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Finite size effect on hydrogen gas sensing performance in single Pd nanowires

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Abstract
We present the hydrogen sensing performance of individual Pd nanowires grown by electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates investigated as a function of the nanowire diameter. Four-terminal devices based on individual Pd nanowires were found to successfully detect hydrogen gas (H_2). Our experimental results show that the H_2 sensing sensitivity increases and the response time decreases with decreasing diameter of Pd nanowires with $d = 400$, 200, 80 and 20 nm, due to the high surface-to-volume ratio and short diffusion paths, respectively. This is in qualitatively good agreement with simulated results obtained from a theoretical model based on a combination of the rate equation and diffusion equation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The palladium/hydrogen system has been a longstanding topic as a metal/gas system for more than a century [1]. Comprehensive studies on the Pd/H system were performed by Lewis [2] 40 years ago. Since then, the Pd/H system had continued to create intense interest for use in hydrogen storage, hydrogenation catalysts and hydrogen gas sensors. Recently, there has been a dramatic change to re-awake our interest in the Pd/H system due to the high possibility of hydrogen gas (H_2) sensor applications, fueled mainly by the development of nanotechnology in the fabrication of Pd nanostructures, e.g. nanowires [3, 4], nanochains [5, 6] and nanotubes [7, 8]. The Pd nanostructures became well known for detecting hydrogen gas at room temperature as well as to be highly sensitive and to respond fast.

In particular, Pd nanochains [5, 6] have recently attracted considerable interest due to its fast hydrogen response originating from the closing of nanoscopic gaps in the wires upon hydrogen absorption. Also, single nanowires with $d = 70$–300 nm grown between two Au electrodes by electrodeposition were demonstrated to show a fast response time with ultra-low power consumption [4]. Even though there have been a few recent efforts to describe the hydrogen gas (H_2) sensing performance in various Pd nanostructures, to date the finite size effects of single Pd nanowires as a hydrogen sensor have not been studied. The finite size effects on the hydrogen sensing performance are of particular interest in this context since it is believed that smaller diameter Pd nanowires will result in a much faster response due to the higher surface-to-volume ratio.

In this paper, we report on a novel approach to fabrication of ultra-high-sensitivity hydrogen sensors using single Pd nanowires grown by electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates. We discuss the finite size effects on the hydrogen sensing performance of single Pd nanowires such as sensitivity, detection limit and response time. Our experimental results demonstrate that sensitivity increases and response time decreases with decreasing diameter of the Pd nanowires, which is in qualitatively good agreement with simulated results. Our theoretical model was based on a combination of the rate equation for the surface and subsurface and the diffusion equation for bulk hydrogen concentration by using the

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relaxation method algorithm and an algorithm for the band diagonal system of equations.

2. Experiment and model

Arrays of Pd nanowires with diameters of 20, 80, 200 and 400 nm were grown by three-probe dc electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates from an aqueous electroplating solution of 0.034 mol/250 ml $PdCl_2$ and 0.1 mol/250 ml HCl solution at room temperature (see figure 1(a)). The Pd nanowires were liberated from the electroplated AAO template by dissolution in a solution of 2% hydrofluoric acid (HF). After removal of the AAO template, the Pd nanowires on the Au layer, which was used as a cathode, were rinsed with methanol for 20 min and immersed in isopropyl alcohol (IPA) (see figure 1(b)). High-resolution transmission electron microscopy (HRTEM) was employed to investigate the microstructures of the Pd nanowires and energy-dispersive x-ray (EDX) analysis revealed that there are no appreciable impurities in the Pd nanowires.

The Pd nanowires were dispersed by applying a drop of IPA containing the nanowires onto a thermally oxidized Si(100) substrate with patterned outer Au electrodes by photolithography and a lift-off process. The spatial positions and orientations of each nanowire were recorded by digitizing the coordinates from optical microscopy images. A combination of electron beam lithography and a lift-off process was utilized to fabricate inner micron-scaled Au electrodes connecting a Pd nanowire with the outer electrodes. Ultra-high vacuum (UHV) dc magnetron sputtering was used for the deposition of the inner Au electrodes. A representative single isolated Pd nanowire device with $d = 20$ nm is presented in figure 1(c).

