

Individual Pd nanowire hydrogen sensors fabricated by electron-beam lithography

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Abstract

We report on the hydrogen gas (H₂) sensing performance of lithographically patterned Pd nanowires as a function of the nanowire thickness and H₂ concentration. A combination of electron-beam lithography and a lift-off process has been utilized to fabricate four-terminal devices based on individual Pd nanowires with width $w = 300$ nm, length $l = 10$ μ m, and thickness $t = 20$ – 400 nm from continuous Pd films. The variation of the resistance and sensitivity at 20 000 ppm H₂ of Pd nanowires was found to be much larger than at 10 000 ppm H₂, which can be explained by an α – β phase transition occurring at 20 000 ppm H₂. This is confirmed by the observation of hysteresis behavior in the resistance versus H₂ concentration for Pd thin films. The response time was found to decrease with decreasing thickness regardless of H₂ concentration due to a higher surface-to-volume ratio and a higher clamping effect. A single Pd nanowire with $t = 100$ nm was found to successfully detect H₂ at a detection limit of 20 ppm. Our results suggest that lithographically patterned Pd nanowires can be used as hydrogen gas sensors to quantitatively detect H₂ over a wide range of concentrations.

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

1. Introduction

The palladium–hydrogen (Pd–H) system was investigated intensively by Lewis [1] 40 years ago. Since then, the Pd–H system has continued providing opportunities for use as hydrogen storage, hydrogenation catalysts and hydrogen gas sensors. Reliable, cheap, and compact sensors to measure the hydrogen gas (H₂) concentration in gas flows and to monitor gas leaks during H₂ production, storage, transportation, and utilization are in high demand. Recently, the development of nanotechnology in the fabrication of Pd nanostructures, e.g. nanowires [2, 3], nanochains [4, 5], and nanotubes [6, 7], has increased interest in the H₂ sensor applications of the Pd–H system.

The absorption of molecular hydrogen by Pd to form Pd–H hydride can cause physical property changes in mass, volume, and electric resistance, all of which can be used to signal H₂ partial pressure changes [8–10]. Pd nanostructures have become well recognized for their highly sensitive H₂ detection at room temperature, but for use as sensors, there are

many problems that need to be addressed [4–7]. Up to now, thin Pd films or thin Pd-based alloy films have been studied for sensor applications due to their simplicity and promising sensing abilities. For pure Pd thin films, peel-off [11] and the α – β phase transition occur when they are exposed to a H₂ concentration greater than 1% at room temperature [10]. To solve these problems in pure Pd thin films, Pd-based alloy thin films [12–14] and Pd nanostructures [2–7] have been investigated extensively. The chemical and mechanical properties of Pd thin films were found to depend on their dimensions [15, 16]. However, the size-dependent H₂ sensing properties of patterned individual nanowires have not yet been studied.

In this work, we present a simple method for the fabrication of individual Pd nanowires patterned by electron-beam lithography. The hydrogen sensing performance of individual patterned Pd nanowires has been investigated as a function of the patterned nanowire thickness. We discuss the effect of nanowire thickness on the hydrogen gas (H₂) sensing performance of Pd nanowires, such as sensitivity, response time, and low detection limit, with respect to surface clamping effect and surface-to-volume ratio. We also discuss

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the variation of electrical resistance and sensitivity of the Pd nanowires according to the H_2 concentration in terms of the α - β phase transition.

2. Experiment

Pd nanowires were sputtered on a thermally oxidized Si(100) substrate using a dc magnetron sputtering system with a base pressure of 4×10^{-8} Torr. A combination of electron-beam lithography and a lift-off process was used to fabricate single Pd nanowires (width $w = 300$ nm, length $l = 10 \mu\text{m}$) with thickness $t = 20$ – 400 nm from continuous Pd films. The thickness of the films was controlled by adjusting the deposition time. Outer Ti/Au electrodes were fabricated by a photo-lithography and lift-off process, and inner micron-scaled Ti/Au electrodes connecting a Pd nanowire with the outer electrodes were made using electron-beam lithography, as shown in figure 1(a). A single lithographically patterned Pd nanowire with dimensions $t = 100$ nm, $w = 300$ nm, and $l = 10 \mu\text{m}$ is presented in figure 1(b). Four-terminal devices based on the individual Pd nanowires were found to successfully detect H_2 . A H_2 sensing experimental setup consists of a sealed chamber of ~ 250 mL, mass flow controllers for monitoring the ratio of H_2 and N_2 , a power source, and digital multimeters connected to a personal computer. The concentration of H_2 is controlled on a N_2 base at atmospheric pressure. The real-time electrical resistance response to H_2 was measured for single Pd nanowires with thickness $t = 400$, 200, 100, and 20 nm at room temperature. All data acquisitions were carried out with a LabView software program through a GPIB interface card.

