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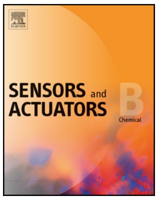

Nanogap-controlled Pd coating for hydrogen sensitive switches and hydrogen sensors

Young-Seok Shim[a,b,c,1], Byungjin Jang[a,1], Jun Min Suh[b], Myoung Sub Noh[c,d], Sangtae Kim[c], Soo Deok Han[c,d], Young Geun Song[c], Do Hong Kim[b], Chong-Yun Kang[c,d], Ho Won Jang[b,*], Wooyoung Lee[a,*]

[a] *Department of Materials Science and Engineering, Yonsei University, Seoul 03722, South Korea*
[b] *Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 08826, South Korea*
[c] *Center for Electronic Materials, Korea Institute of Science and Technology (KIST), Seoul 02791, South Korea*
[d] *KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, South Korea*

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ABSTRACT

We present a simple and facile method for producing high-performance hydrogen (H_2) sensors based on vertically ordered metal-oxide nanorods with a Pd films on a 4-inch SiO_2/Si substrate by a glancing-angle deposition. Firstly, optimal density of nanorods was formed by changing an incident angle of vapor flux. Secondly, nanogaps between each nanorod were precisely controlled by manipulating thickness of Pd films. At room temperature in ambient air, 15-nm-thick Pd-coated SiO_2 nanorods showed the rapid on-off switches. The average response time was approximately 2.8 s (the longest response time: 5 s), and the recovery time was less than 1 s for 2%–0.8% H_2. For 20-nm-thick Pd-coated SiO_2 nanorods, detection of limit was reduced to 10 ppm due to semi-on-off operation. The reproducibility of our approaches was investigated by fabricating the Pd-coated SnO_2 nanorods. They also exhibited the high H_2 sensing performance as Pd-coated SiO_2 nanorods. We strongly believe that high H_2 sensing performance of Pd nanogap controlled metal oxide nanorods provides a new perspective for room-temperature H_2 switches and sensors based on H_2-induced lattice expansion.

1. Introduction

Hydrogen (H_2) has excellent combustion characteristics such as a low ignition energy,high heat of combustion (142 kJ/g H_2), wide flammable range (4–75%), and high burning velocity compared with other combustible gases [1,2]. Moreover, H_2 is abundant and eco-friendly which are the most important factors to be considered as the next generation energy sources [3,4]. For these reasons, studies on the economical production, high-volume storage, and effective utilization of H_2 have been carried out [5,6]. However, colorless, odorless, and tasteless characteristics of H_2 have been regarded as obstacles in handling its safety, since it is highly flammable and explosive when its concentration exceeds 4% in air [7]. In order to safely use H_2, highly sensitive, selective, fast, and reliable sensors for H_2 detection are desirable to prevent the risk of explosions.

Recently, the functional convergence of the Internet with radio-frequency identification and sensors has led to the era of the Internet of Things (IoT), which is a computing concept in which everyday objects are online and communicate via the Internet [8,9]. In particular, the IoT is effective and appropriate for monitoring and controlling objects in hazardous environments to enable people to access them [10]. For applying H_2 sensors in IoT, 4S (high sensitivity, precise selectivity, great speed for response/recovery, and stability for long-term operation) with 2L (low power consumption and low cost fabrication) are required [11]. Among the various requirements to fulfill 4S with 2L, operation atroom temperature is vitally important for H_2 sensors to not only achieve low power consumption but also to prevent potential explosion or accident. Accordingly, various H_2 sensors based on thermally conductive, catalytic, electrochemical, and metal-oxide sensors have been developed and investigated to satisfy operation at room temperature [3,12]. Among them, the Pd based sensors using H_2-induced lattice expansion

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* Corresponding authors.
E-mail addresses: hwjang@snu.ac.kr (H.W. Jang), wooyoung@yonsei.ac.kr (W. Lee).

[1] These authors contributed equally.

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(HILE) have received considerable attention and become superior candidates for H_2 sensor, since these sensors can easily achieve the requirements and it is hardly influenced by external factors such as humidity and other gases [13–15,30–45]. Generally, the H_2 sensing mechanisms of Pd based sensors using HILE are classified into two categories. Firstly, H atom act as electron scattering source in Pd structures and then increases the resistance as H_2 concentration is increased. The second mechanism is based on the Pd nanogap structure which operates the electrical connect/disconnect before and after H_2 exposure by volume expansion of Pd film, respectively.

To maximize the HILE, the Pd nanogaps, nanocracks, or porous structures induced by electrodeposition, pressure-injection of Pd into the nanochannels of a porous membrane such as anodic aluminum oxide (AAO), or top-down patterning from a Pd thin film using electron-beam lithography have been employed (Table S1 in Supplementary data) [16–21]. Despite their decent H_2 sensing properties, they have not been able to overcome poor stability, namely, buckling and peeling after long-term operation and cycling, and relatively high limit of detection (LOD). In addition, most researches conducted H_2 sensing measurement in N_2 ambient because O_2 in air reduces Pd adsorption sites by forming H_2O [22]. In our previous works, in order to overcome aforementioned shortcomings, we fabricated Pd nanogaps induced by tensile stress on elastomeric substrates (polydimethylsiloxane) [23]. It is easy, scalable, and lithography-free compared with other methods, resulting in high sensing performance for H_2 detection. More recently, Pak et al. showed the more enhanced H_2 sensing properties using polymer based substrates with well-aligned Pd nanogaps [24]. However, since the nanogaps in elastomeric or flexible substrates are easily changed as a function of ambient temperature and humidity, achievement of a durable nanogaps with well-established processes have still remained challenges for the utilization of Pd nanogap-based H_2 sensors in the IoT.

