A Hydrogen Sensor Based on Pd-Functionalized Microcantilever with Surface Design

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Abstract

In this study, a hydrogen sensor based on microcantilever with Pd surface functionalization was developed. Since the absorption-actuated cantilever suffers from the junction sliding between functionalization coating and cantilever surface, this work is focused on improving the adhesive properties between Pd and cantilever surface for efficient chemi/mechanical transduction. Experimental results revealed that sputtering deposition technique benefits the adhesion of Pd functionalization for superior hydrogen detections. Furthermore, a surface design via trench-modification is proposed to cantilever surface for interlocking the Pd functionalization with cantilever surface. With this surface design, the trenched-cantilever hydrogen sensor demonstrated the superior sensing characteristics with higher sensitivity and lower detection limit.

Key Words: Cantilever Sensor, Surface Design, Hydrogen Sensing, Pd

1. Introduction

Recently, microcantilevers with surface functionalizations have provided the possibilities of mechanical transductions to chemical detections with high sensitivity [1–3]. These chemi/mechanical transductions are commonly actuated by two chemical reactions; namely adsorption and absorption [4]. In the adsorption mode, the surface functionalization is mostly employed with the self-assembled monolayer (SAM) in scaling of the alkane chain length and anchoring thiol on gold [5]. When the target analyte is adsorbed onto the SAM functionalization, the surface stress of cantilever is changed, which sequentially bends the cantilever beam [6]. In the absorption mode, the surface functionalization is chosen from the specific material with high solubility to target analyte [7]. As illustrated in Figure 1, the absorption of analyte leads to the volumetric expansion of functionalization coating, which causes the bending of cantilever beam [8]. However, without the strongly anchor bond, the absorption-actuated cantilever sensor suffers from the adhesion-related problems between the functionalization coating and cantilever surface. Such poor adhesion often results in interfacial sliding and in ablation, leading to a false response due to abnormal bending. In this respect, the absorption-actuated cantilever sensor presents the inferior detection performances with low response, poor sensitivity, high detection limit as well as short-term stability. In this study, a hydrogen sensor is developed from the microcantilever with Pd functionalization for absorption actuation. However, in order to ameliorate the junction sliding between Pd coating and

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Figure 1. Schematic diagram of the sensing mechanism for the absorption-actuated cantilever sensor.
cantilever surface, a surface design on cantilever beam is newly proposed to interlock the Pd with cantilever surface. The objective of this study is aimed to enhance the adhesive properties between Pd functionalization and cantilever surface for the superior hydrogen detections.

2. Actuating Principle

With the catalytic property of permselectivity to hydrogen, the hydrogen can dissociatively adsorb onto the Pd surface, and sequentially permeate into the Pd bulk, as shown in Equation (1).

\[
H_2(\text{gas}) + 2Pd_{(\text{surface})} \leftrightarrow 2H - Pd_{(\text{surface})} \leftrightarrow 2H - Pd_{(\text{bulk})}
\]  

(1)

With the absorption of hydrogen, the Pd lattice is expanded from 3.89 Å (α-phase) to 4.10 Å (β-phase) [9], which bends the cantilever beam. From Stoney’s formula [10], the cantilever bending (Δz) can be related to the change of surface stress (Δσ) as

\[
\Delta z = \frac{3L^2(1-\nu)}{Et^3} \Delta \sigma
\]

(2)

where \( L \) represents the length of cantilever beam, \( t \) the thickness of cantilever, \( \nu \) the Poisson’s ratio (0.28 for Si), and \( E \) the Young’s modulus (130.9 GPa for Si). Accordingly, the swelling effect upon Δσ can be evaluated from the Δz read-out.

3. Experimental

The commercial silicon cantilever (Arrow™ TL2, NanoWorld) with 500 μm in length, 100 μm in width, and 1 μm in thickness was directly used in this work. The spring constant \( k \) is commercially referred as 0.03 N m⁻¹. After the proper pretreatment of cleaning, the surface of cantilever was grooved by focused ion beam (FET Nova 200, NanoLab) with the 50 nm-deep trenches across the width of cantilever, as shown in Figure 2. And then, the 50-nm Pd was deposited onto the cantilever surface as functionalization layer. Herein, two Pd depositions, i.e. sputtering and e-gun, were employed for comparisons. The hydrogen detections were performed in a flow-type chamber at 303 K. The testing hydrogen/nitrogen synthetic gases were ranged from 30 to 200 ppm with a flow rate of 100 sccm. The laser displacement detector (LT-9010M, Keyence) was employed for measuring the Δz value.

