# Effects of Surface Roughness on Hydrogen Gas Sensing Properties of Single Pd Nanowires

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We report on the effects of surface roughness resulting from an ion milling technique on the hydrogen gas sensing performance of a single Pd nanowire grown by electrodeposition into nanochannels in anodized aluminum oxide templates. A combination of electron beam lithography and a lift-off process was utilized to fabricate four-terminal devices based on individual Pd nanowires. These results are the first demonstration of the effect of ion milling on the response time in a single Pd nanowire used as a hydrogen sensor. The response time of the single Pd nanowire surface-treated by ion milling was 20 times faster than that of a sample without surface treatment. The faster response time was due to the surface roughness effects of the surface treatment, an increase in the surface-to-volume ratio of the ion-milled nanowire.

**Keywords:** Anodized Aluminum Oxide, Pd Nanowire, Hydrogen Gas, Surface Treatment.

**RESEARCH ARTICLE**

## 1. INTRODUCTION

As environmentally friendly technologies become more necessary, recent studies focused on hydrogen gas as a clean energy source has shown promising results.[1–3] The accurate and fast detection of hydrogen gas has arisen as an indispensable requirement for any practical implementation of hydrogen fuel due to its flammable and explosive properties when the concentration exceeds 4% in air.[4] Palladium is a well-established material in applications using $H_2$ sensing,[5–7] specifically in hydrogenation catalysts[8,9] and hydrogen storage.[10,11] The Pd/H system has significant potential in $H_2$ sensor applications due to the development of nanotechnology in the fabrication of Pd nanostructures, such as nanowires,[12,13] nanochains,[14,15] and nanotubes.[8,9]

We have investigated the $H_2$ sensing performance of individual Pd nanowires grown using electrodeposition into nanochannels of anodized aluminum oxide (AAO) templates as a function of the nanowire diameter.[16] The $H_2$ sensing response increased and response time was reduced with decreasing diameter of Pd nanowire due to a high surface-to-volume ratio and a short diffusion path.[16] The results were qualitatively consistent with those of simulations obtained from a theoretical model using a combination of rate and diffusion equations.[16]

Metals are well known to be preferentially removed from their original surfaces or from their bulk by ion milling with a noble gas such as argon.[17,18] Thus the surface roughness effects on an individual Pd nanowire caused by the ion milling technique lead to a high surface-to-volume ratio. The surface roughness of a Pd nanowire is expected to facilitate the thermodynamic processes that minimize the free energy. Hsieh et al.[19] have demonstrated variations in the conduction path and in the number of adsorption sites among the different crystal morphologies. They have shown enhanced properties, including response time, caused by the effects of film thickness and crystal morphology. Althaim et al.[20] have synthesized microgranular layers of iron oxide and compared them with compact iron oxide films. The surface roughness caused a fast response time, indicating considerable dependence on the morphologies of the oxide layers, but the average responses of the samples were similar.[20] Huang et al.[21] modified $SnO_2$ thin films with nanorods using a plasma treatment. The large surface-to-volume ratio of the nanorods allowed for a faster response time than that seen in the as-deposited $SnO_2$ thin films.

In this work, we investigated the effects of surface roughness induced by ion milling on the $H_2$ sensing performance of single Pd nanowires grown using electrodeposition into nanochannels of AAO templates. The effects of surface roughness of a single 400 nm Pd nanowire on the response time are discussed herein.

## 2. EXPERIMENTAL PROCEDURES

The Pd nanowires were electrodeposited into the nanoholes of an AAO using a three-probe dc method

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in a solution containing 0.034 mol/250 ml $PdCl_2$ and 0.1 mol/250 ml HCl at room temperature [see Figs. 1(a and b)]. A layer of Au was sputtered onto one side of the AAO to serve as the working electrode in a standard three-electrode electrochemical cell. The electrodeposition was performed at a potential of 0.1 V with a silver–silver chloride electrode, with carbonate in a glass cell serving as the counter electrode. After the electrodeposition, the Pd nanowires in the AAO were rinsed with de-ionized water and dried in air at room temperature.