In this paper, we demonstrated the wafer-scale fabrication of extremely sensitive H_2 switches and sensors using physical vapor deposition with an in-situ process for the first time. Vertically ordered one-dimensional (1D) SiO_2 nanorods with Pd films were successfully synthesized using a glancing-angle deposition (GLAD). The nanogaps between the individual nanorods are controlled by changing an incident angle of the vapor flux and thickness of Pd films. Upon exposure to H_2, the current path on the vertically ordered 1D SiO_2 nanorods with Pd films was repeatedly linked or broken in accordance with the volume expansion or contraction of the Pd films, resulting in an electrical open or short state (15-nm-thick Pd-coated 83° SiO_2 nanorods). 20-nm-thick Pd-coated 83° SiO_2 nanorods exhibited a as low limit of detection as 10 ppm due to semi-on–off operation. Furthermore, SnO_2 nanorods with Pd films, which have similar morphologies to SiO_2 nanorods also exhibit high H_2 sensing performance to show a reproducibility of our methods.

2. Experimental

2.1. Fabrication

4-inch SiO_2/Si (1 μm/550 μm thick) was used as the substrate, which was precisely cut into 10 mm × 10 mm samples by a dicing saw (Fig. S1 in Supplementary data). Before depositing the SiO_2 and SnO_2 films, the SiO_2/Si substrates were sequentially cleaned in acetone, ethanol, and isopropanol followed by drying in nitrogen gas. Approximately 2–5 nm SnO_2, SiO_2 grains, and Pd pellets with a 99.99% purity (Kojundo Chemistry) were utilized for film deposition. To fabricate the vertically ordered SiO_2 and SnO_2 nanorods, the GLAD method using an electron-beam evaporator was employed. The SiO_2/Si substrate was perpendicularly located 50 cm from the crucible. SiO_2 and SnO_2 films were deposited onto a tilted substrate rotating at a speed of 60 rpm. The base pressure and growth rate were 2.4×10^{-6} Torr and 5 Å/s. All samples were annealed at 550 °C for 60 min in air. Then, Pd films were deposited onto the vertically ordered SiO_2 and SnO_2 nanorods at the original position (0°) with a growth rate of 0.5 Å/s.

2.2. Sample characterization

The morphologies of the fabricated SiO_2 and SnO_2 nanorods were characterized by an environmental scanning electron microscope (XL30 FEG ESEM, FEI) using an accelerating voltage of 15 kV and a working distance of 10 mm.

2.3. Sensor measurement

The vertically ordered SiO_2 and SnO_2 nanorods with Pd were loaded onto a printed circuit board (PCB), and silver paste (P-100, Cans Inc.) was used to wire the sample to the PCB. The PCB with the sample was then placed in a test chamber, in which electrical measurements were performed at room temperature using a workstation with a current measurement unit (Keithley 236, Keithley Instruments, Inc., USA) and a compatible PC Labview program (Fig. S2 in Supplementary data). All measurements were carried out using a mass flow controller (MFC) under controlled gas conditions. The detailed specifications of the chamber and the test methods are described elsewhere. Air was used as the primary gas as a carrier for H_2 and for venting the system.

3. Results and discussion

It is well known that the GLAD technique can lead to a variety of vertically ordered 1D metal-oxide nanostructures such as nanorods, nanoblades, and zigzag nanocolumns by controlling the incident angle of the vapor flux, orientation of substrate, and rotation speed [25,26]. A schematics of the GLAD setup using an electron-beam evaporator and the fabrication procedure for the vertically ordered SiO_2 and SnO_2 nanorods with Pd films on 4-inch SiO_2/Si substrate are shown in Fig. 1(a) and (b). First, to examine the morphologies and adjust the gap between the individual nanorods, we directly deposited a SiO_2 nanorods on a tilted SiO_2/Si substrate (73°, 77°, 83°, 85°, and 87°) rotating at a speed of 60 rpm. Fig. 1(c–g) show the cross-sectional SEM images of the SiO_2 nanorods as a function of incident angle. Even though all samples were deposited at same conditions, the thickness of SiO_2 nanorods gradually decreased with the increasing incident angle. Reversely, diameter and gap between the nanorods were increased. These results can be explained by the self-shadowing effects. As the self-shadowing regions are increased, the size of initial nucleus is increased, resulting in a formation of wide gap between the nanorods with a large diameter [27].