3. Results and discussion

Single patterned Pd nanowires with dimensions $t = 20$ – 400 nm, $w = 300$ nm, and $l = 10 \mu\text{m}$ were used to detect hydrogen gas (H_2) in the concentration range 200–20 000 ppm at room temperature by measuring changes in their electrical resistance. Each sample was first exposed to nitrogen gas (N_2) to obtain a baseline, then to a designated concentration of H_2 , and then back to N_2 , thus completing one cycle. A representative electrical resistance response to the presence of H_2 at 500 and 10 000 ppm for Pd nanowires with $t = 20$ and 400 nm is presented in figure 2. The H_2 sensing mechanism in Pd is based on the change of electrical resistivity when H_2 is absorbed at the octahedral interstitial site in the Pd face-centered cubic (fcc) lattice [17]. The resistivity of PdH_x is higher than that of pure Pd, because hydrogen atoms play a key role as additional scattering centers, thereby increasing the Pd resistivity.

When a patterned Pd nanowire is exposed to H_2 , hydrogen atoms are absorbed and the resistance of the nanowire increases, as seen in figure 2. Furthermore, when N_2 is introduced instead of H_2 , hydrogen atoms are desorbed and the resistance of the film decreases. The sensitivity of the nanowires for H_2 sensing is defined as $(R_H - R_N)/R_N \times 100\%$, where R_H and R_N are the resistances in the presence of H_2 and N_2 gas, respectively. The Pd nanowire with $t = 20$ nm had slightly lower sensitivity, but a much faster response time than

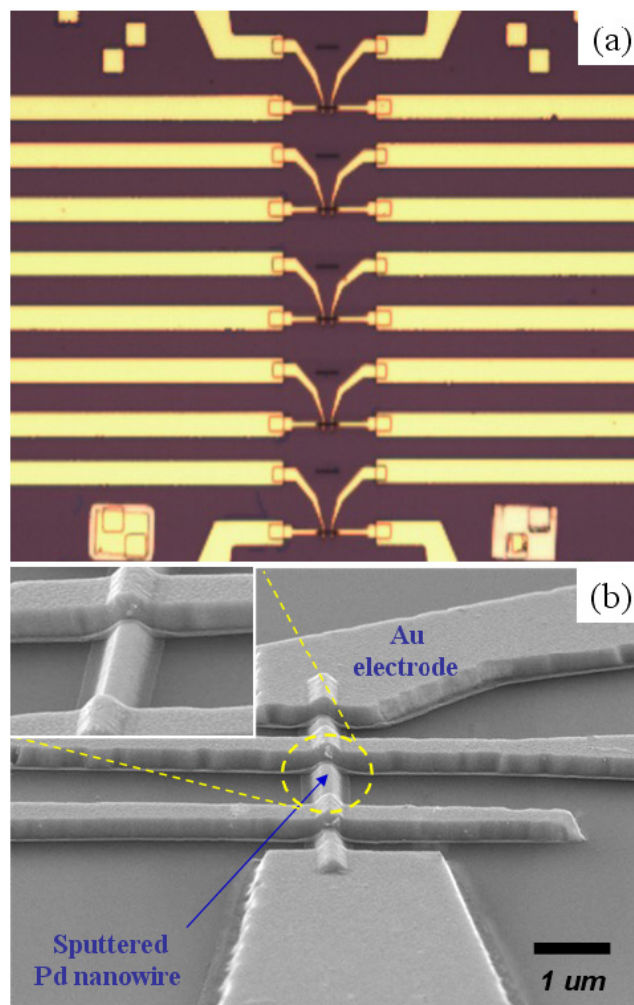


Figure 1. (a) Optical microscope image of a lithographically patterned Pd nanowire sensor array and (b) magnified scanning electron microscopy images of a lithographically patterned Pd nanowire with dimensions $t = 100$ nm, $w = 300$ nm, and $l = 10 \mu\text{m}$.

