

Hydrogen responses of ultrathin Pd films and nanowire networks with a Ti buffer layer

X. Q. Zeng · Y. L. Wang · Z. L. Xiao ·
M. L. Latimer · T. Xu · W. K. Kwok

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Abstract We report on hydrogen responses of ultrathin films and nanowire networks of palladium on titanium buffered silicon substrates and filtration membranes, respectively. We found that in both systems signatures such as retarding responses and saturation of the resistance changes at high hydrogen concentrations associated with the transition from Pd/H solid solution to Pd hydride diminish with decreasing the thickness of the palladium layer from 7 to 2 nm. Our results not only reveal a new way to suppress the phase transition in Pd/H system but also provide an alternative approach to achieve fast and sensitive hydrogen sensors with a wide concentration detection range.

Introduction

Palladium, which can act catalytically to break the H–H bond in diatomic hydrogen (H₂) and allows monatomic hydrogen to diffuse into it, has been pursued as the most selective H₂ sensing material [1]. When bulk Pd is exposed to H₂ [2], it forms a Pd/H solid solution (α -phase) and a Pd hydride (β -phase) at low and high H₂ concentrations,

respectively. At room temperature the maximum and minimum H₂ contents (atomic ratios of H:Pd) for the α - and β -phases are $\alpha_M = 0.015$ and $\beta_m = 0.61$, respectively. A mixed phase ($\alpha + \beta$ phase) exists at intermediate H₂ contents. The H₂-induced resistance change, which is the core of a Pd-based resistive H₂ sensor, is very sensitive to the H₂ content in the α phase and shows only a small increase from α_M up to β_m composition. In the β -phase region, the resistance first increases abruptly, and then stays nearly constant or decreases at higher H₂ contents [2]. The H₂ concentration dependence of the resistance change in Pd films [3], intact nanowires [4, 5] and nanowire networks [6] follows a similar trend with the appearance of the β -phase at concentrations of 1–3 %, depending on the dimensions of the samples and the fabrication methods. Since the resistance of Pd in majority portion of the β -phase does not change monotonically with H₂ concentration, sensors based on Pd films, intact nanowires and nanowire networks can be inapplicable at high H₂ concentrations (>3 %).

This deficiency of the sensor hinders its potential applications, for example, in a fuel processor and as a safety monitor in a vehicle which requires the device to be sensitive to H₂ in the range 1–100 and 0.1–10 %, respectively [6]. Various efforts [7–11] including the use of Pd alloys and reduction of the Pd thickness have been made to suppress the α - to β -phase transition. Recently, Kim et al. [12] found that a Pd film of 50-nm thick on a thermally oxidized silicon (SiO₂/Si) substrate with a titanium (Ti) buffer layer does not have the sensitivity hysteresis at H₂ concentrations of 0.5–1.5 % observed in a film simultaneously deposited on a bare substrate. They concluded that the Ti insertion suppresses the α - to β -phase transition in the 50-nm thick Pd film due to the reinforced film adhesion.

X. Q. Zeng · Y. L. Wang · Z. L. Xiao (✉) ·
M. L. Latimer · T. Xu · W. K. Kwok
Materials Science Division, Argonne National Laboratory,
Argonne, IL 60415, USA
e-mail: xiao@anl.gov; zxiao@niu.edu

X. Q. Zeng · T. Xu
Department of Chemistry and Biochemistry, Northern Illinois
University, DeKalb, IL 60115, USA

Y. L. Wang · Z. L. Xiao · M. L. Latimer
Department of Physics, Northern Illinois University,
DeKalb, IL 60115, USA

It is indeed possible that better film adhesion to the substrate can tolerate larger internal stress in the film, resulting in buckling to occur at a higher H_2 concentration. That is, the transition may still exist but occur (as a sudden increase of the resistance) at a H_2 concentration which may be out of the upper limit of 2 % in the experiments by Kim et al. [12]. Since Ti has been widely used to form a buffer (or adhesion) layer for metal films deposited on oxide substrates [13–15], further experiments on the effect of a Ti buffer layer on the phase transition in Pd/H system not only will be crucial for achieving H_2 sensors with a wide detection range but also can stimulate exploration on new phenomena in Ti-buffered metal systems.

