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Suppression of phase transitions in Pd thin films by insertion of a Ti buffer layer

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Abstract We investigated the effects of a thin titanium (Ti) buffer layer on structural changes and electrical responses of palladium (Pd) thin films. A Ti buffer layer was inserted between a Pd film and the substrate, with varying thickness from 0.5 to 80 nm. Unlike pure Pd films, Ti-buffered Pd films showed no structural deformations after cyclic exposure to hydrogen gas, leading to a linear relationship between sensitivity and hydrogen gas concentration over the measured concentration range of 0 to 2%. This was attributed to the suppression of phase transitions from the α to the β phase in Pd films, due to the reinforced film adhesion by the inserted Ti layer. Our results highlight the practical usability of Pd thin films as reliable and sensible hydrogen sensors, enabled simply by the insertion of a thin Ti buffer layer.

Introduction

Hydrogen (H_2) has received great interest as a green energy source due to its cleanliness, recyclability, and abundance [1, 2]. However, accurate and fast detection of hydrogen is necessary to realize a wide range of H_2-based applications because hydrogen is highly flammable and explosive [3]. For this reason, wide-spread approaches have been pursued for achieving high performance hydrogen sensors, employing different geometries such as hot wire [4] and metal oxide semiconductor [5, 6]. Although a few hydrogen sensors have already been commercialized, they still suffer from critical drawbacks such as high power consumption, poor hydrogen selectivity, and high operating temperature [7, 8].

Palladium (Pd) has recently been recognized as a promising hydrogen sensor material because of its high selectivity to H_2 and good compatibility with the conventional semiconductor integration process [9–13]. In particular, Pd thin films have been intensively investigated because they not only show high sensitivity to H_2, but are also easy to fabricate. From a previous study [14], however, we have found that Pd thin films are structurally deformed and become electrically hysteretic during the H_2 absorption and desorption processes, due to phase transition from the α to the β phase. This might be related to the large difference in lattice expansions in the α and β phase Pd-H systems, both of which have the same crystal structure (face-centered cubic): $\Delta a/a_0$ reaches 0.13 and 3.47% in the respective α and β phases [15]. These issues should be addressed, as Pd films are increasingly considered for use in practical hydrogen sensors. One of our prior studies revealed that the addition of a small amount of nickel (Ni) can suppress the structural deformation, eliminating the hysteresis in electrical resistance [16]. However, this approach complicates the film fabrication process, and Ni is not compatible with semiconductor integration process.

In this study, we investigated structural changes and response behaviors of a thin film stack, where a thin titanium (Ti) buffer layer was inserted between a Pd thin film and the substrate. The suppression of film delamination and hysteretic resistance change in the Ti-buffered Pd films is discussed in comparison with pure Pd films.

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Experiment

A Ti buffer layer was deposited on a thermally oxidized Si (100) substrate by DC magnetron sputtering, varying its thickness from 0.5 to 80 nm (0.5, 1, 4, 5, 10, 20, 40, 80 nm). Subsequently, a Pd thin film was deposited in situ on the Ti buffer layer also by DC magnetron sputtering, with thicknesses of either 50, 100, or 200 nm. The sputter chamber was held under high vacuum (1×10^{-6} Torr) before performing the deposition, and the target-to-substrate distance was 10 cm.

Electrical resistances were measured to evaluate H_2 sensing performance of the Ti-buffered Pd thin films, using a 4-point probe. For the measurements, a sample was mounted onto a printed circuit board (PCB) with an Au wire linked between the two, which was positioned in a test chamber (250 mL in volume). The test chamber was equipped with mass flow controllers for nitrogen (N_2) and hydrogen gases. A gas mixture was fed to the chamber through a gas inlet after intermixing the two gases at the desired ratio beforehand. A check valve was set to open at a pressure higher than ambient pressure so as to maintain the internal pressure of the chamber at atmospheric pressure. The sample in the test chamber was connected to a current source-measurement unit (Keithley 236) and a nanovoltmeter (Keithley 2182), both of which were controlled by a personal computer using a general purpose interface board (GPIB). A current of 1 mA was applied to a sample and a voltage was read out at an interval of 1 s to measure the real-time resistance under specific gas conditions.