In order to precisely control the gap between the nanorods and investigate the H_2 sensing properties, we deposited Pd films on the SiO_2 nanorods with varying thicknesses (5, 10, 15, and 40 nm). Fig. 2 shows the plane-view SEM images of twenty different samples as a function of an incident angle and Pd thickness. The gaps in all samples were decreased with an increasing thickness of Pd films and decreasing incident angle. To clearly investigate the change of morphologies, we converted the plane-view SEM images using MATLAB, as shown in Fig. 3(a). Porosity of all samples is shown in Fig. 3(b), which was calculated by the ratio of black (blank) and red (SiO_2 or Pd-coated SiO_2 nanorods) color. All samples showed the highest and lowest porosity at 5 nm- and 40 nm-thick-Pd films, respectively. For low-incident angle of vapor flux (73° and 77°), SiO_2 nanorods are easily covered by even a small thickness of Pd films due to their high density. Reversely, low density of SiO_2 nanorods

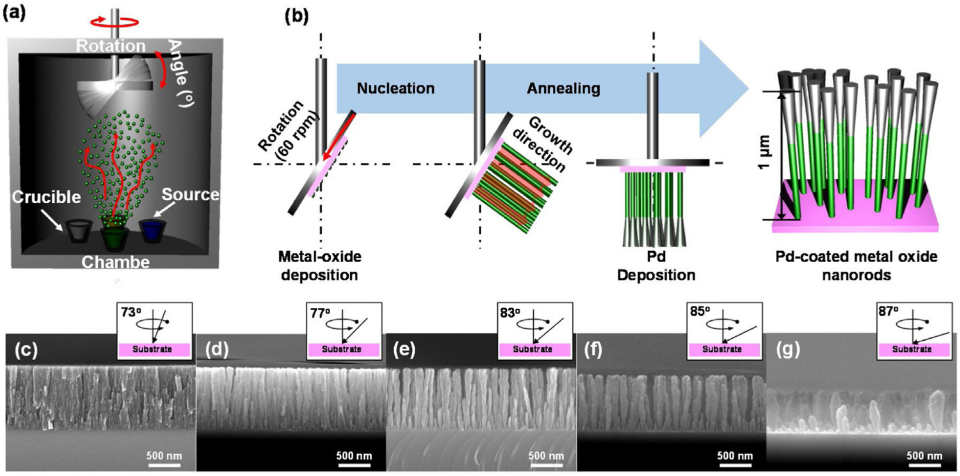

Fig. 1. Schematics of (a) the GLAD setup using an electron-beam evaporator and (b) the fabrication procedures for the Pd-coated metal-oxide nanorods. (c–g) Cross-sectional SEM images of the vertically ordered SiO_2 nanorods. Insets are incident angle of vapor flux.

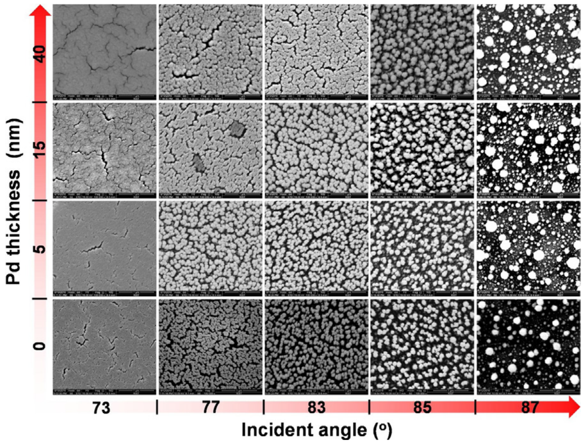

Fig. 2. Plane-view SEM images of the vertically ordered SiO_2 nanorods as a function of incident angle (73°, 77°, 83°, 85°, and 87°) and Pd thickness (0, 5, 15, and 40 nm) on SiO_2 nanorods.

deposited at 85° and 87° is not appropriate for changing the porosity since the distance between individual nanorords is too far from each other. From the slope in Fig. 3, it is noteworthy that porosity of 83° SiO_2 nanorods showed distinct dependency on the thickness of Pd films by optimal density. In other words, we can easily control the nanogap in 83° SiO_2 nanorods compared with others. In order to investigate surface composition and the chemical state, X-ray photoelectron spectroscopy (XPS) measurements were carried out for the Pd film on SiO_2 nanorods. The additional chemical compounds in Pd film are not observed. The XPS spectrum of Pd displays binding energy peaks at 336.1 eV and 341.4 eV, corresponding to electronic transitions of Pd_{3d5A} and Pd_{3d3A}, respectively. The 5.3 eV gap between Pd_{3d5A} and Pd_{3d3A} indicates the value of separated spin-orbit doublet (Fig. S3 in Supplementary data), which accords with the literatures [46,47].

