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Amorphous Pd-assisted H₂ detection of ZnO nanorod gas sensor with enhanced sensitivity and stability

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Highlights:

- Facile synthesis of ultrathin amorphous Pd layer (2 - 5 nm) on ZnO nanorods.
- Comparison of sensing behavior between amorphous and crystalline Pd-coated ZnO nanorods sensors.
- Demonstration of superior sensing response (12,400%) of amorphous Pd-coated ZnO nanorods sensors.
- High stability of amorphous Pd-coated ZnO nanorods sensors.

Abstract

For monitoring H₂ concentrations in air, diverse resistive gas sensors have been demonstrated. In particular, Pd-decorated metal oxides have shown remarkable selectivity and sensing response for H₂ detection. In this work, H₂ sensing behavior of amorphous Pd layer covering ZnO nanorods (am-Pd/ZnO NRs) is investigated. This is the first report on the

enhanced gas sensing performance attained by using an amorphous metal layer. The amorphous Pd layer is generated by reduction reaction with a strong reducing agent (NaBH_4), and it covers the ZnO nanorods completely with a thickness of 2 ~ 5 nm. For comparison, crystalline Pd nanoparticles-decorated ZnO nanorods (c-Pd/ZnO NRs) are produced using a milder reducing agent like hydrazine. Comparing the c-Pd/ZnO NRs sensor and other previously reported hydrogen sensors based on the crystalline Pd and metal oxides, the am-Pd/ZnO NRs sensor exhibits a remarkable sensing response (12,400 % at 2 % H_2). The enhancement is attributed to complete cover of the amorphous Pd layer on the ZnO NRs, inducing larger interfaces between the Pd and ZnO. In addition, the amorphous Pd layer prevents surface contamination of the ZnO NRs. Therefore, the am-Pd/ZnO NRs sensor maintains initial sensing performance even after 5 months.

Keywords: Amorphous palladium, ZnO nanorod, Hydrogen, Gas sensor

1. Introduction

Fuel cells, which are operated by hydrogen (H_2) gas, have been highlighted as a promising energy devices [1,2]. Unfortunately, the flammability of H_2 in air at concentrations higher than 4 % is a considerable safety issue [3]. In this regard, a gas sensor that can detect small amounts of H_2 should be developed for monitoring H_2 gas leakages. There are various approaches for fabricating H_2 gas sensors in the forms of electrochemical [3,4], optical [5,6] or resistive devices [7-9]. Among them, the resistive gas sensors are attractive because of their simple fabricating process, portability, and miniaturization.

The channels of the resistive gas sensors are conventionally based on metal oxides

such as SnO_2 [10], ZnO [11] or WO_3 [12]. As film-typed channel is not suitable due to fewer adsorption sites present on the surface, one-dimensional (1D) metal oxide nanostructures have been researched as promising channels for sensitive gas sensors [13,14], including 1D ZnO nanorods [15,18-21] or nanowires [22,23] owing to their high surface to volume ratio, conductivity, and good stability. The resistance of metal oxide changes reversibly with the adsorption or desorption of gas molecules on the channel surface. Sensing mechanism also depends on both the metal oxide type and the target gas molecules [14]. ZnO , which is an n-type semiconductor, loses some intrinsic carriers (electrons) to the chemisorbed oxygen on the ZnO surface. If the ZnO is exposed to H_2 gas, the strong reducing H_2 gas reacts with the chemisorbed oxygen species, giving byproducts of water (H_2O). Then, electrons return to the ZnO , increasing the conductivity or decreasing the resistance within the channel [14,24,26].

In general, the metal oxide-based gas sensors require high operating temperatures of approximately 200-400 °C [13-24] or UV activation [23,26] to produce a suitable sensing atmosphere for eliminating moisture and other adsorbed chemical species to induce chemisorption of oxygen species on the ZnO surface. However, the embedded heaters or UV lamps require additional energy consumption, limiting the commercialization of such sensors. For reducing the operating temperature, noble metals such as Au [27,28], Pt [29,30] or Pd [8,31-35] have been applied as catalysts for enhancing the adsorption and desorption of gas molecules. Specifically, the Pd can dissociate H_2 molecules and store H atoms at interstitial sites. Therefore, metal oxides composited with the noble metal show a remarkable resistance change to H_2 gas exposure. Diverse approaches have been attempted for H_2 gas sensors by combining ZnO and Pd [24,36]. Various Pd nanostructures have been introduced to enhance the catalytic effect [37-39]. Several studies have been attempted to tune the intrinsic properties

of Pd by alloying with other metals to enhance the catalytic activity for H₂ dissociation [40,41]. Unfortunately, it is reported that the sensing performance deteriorated with metal oxide surface contamination by strong adsorbates such as sulfur [42,43]. Therefore, regeneration process at a high temperature above 400 °C was required to remove the adsorbates but, the noble metals were easily aggregated at this temperature, resulting in a poor gas sensing performance owing to the resultant less catalytic area [43].