An H_2 sensing experimental set-up consists of a sealed chamber of ~250 ml, mass flow controllers for monitoring the ratio of H_2 and N_2 and digital multimeters connected to a personal computer. The gas chamber has a gas inlet and a gas outlet. The two gases were mixed from different lines and fed though the gas inlet line of the chamber. The check valve opens at a higher pressure than the environmental pressure so that the pressure in the chamber is maintained at nearly constant atmospheric pressure. The purity of the N_2 and H_2 gas used was 99.9%. The real-time electrical resistance response to H_2 was measured for single Pd nanowires with diameters $d = 400$, 200, 80 and 20 nm at room temperature. All data acquisition was carried out using the LabView software program through a GPIB interface card.

A model to address the change in electrical resistance in the presence of H_2 for Pd nanowires can be expected. When a Pd nanowire is exposed to H_2, hydrogen molecules are adsorbed on the surface of the Pd nanowire. The absorbed hydrogen molecules are dissociated into hydrogen atoms which diffuse into the interstitial sites along grain boundaries, and then react with Pd atoms to form Pd hydride (PdH_x) of α and β phases, which are dependent upon the H_2 concentration [9]. The gaseous hydrogen pressure, the hydrogen concentration in Pd and electrical resistivity are related in the Pd–H phase diagram. In the Pd–H phase diagram, the α phase, $\alpha + \beta$ phases and β phase form in the case of $x < 0.015$, $0.015 \leqslant x < 0.61$ and $x \geqslant 0.61$ in atomic percent in the Pd hydride (PdH_x) at 278 K, respectively.

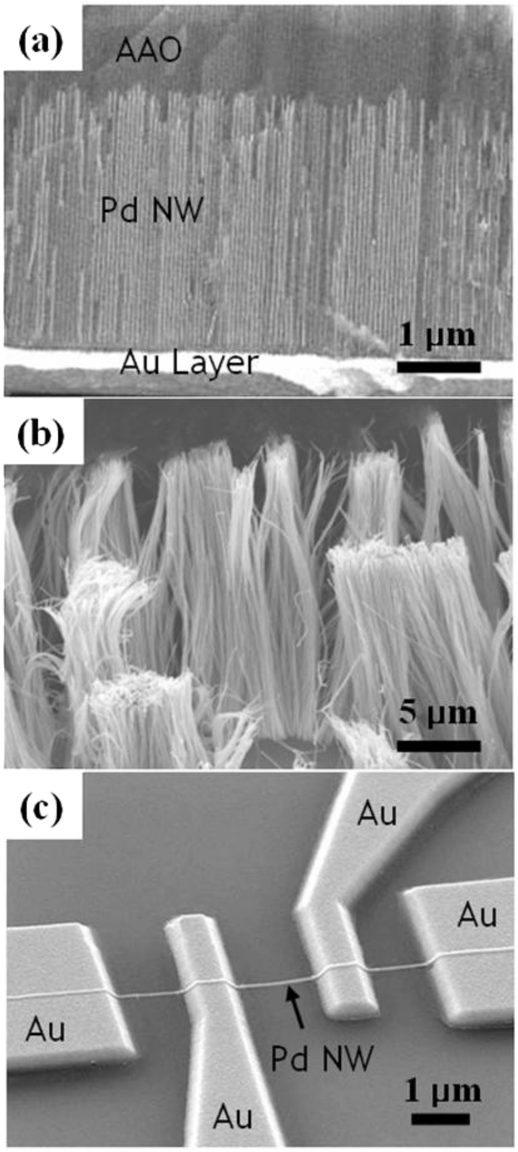

Figure 1. (a) Arrays of Pd nanowires grown by electrodeposition into nanochannels of AAO templates, (b) the Pd nanowires liberated from the electroplated AAO template by dissolution in a 2% hydrofluoric acid solution and (c) a representative individual Pd nanowire device with $d = 20$ nm.