Here we report investigations on H_2 responses of Ti-buffered Pd (Pd/Ti) layers at H_2 concentrations up to 100 %. In addition to the SiO_2/Si substrate used in Ref. 12, we also deposited Pd/Ti layers onto filtration membranes—a new type of substrate to form nanowire networks (see the inset of Fig. 1 for a typical top-view micrograph) which can have shorter response times due to increased surface area to volume ratio [6]. The α - to β -phase transition can be clearly identified in all samples with Pd layers thicker than 5 nm, though it occurs at H_2 concentrations higher than 2 %. On the other hand, we did find a way to diminish the α - to β -phase transition: reducing the thickness of the Pd layer to be 4 nm or less. The suppression of the α - to β -phase transition allows Pd/Ti sensors applicable to H_2 concentrations up to 100 %.

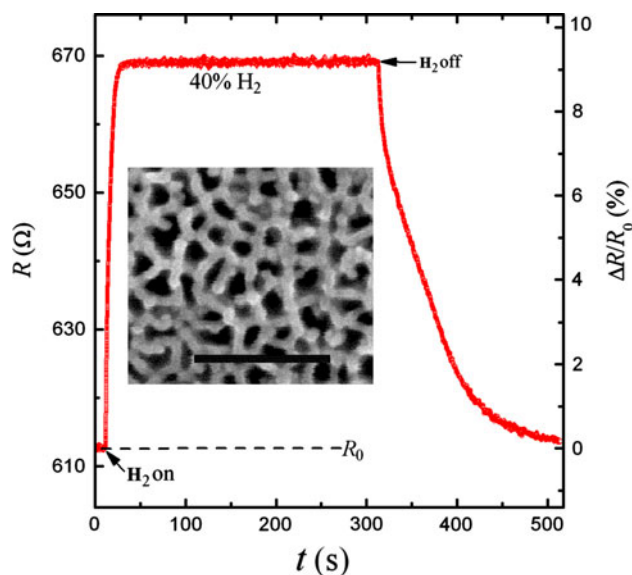


Fig. 1 Responses of a 7-nm Pd/2-nm Ti nanowire network to 40 % H_2 gas. R_0 is the resistance in the absence of H_2 gas and ΔR is defined as the absolute resistance change $R(t) - R_0$. Inset shows a scanning electron microscopy (SEM) image of this 7-nm Pd/2-nm Ti nanowire network deposited onto an Anodisc®13 filtration membrane with a nominal filtration pore diameter of 20 nm. The scale bar is 200 nm

