Hydrogen gas sensing properties of PdO thin films with nano-sized cracks

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Abstract

We report on a novel method for the fabrication of highly sensitive hydrogen gas sensors based on palladium oxide thin films and have investigated their hydrogen sensing properties and nanostructures. To our knowledge, this is the first report on the use of palladium oxide and reduced palladium thin films as hydrogen sensors. The palladium oxide thin films were deposited on thermally oxidized Si substrates using a reactive direct current (DC) magnetron sputtering system. Considerable changes in the resistance of the palladium oxide thin films were observed when they were initially exposed to hydrogen gas, as a result of the reduction process. After the initial exposure to hydrogen gas of $PdO_{30\%}$, its sensitivity increased up to $\sim 4.5 \times 10^3\%$. The morphology of the PdO surface was analyzed using a scanning electron microscope (SEM), in order to investigate the interactions between palladium oxide and hydrogen. The SEM images showed a large number of nano-sized cracks on the surface of the palladium oxide during the reduction process, which acted to increase the effective surface-to-volume ratio. The response behaviors of the reduced Pd films to hydrogen gas were reversible and had an enhanced sensing property when compared with those of the pure Pd films. In addition, their sensitivities and response times were improved due to the nano-sized cracks on the surfaces. The results demonstrate that palladium oxide and reduced palladium thin films can be applied for use in highly sensitive hydrogen sensors.

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

1. Introduction

In recent years, hydrogen has gained much interest as a possible energy source due to several important advantages; it is renewable, abundant and boasts useful properties [1, 2]. In addition, no greenhouse gases are generated in its consumption, and no pollutants of any kind are produced when it is burned, making it the most environmentally friendly fuel. The representative applications for hydrogen as an energy source are fuel for direct combustion and for fuel cells with very high efficiencies. There is, however, a major safety issue in all hydrogen-based applications; it has flammable and explosive properties when the concentration of the hydrogen (H_2) gas exceeds 4% in air [3]. Hence, the immediate detection of hydrogen is extremely important over a wide range of concentrations. A large amount of research has been done for the development of highly sensitive and reliable hydrogen sensing materials, using wide bandgap semiconducting oxides such as SnO_2 [4], In_2O_3 [5] and ZnO [6]. In this study, we focus on palladium oxide (PdO) and reduced palladium (Pd) thin films which can be used as novel sensing metal oxides to detect H_2. To our knowledge, this is the first proposal for the use of PdO and reduced Pd thin films as hydrogen sensors. The fundamental operational principles of PdO are based on changes in its resistance with H_2 absorption/desorption and its reduction process, resulting in the ability to operate at sufficiently low temperatures. It is therefore important to investigate the changes in electrical conductance of PdO due to its reduction process. After the reduction process, PdO is irreversibly changed into Pd, the surface of which contains nano-sized cracks, resulting in a different surface morphology. Generally, Pd is one of the most important materials for the detection of hydrogen due to its high-selectivity and

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high-reactivity [7–12]. For this reason, the interaction between Pd and hydrogen has been investigated to improve the sensing properties [13, 14]. Palladium has been incorporated into nano-technologies to enhance the H_2 sensing properties of nano-wires [7, 8], nano-tubes [9, 10] and nano-chains [11, 12], as well. In this study, we investigated the change in the conductance of PdO with varying oxygen partial pressures upon initial exposure to hydrogen gas, the variation in sensing properties, and the surface morphology of the reduced Pd thin film after the reduction process. The results indicate that this novel fabrication method produces highly effective H_2 sensors that could exhibit a broad dynamic detection range and a fast response time.