A mean-field model with three layers, proposed from previous work [10, 11], was utilized, showing that temperature programed desorption spectra were explained better by introducing a subsurface interlayer. The rate equation and diffusion equation are coupled to compute the hydrogen concentration profile in a Pd nanowire. The Pd nanowires were modeled by an infinitely long cylinder of radius d immersed in a uniform gas with H_2 partial pressure P. The Pd nanowires were assumed to be composed of a homogeneous Pd single crystal, the surface of which was assumed to be clean of contaminants. Grain boundary effects and impurities were neglected. Ambient temperature T was assumed to be uniform

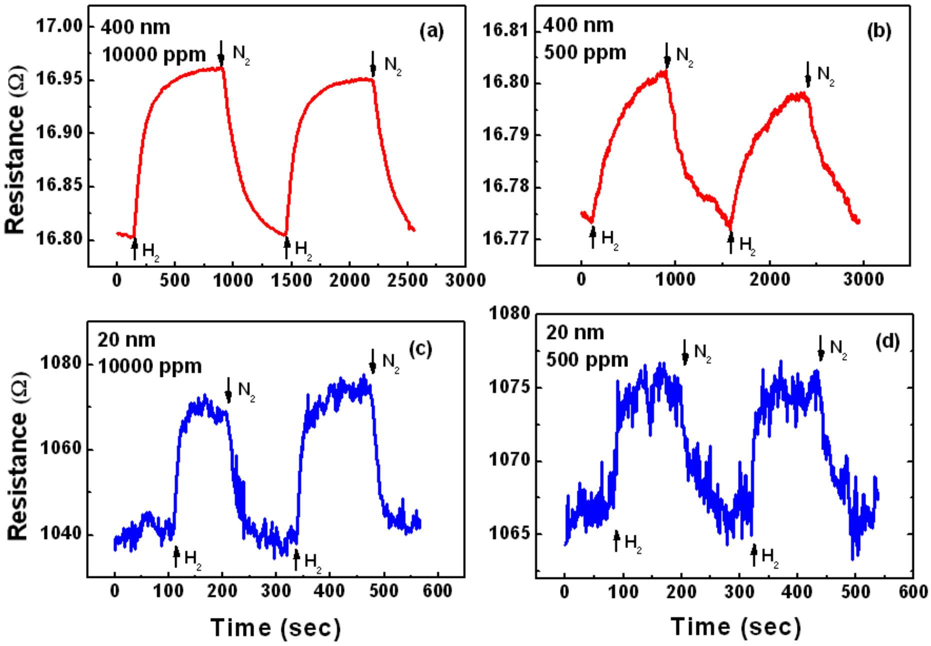

Figure 2. The real-time electrical resistance response to H_2 for single Pd nanowires with diameters $d = 400$ nm ((a), (b)) and $d = 20$ nm ((c), (d)) at 10 000 and 500 ppm partial pressures of H_2, respectively, at room temperature.

throughout the whole nanowire. The transient mass balance for the surface and subsurface layers is described by a rate equation [10]. The hydrogen diffusion into the Pd nanowire is described by the diffusion equation in cylindrical coordinates:

$$\frac{\mathrm{d}Y(r,\tau)}{\mathrm{d}\tau} = \exp\left(-\frac{E_D^*}{RT}\right)\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}Y(r,\tau)}{\mathrm{d}r}\right) \tag{1}$$

where $Y(r,\tau)$ denotes the normalized hydrogen concentration of the bulk nanowire with the bulk site density of hydrogen. R is the gas constant and τ is dimensionless time, which is defined as $(D_0/d^2)t$, where t is real time, and d and r denote the real diameter and dimensionless radial distance of the bulk normalized with radius. $D_0(=2.83 \times 10^{-3}\ \mathrm{cm}^2\ \mathrm{s}^{-1})$ and $E_D^*(=12\ \mathrm{kcal\ mol}^{-1})$ are the pre-exponential factor and activation energy of the Fickian diffusion process in the bulk, respectively. Reasonable values for all parameters have been estimated in the literature [10–14].