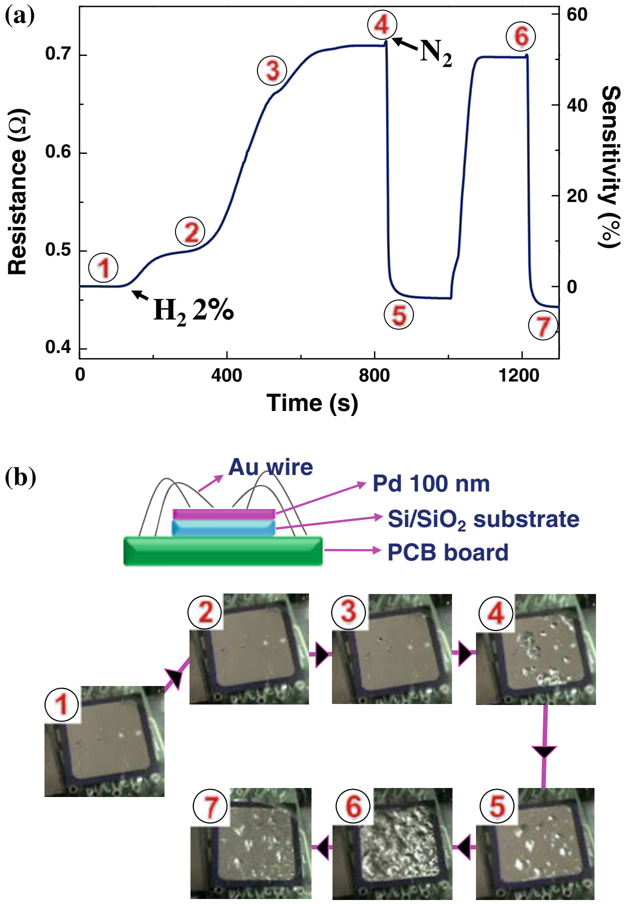


Fig. 1 **a** The real-time electrical resistance and **b** step-by-step morphology evolution of a 100 nm thick pure Pd film in response to cyclic exposures to 2% hydrogen gas (H_2) at room temperature. *Inset* in (**b**) schematically shows the test sample structure

Results

We began by investigating the response behaviors and structural changes of a pure Pd film (100 nm thick) in the presence and absence of H_2. Figure 1 shows the change in electrical resistance and the step-wise evolution of surface morphology for the Pd film at room temperature after initializing the film by exposing it to N_2. The sensitivity on right hand axis in Fig. 1a is defined as:

$$\text{Sensitivity} \quad (\%) = \frac{R_H - R_N}{R_N} \times 100 \qquad (1)$$

where R_H and R_N are the resistance in the presence of H_2 and N_2, respectively [17]. When a Pd film is exposed to H_2 gas, hydrogen molecules diffuse into the film and are broken into H atoms, which occupy interstitial sites of the Pd matrix, leading to changes in physical properties such as volume, mass, density, and electrical resistance [13]. The increase in resistance originates from an increased frequency of charge carrier scattering off the absorbed H atoms [13]. Interestingly, the resistance-increasing pattern observed from the first exposure to H_2 is not monotonic, but includes two intermediate stages with reduced rates of increase, of which the first one is particularly distinct, as seen in Fig. 1a.

The appearance of the intermediate stages can be considered in association with features of crystalline phase and structural deformations in the Pd film [18–20]. The Pd film is in the α phase when a small amount of H_2 is absorbed into the film, filling the interstitial sites with slight volume expansion (resistance increment between stages ① and ②). When the interstitial sites are almost filled, nuclei of β phase palladium hydride (PdH_x) start to form in the original α phase matrix, causing a small increase in resistance (stage ②). Once a sufficient number of β nuclei are created, they grow and encroach on the α phase region until the full matrix is transformed to the β phase, generating a significant latent stress in the film due to large volume expansion (rapid resistance increase between stages ② and ③). Further absorption of H_2 induces structural deformations such as surface delamination to compensate for the large tensile stress at the interface between Pd film and the substrate (stage ③), and substantial morphology change is observed after extended exposure to H_2, as shown in Fig. 1b (stage ④). The structural deformation is irreversible in nature, resulting in only fractional recovery as seen in Fig. 1b (stage ⑤). Once this first cycle is completed, the intermediate stages are found to be very weak because of the large increase in surface area due to the structural deformations from the first cycle. However, the structural deformations become further deteriorated as a result of the cyclic process, as confirmed by an image of stage ⑥ in Fig. 1b, which demonstrates the seriousness of the structural deformations in pure Pd films.