the Pd nanowire with $t = 400$ nm at both H_2 concentrations (see figure 2). For the nanowire with $t = 20$ nm, the substrate is likely to suppress the volume expansion and hydrogen absorption into the nanowire due to tensile stresses resulting from the film–substrate interface, as compared to the nanowire with $t = 400$ nm. This is called the surface clamping effect [18]. The strain parallel to the film–substrate interface of the Pd thin film with $t = 20$ nm was estimated to be at least 60 times smaller than that for a free bulk sample [15, 16]. In our previous study of individual Pd nanowires grown by electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates that were not clamped on the substrate, the smaller diameter Pd nanowires showed a higher sensitivity due to the greater surface-to-volume ratio [17]. By contrast, in this study, we found that the lower sensitivity for a patterned Pd nanowire with $t = 20$ nm was attributable to the surface clamping effect.

The electrical resistance of Pd nanowires in the presence of H_2 increases, and then eventually saturates, with time.

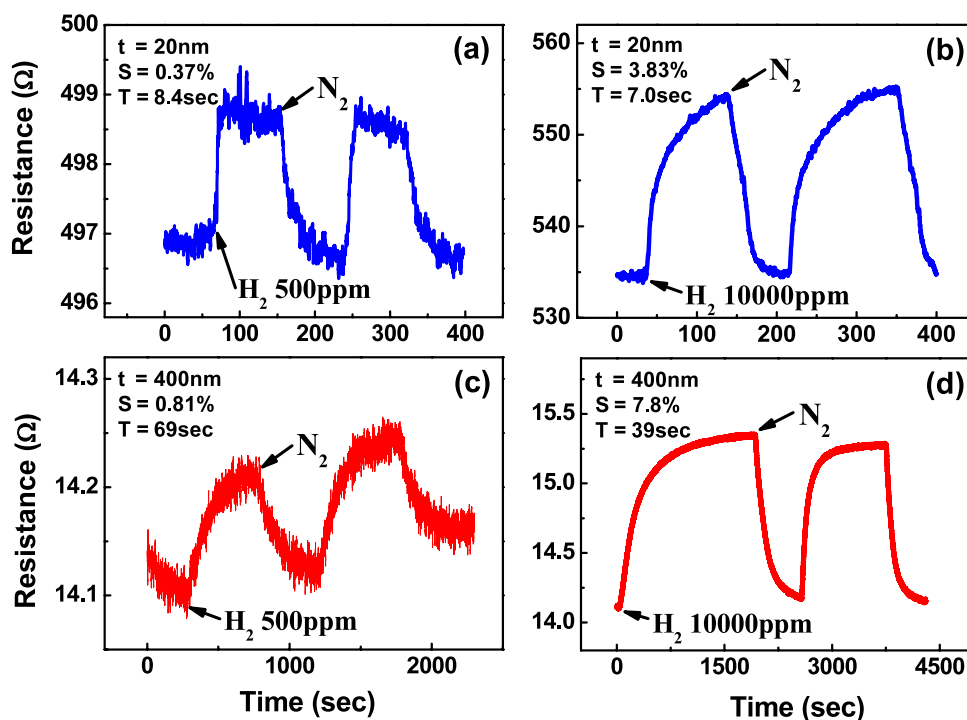


Figure 2. The real-time electrical resistance response to H_2 for lithographically patterned Pd nanowires with $t = 20$ nm (a), (b) and $t = 400$ nm (c), (d) at 500 ppm and 10 000 ppm of H_2 at room temperature.