Experiment

SiO_2/Si substrates of 6–10 mm in length and 2–3 mm in width were cut from a silicon wafer (Nova Electronic Materials, Inc) with a 200-nm thick SiO_2 layer. Filtration membranes with a nominal filtration pore diameter of 20 nm were purchased from Whatman Company (Anodisc® 13). They were cleaned in acetone for 10 min in an ultrasonic bath and then rinsed with deionized water followed with an ethanol rinse. They were dried using high-purity nitrogen gas. Ti and Pd were sputtered sequentially onto the substrate by employing an ACT-2400 thin film deposition system under a base vacuum of $\sim 1 \times 10^{-7}$ Torr. The working gas was argon (Ar) at a pressure of 3-m Torr. The deposition rates of Ti and Pd were 0.64 and 1.14 Å/s, respectively, determined by an in situ quartz crystal microbalance (QCM) thickness monitor (model TM-350 from Maxtek, Inc.). The sputtering time for a deposited metal was defined by using a desired nominal thickness divided by the deposition rate. A high-resolution field emission scanning electron microscope (FESEM) (Hitachi S-4700II) was used to image the morphology of the fabricated samples. Rectangle-shaped samples, those on Si substrates and cut from Pd/Ti-coated filtration membranes, were glued onto a sample holder with the Pd/Ti-coated surface facing up. Four Au wires of 50 μm in diameter were attached to the sample with silver paste and the distances between the two voltage leads are 3 ± 1 mm. The H_2 sensor testing was performed by placing the sample in a sealed flow cell with a total dead volume of 2–3 mL. An array of ultrafast solenoid valves (response time of 25 ms) and minimized dead volume of the gas passages were used to accurately characterize these sensors with response times down to tens of milliseconds. H_2 gas (Airgas, ultrahigh purity) was premixed with N_2 gas (Airgas, ultrahigh purity) to the desired concentrations using mass flow controllers (Aalborg GFC17A). The purging gas is N_2 . The total gas flow rate was 200 sccm. The resistance of the sample was measured in constant current mode with a current source (Keithley 6221). The voltage was recorded with a precision high-speed digital-to-analog (DAC) board (NI6259, 16 bits, sampling rate up to 1 MS/s) via a voltage preamplifier (Stanford Research Systems, SR560). All tests were carried out at room temperature.

Results and discussion

In previous experiments [6] we found that the H_2 response of a thinner Pd layer is faster and a nominal thickness of 7 nm is needed for the Pd nanowire networks and film to be continuous. Since the Ti layer which is 1–3-nm thick also adds to the total thickness of the sample, we focused on

Pd/Ti samples with Pd layer thickness of 7 nm and less. Figure 1 presents a typical evolution of the resistance for a 7-nm Pd/2-nm Ti sample when the flow of H₂ gas is on and off: with the presence of H₂ the sample resistance increases from the baseline value R_0 and eventually reaches a steady state. This resistance change is reversible once H₂ is removed. Such a H₂ response is similar to that observed in continuous Pd films, intact Pd nanowires, and nanowire networks [3–6].

As revealed by combined analyses with X-ray diffraction and resistive measurements, bulk Pd/H system exhibits an α - to β -phase transition at H₂ concentration of 1–2 % and its resistivity in the β -phase is insensitive to the change of H₂ concentration [2]. Similar behavior has been reported for thin films [3], individual nanowires [4, 5] and nanowire networks [6] of pure Pd. Since the diffusion paths for protons are extremely short in Pd nanostructures, the H₂ response rate is limited by adsorption process. The associated energy barrier is found to be larger in the β -phase than that of the α -phase. That is, the β -phase has a slower response rate, leading to a retarding response once the β -phase starts to form [5] and a bump or a peak in the concentration dependence of the response time. The anomalies in both the concentration dependences of the resistance change $\Delta R_M/R_0$ and the response time have been considered as signatures for the α - to β -phase transition in Pd nanostructures [4–6, 10]. Figure 2a shows data for samples with 7-nm thick Pd layer buffered with a Ti layer of 2-nm thick deposited on both the SiO₂/Si substrate and the filtration membrane. Indeed, peaks appear in the concentration dependence of the response time for both types of samples. As expected, the response times for the Pd/Ti nanowire network are shorter than those of the film at all H₂ concentrations. The concentration dependence of the resistance change $\Delta R_M/R_0$ for the nanowire network sample also follows the similar trend of that for a pure Pd nanowire network [6] i.e., the resistance first increases quickly and then becomes insensitive with increasing H₂ concentration. In the 7-nm thick Pd nanowire network on a bare filtration membrane [6], the $\Delta R_M/R_0$ versus H₂ concentration relation in the α -phase (up to 3 % H₂) was found to follow Sievert's law [8], i.e. a power-law relation with an exponent of ~ 0.5 . As indicated by the data presented in Fig. 2a, however, the concentration dependence of the resistance change $\Delta R_M/R_0$ for both the Pd/Ti nanowire network and the film samples deviates significantly from a power-law relation. The retarding response in these samples also occurs at higher H₂ concentrations. Furthermore, the $\Delta R_M/R_0$ for the thin film sample even starts to decrease after reaching a maximum at H₂ concentration of 30 %. These results indicate that the Ti-buffered samples indeed behave differently from their counterparts on bare substrates [6]. The α - to β -phase transition, however, can be

