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Cracked palladium films on an elastomeric substrate for use as hydrogen sensors

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ABSTRACT

We have investigated a lithography-free technique for On-Off type hydrogen sensors using a cracked palladium (Pd) film on an elastomeric substrate. Cracks were induced in a sputtered Pd film simply by undergoing hydrogen absorption and desorption processes. Compared to the same thickness of a Pd film on a Si/SiO_2 substrate that relied on the electron scattering mechanism, a cracked Pd film on an elastomeric substrate operated as a reversible On-Off hydrogen sensor based on the crack open-close mechanism when exposed to hydrogen. The thickness of a Pd film on the elastomeric substrate plays a significant role in determining the sensing mode of the cracked Pd film. The cracked Pd film with a thickness of 9–11 nm on the elastomeric substrate showed reversible and perfect On-Off responses under a wide range of hydrogen concentrations with large current variations and a fast response time of less than 1 s.

1. Introduction

The expectation of the advent of the hydrogen age has been growing since hydrogen gas (H_2) emerged as a new source of green energy. However, the safety issues associated with using H_2 must be addressed before expanding H_2-based applications because H_2 is highly explosive when its concentration exceeds 4% in air [1]. Among the many candidate materials for precisely detecting H_2, palladium (Pd) has been intensively investigated due to its distinct ability to naturally absorb and desorb hydrogen at room temperature, depending upon its environment [2]. Although many Pd-based nanostructures such as nanoparticles [3,4], nanowires [5,6], and thin films [7,8] have been reported, Pd thin films are expected to be commercialized due to their easy and cheap fabrication processes. However, the slower responses and lower sensitivities of Pd thin films compared to other types of Pd nanostructures have slowed the commercialization of H_2 sensors based on thin films. Recently, Penner et al. [9]. developed Pd mesowire-based H_2 sensors, which were fabricated by Pd electrodeposition on step edges of single-crystalline graphite and included many nanogaps in the structure. They showed very fast responses and behaved like an On-Off type H_2 sensor, igniting a wide range of research studies concerning similar H_2 sensors with On-Off responses to H_2 [10–12]. Despite their strong benefits, however, these sensors also possess drawbacks such as a complex fabrication process and limitations in detecting low H_2 concentrations. To overcome these disadvantages, we previously reported a nanogap-based sensing method that utilizes crack formation in a Pd (and PdNi) thin film generated by stretching the thin film on an elastomeric substrate, termed highly mobile

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thin films on an elastomeric substrate (MOTIFE) [13]. The MOTIFE H_2 sensors operated perfectly as On-Off sensors with high performance resulting from nanogaps on the surface of the sensors formed by mechanical stretching. Even though the MOTIFE sensors seem to resolve many shortcomings, stretching is required to create uniform nanogaps over large areas in the devices.

Here, we present a novel cracked Pd film on an elastomeric substrate (CPE) as a high-performance H_2 sensor that requires no mechanical handling procedure. Hydrogen absorption on the Pd film applies a strain to the silica-like surface of the elastomeric substrate, generating random cracks on the elastomeric substrate. Then, the random cracks propagate to the Pd film during hydrogen desorption. The easy-to-fabricate CPE shows On-Off behaviors with good repeatability, fast response, and a high sensitivity to H_2.

2. Experimental procedures

2.1. *Fabrication method for the CPE*

Polydimethylsiloxane (PDMS) elastomer (Sylgard 184, Dow Corning) substrates were prepared by mixing a base resin with a curing agent at a weight ratio of 10:1 and then by curing at 70 °C for 3 h. The thickness of the PDMS substrate was 0.75 mm. To fabricate H_2 sensors, a Pd film was deposited on the PDMS substrate under ultra-high vacuum (UHV), using direct current (DC) magnetron sputtering. Before deposition, the chamber pressure was kept in the range of