In order to suppress the structural deformations, we inserted a Ti buffer layer between the Pd film and the substrate. Figure 2 shows electrical responses to 2% H_2 at room temperature as a function of thicknesses of respective Ti and Pd films. The start-up points of H_2 and N_2 gas inflow are indicated by arrows on each response curve. Most notably, no curve exhibits any intermediate stage with an inflection point in it, even for the first cycle of H_2 exposure. This suggests that no structural deformations occur during H_2 absorption process, as would be later confirmed by laser scanning microscopy. As compared to the sensitivity (46.5%) of 100 nm thick pure Pd film (see Fig. 1a), the Ti-buffered Pd films with an identical Pd thickness of 100 nm show smaller sensitivities: 9.2% for 1 nm Ti (Fig. 2c) and 8.0% for 5 nm Ti (Fig. 2b). This is attributed to the Ti-mediated improvement of Pd film adhesion to the substrate. Similar to the so-called "clamping effect" [21], the improved adhesion restricts global volume expansion of the Pd film, lowering the level of H_2 in-take. The small decrease in the sensitivity for the thicker Ti buffer indicates that the restriction of volume expansion primarily occurs in the vicinity of the Pd film/substrate interface, and the degree of restriction decreases farther from the interface. For this reason, the effect of improved adhesion is also observed in the very thin Ti buffer, as indicated by inflectionless resistance increase for a Ti buffer with a thickness of 0.5 nm in Fig. 2d. Comparing Pd films with different thicknesses on the same 5 nm thick Ti buffer (see Fig. 2a, b), the thinner Pd film shows a slightly larger sensitivity (8.9%) and shorter response time (21 s) than those (8.0%, 37 s) of the thicker one. Here, the response time is defined as the time to reach 36.8% (e^{-1}) of the total resistance change [22]. This is because slightly more hydrogen molecules can more rapidly diffuse into the thinner film owing to the shorter diffusion distance, just as in the Pd film case without a Ti buffer. Because of the Pd film thickness effects, the sensitivity (7.3%) becomes lower for the thicker Pd film, as seen in Fig. 2d. When the response time is considered in association with the intensity of the Pd film adhesion to the substrate, however, it is found that the longer diffusion distance effect for the thicker Pd film is compensated for by the weaker adhesion in the thinner Ti buffer layer (e.g., 19 s and 22 s for Fig. 2c, d).

The inflectionless monotonic resistance increase observed from Pd films on Ti buffer is expected to be related to Pd film morphology. To closely examine the relationship between the electrical response and film morphology, we investigated structural deformations and surface morphologies of the pure Pd and Ti-buffered Pd films using confocal