Amorphous materials were synthesized and applied as catalysts [44-46]. Owing to the nature of their disordered atoms and irregular surfaces, amorphous materials are apparently different to crystalline ones. The atomic arrangement of a solid surface is directly related to its interactions with the interfacing gases or liquids, e. g. adsorption or desorption. Some chemical reactions that occur at solid-gas or solid-liquid interfaces can be altered when amorphous solids are utilized. For example, it is reported that several amorphous catalysts such as Pd nanoparticles [45] or cobalt iron oxide [46] demonstrated a superior catalytic activity for oxygen reduction or evolution reactions compared to crystalline ones. Despite of their superior catalytic activities and unique intrinsic properties, amorphous metals have not been studied in the field of the resistive gas sensors.

In this report, an amorphous Pd layer was uniformly synthesized on the hydrothermally grown ZnO nanorods (am-Pd/ZnO NRs) via a facile method using a strong reducing agent (NaBH₄), and this system was investigated as a resistive-typed H₂ gas sensor. With a similar synthetic process using a milder reducing agent (hydrazine), crystalline Pd nanoparticles were also decorated onto the ZnO NRs (c-Pd/ZnO NRs) to compare their H₂ gas sensing performance.

2. Experimental method

2.1. Materials

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %, Sigma-Aldrich), hexamethylenetetramine (HMTA, 99.0 %, Sigma-Aldrich), deionized water (DI, 18 M Ω cm, Millipore), PdCl_2 (99 %, Sigma-Aldrich), KCl (99.0 - 100.5 %, Sigma-Aldrich), NaBH_4 (99 %, Sigma-Aldrich) and hydrazine monohydrate (98 %, Sigma-Aldrich) were purchased and used without any further purification.

2.2. Synthesis of the ZnO NRs

ZnO NRs were grown using a hydrothermal process. A ZnO seed layer was deposited onto a SiO_2/Si substrate via a sputtering process (RF & DC Magnetron Sputtering System, KVS-2003L). The thickness of the seed layer was adjusted to 50 nm. The seed layer was treated with a UV-ozone cleaner (UVO cleaner, AHTECH LTS) to induce a hydrophilic surface. The layer was then dipped into an aqueous solution consisting of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25 mM) and HMTA (25 mM) for the ZnO NRs growth at 92 °C for 6 hrs. Finally, the sample was washed with DI water and blow-dried with a nitrogen gun.

2.3. Synthesis of the am-Pd/ZnO NRs

The amorphous Pd on the ZnO NRs was formed by using a reduction method with NaBH_4 . Initially, a 3 mM aqueous solution of K_2PdCl_4 was prepared by adding PdCl_2 (3 mM) and KCl (6 mM) in DI water. The precursor solution was spin-coated on the ZnO NR substrate and the sample was placed into a NaBH_4 solution (0.01 M) at room temperature. After 2 hrs, the sample (am-Pd/ZnO NRs) was washed with DI water and blow-dried with a nitrogen gun.

2.4. Synthesis of the c-Pd/ZnO NRs

Following the same synthetic process as the am-Pd/ZnO NRs until the coating of K_2PdCl_4 precursor on the ZnO NRs, the Pd precursor was reduced by hydrazine (0.01 M) dissolved in DI water. The other conditions, such as the reaction time and temperature, were same for the am-Pd/ZnO NRs synthesis. Lastly, the sample was placed on a hot plate at 100 °C for 30 min to enhance crystallinity of the Pd.