The hydrogen concentration represents flux continuity at the subsurface–bulk interface and at the center of the nanowire by using the continuity equation. At the subsurface–bulk interface, the following boundary condition should be satisfied:

$$\left(\frac{\partial Y(r,\tau)}{\partial\tau}\right)_{r=1} = \frac{\mathrm{d}/2}{D_0\exp(-E_D^*/RT)}\left(\frac{X_{2\mathrm{s}}}{Y_\mathrm{b}}\right) \times [R_{21} - R_{12}] - \left(\frac{\partial Y}{\partial r}\right)_{r=1} \tag{2}$$

where $Y(r,\tau)_{r=1}$ denotes the normalized hydrogen concentration in the topmost layer of the bulk nanowire, X_{2s} denotes subsurface site density, Y_b denotes the site density of the bulk, and R_{21} and R_{12} denote the migration from subsurface to bulk and vice versa, respectively. $Y(r,\tau)$ is numerically calculated by using the relaxation method algorithm and an algorithm for the band diagonal system of equations. The resistivity of the palladium/hydrogen system is proportional to the absorbed H concentration, since absorbed hydrogen atoms act as scattering centers [2, 9]. In the present work, only the α phase of the palladium hydride will be discussed in terms of the sensitivity and response time because of the partial pressure being lower than 10 000 ppm. The sensitivity, S, is defined by the relative variation of resistance and it is approximately given by the following expression in terms of the H to Pd concentration in the α phase:

$$S = \frac{\Delta R}{R} = \frac{\Delta\rho}{\rho_0} = \gamma[\mathrm{H/Pd}] \tag{3}$$

where $\Delta\rho$ is the difference in resistivities between the absence and the presence of H_2, ρ_0 is the resistivity of Pd in the absence of H_2 and γ is a proportionality constant. The total [H/Pd] is the ratio of total absorbed hydrogen atoms against Pd atoms throughout the nanowire i.e. surface, subsurface and bulk. It can be calculated from $Y(t)$, $X_2(t)$ and $X_3(t)$ in the following:

$$[\mathrm{H/Pd}] = \frac{2\pi\frac{d}{2}l(X_2(t)X_{2s} + X_3(t)X_{3s}) + \pi\left(\frac{d}{2}\right)^2 lY(t)Y_b}{2\cdot 2\pi\frac{d}{2}lN_s + \pi\left(\frac{d}{2}\right)^2 lN_b} = \frac{2[X_2(t)X_{2s} + X_3(t)X_{3s}] + \frac{d}{2}Y(t)Y_b}{4N_s + \frac{d}{2}N_b}, \tag{4}$$

$$Y(t) = \int_0^1 rY(r,t)\,\mathrm{d}r, \tag{5}$$

where $X_3(t)$ and $X_2(t)$ represent the surface and subsurface normalized concentrations of hydrogen, with $X_{3s}(=9.4 \times 10^{14}\ \mathrm{sites\ cm}^{-2})$ and $X_{2s}(=4.7 \times 10^{14}\ \mathrm{sites\ cm}^{-2})$ denoting the corresponding surface and subsurface site densities, respectively. l is the length of the nanowire and Y_s represents the bulk site density, having the value of

4.7×10^{20} sites cm^{-3}. $N_s(= 1.69 \times 10^{15}$ atoms cm$^{-2})$ and $N_b(= 6.81 \times 10^{22}$ atoms cm$^{-3})$ are Pd atom concentrations at surface and bulk, respectively and we assume the Pd atom concentration in the subsurface is equal to that in the surface.

3. Results and discussion

Single Pd nanowires with $d = 20$–400 nm were used to detect hydrogen gas in the concentration range 500–10 000 ppm at atmospheric pressure and at room temperature by measuring the change in electrical resistance. Each sample was first exposed to nitrogen gas (N_2) in order to obtain a baseline, then to a desired concentration of hydrogen gas (H_2), and then back to N_2, completing one cycle. Figure 2 exhibits the representative electrical resistance response to the presence of H_2 of 500 and 10 000 ppm for Pd nanowires with $d = 400$ and 20 nm. The hydrogen sensing mechanism in Pd is based on the change in electrical resistivity as hydrogen is absorbed at the octahedral interstitial site in the Pd fcc lattice. The resistivity of PdH_x is higher than pure Pd, since hydrogen atoms play a role as additional scattering sources, giving rise to the increase in the resistivity of the nanowires, as described previously in detail. The single Pd nanowire with $d = 20$ nm was found to successfully detect H_2 at 500 ppm. It was also found that a single Pd nanowire with $d = 400$ nm sensed H_2 even at 200 ppm as a low detection limit. Reduced currents were applied to prevent us from burning the nanowire with $d = 20$ nm due to Joule heating, leading to rather noisy signals. It is obvious that the sensitivity and response time of the Pd nanowire with $d = 20$ nm are higher and faster than for Pd nanowires with $d = 400$ nm at both concentrations. Further details of the sensitivity and response time for Pd nanowires as a function of the nanowire diameter will be discussed below.