We measured the resistance of all samples using digital multimeter to find the optimal thickness of the Pd films for H_2 sensors. For SiO_2 nanorods deposited at 73° and 77°, they were too dense to find the gap between the SiO_2 nanorods, leading to low resistance values (3 Ω), which indicates that all nanorods were perfectly connected. In contrast, the SiO_2 nanorods deposited at 85° and 87° had a sparse distribution, and the gaps between the individual SiO_2 nanorod deposited at 85° and 87° were greater than 100 and 300 nm, respectively. Hence, they exhibited the insulating properties although the thickness of Pd films is 40 nm. For the SiO_2 nanorods deposited at 83°, a semi-dense distribution was observed compared to other samples. When the thickness of the Pd films reached 40 nm, the SiO_2 nanorods deposited at 83° abruptly exhibited the low resistance. Since the SiO_2 nanorods deposited at 83° below the 40-nm-thick Pd films were insulators, these results clearly point out that the optimal nanogap exists at a Pd film thickness of less than 40 nm for on–off operation to H_2. Therefore, we controlled deposition thickness of the Pd films and gas-sensing properties such as response, detection limit, and stability were also evaluated under multiple exposures to various H_2 concentrations.

Fig. 4 shows a representative response curves of the 15- and 20-nm-thick Pd-coated 83° SiO_2 nanorods as a function of H_2 concentration (in an air carrier gas). In order to promote the formation

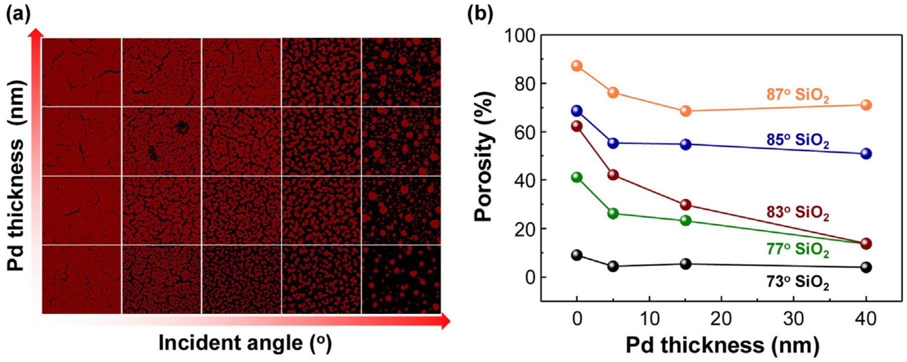

Fig. 3. (a) Converted images of plane-view SEM images by MATLAB. (b) Porosity of Pd-coated SiO_2 nanorods calculated from MATLAB.

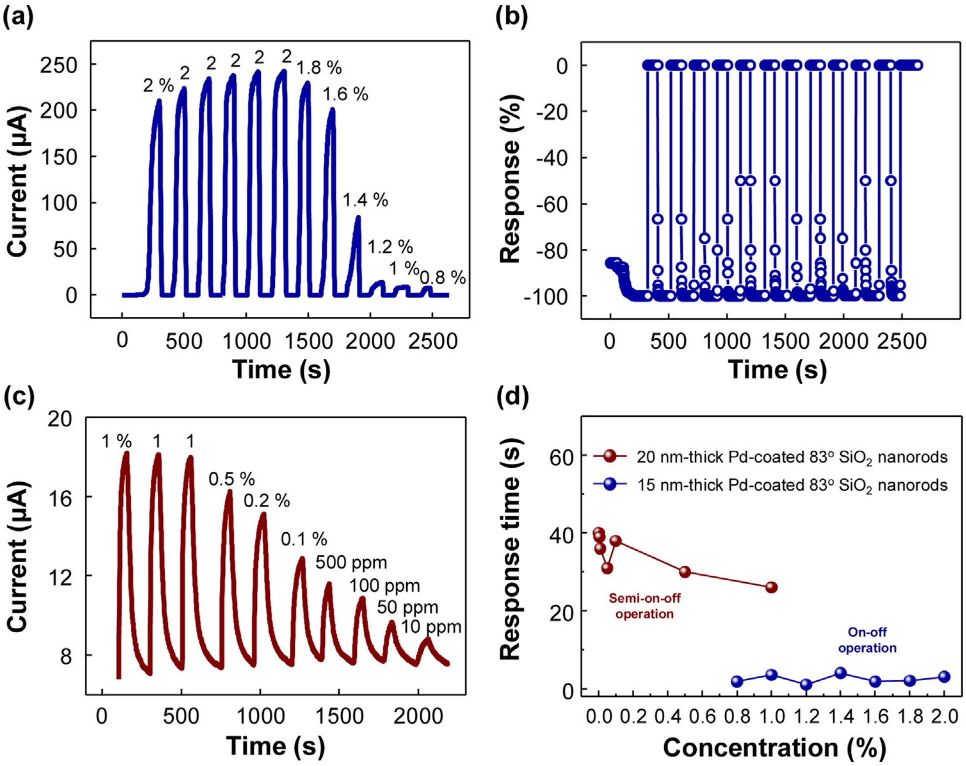

Fig. 4. (a) The real-time electrical response of the 15-nm-thick Pd-coated 83° SiO_2 nanorods to 2–0.8% H_2 in air carrier at room temperature. (b) The response versus time curve for the 15-nm-thick Pd-coated 83° SiO_2 nanorods. (c) The real-time electrical response curves of 20-nm Pd-coated 83° SiO_2 nanorods to 1%–10 ppm H_2 in air carrier at room temperature. (d) Response time of 15- and 20-nm-thick Pd-coated 83° SiO_2 nanorods to exposure concentration.