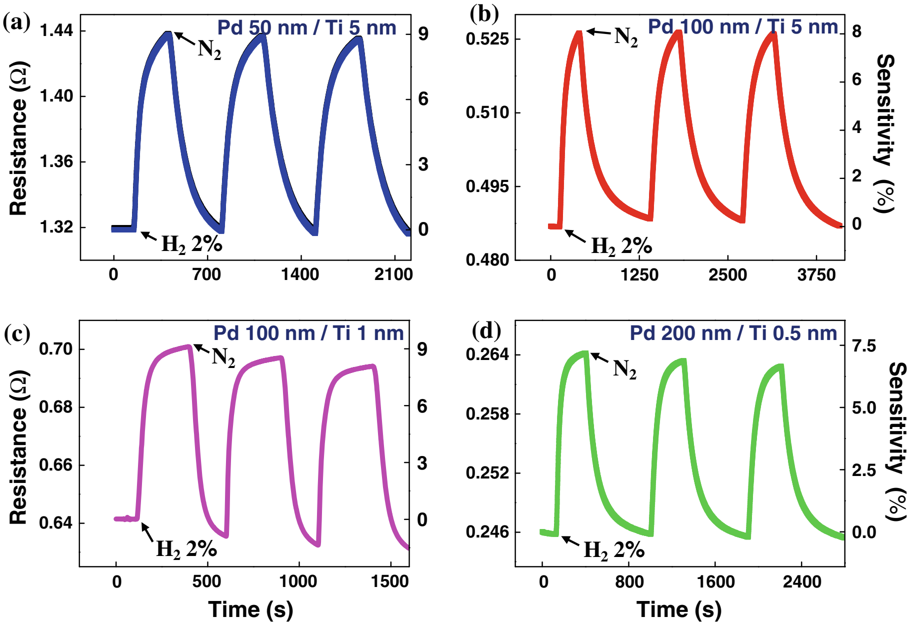
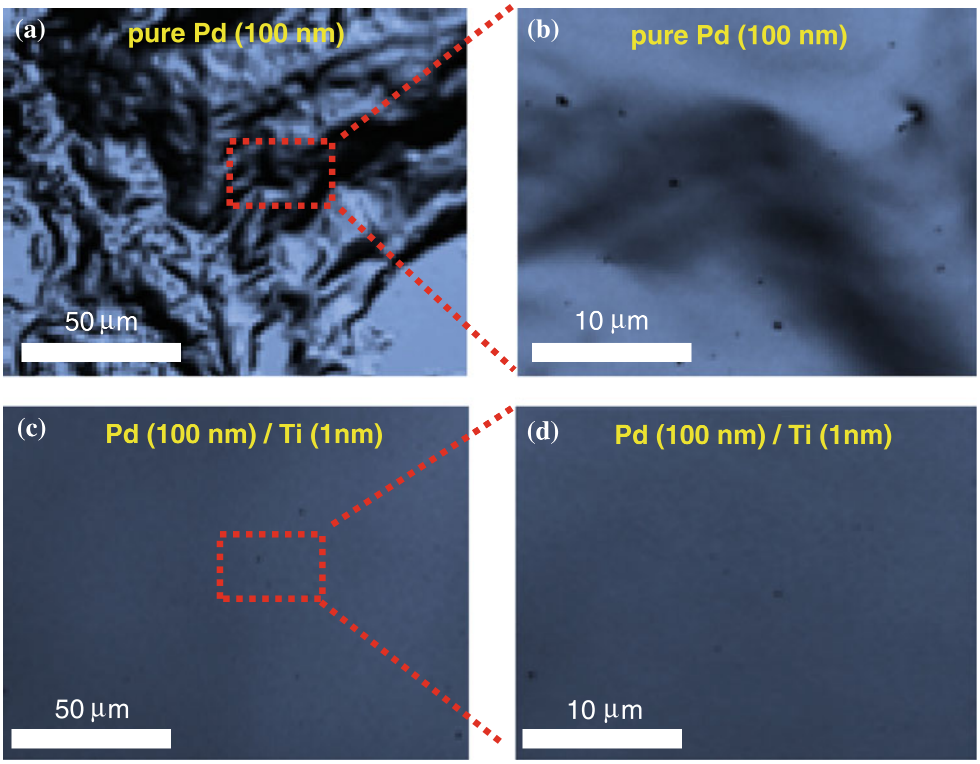


Fig. 2 The real-time electrical responses of Pd films on a Ti buffer layer with different thickness combinations of Pd and Ti: **a** 50 (Pd)/5 (Ti) nm, **b** 100/5 nm, **c** 100/1 nm, and **d** 200/0.5 nm. Measurements were performed at room temperature, using 2% H_2

Fig. 3 Confocal laser scanning microscopy images of surface morphologies of a pure Pd and a Ti-buffered Pd film after exposure to 2% H_2. The thicknesses of the Pd film and Ti buffer layer were 100 and 1 nm, respectively



laser scanning microscopy. Figure 3 shows confocal laser scanning microscopy images of the 100 nm thick Pd films without and with Ti buffer layer after exposure to 2% H_2. Indeed, the Ti-buffered Pd film shows a clean surface without noticeable defects (Fig. 3c, d), while surface delamination caused by structural deformations is observed on the pure Pd film (Fig. 3a, b). This observation justifies that the insertion of a thin Ti buffer layer suppresses structural deformations, leading to monotonic electrical response behavior.