2. Experiments

Palladium oxide ($PdO_{x\%}$) thin films were deposited onto thermally oxidized Si(100) substrates using a pure palladium (Pd) target (99.99% purity) using a reactive sputtering system (base pressure $= 4 \times 10^{-8}$ Torr) at room temperature [15, 16]. The flows of Ar and O_2 were controlled by mass flow controllers (MFCs). The sputtering gas mass flow ratio of oxygen (f_g) is defined as

$$f_g = \frac{f(O_2)}{f(O_2) + f(Ar)} \times 100(\%), \quad (1)$$

where $f(O_2)$ and $f(Ar)$ are the mass flows of Ar and O_2 gases, respectively. $PdO_{x\%}$ represents the PdO thin film which is deposited at $x\%$ oxygen partial pressure. The total mass flow of the Ar and O_2 gases was kept at 22.5 sccm. Six types of $PdO_{x\%}$ thin films were fabricated at different oxygen ratios, up to a maximum of 30% ($f_g = 5\%$, 10%, 15%, 20%, 25% and 30%). It was reported that over 30% the oxygen ratio had a critical effect on the PdO thin films in air due to the film stress, resulting in a telephone cord morphology [17]. The thickness of each $PdO_{x\%}$ thin film was 40 nm. In order to measure the electrical properties of the samples, they were wired using a wire bonder. The measurement system consisted of a sealed chamber (~250 ml), mass flow controllers for monitoring the ratio of H_2 to N_2, and digital multimeters connected to a personal computer. The gas chamber had both a gas inlet and a gas outlet. The two gases were mixed from different lines and flowed together into the chamber though the gas inlet line. The pressure in the chamber was maintained at a nearly constant atmospheric pressure. The real-time electrical resistance responses to H_2 were measured from the samples. All of the data acquisitions were carried out using LabView software through a general purpose interface bus (GPIB) interface card. The surface morphologies of the samples were observed using an SEM at an accelerating voltage of 10.

3. Results and discussion

Figure 1 shows the normal sensitivity behaviors of the $PdO_{x\%}$ thin film when exposed to 2% (i.e., 20 000 ppm) H_2 (N_2 base) and N_2 in sequence. The sensitivity (S) of the films for H_2
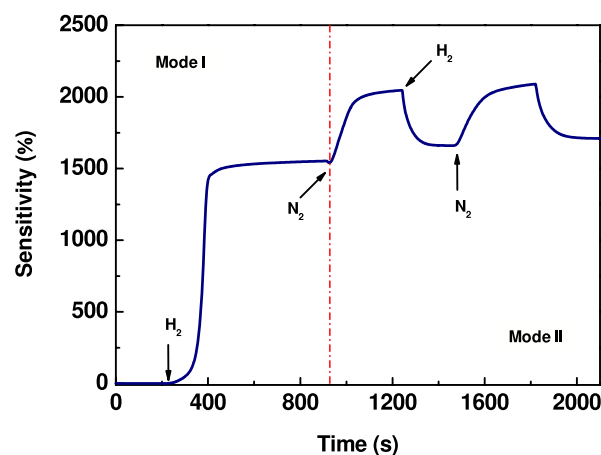
Figure 1. Sensitivity behaviors of $PdO_{x\%}$ (Mode I) and reduced $PdO_{x\%}$ (Mode II) thin films when exposed to hydrogen gas.

sensing is defined as

$$S = \frac{G_H - G_N}{G_N} \times 100(\%), \quad (2)$$

where G_H and G_N are the conductances in the presence of H_2 and N_2 gases, respectively. There are two different modes observed, as shown in figure 1. One is the reduction process of the PdO thin film (Mode I) and the other is the hydrogen absorption/desorption process of the reduced Pd thin film (Mode II). The sensing mechanism of a PdO sensor is quite different from that of a Pd sensor. In the case of the PdO-based sensors, their resistances decrease due to the reduction process when exposed to H_2. The following reaction can be used to describe the reduction process in the PdO sensors [18]:

$$PdO + H_{2(g)} \rightarrow Pd + H_2O_{(g)}. \quad (3)$$

PdO is unstable at room temperature due to oxygen in the bulk. Therefore, when the PdO film was exposed to hydrogen gas, the reduction process easily occurred on the surface of the PdO film. As a result, the resistance of the PdO thin film significantly decreases when reacted with hydrogen gas due to the deoxidization process. The hydrogen sensing mechanism in Pd is based on an increase in the electrical resistance as H_2 is absorbed. When a Pd sensor is exposed to H_2, hydrogen molecules are adsorbed onto the surface of the Pd surface and then dissociate into hydrogen atoms ($H_2 \xrightarrow{Pd} 2H$) that diffuse into the interstitial sites in the Pd fcc structure. Therefore, hydrogen atoms play an important role as one of the scattering sources. As a result, the resistance of a Pd thin film increases when hydrogen gas is absorbed due to the formation of Pd hydride [19, 20] and the hydrogen-induced lattice expansion [9, 10, 21, 22].