and secure the stability of Pd nanogaps, all samples were cyclically exposed to H_2 in air. Upon exposure to ambient air, they showed the insulating properties with extremely low current level. When the sample was exposed to 2% H_2, their current level abruptly increased, revealing a notable on-off behavior at room temperature (Fig. 4(a)). The amplitude of the current is related to extent of the volume expansion in the Pd films. The optimal nanogap of the 15-nm-thick Pd-coated 83° SiO_2 nanorods was enough to electrically connect them upon exposure to H_2, resulting in enhancement of current changes (~240 μA at 2% H_2). However, below low concentration (<0.8% H_2), current level of the 15-nm-thick Pd-coated 83° SiO_2 nanorods did not change since the concentration is not enough to connect the nanogap, resulting in insulating property. In order to investigate the response/recovery time of the 15-nm-thick Pd-coated 83° SiO_2 nanorods, the electrical response curves in Fig. 4(a) were converted to the response as shown in Fig. 4(b). The input constant (0.1 V) was divided by each current value and converted to a resistance by Ohm's law. The average response time was approximately 2.8 s (the longest response time: 5 s), and the recovery time was less than 1 s, which is similar to results previously reported studies based on H_2 sensors using polymer [21].

For more effective on-off operation with a high response and low LOD, we fabricated 20-nm-thick Pd-coated SiO_2 nanorods to reduce the nanogaps. Their resistances were approximately 734 kΩ, which indicates that Pd films on individual SiO_2 nanorods are slightly linked. For this reason, we call the operating mechanism of the sensor as 'semi-on-off operation'. When the 20-nm-thick Pd-coated 83° SiO_2 nanorods were exposed to 1% H_2, current was increased and recovered to their initial current level after multiple exposures to target gas at room temperature, repeatedly (Fig. 4(c)). Further, we continuously exposed the sample to a low concentration of H_2. The sensor response is defined as $(R_{H2} - R_{air})/R_{air} \times 100$,

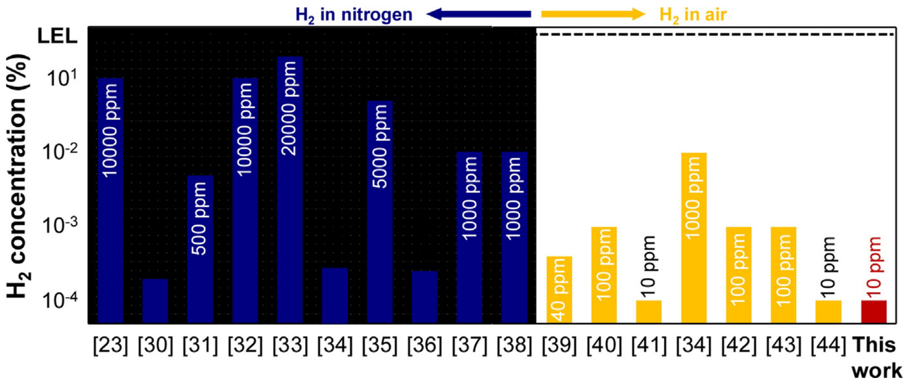

Fig. 5. Limit of detection (LOD) for resistance-based H_2 sensors in N_2 or air at room temperature, as reported in the interature [11–27] and the present study. Dotted line indicates the lower explosion limit (LEL) of H_2.