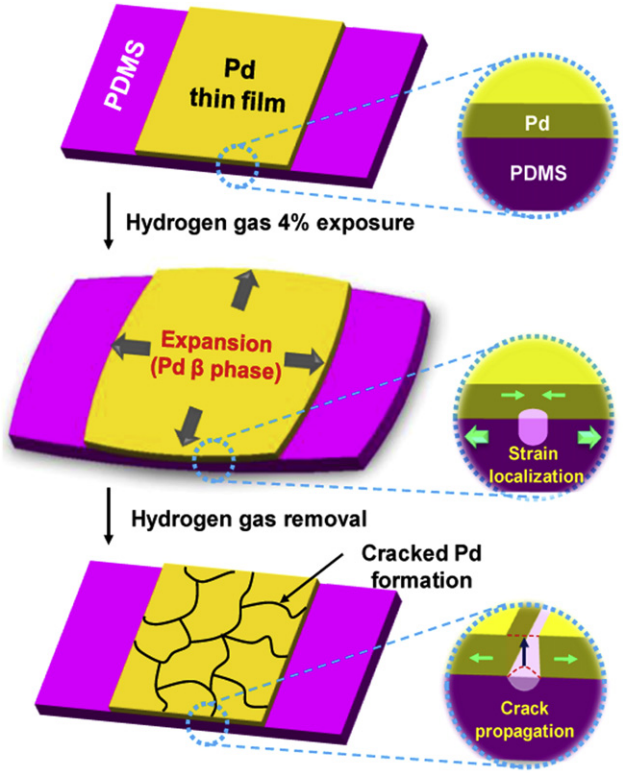

Fig. 1 – Schematic of the fabrication process used for the CPE. (Step 1) Deposition of a Pd thin film onto a PDMS substrate using ultra high-vacuum DC magnetron sputtering. (Step 2) Expansion of the Pd thin film caused by the absorption of hydrogen atoms. (Step 3) Formation of random cracks on the retracted Pd thin film upon desorption of H_2 from the film.

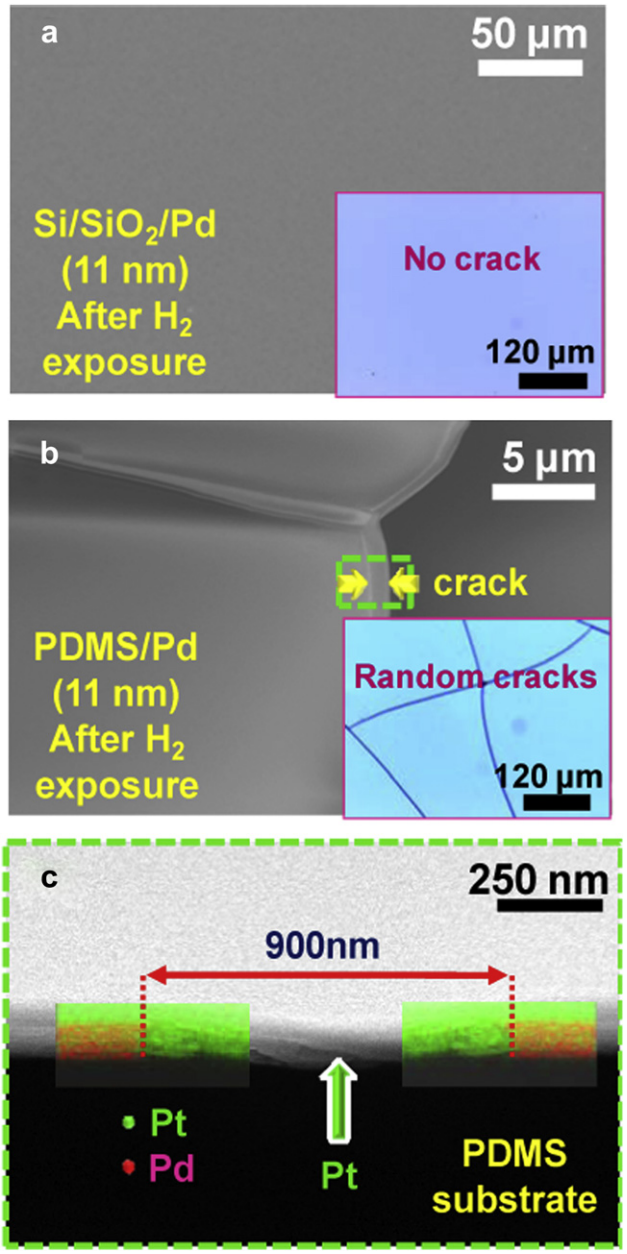

Fig. 2 – (a) An SEM image of a Pd thin film on a Si/SiO_2 substrate. There are no cracks on the surface of the film after exposure to H_2. The inset shows an optical microscope image of the film. (b) An SEM image of a Pd thin film on a PDMS substrate. Unlike the film in (a), there are random cracks on the surface of the film after exposure to H_2. The optical microscope image in the inset clearly shows the random cracks. (c) A cross-sectional TEM image of the crack. The crack formed on the top surface of PDMS was measured to be ~900 nm wide. Pt was used for the FIB milling.