A noticeable change in the conductance was observed during the reduction process of the PdO thin film (Mode I). In Mode I, the sensitivity of the $PdO_{30\%}$ thin film was as high as $\sim4.5 \times 10^3\%$. The response time (τ) is defined as the time required to reach 90% of the maximum change in the electrical resistance for a given H_2 concentration. The response
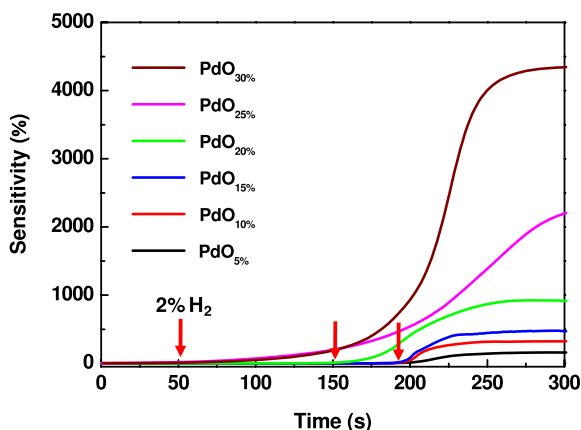
Figure 2. Sensitivity behaviors of as-deposited PdO thin films with different oxygen partial pressures upon initial exposure to 2% H_2.
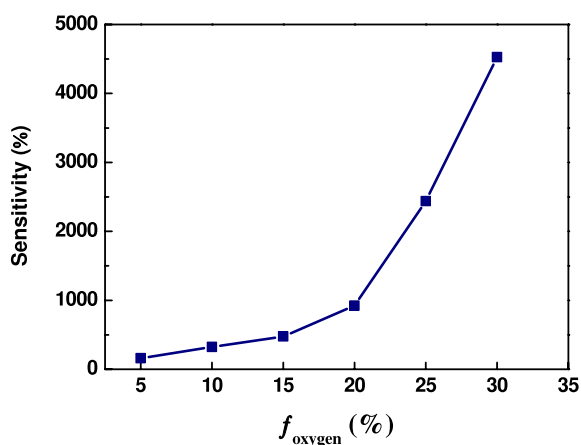

Figure 3. Sensitivity changes of PdO$_{X\%}$ films when deposited with different oxygen partial pressures.

time of the PdO$_{30\%}$ thin film was as short as 16 s when the sensor was exposed to 2% H_2. Although the PdO thin films were valuable as hydrogen sensing materials, the irreversible reaction is a critical drawback. However, as can be seen in figure 1 (see Mode II), recovery behaviors of the reduced Pd thin films were observed and will be discussed later in this paper. During the irreversible reduction process upon the initial exposure to hydrogen gas, nano-sized cracks were generated on the surfaces of the PdO$_{x\%}$ thin films. Namely, there were numerous small water drops on the surfaces of the films after the reduction process.

Figure 2 presents the sensitivity behaviors of the as-deposited PdO films with the different oxygen partial pressures upon initial exposure to 2% H_2, at room temperature. The amplitude of the sensitivity change was significantly dependent on the oxygen partial pressure. The resistivity of pure palladium is ~ 10.8 $\mu\Omega$ cm (@20 °C) and palladium is a member of the platinum group of metals. However, palladium oxide compounds are not conductive materials. For that reason, the resistance change magnitude of the PdO samples was proportional to the oxygen ratio in the PdO$_{x\%}$ samples.