The effect of nanowire diameter on the H_2 sensing sensitivity for single Pd nanowires with $d = 20$–400 nm has been investigated. Figure 3(a) shows the variation in sensitivity as a function of the nanowire diameter for single Pd nanowires with $d = 20$, 80, 200 and 400 nm in the concentration range 1000–10 000 ppm. The sensitivity S of the nanowires for H_2 sensing is defined as $S = (R_H - R_N)/R_N \times 100\%$, where R_H and R_N are the resistances in the presence of H_2 and N_2 gas, respectively. The sensitivity was found to decrease with increasing nanowire diameter up to $d = 200$ nm. There is no significant difference in the sensitivity between nanowires with $d = 200$ and 400 nm. The inset of figure 3(a) shows that the sensitivity is linear to H_2 concentration in the range 500–10 000 ppm for the nanowires with $d = 20$ and 80 nm, indicating that a Pd single nanowire can be used as an H_2 sensor to quantitatively detect H_2 in the wide range of H_2 concentrations given.

Figure 3(b) displays the variation of total [H/Pd] as a function of the diameter of the nanowires at 10 000 ppm H_2 obtained by theoretical modeling. The total [H/Pd] was found to decrease with increasing nanowire diameter. In other words, the simulated results were found to be in qualitatively good agreement with the experimental results, as seen in figure 3(a), according to equation (3), showing that total [H/Pd] is proportional to the sensitivity S. Surface, subsurface and bulk are the order of [H/Pd] values for a Pd nanowire in a mean-field model with three layers. Therefore, the smaller diameter exhibits the higher sensitivity according to equation (4). This is because the ratio of hydrogen sites to palladium atoms at the surface and subsurface, $(X_{2s} + X_{3s})/2N_s$, is ~60 times higher than that in the bulk, Y_b/N_b, for a Pd nanowire. In addition, the occupation probability of hydrogen atoms at the surface, $(X_2 + X_s)/2$, is more than four times higher than that in the bulk, Y, according to the simulated results. The experimental and simulated results of the diameter dependence of response time at 1% H_2 for nanowires with $d = 20$, 80, 200 and 400 nm are presented in figure 4. The electrical resistance in the Pd nanowires in the presence of H_2 increases with time until eventually it can no longer be saturated. The response time corresponds to the hydrogenation process time as follows. When a Pd nanowire is exposed to H_2, hydrogen molecules are adsorbed on the surface of the Pd nanowire. The absorbed hydrogen molecules are dissociated into hydrogen atoms which diffuse into the interstitial sites determined by the activation energy of the Fickian diffusion process and the gradient of hydrogen concentration, and then they react with Pd atoms to form Pd hydride. The response time can be defined as the time to reach 36.8 % $(=e^{-1})$ of the total change of the electrical resistance at a given H_2 concentration. The