4. Results and Discussion

Figure 3 shows the typical hydrogen transient detections of the Pd-functionalized cantilever at different hydrogen concentration. When the hydrogen concentration is raised from 200 to 1000 ppm, the Δz value increases from 17.5 to 28.2 μm, and the Δσ value correspondingly increases from 4.2 to 6.8 N m⁻¹. As from XPS analysis in Figure 4, about 60% of Pd film is found as the oxygenated species or palladium oxides, i.e. PdO and PdO₂. It is believed that these oxides will block and consume the initial hydrogen adsorbates [8,9], thereby leading the inferior 100 ppm detection in Figure 3. Accordingly, prior to the hydrogen detection, a trace of hydrogen is required to reduce the oxides as activation procedure.

Figure 5 makes the comparisons of hydrogen sensing performances between different Pd depositions on cantilever surfaces. Experimental results indicate the sputtered Pd-functionalization exhibits the superior sensing characteristics than e-gun one. For example of 50 ppm
detection, the e-gun Pd deposition reveals unsatisfactory coating adhesion, which was obliged to insert a Cr adhesion layer for more Δz transduction from 2.7 to 5.1 μm. But, the sputtered Pd-cantilever junction, suffering the deposition momentum via sputtering bombardment, demonstrates the effective Pd coating adhesion for large Δz and Δσ responses of 8.7 μm and 2.1 N m⁻¹. As shown in Figure 6, for further enhancing the adhesion of Pd sputtering, the surface design via trench-modification on cantilever sensor is characterized. For the hydrogen detections from 50 to 100 ppm, the 30-trench modified cantilever sensor demonstrates the remarkable Δz value from 22.0 to 28.0 μm, and the initial response rate also increases from 30.4 to 42.5 μm h⁻¹. These sensing results largely prevail over the hydrogen detections of cantilever sensor without trench-modification. It is proposed that the trench-modification provides the mechanical interlock between cantilever surface and Pd functionalization for efficient bending transduction.

In order to verify the effect of interlock from trench-modification, two experiments were attempted to clarify this issue. As shown in Figure 7, with the thinner Pd deposition (40 nm-thick), the cantilever with 50 trenches presents the inferior Δz responses than the cantilever without trench-modification. Different from the 50 nm-Pd functionalization, the discontinuous 40 nm-Pd functionalization leads the incomplete transduction of Pd ex-
expansion. This validates that the surface design via trench-modification truly interlocks the Pd layer with cantilever surface for superior hydrogen sensing performances. Furthermore, the force curves of studied cantilevers were also characterized by AFM (SPA-300, SEIKO). The force constants ($k$) of the cantilevers with and without surface modification are 1.93 × 10^{-2} (non-trench), 6.90 × 10^{-3} (30-trench), and 3.55 × 10^{-4} (50-trench) N m^{-1}. After the 40 nm-Pd sputtering functionalization, the composite cantilevers become more rigid, yielding the $k$ values as 5.82 × 10^{-2} (non-trench), 5.54 × 10^{-2} (30-trench), and 5.79 × 10^{-2} (50-trench) N m^{-1}. The trench-modification does not reduce appreciably the $k$ values of these Pd functionalized cantilevers. It clearly indicates these high hydrogen responses of cantilever with trench-modification are mainly attributed to the improvement of functionalization adhesion, not due to the reduction in rigidity of cantilever.

5. Conclusion

In this study, the junction adhesion between Pd functionalization and cantilever surface has been verified as a key point to hydrogen sensing performances. It was found the sputtered Pd-cantilever junction receives the effective momentum bombardment, which leads the superior hydrogen sensing transductions than e-gun Pd deposition. Besides, a surface design via trench-modification is newly employed to interlock the Pd functionalization with cantilever surface for enhancing the chemi/mechanical transduction. Such surface design has been verified to prohibit the junction sliding due to the Pd expansion. Experimental results revealed that the Pd-functionalized cantilever with trench-modification exhibits the preferable hydrogen detections with higher sensitivity and lower detection limit.

References