When a Pd nanowire is exposed to H_2 , hydrogen molecules are adsorbed on the surface of the Pd nanowire. The adsorbed hydrogen molecules are subsequently 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. The hydrogen atoms then react with Pd atoms to form Pd hydride [10, 19]. The response time can be defined as the time required to reach 36.8% ($=e^{-1}$) of the total change of the electric resistance at a given H_2 concentration. The much faster response time in the Pd nanowire with $t = 20$ nm is ascribed to the higher surface-to-volume ratio originating from the shorter and more numerous diffusion paths [17], and a higher surface clamping effect causing lower hydride site density, as compared to the $t = 400$ nm nanowire. The thickness effect for Pd nanowires relating to sensitivity and response time will be described in further detail.

Figure 3 shows the variation in sensitivity with time upon exposure to 10 000 ppm and 20 000 ppm H_2 for single Pd nanowires with (a) $t = 20$ nm and (b) $t = 400$ nm, respectively. Distinct variations in the sensitivity due to electric resistance responses upon exposure to 10 000 and 20 000 ppm H_2 were observed with time for single Pd nanowires with $t = 20$ and 400 nm. As the amount of absorbed hydrogen atoms in the Pd nanowires increases with time after exposure to 10 000 ppm H_2 , the sensitivity was clearly observed to increase monotonically and then reach saturated values (see figures 3(a) and (b)). The increase in resistance and sensitivity to H_2 concentration is due to scattering by the diffused hydrogen atoms in the interstitial sites, indicating α -phase formation of a solid solution. However, the variation of resistance and

sensitivity at 20 000 ppm H_2 was found to be much greater than at 10 000 ppm H_2 for Pd nanowires with $t = 20$ nm and $t = 400$ nm, respectively. The arrows in the resistance curves with time at 20 000 ppm H_2 also indicates the point at which the α - β phase transition starts to occur. These results can be explained by observation of the hysteresis behavior when comparing resistance versus H_2 concentration for Pd thin films. To investigate the variation in resistance and sensitivity of the sensor as a function of H_2 concentration, variations in electric resistance and sensitivity were measured with gradually increasing H_2 concentration during the absorption process and with decreasing H_2 concentration during the desorption process. The insets of figures 3(a) and (b) show the variations in resistance and sensitivity as a function of H_2 concentration during absorption and desorption for Pd thin films with $t = 20$ nm and $t = 400$ nm, respectively. Hysteresis behavior is clear in the resistance versus H_2 concentration plot for the Pd thin film with $t = 400$ nm, whereas little hysteresis was observed for the Pd thin film with $t = 20$ nm.

There are three hysteresis regions in the resistance versus H_2 concentration plot for the $t = 400$ nm Pd thin film, as shown in the inset of figure 3(b). The first region, where the resistance (sensitivity) gradually increases with increasing H_2 up to 1.3%, represents the α single phase (solid solution) at room temperature. The second region, where the resistance abruptly increases for the concentration range 1.3–1.5%, represents the mixture of α and β phases ($\alpha + \beta$ co-existing region). The third region, where the resistance eventually saturates with H_2 concentration, denotes the Pd–H hydride β phase. Absorption and desorption in the Pd–H system occur as a result of H–H and Pd–H interactions. We