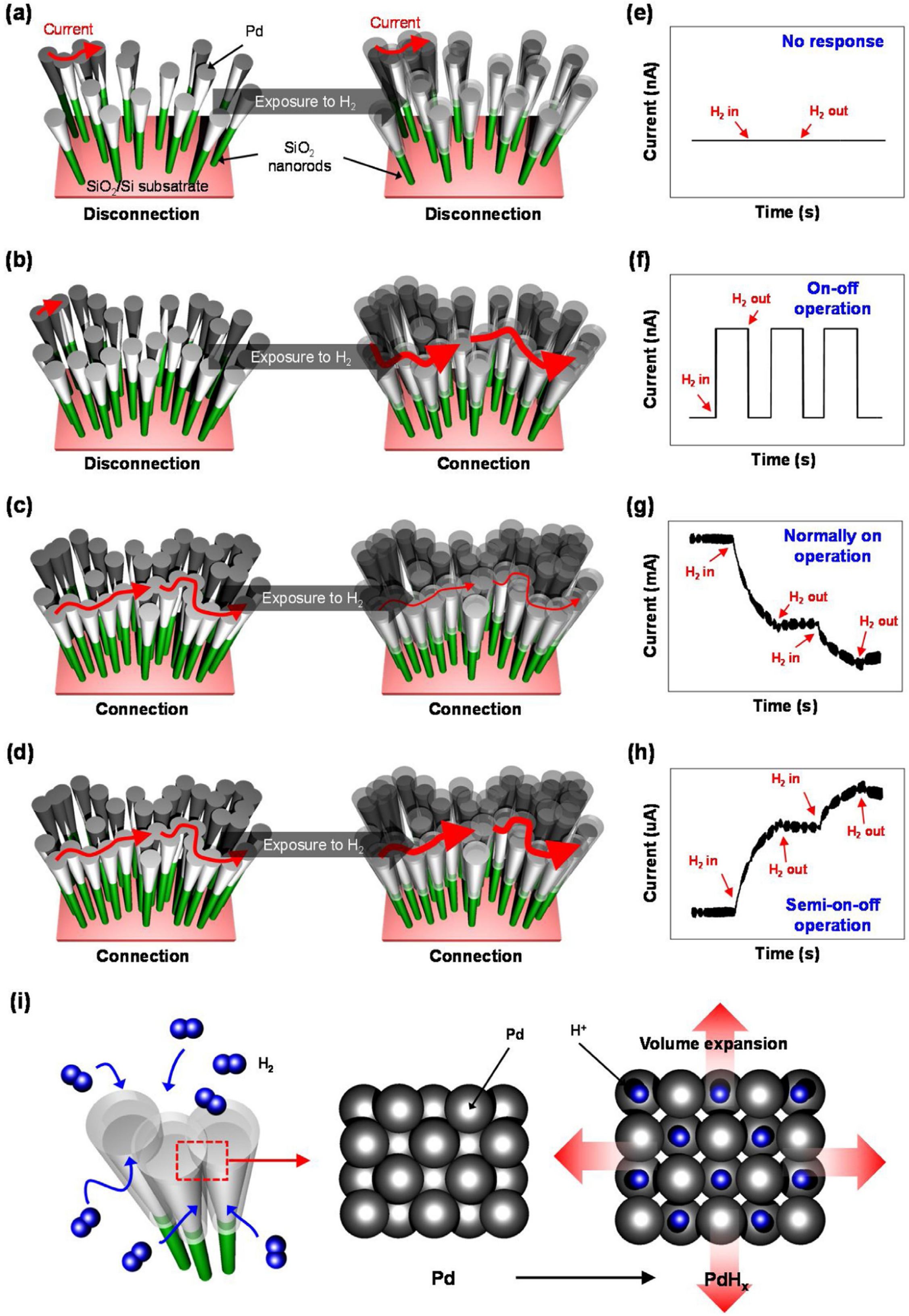

Fig. 6. Schematics of H_2 sensing behavior of the Pd-coated metal-oxide nanorods as a function of geometric configuration and thickness of Pd films; (a) large and (b) small nanogaps between metal-oxide nanorods with the Pd films, (c) fully and (d) partially connected Pd films on metal-oxide nanorods before and after exposure to H_2. The arrows indicate the current flow, and the size of each arrow denotes the magnitude of the current. (e–h) Representative response curves of H_2 sensing behaviors. (i) Diffusion path of H_2 to the Pd film on vertically ordered metal-oxide nanorods, and volume expansion of Pd films before and after exposure to H_2.

where R_{H2} and R_{air} are the electrical resistances in H_2 and dry air, respectively. The response of the 20-nm-thick Pd-coated 83° SiO_2 nanorods to 1%, 0.5%, 0.1%, 500 ppm, 100 ppm, 50 ppm, and 10 ppm were 145.5, 118.5, 69.3, 48.5, 40.8, 24.7, and 16, Furthermore, their response times were less than 60 s. However, metal-oxide nanorods as a substrate are rigid and do not have elasticity, leading to relatively slow recovery. In order to compare the sensing properties of each sample, we plotted the response time and LOD as a function of H_2 concentration (Fig. 4(d)). Interestingly, their plot regions were clearly separated into one with relatively fast response time (<3 s) and high LOD (0.8%) (15-nm Pd coated 83° SiO_2) and the other with relatively slow response time and low LOD (10 ppm) (20-nm Pd coated 83° SiO_2). Such a low LOD for the 20-nm-thick Pd-coated 83° SiO_2 is superior to those of previously reported highly sensitive H_2 sensors operating at room temperature, as shown in Fig. 5. Additionally, according to performance metrics for H_2 gas sensors defined by the U.S Department of Energy (DOE), the sensor's response and response time to 1% H_2 are required to be 0.25 and <60 s in ambient air, respectively [22]. Since both of them are fulfilled, our sensors are suitable for application in H_2 switches in explosion hazard and high sensitive H_2 sensors at explosive and hazardous condition, and high sensitive H_2 sensors.