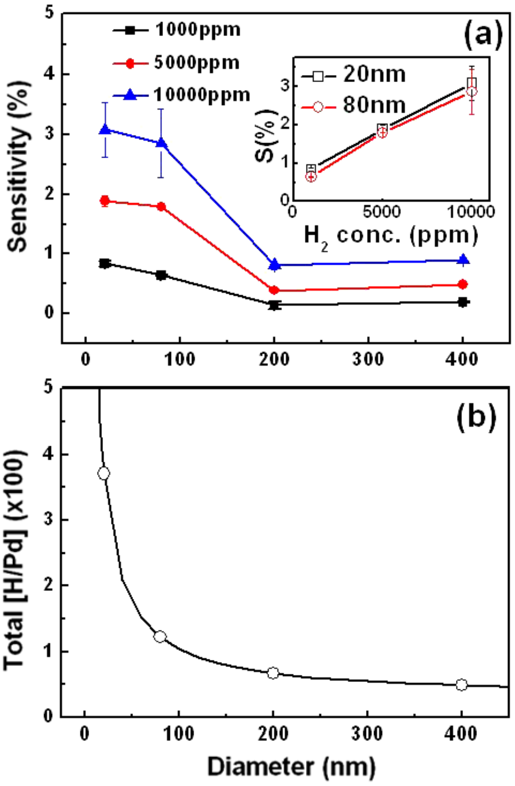

Figure 3. (a) The variation of sensitivity as a function of nanowire diameter for single Pd nanowires with $d = 20$, 80, 200 and 400 nm in the H_2 concentration range 1000–10 000 ppm. The inset of (a) shows the linearity of the sensitivity with H_2 concentration, illustrating that a Pd single nanowire can be used as an H_2 sensor to quantitatively detect H_2 over the wide range of H_2 concentrations. (b) The simulated total [H/Pd] as a function of nanowire diameter at 10 000 ppm H_2 obtained by theoretical modeling.

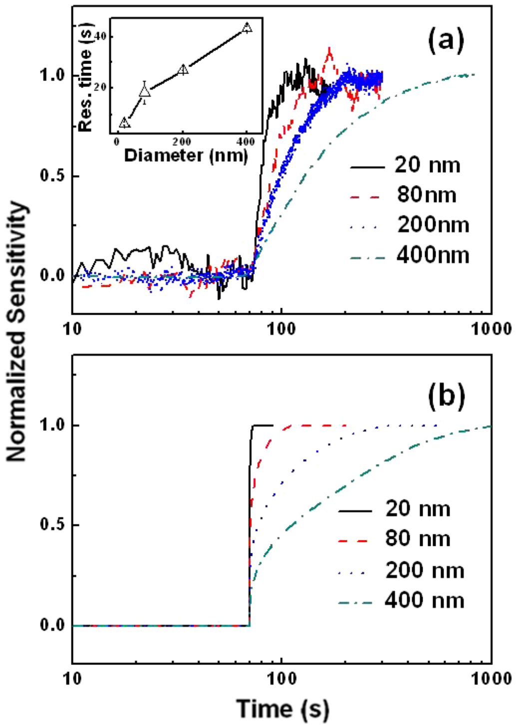

Figure 4. The experimental (a) and simulated (b) results of the diameter dependence of response time at 1% H_2 for Pd nanowires with $d = 20$, 80, 200 and 400 nm, showing that the response time decreases with decreasing nanowire diameter. The inset of (a) shows the variation of the response time with nanowire diameter.