2.5. Characterization

Field emission-scanning electron microscopy (FE-SEM, JEOL 7300, 5 kV, 20 μ A) and high -resolution transmission electron microscopy (HR-TEM, Technai G2 F30, 300 keV) were used for observing the morphology of the materials. The crystallographic properties were confirmed by X-ray diffraction (XRD, Rigaku Ru-200B) with a $CuK\alpha$ source. The 2θ range was selected between 25° and 60° with a scan rate of 1° min⁻¹. Surface compositions and electronic states were investigated by X-ray photoelectron spectroscopy (XPS, MULTILAB 2000) with a monochromic Al $K\alpha$ X-ray source.

2.6. Sensor fabrication and measurement

For constructing the resistive H_2 sensors, a Cr (10 nm)/Au (20 nm) interdigitated electrode with a finger width of 1500 μ m and inter-finger spacing of 100 μ m was deposited on a SiO_2/Si substrate. A ZnO seed layer was then deposited locally at the center region of the interdigitated electrode area by using a shadow mask. Then, ZnO NRs growth and Pd layer coating were performed as described above. The sequential processes are depicted in Scheme

1.

H₂ gas sensing was measured at 20 °C via a homemade gas chamber connected to a vacuum pump and mass flow controllers (SEC-7400), which maintained a desired gas concentration. The gas concentration was controlled by varying the flow rates of air and H₂ gas while the total flow rate (3000 sccm) was fixed. The current of gas sensor was measured continuously through a sourcemeter (Keithley 2400) at 1 V. Prior to measurements, a stable base current was achieved after exposing in air for 30 min.

3. Result and discussion

3.1. Synthesis and characterization of Pd/ZnO NRs

The ZnO NRs were hydrothermally grown on the ZnO seed layer [47]. After spin-coating the K₂PdCl₄ precursor solution on the ZnO NRs sample, the solution selectively soaked the ZnO NRs because abundant hydroxyl groups (Zn-OHs) [47,48] were present on the ZnO NRs, making them more hydrophilic compared to the other regions of SiO₂ and the Au electrode. The coated Pd precursors were converted into a metallic phase by dipping the sample into a reducing agent. Two reducing agents, NaBH₄ and hydrazine, were utilized to generate different Pd phases. The reduction rate of the Pd precursor layer determined the Pd metallic phase. The NaBH₄, which is one of the strong reducing agents, rapidly generated amorphous metallic layer within several seconds [49,50]. In contrast, the hydrazine, a relatively mild reducing agent, reduced the Pd precursors into crystalline metal nanoparticles [45].

The synthesized materials were observed by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). ZnO NRs were densely grown on the seed layer (Fig. 1a) with a hexagonal top facet (Fig. 1b) with a diameter in the range of 50 ~ 100 nm and a length of approximately 2 μm (Fig. S1). In general, the diameter depends on the

concentration of the precursor solution ($\text{Zn}(\text{NO}_3)_2$ and HMTA), and the length was controlled by the reaction time [51]. After the reduction process, the ZnO NRs surface appeared rougher without noticeable destruction of the nanorod (Fig. 1c and 1d, and Fig. S2).

TEM images (Fig. 2) shows more detailed information on the Pd layer, including crystallographic information. Single crystalline characteristic of the ZnO NR was identified in Fig 2a and 2b. The indicated plane in Fig. 2b represents the (002) crystal plane with a spacing of 0.26 nm. The Pd layer, synthesized via the NaBH_4 reducing agent, completely covered the ZnO NR surface with a thickness of 2 ~ 5 nm (Fig. 2c and 2d). HR-TEM image (Fig. 2d) demonstrated the single crystalline ZnO NR-core covered with amorphous Pd-shell. The fast Fourier transform (FFT) pattern of Fig. 2d represented only ZnO (002) crystal plane. The corresponding selected area electron diffraction (SAED) pattern also revealed diffraction spots derived only from the single crystalline ZnO NR, verifying the amorphous phase of Pd layer (Fig. S3a). The amorphous Pd-coated ZnO NRs are hereafter denoted as am-Pd/ZnO NRs.

After being treated with the hydrazine, the Pd precursor layer was converted into Pd nanoparticles with a diameter of 4 ~ 6 nm, which attached to the ZnO NR surface as shown in Fig. 2e and 2f. In comparison to the am-Pd/ZnO NR, the FFT and SAED patterns of hydrazine-treated sample (Fig. 2f and Fig. S3b, respectively) had diffraction spots coming from both the crystalline ZnO and Pd nanoparticles, indicating the crystallinity of the Pd nanoparticles. The crystalline Pd nanoparticles-attached ZnO NRs are hereafter denoted as c-Pd/ZnO NRs.