The Pd nanowires were liberated from the electroplated AAO template by dissolution in a solution of 2% hydrofluoric acid. After removal of the template, the Pd nanowires on the Au electrode were rinsed with methanol for 20 min and immersed in isopropyl alcohol. The Pd nanowires were dispersed by applying a drop of nanowire-containing IPA onto a thermally oxidized Si(100) substrate having outer Au electrodes patterned with photo-lithography and a lift-off process. A combination of electron beam lithography and a lift-off process was utilized to fabricate the inner micron-scaled Au electrodes connecting the Pd nanowire to the outer electrodes.[16] A representative single Pd nanowire device is shown in Figure 1(c). The $H_2$ sensing setup consisted of a 250 mL sealed chamber, mass flow controllers for monitoring the ratio of $H_2$ and $N_2$, and digital multimeters connected to a personal computer.
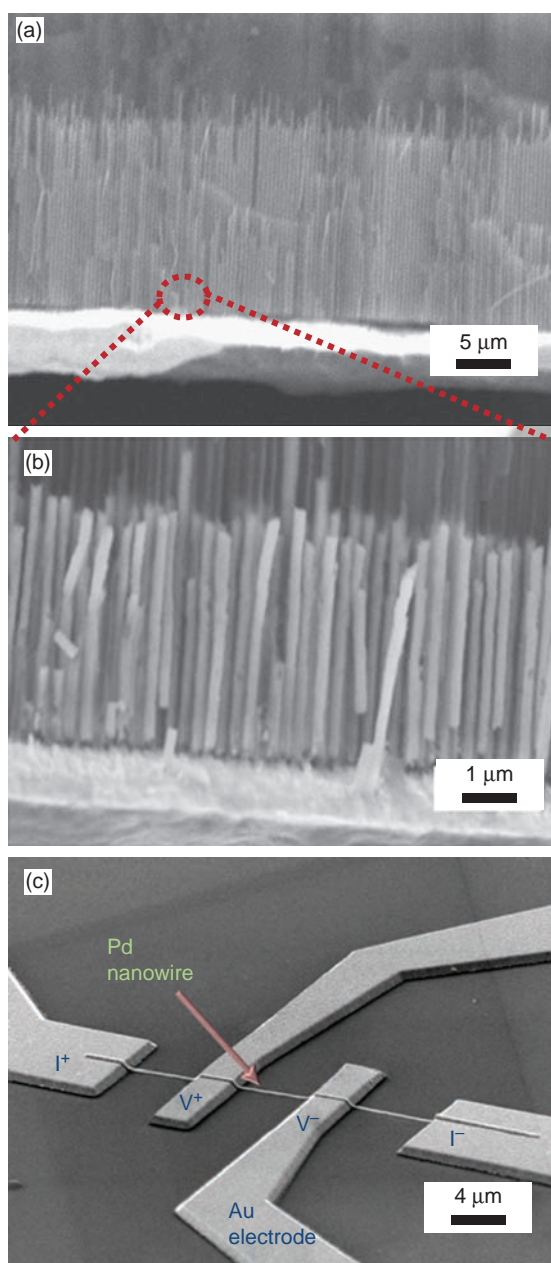


Fig. 1. (a) SEM image of Pd nanowires arrays grown in AAO templates using an electrodeposition method, (b) enlarged image of (a), (c) a representative individual Pd nanowire.
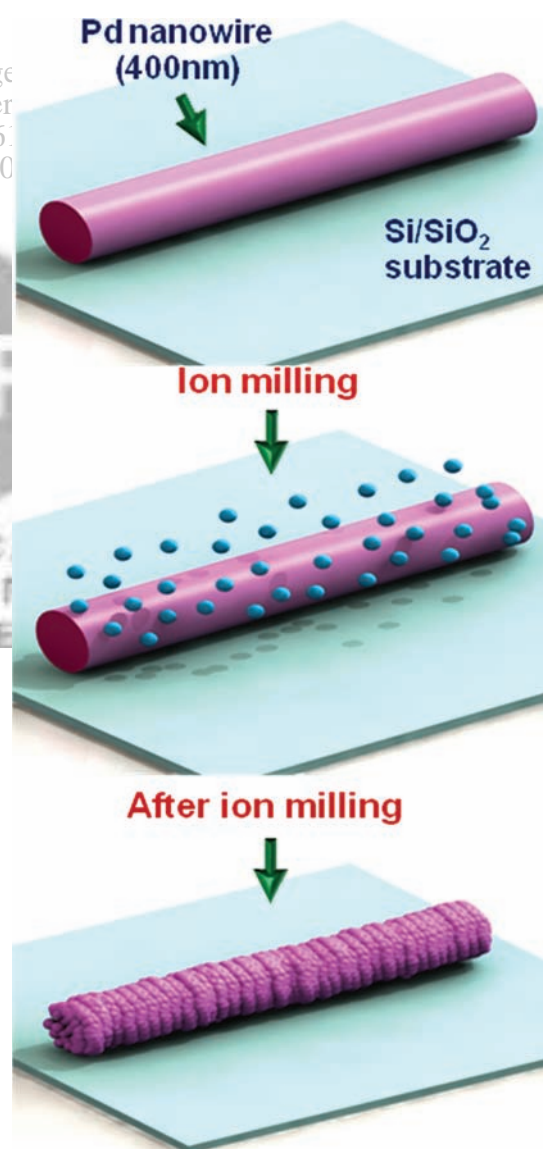