It is apparent that the H_2 sensing properties including the response and response/recovery time can be tuned and enhanced by controlling the morphology of the SiO_2 nanorods and the thickness of the Pd films. A proposed model of the H_2 sensing mechanism with representative electrical response curves of the vertically ordered metal-oxide nanorods with Pd films is illustrated in Fig. 6. As explained above, the Pd-coated metal-oxide nanorods consist of many nanorod clusters with various nanogaps between themselves. For a low density and sparse distribution of metal-oxide nanorods, long distance interrupts the connection of each Pd film to the adjacent nanorods in the H_2 atmosphere (Fig. 6(a)). In contrast, the optimal distance of metal-oxide nanorods with an ideal thickness of the Pd films, namely, the 15-nm-thick Pd-coated 83° SiO_2 nanorods, can form the effective nanogaps at which the Pd films are connected/disconnected by expansion/contraction upon exposure to H_2, resulting in excellent on-off operation (Fig. 6(b)). There are two H_2 sensing mechanisms for metal-oxide nanorods in high density. First, since the Pd films on adjacent nanorods are already linked, on–off electrical switching is not possible, but the resistance of the linked Pd films is increased in H_2 atmosphere due to multiple carrier scattering on H_2 absorption, resulting in low response, which is referred to "normally on operation" (Fig. 6(c)) [29]. Second, the partially connected Pd films on metal-oxide nanorods, such as 20-nm-thick Pd-coated 83° SiO_2 can operate as **"**semi-on-off operation**"**. Upon exposure to H_2, contact areas between the Pd films on the metal-oxide nanorods are enlarged by the volume expansion of the Pd films. After removing H_2, current level is reversibly recovered to their initial current level. The LOD of the 20-nm-thick Pd-coated 83° SiO_2 nanorods is much lower than those of the 15-nm-thick Pd-coated 83° SiO_2 nanorods, which indicates that numerous connections can be simultaneously formed in the innumerable Pd films on metal-oxide nanorods, mutually contributing to the enhanced conductance (Fig. 6(d)). In addition, vertically ordered 1D nanostructures induce an improvement in H_2 diffusion in Pd films owing to an extremely porous surface. Fig. 6(e) shows the magnified scheme for volume expansion of Pd film on metal-oxide nanorods after exposure to H_2. In the case of Pd nanogap sensors on elastomeric substrates, a previously reported platform for H_2 sensors, the diffusion path of H_2 is limited to the surface and the crack on the Pd films (Fig. S4 in Supplementary data) [28,29]. On the other hand, it is easy for H_2 to access the Pd films with many nanogaps because the Pd films on vertically ordered 1D nanostructures are entirely exposed to open space, resulting in a high response and fast response time at low H_2 concentrations [48]. In other words, the vertically ordered Pd-coated metal-oxide nanorods can maximize the H_2 sensing properties for the given geometric configuration.

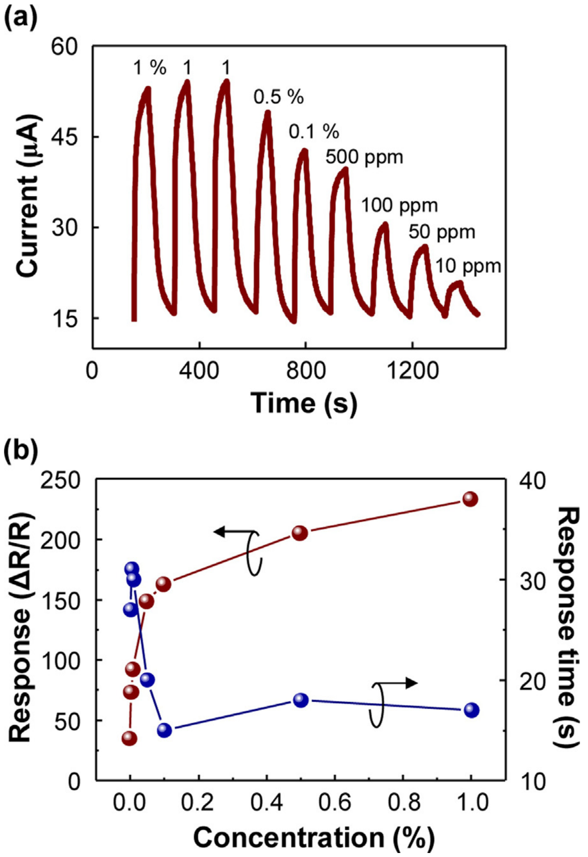

Fig. 7. (a) The real-time electrical response curves of 10-nm-thick Pd-coated 80° SnO_2 nanorods to 1%–10 ppm H_2. (b) Response and response times versus H_2 concentration of the 10-nm-thick Pd-coated SnO_2 nanorods.

Additionally, in order to demonstrate the reproducibility of our structures for highly sensitive H_2 sensors, we fabricated SnO_2 nanorods on a tilted SiO_2/Si substrate (80°), which have a similar length, morphology, and density to SiO_2 nanorods (Fig. S5 in Supplementary data). When the thickness of the Pd films on the vertically ordered SnO_2 nanorods reached 10 nm, a smaller thickness than that for the SiO_2 nanorods, they exhibited H_2 sensing properties because the SnO_2 nanorods were slightly denser and rougher than the SiO_2 nanorods. The real-time electrical responses of 10-nm-thick Pd-coated 80° SnO_2 nanorods were measured, as shown in Fig. 7(a). Measurement of the current was conducted in the same manner. Like the 20-nm-thick Pd-coated 83° SiO_2 nanorods, their sensing behavior was semi-on-off operation and LOD of the 10-nm-thick Pd-coated 80° SnO_2 nanorods to H_2 was also as low as 10 ppm. Fig. 7(b) shows the response and response time of the 10 nm-thick Pd-coated 80° SnO_2 nanorods as a function of the H_2 concentration. The responses to 1%, 0.5%, 0.1%, 500 ppm, 100 ppm, 50 ppm, and 10 ppm H_2 were 233, 205.4, 162.8, 148.7, 92.3, 73.5, and 35.1, respectively. Both response and response time of the 10 nm-thick Pd-coated 80° SnO_2 nanorods also meet the requirements of DOE. Although H_2 sensing properties are different depending on the region on SiO_2/Si substrate where sample is fabricated due to the thickness deviation between the center and the edge of 4-inch SiO_2/Si substrate, they still exhibited high H_2 sensing characteristics as H_2 switches and H_2 sensors (Fig. S6 in Supplementary data).