For more crystallographic information, X-ray diffraction (XRD) patterns were also measured (Fig. S4). The XRD pattern of the grown ZnO NRs (Fig. S4a) showed three assigned peaks at 31.8° , 34.3° , and 36.3° , representing the (100), (002), and (101) planes, respectively (PDF# 36-1451). The peak located at 38.2° was attributed to the (111) plane of the Au electrode

(PDF# 00-004-0784). However, there were no Pd peaks in both the am-Pd/ZnO NRs and c-Pd/ZnO NRs. It appeared that the amount of Pd precursor on the ZnO NRs was too small to be detected. To evidence this, the Pd precursor solution was drop-casted on a dummy SiO₂ substrate and reduced with the NaBH₄ or hydrazine (Fig. S4b). A peak for potassium chloride (KCl), which was a byproduct of the reaction with K₂PdCl₄, was observed in both samples. Two peaks at 40.3° and 46.6° corresponding to the Pd (111) and (002) planes, respectively (PDF# 05-0681), were observed only in the sample treated with the hydrazine, indicating that crystalline Pd was generated.

X-ray photoelectron spectroscopy (XPS) was measured to analyze the compositions and electronic states of the elements at the surface. The wide XPS spectra of the am-Pd/ZnO NRs, c-Pd/ZnO NRs, and pure ZnO NRs predominantly contained Zn2p and O1s peaks (Fig. S5). The Pd3d peak was present in both the am-Pd/ZnO NRs and c-Pd/ZnO NRs, in which the atomic content of Pd with respect to Zn (Pd/Zn) was 0.096 and 0.060, respectively. The lower Pd content ratio of c-Pd/ZnO NRs than that of the am-Pd/ZnO NRs was ascribed to partial exposure of the ZnO NRs surface.

The narrow O1s XPS spectra (Fig. 3a) were fitted with three O species: fully coordinated O²⁻ ions in the ZnO lattice (denoted as O1), O²⁻ ions around defect sites or OH groups (denoted as O2), and chemisorbed oxygen on the ZnO surface (denoted as O3) [52,53]. The atomic percent of O3 in the total oxygen species was 11.5, 30.4 and 18.9 % for the am-Pd/ZnO NRs, c-Pd/ZnO NRs and pure ZnO NRs, respectively. Oxygen can be chemisorbed on a ZnO NR surface in the forms of O⁻, O²⁻ or O₂⁻. The chemisorbed oxygens are generated after dissociation of the O₂ molecules [25]. In general, noble metal catalysts (Pt or Pd) can facilitate O₂ dissociation and increase the number of chemisorbed oxygens on the metal oxide surface.

The higher O₃ content (more chemisorbed oxygens) on the c-Pd/ZnO NRs than that of the pure ZnO NRs was caused by the catalytic effect of the Pd nanoparticles deposited on the ZnO NRs. In contrast, the lower chemisorbed oxygen content on the am-Pd/ZnO NRs than that of the pristine ZnO NRs can be explained by the uniform coating of the amorphous Pd layer on the ZnO NR surface, which prevented the chemisorption of the oxygen species.

In Fig. 3b, the Pd3d peaks of the am-Pd/ZnO NRs and c-Pd/ZnO NRs are compared and fitted with Pd-O and metallic Pd. Similar amounts of Pd-O were formed regardless of the reducing agents (29 % and 26 % for the am-Pd and c-Pd, respectively). The metallic Pd peak position of the am-Pd/ZnO NRs was located at 335.71 eV, which was 0.26 eV higher than that of the c-Pd/ZnO NRs. As the peak position of Pd3d shifts to a higher voltage with increasing the coordination number, more 3d electrons in the am-Pd/ZnO NRs are engaged with higher coordinated atoms [53,54].