Fig. 2. Schematic images of the ion milling process for a single Pd nanowire.

The purities of the $N_2$ and $H_2$ were 99.9%. The real-time electrical resistance response to $H_2$ was measured for individual Pd nanowires at room temperature. All data acquisition was performed using the LabView software program through a GPIB interface card. Figure 2 presents schematic images of the ion milling process for a single Pd nanowire. A Pd nanowire was treated with Ar ion milling using an electron cyclotron resonance ion beam source. The ion milling conditions were as follows: beam energy of 500 eV, beam current density of 5 $\mu A/cm^2$, milling angle 0–6° with respect to the normal of the nanowire surface, and a process time of 10 min.

## 3. RESULTS AND DISCUSSION

In previous work, we have studied experimentally and theoretically the finite size effects on the $H_2$ sensing performance in single Pd nanowires.[16] Single Pd nanowires with various diameters were investigated to detect $H_2$ in a wide concentration range at room temperature by measuring the changes in their electrical resistances. Smaller-diameter Pd nanowires had a much faster response due to their higher surface-to-volume ratios. The ion milling treatment is of particular interest in this context, as the surface condition of a single nanowire is an important factor in its $H_2$ sensing properties. The scanning electron microscopy (SEM) images of the surface of a Pd nanowire (a) before and (b) after ion milling treatment are shown in Figure 3. The surface of the Pd nanowire before ion milling was clean and smooth based on the surface of the nanochannels of the AAO template. In contrast, the surface of the Pd nanowire after ion milling was rough and coarse, as shown in Figure 3(b). As a result, the ion milling treatment successfully demonstrated surface roughness effects on $H_2$ sensing performance.

The variation in response (%) at 10,000 ppm $H_2$ of a single Pd nanowire before and after ion milling treatment is shown in Figure 4. These results are the first demonstration of the effect of ion milling on the response time in a single Pd nanowire used as a hydrogen sensor. The response of the nanowire for $H_2$ is defined as

$$\text{Response} = \frac{R_H - R_N}{R_N} \times 100(\%)$$

where $R_H$ and $R_N$ are the resistances in the presence of $H_2$ and $N_2$, respectively. Each sample was exposed to a gas cycle: first to $N_2$ to obtain a baseline, then to a desired concentration of $H_2$, and then to $N_2$ again. The response time was defined as the time needed to reach 90% of the total change in electrical resistance at a given $H_2$ concentration. The response time of the ion-milled nanowire was 25 s, which was much faster than that of an untreated nanowire (500 s). The single Pd nanowire surface-treated with ion milling responded to $H_2$ approximately 20 times faster than did those without surface treatment. This difference is attributed to the surface roughness effects caused by ion milling, which increased the surface-to-volume ratio and corresponded to the higher initial $H_2$ adsorption rate. In our previous work,[16] the response time of 20–400 nm Pd nanowires decreased with decreasing nanowire diameter, indicating a higher surface-to-volume ratio and a shorter diffusion path in the smaller nanowires. However, in this study, not the diffusion path but the surface-to-volume ratio was the predominant reason for the faster response time in the ion-milled nanowire. The response time corresponded to the following hydrogenation process. When a Pd nanowire is exposed to $H_2$, hydrogen molecules are adsorbed onto the surface of the Pd nanowires and then dissociate into hydrogen atoms that diffuse into the interstitial sites in the Pd fcc structure as determined by the activation energy of the Fickian diffusion process and the hydrogen concentration gradient. The hydrogen atoms then react with Pd atoms to form Pd hydride, which then acts as an additional scattering source,
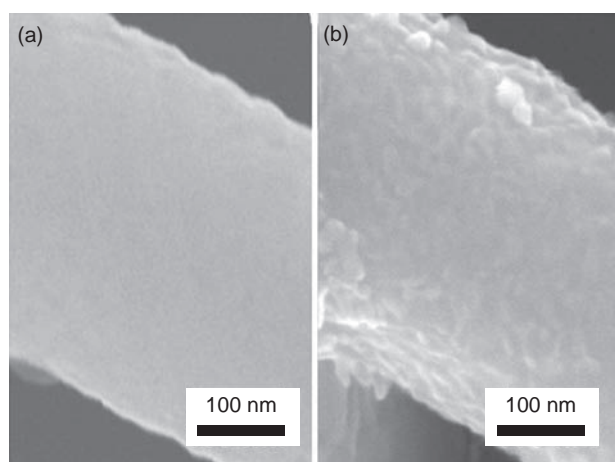


