sensing performance of Pd was studied by measuring the resistance change of the film on switching the gaseous environment from  $N_2$  to  $H_2$  in cyclic manner. All the films exhibited an increase in resistance upon  $H_2$  exposure. The dissociation rate of hydrogen molecule into hydrogen atom on Pd films depends on the active surface area presented by Pd particles in the film. This determines the response time of  $H_2$  sensor.  $H_2$  atoms diffuse into the Pd lattice to form the Pd-hydride [23]. Moreover, the hydrogen adsorption by Pd is driven by adsorption at grain boundaries suggesting a vital role of tuning the grain size and the particle packing density in tailoring the gas sensors properties. Figure 5 shows the typical gas sensing response in terms of resistance change with time by changing gas from  $N_2$  to  $H_2$  for electrochemically grown films. The % change in resistance, which is the sensor signal in the present case, is defined as:

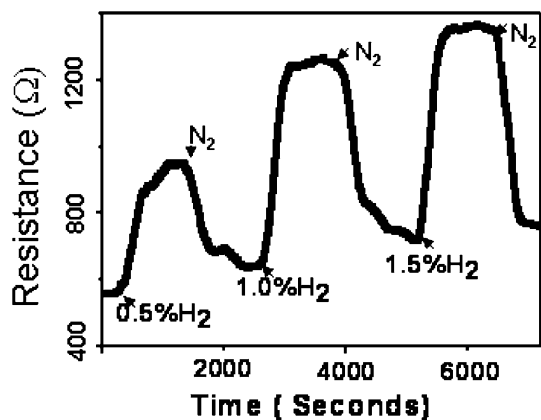
$$\text{Sensor signal} = \left( \frac{R_{\max} - R_{\min}}{R_{\max}} \right) (100).$$

The gas sensor signal ( $(\Delta R/R) \cdot 100$ ) increases gradually with decrease in average grain size as shown in Fig. 6a for

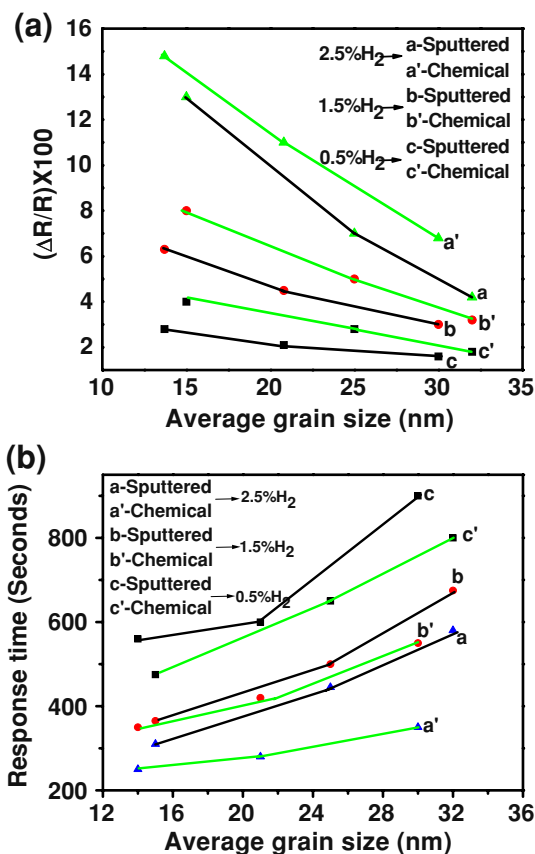


**Fig. 4** AFM image showing the topography of thin film Pd deposited at (a) 75 mTorr, and (b) 100 mTorr by sputtering method

chemically grown as well as sputter deposited films. Figure 6b shows the variation of response time with average grains size for the chemically grown and sputtered deposited films. Response time is the time needed for the resistance of the gas sensor to obtain 90% of the maximum resistance when hydrogen gas is introduced into an environment of nitrogen. Response time decreases with increase of particle size for all hydrogen concentrations. Overall the gas sensing response is observed to be increased in lower grain size which is attributed to the activation of surface state in nanodimensional regime leading to improved chemical sensitization phenomena



**Fig. 5** Typical change of resistance with time on switching the gas from nitrogen to hydrogen for electrochemically grown Pd nanoparticle film with thickness of 150 nm



**Fig. 6** Variation of **a** sensor signal and **b** response time for different concentration of hydrogen with average grain size of the Pd nanoparticle films with thickness of 150 nm deposited by electrochemical and sputtering method

[24–27]. It is known that the density of these activated centers is higher for the lower particle size. It was interesting to note that the chemically synthesized Pd nanoparticles show better sensing response than the sputter deposited Pd thin films due to the large number of possible

active surface states caused due the solution preparation methods and higher surface roughness of the nanoparticles. This behavior in the gas sensing response in terms of the increase in sensor signal and decrease in response times on reducing the size of Pd particles shows the occurrence of chemical sensitization in the film. The chemical sensitization is a gas sensing mechanism, which has been studied extensively for the metal-supported metal oxide sensors but the observance of such mechanism for the metal-only sensors has not been reported so far. In the case of metal–metal oxide sensors, the chemical sensitization is known to be a two step process, namely the gas-semiconductor surface interaction and spillover effect [26, 27]. However, we believe in the case of ‘metal-only’ sensors the only process that is likely to be in existence is the direct interaction between gas and metal surface. This leads to the change of surface potential resulting into chemical sensitization phenomenon. Thus, the sensing process reduces the mechanism into a one step sensing phenomena, which is possibly the reason for the observed room temperature sensor response.

As the Pd particle size approaches the nanoscale dimensions, the probability of forming Pd-hydride increases due to a very strong affinity of Pd toward H<sub>2</sub> absorption which should be more in the nanodimension due to high specific surface area of Pd [14]. The formation of Pd-hydride, which is a process of lattice modifications [14], results in the band structure alteration and changing the work function on hydrogen exposure. We have observed a systematic change in the work function on H<sub>2</sub> exposure to the Pd nanoparticles and thin films using X-ray photoelectron spectroscopy techniques. The experimentally observed very higher value of recovery times for these sensors can be correlated to the formation of Pd-hydride. Once Pd is transformed as Pd-hydride, the lattice structure of the palladium changes, in terms of expansion. This causes the sensor to recover more slowly to the baseline resistance. The change in work function due to gas adsorption suggests the presence of electronic sensitization on the films [24, 25]. Therefore, we believe that hydrogen sensing by Pd is attributed to the dual (chemical and electronic) sensitization mechanism. Enhancement in sensing response with lower particle size is attributed to the chemical sensitization whereas the improved sensing due to experimentally observed change in work function on hydrogen exposure is attributed to electronic sensitization.

**Conclusions**

Electrochemically grown Pd nanoparticles and sputtered Pd thin films have been used to detect hydrogen at room temperature. Comparative study shows that electrochemically

grown Pd nanoparticles have better H<sub>2</sub> sensing characteristics than the sputtered palladium thin films. Gas sensing response has been observed to improve with lower grain size in the both type of systems. Chemical and electronic sensitization mechanisms were observed to be responsible for the enhanced gas sensing behavior with lower grain size. The Pd based conductive sensors, tested for different concentration of H<sub>2</sub>, were observed to be highly stable and reproducible.

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