3.2. H₂ sensing behaviors at high concentrations

Sensor performances were investigated using a real-time current measurement at different H₂ gas concentrations. The sensing response is defined as $S(\%) = [(I_g - I_a) / I_a \times 100]$, where I_a is the measured current in the presence of air only and I_g is the current when the sensor is exposed to H₂ gas. As a preliminary step, the effect of K₂PdCl₄ precursor concentration (0.5 ~ 30 mM) on the sensing response was investigated (Fig. S6). The sensing response was calculated based on the current recorded after 5 min exposure of H₂ gas. The optimized concentration of K₂PdCl₄ precursor solution was 3 mM, considering the higher sensing response especially at lower H₂ concentrations less than 2 %. The sensor prepared at a lower concentration of K₂PdCl₄ did not produce enough catalytic sites for sensing. On the other hand,

at high K_2PdCl_4 concentration, thick amorphous Pd layer was generated, which disturbed the adsorbed hydrogen to diffuse into the surface of ZnO NR. Therefore, the conductivity of ZnO NR was not that much altered after hydrogen exposure. The following experiments were conducted with the sensors spin-coated with the 3 mM of K_2PdCl_4 precursor solution.

Fig. 4a shows the steady-state resistance responses of the am-Pd/ZnO NRs and c-Pd/ZnO NRs sensors at various H_2 concentrations in the range of 0.5 ~ 6 % along with their corresponding sensing response curves in Fig. 4b. Each cycle was conducted with 5 min of H_2 gas exposure followed by 10 min of recovery. The sensing response linearly increased with the H_2 concentration. In the case of am-Pd/ZnO NRs sensor, the sensing response reached a value of 17,400 % at 6 % concentration. Repeatability test was also performed for 10 cycles at 0.5 % H_2 concentration (Fig. S7), and the same sensing performance was recorded in each sensing cycle. The sensing response of the am-Pd/ZnO NRs sensor measured at 1 % H_2 concentration (7,950 %) was superior to other previously reported hydrogen gas sensors, operating at room temperature (Table S1). The sensing response of c-Pd/ZnO NRs sensor was 800 % at 0.5 % concentration, increased to 2,500 % at 4 % concentration, and then saturated.

The sensing response curves of the am-Pd/ZnO NRs and c-Pd/ZnO NRs sensors at 2 % concentration are compared in Fig. 4c. The sensing response of am-Pd/ZnO NRs sensor (12,400 %) was 5 times that of the c-Pd (2,400 %). They were normalized with S_{max} , which was the maximum response value after 5 min of H_2 exposure, for comparing the response and recovery behavior (inset of Fig. 4c). The response and recovery times are defined as the required time to approach 90 % of S_{max} during the H_2 exposure and 10 % of S_{max} during the recovery, respectively [31,35]. The c-Pd/ZnO NRs sensor demonstrated a faster response time of 156 sec and recovery time of 61 sec than those of 227 sec and 95 sec for the am-Pd/ZnO

NRs sensor, respectively.

In general, metal oxide conductivity changes depending on the amount of chemisorbed oxygens (Mechanism I, Fig. S8) [24,25,36]. The Pd nanoparticles act as catalysts for splitting O_2 or H_2 molecules. First, O_2 molecules are dissociated on the Pd catalysts and diffuse into the ZnO surface. Then, some electrons in the ZnO move to the adsorbed O; depletion regions are formed at the interface of Pd particles/ZnO; and the conductivity of ZnO is reduced. After exposure to H_2 gas, the Pd also facilitates the dissociation of H_2 molecules into two H atoms. The H atoms react with the adsorbed O on the ZnO surface with a byproduct of water. Then, the electrons captured in the adsorbed O return to the ZnO, and the conductivity increases owing to the increased carriers within the ZnO. The c-Pd/ZnO NRs sensor followed Mechanism I due to the abundant chemisorbed oxygen on the ZnO surface, as confirmed from the O1s XPS spectra (Fig. 3a).

However, the higher sensing response of the am-Pd/ZnO NRs sensor could not be explained using the Mechanism I, considering the lower amount of chemisorbed oxygens. Instead, it can be explained by the lowering of Pd work function (Mechanism II, Fig. S9), associated with the diffusion of dissociated H into the Pd. The work function of Pd decreases with increasing the interstitial H atoms within the Pd [55]. Due to the Schottky barrier formed between Pd and ZnO, the electron flow at the interface becomes limited. After lowering the work function of Pd during H_2 exposure, the Schottky barrier height decreases and thus, electron transfer between the Pd layer and ZnO becomes more facile, enabling higher conductivity [25,37]. In this case, the amount of chemisorbed oxygens on the ZnO surface have nothing to do with the increased conductivity. The slower response of the am-Pd/ZnO NRs sensor was ascribed to the delay time for interstitial diffusion of H atoms into the deep Pd layer,

which was interfacing the ZnO [56]. Meanwhile, in the case of c-Pd/ZnO NRs sensor, as the sensing reaction occurred at the chemisorbed oxygens located at the exposed ZnO surface, the delay time for interstitial diffusion of H atoms was no longer concerned, exhibiting the relatively faster response. The interfacial area between the Pd and ZnO played an important role in both mechanisms. The remarkable sensing response of the am-Pd/ZnO NRs sensor was attributed to the larger Pd/ZnO interface area.