The sensitivity change as a function of the oxygen partial pressure indicates that the change in sensitivity is exponentially
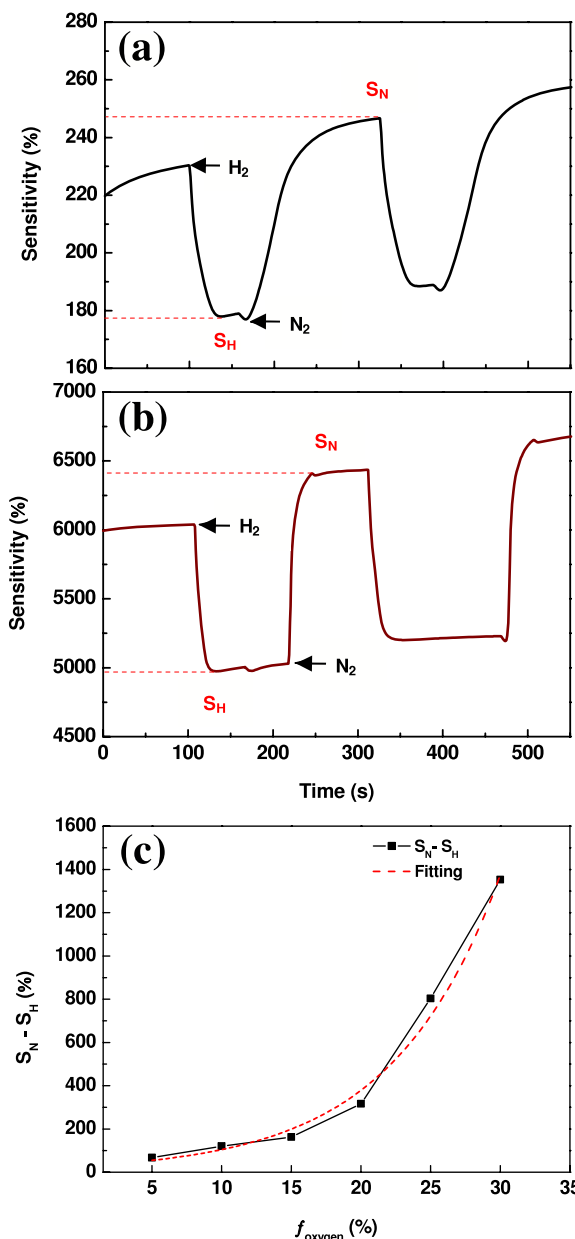

Figure 4. Change in resistance as a function of time of reduced Pd thin films (a) PdO$_{5\%}$ thin film and (b) PdO$_{30\%}$ thin film, where S_H is the maximum sensitivity for H_2 and S_N is the stable sensitivity for N_2 purging. (c) A plot of the $S_N - S_H$ change as a function of oxygen partial pressure.

proportional to the oxygen ratio, as shown in figure 3. The sensitivity was seriously dependent on the oxygen partial pressure in the as-deposited PdO thin films. Based on the variation in sensitivity with increasing oxygen ratio, the PdO films with higher amounts of oxygen added could be used as the most effective hydrogen gas sensors.