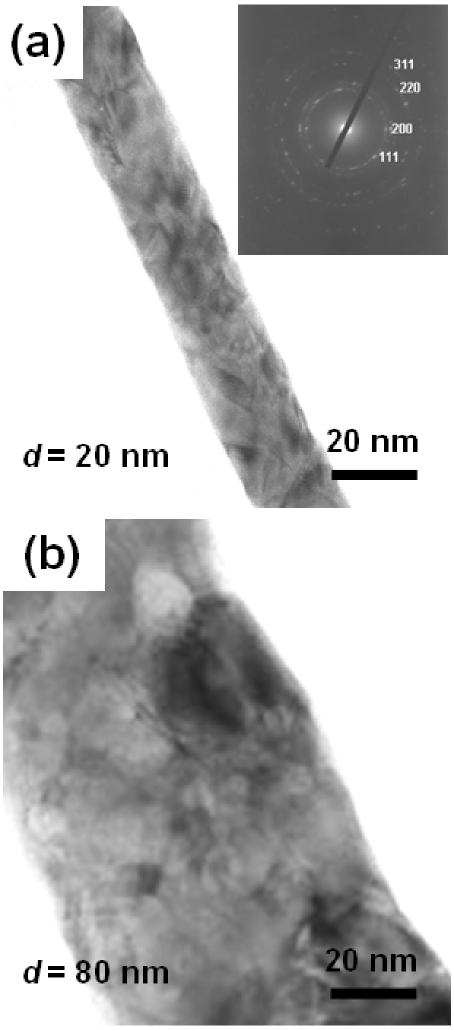

Figure 5. High-resolution transmission electron microscopy (HRTEM) image of the microstructures of single Pd nanowires with $d = 20$ nm (a) and $d = 80$ nm (b). The inset of (a) shows the electron diffraction ring patterns obtained from the Pd nanowire with $d = 20$ nm, providing direct evidence that the Pd nanowire is polycrystalline. From the determination of the distance spacing of planes (111), (200), (220) and (311) for the nanowire, the lattice constant of cubic Pd was found to be 3.936 Å, consistent with the lattice constant (3.889 Å) of H-free Pd.

response time was found to decrease with decreasing nanowire diameter, as seen in the inset of figure 4(a). This is attributable to the higher surface-to-volume ratio, corresponding to the higher initial H_2 adsorption rate, and the shorter diffusion paths for the narrower nanowire, as predicted in our model. Our results are the first experimental demonstration of the diameter dependence ($d = 20$–400 nm) of response time in a Pd single nanowire, which is qualitatively consistent with a theoretical model predicting that the response time of a Pd nanowire decreases with decreasing diameter, as shown in figure 4(b). In this work, the fastest response time of ~6 s was obtained in a Pd single nanowire with $d = 20$ nm.

High-resolution transmission electron microscopy (HRTEM) was exploited to observe the microstructures of the single Pd nanowires with $d = 20$ and 80 nm (see figure 5). The inset of figure 5(a) shows the electron diffraction patterns obtained from the Pd nanowire with $d = 20$ nm. From the determination of the distance spacing of planes (111), (200), (220) and (311) for the nanowire, the lattice constant of cubic Pd was found to be 3.936 Å, in good agreement with the lattice constant (3.889 Å) of H-free Pd. The ring patterns provide direct evidence that the Pd nanowire is polycrystalline. While the mean grain size of the Pd nanowire with $d = 20$ nm was found to be 9.8 nm, the mean grain size of the Pd nanowire with $d = 80$ nm was observed to be 21.6 nm. Hydrogen atoms are believed to diffuse into the octahedral interstitial sites of the Pd nanowire along grain boundaries [15], indicating that smaller mean grain size means more grain boundaries. Therefore, the Pd nanowire with $d = 20$ nm is able to provide more paths for hydrogen atoms to diffuse along, leading to a faster response than for the Pd nanowire with $d = 80$ nm, as seen in figure 4(a). The experimental results on the sensitivity and response time for the Pd nanowires were found to be in qualitatively good agreement with the simulated results obtained from our theoretical model, in which the Pd nanowire was assumed to be a single crystal, even though the Pd nanowires obtained from AAO templates were observed to be polycrystalline having defects, grain boundaries, rough surfaces, etc.

4. Conclusion

The finite size effect on the hydrogen gas sensing performance in Pd nanowires as a function of nanowire diameter in the range $d = 20$–400 nm has been investigated. A combination of electron beam lithography and a lift-off process was utilized to fabricate four-terminal devices based on individual Pd nanowires, which were grown by electrodeposition in the nanochannels of anodized aluminum oxide (AAO) templates. A single Pd nanowire with $d = 400$ nm was found to successfully detect H_2, even at 200 ppm as a low detection limit.

The H_2 sensing sensitivity for Pd nanowires with $d = 20$–400 nm was found to decrease with increasing nanowire diameter. This is due to the higher surface-to-volume ratio, corresponding to a higher initial H_2 adsorption rate, for the narrower nanowire. The response time for the Pd nanowires with $d = 20$–400 nm was found to decrease with decreasing nanowire diameter, indicating the higher surface-to-volume ratio and the shorter diffusion paths for the narrower nanowire. Our results demonstrate that the sensitivity and response time are dependent on the Pd nanowire diameter, which is qualitatively consistent with simulated results.

Acknowledgments

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