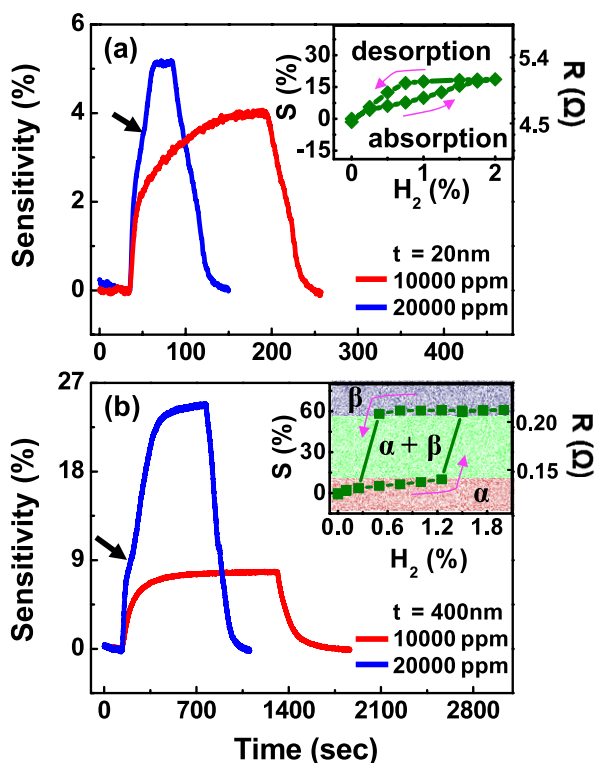


Figure 3. The variation in electric resistance and sensitivity with time upon exposure to 10 000 and 20 000 ppm H_2 of single Pd nanowires with (a) $t = 20$ nm and (b) $t = 400$ nm. The insets of (a) and (b) indicate the variation in resistance and sensitivity of the nanowires as a function of H_2 concentration during absorption and desorption.

speculate that the hysteresis behavior observed in the resistance versus H_2 concentration plot is due to different contributions of the H–H and Pd–H interactions. In contrast, because only a small hysteresis behavior was observed for the $t = 20$ nm Pd thin film, the surface clamping effect appears to have dominated the $t = 20$ nm Pd thin film and suppressed the hysteresis behavior.

In addition, the ratio of the sensitivity for 10 000 and 20 000 ppm H_2 was observed to be 1.3 for the 20 nm thick nanowire and 3 for the 400 nm thick nanowire. H_2 absorption was suppressed in the thinner nanowire due to the surface clamping effect. For further discussion of the hysteresis and surface clamping effects in Pd thin films, see [20].

The effect of nanowire thickness on the H_2 sensing performance for single Pd nanowires with $t = 20, 100, 200,$ and 400 nm was also investigated. Figure 4 displays the variations of (a) sensitivity and (b) response time as a function of nanowire thickness in the H_2 concentration range 500–20 000 ppm. The sensitivity was found to increase with increasing nanowire thickness in the range $t = 20$ –100 nm for various H_2 concentrations. However, there was no significant difference in the sensitivity of Pd nanowires between $t = 100$ and 400 nm for any H_2 concentration. In our previous study [17], we showed that the H_2 sensing sensitivity of individual Pd nanowires grown by electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates increases with decreasing Pd nanowire diameter due to a

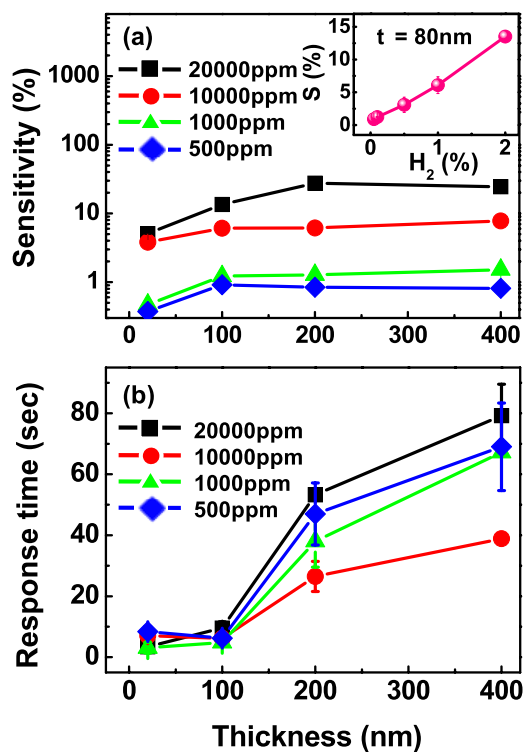


Figure 4. The variation in (a) sensitivity and (b) response time as a function of the nanowire thickness of lithographically patterned Pd nanowires with $t = 20, 100, 200,$ and 400 nm in the H_2 concentration range 500–20 000 ppm. The inset of (a) shows that the sensitivity is linear in the H_2 concentration range 500–10 000 ppm for the nanowire with $t = 80$ nm.

high surface-to-volume ratio. By contrast, in this study, the sensitivity of Pd nanowires with $t = 20$ nm was dominated by the surface clamping effect, rather than the surface-to-volume ratio. However, the surface clamping effect and surface-to-volume ratio are likely to counterbalance each other for Pd nanowires with $t = 100$ –400 nm for all H_2 concentrations.