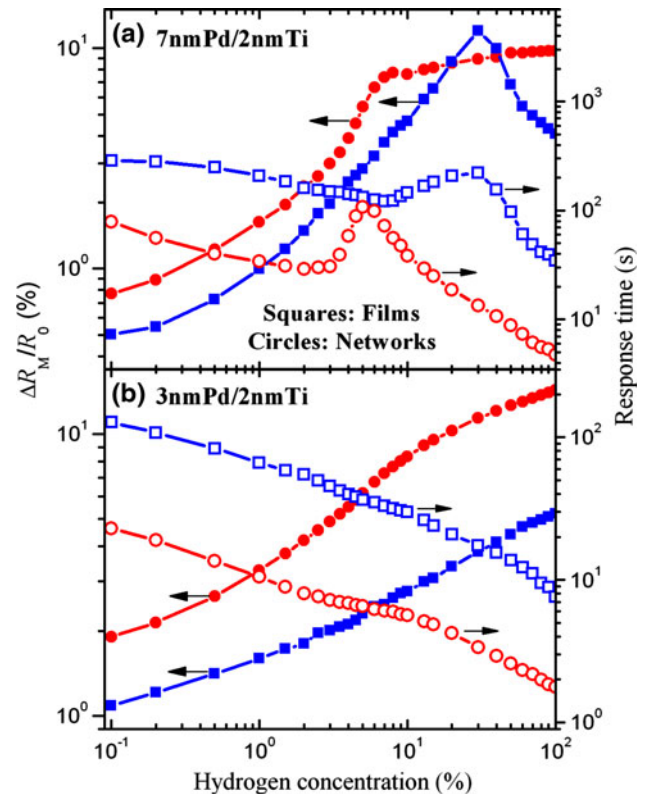


Fig. 2 Concentration dependences of the maximal resistance change $\Delta R_M/R_0$ and the response time for both continuous films (*squares*) on SiO₂/Si substrates and nanowire networks (*circles*) formed on filtration membranes buffered with a 2-nm thick Ti layer. The nominal thicknesses of the Pd layers are 7 nm (**a**) and 3 nm (**b**), respectively. ΔR_M is the maximal resistance change at a specific concentration. The response time is defined as the rise time to reach 90 % of its maximal change, i.e., $\Delta R/\Delta R_M = 0.9$

clearly identified with signatures such as the non-monotonic decrease of the response time with increasing H₂ concentration, though it occurs at concentrations higher than 2 %—the upper limit in the experiments by Kim et al. [12].

Previous experiments [6] reveal that the location of the α - to β -phase transition in Pd nanowire networks on bare filtration membranes does not change with increasing the nominal thickness from 7 to 30 nm while the retarding response evolves from a bump to a peak, i.e., the β -phase becomes dominant in the co-existence state of a thicker sample. On the other hand, no α - to β -phase transition could be detected in 3.8 nm sized Pd-nanoclusters [16] by x-ray diffraction measurements and in 2–3-nm thick Pd nanowire networks [10] on filtration membranes with a chromium layer of 2-nm thick through resistive measurements. Thus, we examined the H₂ responses of Pd/Ti samples with thinner Pd layers. Figure 2b presents the results for 3-nm Pd/2-nm Ti samples on both types of substrates. Indeed, signatures for the α - to β -phase

transition do not appear in the H_2 responses of the Pd/Ti sample on a SiO_2/Si substrate and are dramatically suppressed in those of the nanowire network.