As we mentioned before, the PdO thin films have a critical issue which is irreversible to H_2. For this reason, the recovery behavior of the reduced Pd thin films was investigated. Changes in the resistance of the reduced Pd thin films as a function of time are shown in figures 4(a) and (b) for the reduced Pd thin films of $f_g = 5\%$ and 30%, respectively.
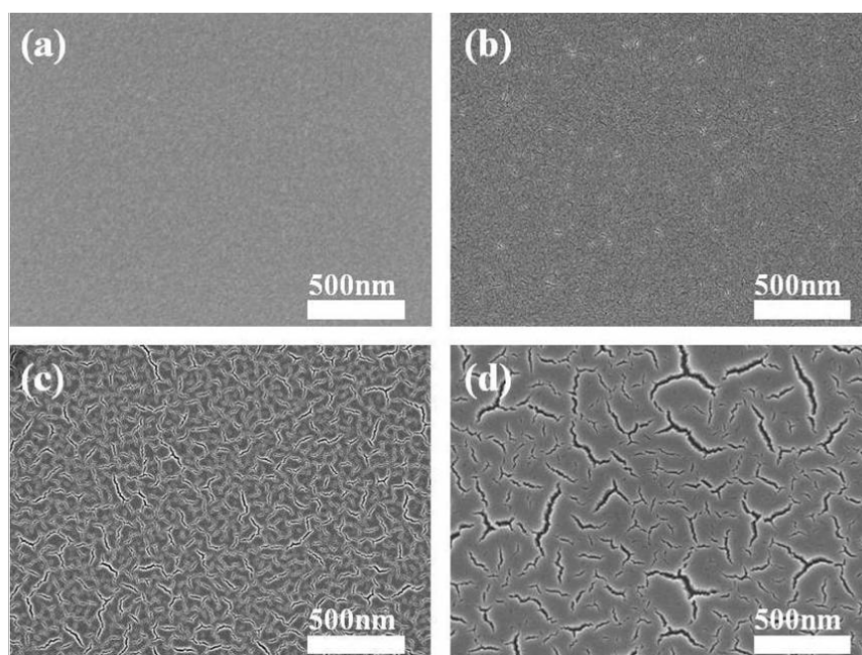
Figure 5. SEM images showing the nano-sized cracks generated on the surfaces of reduced Pd thin films, (a) $PdO_{15\%}$, (b) $PdO_{20\%}$, (c) $PdO_{25\%}$, and (d) $PdO_{30\%}$.

To measure the variations in their electrical properties with gas absorption/desorption, the sensors were first exposed to N_2 to obtain a baseline, then to a 2% concentration of H_2, and then back to N_2, thus completing one cycle. The reduced $PdO_{30\%}$ film had a faster response time and a higher sensitivity when compared to those of the reduced $PdO_{5\%}$ film. The nano-cracks generated on the surface of the reduced Pd thin films had positive effects on the sensitivity and response time. The sensitivity differences between the S_N and S_H of the samples are shown in figure 4(c) where S_H is the maximum sensitivity for H_2 and S_N is the stable sensitivity for N_2 purging. The fitting curve of S_N-S_H changes as a function of the oxygen partial pressure overlapped for all of the samples. The fitting line obeying the following equation is in good agreement with all of the data:

$$(S_N - S_H) \times 100 \ (\%) = A \exp(B f_g) \qquad (4)$$

where A and B are the constant values 29 and 0.13, respectively. As illustrated, the change in the sensitivity of the reduced Pd thin films was exponentially proportional to the oxygen partial pressure, up to a pressure of 30%.

The surfaces of the reduced Pd thin films had a different morphology as compared to that of pure Pd after exposure to H_2. These surface changes were observed using an SEM and are shown in figure 5. The SEM images are the (a) $PdO_{15\%}$, (b) $PdO_{20\%}$, (c) $PdO_{25\%}$ and (d) $PdO_{30\%}$ thin films, respectively, after the initial exposure to hydrogen gas. When compared with the as-deposited PdO and Pd [23] films, the significant change in surface morphology of the reduced Pd thin films can be attributed to the desorption of oxygen from the $PdO_{x\%}$ surface, creating a large number of nano-scaled cracks. Pan *et al* [24] demonstrated nanoflake formation on a PdO thin film grown on a Pt substrate, which was ascribed to a large interfacial stress due to a lattice mismatch between PdO and Pt. However, we could not discern any cracks in the thin films with oxygen ratios of less than 15%. Figure 5(b) is the SEM image of the reduced $PdO_{20\%}$ thin film, on the surface of which very small defects were observed. Numerous nano-cracks were seen on the entire surface of the $PdO_{25\%}$ film (shown in figure 5(c)), with nano-cracks found at the edge of the film upon the initial exposure to H_2. Figure 5(d) shows that the number of nano-cracks of the $PdO_{30\%}$ thin film was greater than that of the $PdO_{25\%}$ thin film. We believe that as the nano-cracks were generated, the performance of the reduced Pd sensors improved dramatically due to the increase in the surface-to-volume ratio.