4. Conclusion

In summary, we fabricated H_2 sensitive switches and sensors based on vertically ordered Pd-coated metal-oxide nanorods on 4-inch SiO_2/Si substrate. The configuration of the nanorods was primarily controlled by changing an incident angle of the vapor flux with successive deposition of Pd films. Upon exposure to H_2, both the 15- and 20-nm-thick Pd-coated 83° SiO_2 nanorods exhibited excellent sensing performance with a fast response time, low power consumption, and operation at room temperature. By maintaining the optimal density of nanorods, we also obtained the high H_2 sensing performance for the 10-nm-thick Pd-coated 80° SnO_2 nanorods. These results indicate that various metal-oxides can be repeatedly produced as H_2 sensors with our methods. Consequently, our approaches are reproducible and effective methods and suitable for fabricating high-performance H_2 sensors for the IoT.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2017.08.198.

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Biographies

Young-Seok Shim received his Ph.D. degree from Department of Materials Science and Engineering of Yonsei University in 2016. Now he is a postdoctoral researcher in KIST. His research interests are the synthesis nanostructured oxide thin films and their applications to various devices including sensor and solar water splitting cells.

Byungjin Jang was born in 1987 in Seoul, Republic of Korea. He received a BS degree in Material Science and Engineering at Yonsei University in 2012. He is currently studying MOTIFE sensors using Pd as a step toward his Ph.D. degree in hydrogen sensor devices at Yonsei University.

Jun Min Suh is a Combined Master's-Ph.D. candidate under the supervision of Prof. Ho Won Jang at School of Materials Science and Engineering, Seoul National University. His doctoral research focuses on gas sensors using metal oxide nanostructures, solution sensors using 2-dimensional materials and laser-assisted electrochemical synthesis of metal oxide nanostructures.

Myoung-Sub Noh received his BSc degree in Department of Materials Science and Engineering of Suwon University. He is a Combined MS-Ph.D candidate at KU-KIST Graduate School of Converging Science and Technology in Korea University. His doctoral research focuses on development of the flexible piezoelectric thin films using laser lift-off(LLO) and excimer laser annealing(ELA) methods.

Sangtae Kim received his Ph.D. from Department of Materials Science and Engineering at Massachusetts Institute of Technology in 2016. He is a researcher at KIST, pursuing research in energy harvesting, ferroelectrics and electrochemistry.

Soo Deok Han received his BSc degree in Department of Materials Science and Engineering of Korea University. Now, he is a Ph.D. candidate at KU-KIST Graduate School of Converging Science and Technology in Korea University and KIST. His research interests concentrate on the nanostructured functional metal oxides and their applications.

Young Geun Song received his B.S. form Pusan National University, Korea, in 2016. He is currently a M.S. course student in the Department of Electrical Engineering, Korea University. His research interests include fabrication of metal oxide nanostructure, and chemical sensor applications.

Do Hong Kim received his Ph.D. degree from Department of Materials Science and Engineering of Korea University in 2017. Now he is a postdoctoral researcher in Korea University. His research interests include the synthesis of nanostructured metal oxide thin films and their electrical and optical characteristics.

Chong-Yun Kang received his Ph.D. from the Department of Electrical Engineering of Yonsei University in 2000. Now he is a Principal Research Scientist in KIST from 2000 and a professor of KU-KIST Graduate School of Converging Science and Technology in Korea University from 2012. His research interests include smart materials and devices, expecially, piezoelectric energy harvesting and actuators, electrocaloric effect materials, and nanostructured oxide semiconductor gas sensors.

Ho Won Jang received his Ph.D. from the Department of Materials Science and Engineering of POSTECH in 2004. He joined the Department of Materials Science and Engineering of Seoul National University in 2012 and is working as an associate professor. His research interests are the synthesis of nanostructured oxide thin films and their applications to various devices including sensors, solar water splitting cells, light-emitting diodes, photovoltaics, and memristors.

Wooyoung Lee is a professor of Department of Materials Science and Engineering, the chairman of Yonsei Institute of Convergence Technology and the Head of Institute of Nanoscience and Nanotechnology at Yonsei University in Korea. He received a BS degree in metallurgical engineering in 1986, a MS degree in metallurgical engineering from the Yonsei University in 1988. He received a Ph.D. degree in physics from University of Cambridge, England in 2000. He is also the director in Korea-Israel Industrial R&D Foundation and the advisor in National Assembly Research Service. In recent years, his research interests have centered on thermoelectric devices, spintronics, hydrogen sensors and hydrogen storage materials. He has received a number of awards in nano-related research areas and a Service Merit Medal (2008) from the Korean Governments due to contribution on the development of intellectual properties. He has authored and co-authored over 150 publications, and has edited a few of special books on nano-structured materials and devices.