As indicated by the data in Fig. 2, the Pd/Ti nanowire networks and the films have significant differences in responding to H_2 , e.g., the locations of the α - to β -phase transition and the H_2 -induced resistance change in the β -phase as shown in Fig. 2a. That is, a 2-nm thick Ti buffer layer plays different roles on different types of substrates. This is in fact understandable because a substrate with a perfect surface allows a layer by layer growth of a buffer layer while that with a reduced surface promotes a three-dimensional (3D) growth process [17]. This implies that the Ti layer on the SiO_2/Si substrate may form intact thin layer while that on a filtration membrane can be granular, resulting in different morphologies/crystallinities and H_2 responses of the Pd/Ti layers. The $\Delta R_M/R_0$ versus concentration relation of the 7-nm Pd/2-nm Ti layer on a SiO_2/Si substrate is very similar to that observed in some bulk Pd samples, indicating the good crystallinity and intactness of its Pd layer.

The different morphologies of the Ti buffer layers on different types of substrates may also be the origin for the significantly larger values of the $\Delta R_M/R_0$ for the nanowire network than that for the film as shown in Fig. 2b: on the filtration membrane, the 3-nm Pd layer probably forms PdTi alloy with the Ti granules which have larger surface area than the intact Ti layer on SiO_2/Si substrate. Furthermore, the Ti granules may not be completely covered by the 3-nm thick Pd, promoting Ti diffusion and alloying of Pd and Ti [13]. On the other hand, the 3-nm Pd/2-nm Ti sample on the SiO_2/Si substrate behaves more like a pure Pd layer due to its excellent intactness which reduces both the Ti diffusion and the contact area between Pd and Ti. Data presented in Fig. 3 and 4 for the H_2 responses of 2-nm thick Ti-buffered samples with Pd layers of different thicknesses support this interpretation: H_2 -induced resistance changes of the 4-nm Pd/2-nm Ti nanowire network are smaller than those with 2- and 3-nm thick Pd layers while the films have larger resistance changes with increasing thickness for the Pd layer. This indicates that on the filtration membrane the Pd and Ti most likely form PdTi alloy if the Pd layer is 4 nm or thinner. However, the Pd:Ti ratio in the alloy changes in samples with different nominal thicknesses of the Pd layer and can even decrease in the Ti diffusion direction. It is possible that the content of Ti is reduced to zero on the surface of the sample with 4-nm thick Pd. Deposition of more Pd, e.g. with a nominal thickness of 5 nm or above produces an additional conduction path of pure Pd in parallel to the PdTi alloy layer. This is in fact consistent with the data in Fig. 3a that the resistance change of the Pd/Ti sample becomes larger when the nominal thickness of the Pd layer is increased from 4 to