**Fig. 3.** SEM images of the surface of a Pd nanowire (a) before and (b) after ion milling treatment.
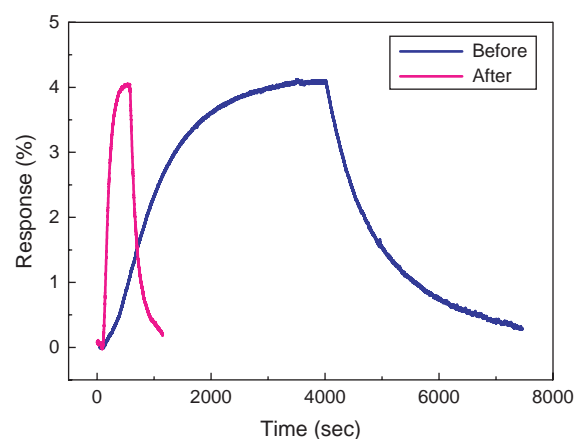


**Fig. 4.** The variation in response (%) for a single Pd nanowire at 10,000 ppm partial pressure $H_2$ before and after ion milling treatment.

thereby increasing the resistivity in the nanowires. Therefore, when the Pd nanowire was exposed to $H_2$, hydrogen atoms were absorbed, and the resistance of the nanowire increased. However, when $N_2$ was introduced, instead of $H_2$, hydrogen atoms were desorbed, and the resistance of the nanowire decreased.

The single Pd nanowire successfully detected $H_2$ at 10,000 ppm, regardless of ion milling treatment. The responses were nearly identical before and after ion milling treatment at $\sim$1%. An enhanced response due to the increased surface-to-volume ratio was not observed for the ion-milled Pd nanowire. The response (%) was defined by the relative variation in the resistance and is approximately given by the following expression in terms of the H and Pd concentrations in the $\alpha$ phase:

$$\text{Response} = \frac{\Delta R}{R} = \frac{\Delta \rho}{\rho_0} = \gamma[H/Pd]$$

where $\Delta \rho$ is the difference in resistivities in the absence and the presence of $H_2$, $\rho_0$ is the resistivity of Pd in the absence of $H_2$, and $\gamma$ is a proportionality constant. The total [H/Pd] is the ratio of total absorbed hydrogen atoms against that of Pd atoms throughout the nanowire, (surface, subsurface, and bulk). The responses of single Pd nanowires sharply increased with increasing nanowire diameter in the range of $d < 80$ nm. There were no significant differences in the responses for $d > 80$ nm, which was qualitatively consistent with the theoretical model.[16] Therefore, the increased surface-to-volume ratio due to ion milling in the single Pd nanowire had a significant effect on the response time and almost no effect on the response.

## 4. CONCLUSIONS

In summary, the effects of surface roughness induced by ion milling on the $H_2$ sensing performance of a single 400 nm Pd nanowire was investigated. The responses were nearly identical in the single Pd nanowires, regardless of ion milling treatment, whereas the response time of the ion-milled nanowire was much faster than that of the untreated nanowire. The faster response time was ascribed to surface roughness effects, which provided a higher surface-to-volume ratio in the ion-milled nanowire. Our results demonstrate that the effects of surface roughness on the response time were dominant in single Pd nanowires.

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