Figure 6 demonstrates the effects of the oxygen partial pressure (f_g = 5%–30%) on the H_2 sensing properties for the reduced $PdO_{x\%}$ films. When compared to pure Pd of the same thickness, the reduced $PdO_{x\%}$ thin films, as reported here, had a higher response and a faster recovery time. Figures 6(a) and (b) illustrate the response time with exposure to H_2 and the recovery time with exposure to N_2, for the reduced Pd thin films, respectively. The response time was defined as the time to reach 90% changes of total transition in the electrical resistance at a given H_2 concentration. The recovery time is defined as the time required to return to the baseline electrical resistance at ambient N_2. The changes in the response and recovery times as a function of the oxygen partial pressure decreased exponentially. These results indicate that reduced Pd sensors have great potential for the detection of H_2 as compared to those of pure Pd. The noticeable sensing properties of the reduced Pd thin films are primarily derived from the nano-sized cracks generated during the irreversible reduction process upon the initial exposure to H_2. We believe that the nano-cracks make it possible to dramatically improve the sensing properties of the reduced $PdO_{x\%}$ sensors due to the increase in the surface-to-volume ratio.
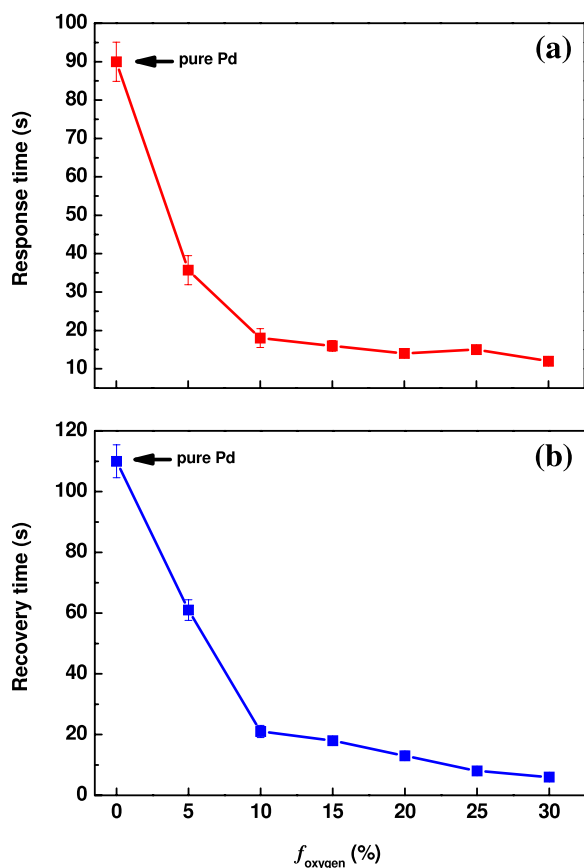
Figure 6. Comparison between pure Pd and reduced Pd thin films upon exposure to H_2 with respect to (a) response time and (b) recovery time.

4. Conclusions

We have successfully fabricated highly sensitive hydrogen gas sensors based on palladium oxide (PdO) thin films. To our knowledge, this is the first report on the use of PdO and reduced Pd thin films as hydrogen sensors. The PdO thin films were deposited onto thermally oxidized Si(100) substrates using a reactive DC magnetron sputtering system. The hydrogen sensing properties of the PdO thin films were investigated in two different ways. One is based on the reduction process of the PdO thin films, and the other uses reduced Pd thin films. In the reduction process of PdO thin films, a remarkable change in conductance was observed upon initial exposure to 2% H_2 at room temperature. In particular, numerous nano-cracks were generated on the surface of the PdO during the reduction process. The nano-sized cracks can be controlled by adjusting the oxygen concentration, and the sizes of the cracks are dependent on the oxygen flow rate. As a result, the PdO sensors demonstrated an ultra-high sensitivity ($\sim 4.5 \times 10^3 \%$) and a fast response time at room temperature. Furthermore, the reduced Pd thin films had a significant electrical conductance modulation upon exposure to H_2 when compared with pure

Pd. Consequently, it is possible to fabricate highly sensitive H_2 sensors that exhibit high sensitivity and fast response and recovery times using PdO and reduced Pd thin films.

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