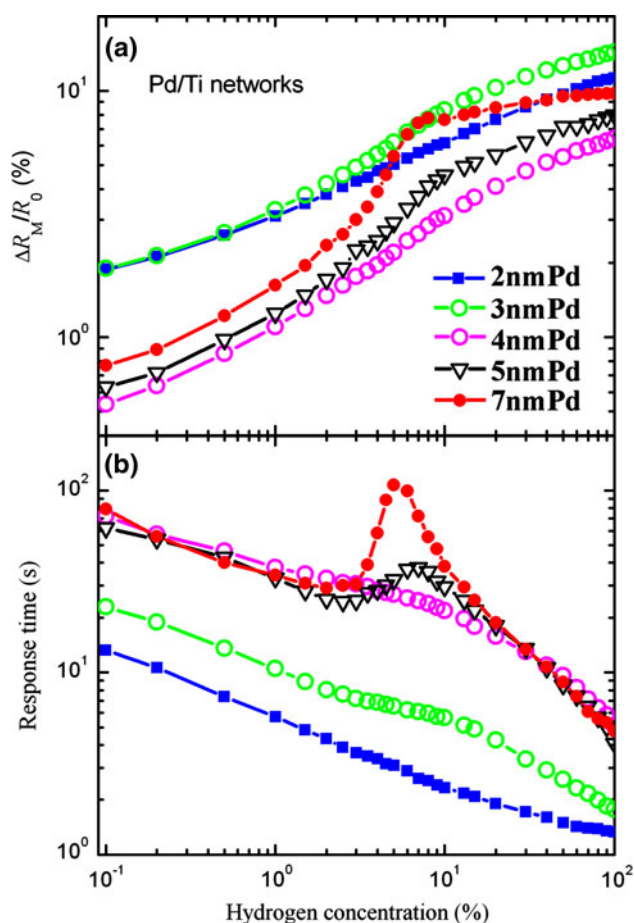


Fig. 3 Concentration dependences of the maximal resistance change $\Delta R_M/R_0$ (a) and the response times (b) for Pd/Ti nanowire networks with various nominal thicknesses for the Pd layers. The thickness of the Ti buffer layer is 2 nm for all samples

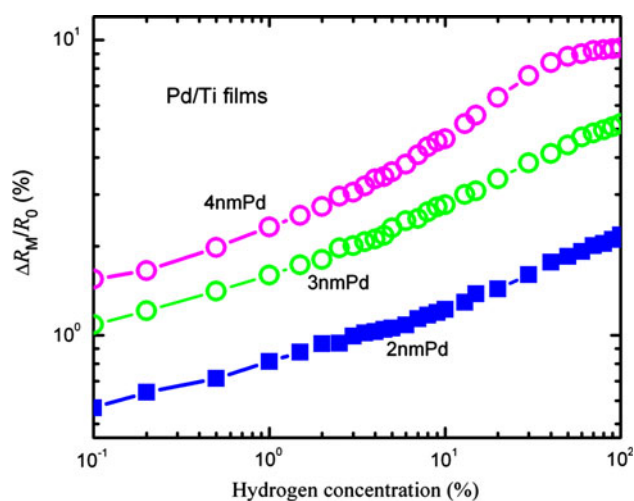


Fig. 4 Concentration dependences of the maximal resistance change $\Delta R_M/R_0$ for Pd/Ti films on SiO_2/Si substrates with various nominal thicknesses for the Pd layers. The thickness of the Ti buffer layer is 2 nm for all samples

7 nm, a typical behavior of the nanowire networks of pure Pd sputtered onto filtration membranes. Furthermore, the resistance change of 10 % for the 2-nm Pd/2-nm Ti nanowire network at 100 % H₂ is larger than the maximal resistance change of 6 % for the α -phase in pure Pd [2], though no anomalies associated with the α - to β -phase transition can be identified. This implies that nanowire networks of PdTi alloys can be promising candidates for achieving H₂ sensors which are not only fast but also sensitive. Previous experiments investigated H₂ responses of bulk PdTi alloys with Ti compositions up to 10 % and observed H₂-induced resistance increase slightly smaller than that of pure Pd [18]. Our results indicate that it would be interesting to study PdTi alloys with higher Ti compositions.

Conclusions

We explored H₂ responses of ultrathin nanowire networks and films consisting of Ti and Pd layers sputter-deposited sequentially on filtration membranes and thermally oxidized silicon substrates, respectively. We observed no signatures for a H₂ related α - to β -phase transition in 2-nm Pd/2-nm Ti nanowire network and (2-, 3-nm Pd)/2-nm Ti films while clearly identified this phase transition in samples on both types of substrates if the Pd layers are thicker than 4 nm. We found that the Pd/Ti nanowire networks with layers of 3 nm or thinner have larger H₂-induced resistance changes than the intact films and attributed the results to the formation of PdTi alloys due to the Ti diffusion in the granular nanowire networks. Our results indicate that the ultrathin Pd/Ti nanowire networks can eliminate a crucial drawback caused by the α - to β -phase transition and is capable of distinguishing H₂ concentrations up to 100 %. Furthermore, their sensitivities also exceed those of pure Pd in the α -phase.

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