We examined the relationships between the existence (pure Pd films) or absence (Ti-buffered Pd films) of structural deformations with the different phase transition behaviors in the respective Pd films. It was found that the different phase transition behaviors make a difference in electrical responses to H_2 absorption and desorption, as shown in Fig. 4. As displayed in Fig. 4a and as explained via Fig. 1, a pure Pd film is in the α phase and shows little volume expansion (<0.15%) when it is exposed to a low concentration of H_2 (<0.5%), producing no significant structural change. However, β phases nucleate and grow in the α phase matrix as H_2 concentration increases, imposing gradually increasing tensile stress on the film/substrate interface. At last, a complete phase transition from the α to β phase occurs when H_2 concentration exceeds 1.5%, generating a large volume expansion of 3.5% [23]. The large volume expansion and accumulated stress at the interface deform the crystal structures and peel the film off the substrate, as seen in Figs. 1b, 3a, b. The large amount of H_2 in-take and structural deformations lead to a leap in electrical resistance. As the structural deformations are only partially recovered, the high-resistance (sensitivity) state remains for low concentrations (~0.7%) in the stepwise H_2 desorption process, producing a hysteresis in electrical response. In contrast, the sensitivity of a Ti-buffered Pd film linearly increases with increasing H_2 concentration, without a drastic change, as shown in Fig. 4b. The sensitivity change in response to gradual H_2 desorption is exactly superimposed on that of the H_2 absorption process, showing no hysteresis. Moreover, the sensitivity of this Ti-buffered Pd film is more than four times smaller than that of the pure Pd film at an identical H_2 concentration of 2%. These results indicate that the insertion of a thin Ti buffer layer effectively suppresses the α to β phase transition by an enhanced adhesion of Pd film, thereby reducing the number of H_2 molecules that diffuse into the Pd film.

Conclusions

We demonstrated that serious structural deformation problems observed in H_2 sensing using pure Pd films can be remedied by the insertion of thin Ti buffer layer between a Pd film and the substrate. The structural deformation and film delamination were attributed to the phase transition

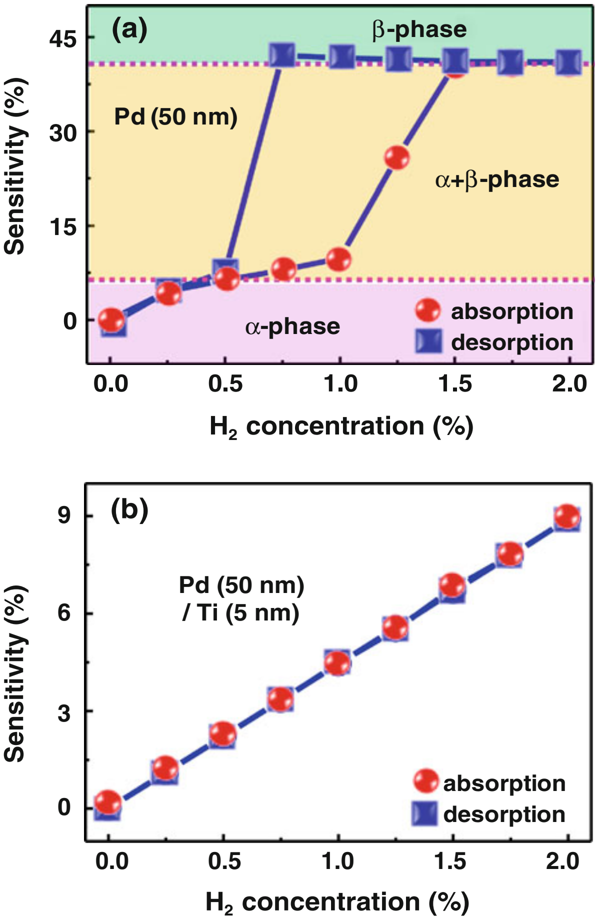


Fig. 4 Sensitivity changes in (**a**) a pure Pd film and (**b**) a Ti-buffered Pd film as a function of H_2 concentration. Pd film and Ti layer thicknesses were 50 and 5 nm. *Circle* and *square* symbols represent data obtained from gradual increase and decrease in H_2 concentration, respectively

from α to β phase occurring at about 1.5% H_2, resulting in intermediate stages and a hysteresis in real-time and cyclic responses, respectively. When a thin Ti buffer, as little as 0.5 nm in thickness, was inserted, no structural deformation was observed due to the suppression of the α to β phase transition, leading to inflectionless monotonic resistance change and a hysteresis-free linear response relationship with H_2 concentrations. The Ti buffer layer made the Pd film tightly bound to the substrate, consequently reducing the free volume of a Pd film for accommodating hydrogen atoms. Our results suggest that Pd thin films can be practically used as reliable and sensitive hydrogen sensors by simply inserting a thin Ti buffer layer between the Pd film and substrate.

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