On the other hand, the response time was found to decrease with decreasing thickness for all H_2 concentrations, as shown in figure 4(b). This could be due to the higher surface-to-volume ratio inducing shorter, more numerous diffusion paths, and the greater clamping effect causing a reduction in the density of hydride sites. In this work, the fastest response time of ~ 3 s was obtained from the single Pd nanowire with $t = 20$ nm. The response time was found to decrease with increasing H_2 concentration due to a higher concentration gradient in the α phase region, i.e. lower than 10 000 ppm. However, at 20 000 ppm H_2 , the response time was delayed by the α – β phase transition, appearing as a step-like increase in resistance. For nanowires with $t = 20$ and 100 nm, the response time for all H_2 concentrations is very fast because the surface clamping effect suppresses the α – β phase transition.

A lithographically patterned Pd nanowire with dimensions $t = 100$ nm, $w = 300$ nm, and $l = 10$ μm would be a good candidate for H_2 sensor applications because of its high sensitivity and fast response time, as well as easy fabrication. We confirmed in this study that lithographically patterned Pd nanowire arrays showed identical H_2 sensing performance.

The inset of figure 4(a) shows that the sensitivity is linear in the H₂ concentration range 500–10 000 ppm for Pd nanowires with $t = 80$ nm, indicating that patterned Pd nanowires can be used as hydrogen gas sensors to quantitatively detect H₂ over a wide range of H₂ concentrations. It should be noted that a single Pd nanowire with $t = 100$ nm could successfully detect H₂ at concentrations as low as 20 ppm. In the present work, we showed that the H₂ sensing properties of lithographically patterned Pd nanowires are different from those of Pd nanowires grown by electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates. This is because the patterned Pd nanowires adhere to the surface of a substrate and hydrogen absorption is restricted by the surface clamping effect for thinner nanowires. To fabricate robust hydrogen sensors based on patterned Pd nanowires, there is a trade-off between sensitivity and response time according to the nanowire thickness.

4. Conclusion

We investigated the finite size effect on the hydrogen gas sensing performance of lithographically patterned Pd individual nanowires with dimensions $t = 20$ –400 nm, $w = 300$ nm, and $l = 10$ μ m as a function of nanowire thickness. Individual patterned Pd nanowires with $t = 20$ –400 nm, $w = 300$ nm, and $l = 10$ μ m could detect hydrogen gas (H₂) in the concentration range 20–20 000 ppm at room temperature, as measured by changes in the electrical resistance of the nanowires. The variation in resistance and sensitivity at 20 000 ppm H₂ was much larger than that at 10 000 ppm H₂ for Pd nanowires with $t = 20$ nm and $t = 400$ nm, respectively. This can be explained by the α – β phase transition, which occurs at 20 000 ppm H₂. The hysteresis behavior in the resistance versus H₂ concentration plot for Pd thin films demonstrated the variations in the resistance and sensitivity of Pd nanowires at 10 000 and 20 000 ppm H₂. Hysteresis behavior was obvious in the resistance versus H₂ concentration plot for the $t = 400$ nm Pd thin film, whereas little hysteresis was observed for the $t = 20$ nm Pd thin film. The sensitivity for the Pd nanowires with $t = 20$ nm was found to be dominated by the surface clamping effect rather than the surface-to-volume ratio, indicating the suppression of H₂ absorption in the thinner nanowire. However, there was no significant difference in the sensitivity of Pd nanowires with $t = 100$ –400 nm for any H₂ concentration, because the surface clamping effect and surface-to-volume ratio counteract each other. The response time was found to decrease with decreasing thickness for all H₂ concentrations due to the higher

surface-to-volume ratio, which gives rise to shorter, more numerous diffusion paths, and the higher clamping effect, which reduces the hydride site density. We have demonstrated that these lithographically patterned Pd nanowires are good hydrogen gas sensor candidates due to their high sensitivity, rapid response time, and easy fabrication.

Acknowledgments

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