3.3. H₂ sensing behaviors at low concentrations

Notably, the fabricated sensors worked even at 0.01 % H₂ (100 ppm) with a sensing response of 50 %. The sensing responses at low concentrations below 0.5 % (Fig. 5a) demonstrated different behaviors than those at high H₂ concentrations. Both sensors (am-Pd/ZnO NRs and c-Pd/ZnO NRs) were saturated rapidly with a response time of less than 10 sec. The discrepancy in the sensing responses between the two sensors decreased with decreasing the H₂ concentration, and they had the same sensing response at 0.01 % (100 ppm). Adsorption of gas molecules at low concentration can be modeled based on the Langmuir isotherm theory. For the adsorption behavior of diatomic H₂ on Pd, the adsorption (r_a) and desorption rate (r_d) are described as [37,38]

$$r_a = k_a p (1-\theta)^2 \quad (1)$$

$$r_d = k_d \theta^2 \quad (2)$$

,where k_a and k_d are adsorption and desorption constant, respectively, p is a partial pressure of the H₂ gas, and θ (coverage) is the fraction of hydrogen atoms absorbed on the Pd. At

equilibrium, both rates should be same to maintain steady state. Thus, the following formula can be derived,

$$r_a = r_d \rightarrow \theta/(1-\theta) = (k_a/k_d)^{1/2} p^{1/2} = C p^{1/2} \quad (3)$$

,where C is a function of 'heat of adsorption', which is the amount of heat released during the adsorption. At a low partial pressure of H_2 gas ($\theta \ll 1$), the formula can be approximated by

$$\theta \approx C p^{1/2} \quad (4)$$

Because the sensing response (S) is proportional to the coverage (θ), it is related to the square root of H_2 concentration.

$$S \propto \theta \propto p^{1/2} \quad (5)$$

The sensing response plots vs. $p^{1/2}$ at low concentrations (0.01 ~ 0.5 %) exhibited linearity regardless of the sensor type (Fig. 5b). There are several reports on comparing solubility of H_2 into crystalline and amorphous metals [57,58]. Because of abundant defect sites in the amorphous metals, which is beneficial for H_2 adsorption, the amorphous metals own a higher solubility than the crystalline ones, and therefore the amorphous metal has a higher heat of adsorption, and thus a higher C . The higher slope (proportional to the constant C) of sensing response plots (vs. $p^{1/2}$) of am-Pd/ZnO NRs than that of the c-Pd/ZnO NRs sensor

coincides with the prediction. On the contrary, the plots at high concentrations were not linear (Fig. 5c). The different sensing behaviors could be explained with the Pd phase variation. At a low partial pressure of H_2 , palladium metal is converted into α -phase palladium hydride (α - PdH_x , $x < 0.017$). Meanwhile, at H_2 concentrations over 0.5 %, a new phase called β -phase palladium hydride (β - PdH_x , $x > 0.58$) is generated. Both phases coexist at a concentration range of 0.5 ~ 2 % and the contents of β - PdH_x increase with the H_2 concentration [59]. The abundant interstitial H atoms in the β - PdH_x interrupted the additional adsorption of H atoms, and therefore the sensing response became nonlinear to $p^{1/2}$ and saturated after full conversion into the β - PdH_x as shown in Fig. 5c. In the case of c-Pd/ZnO NRs sensor, there were no significant resistance changes even at higher concentrations of over 2 %, showing a saturated sensing response (Fig. 4a). However, the disordered Pd atoms in amorphous Pd layer provided random adsorption sites or interstitial sites for H atoms in contrast to the crystalline Pd lattice, enabling more adsorption of H atoms into the amorphous Pd layer and shifting the response saturation to a higher concentration.

3.4. Humidity dependence and selectivity of the am-Pd/ZnO NRs sensor

Humidity dependence of the am-Pd/ZnO NRs sensor was explored as shown in Fig. S10. The sensing response at 1 % H_2 concentration decreased with increasing the relative humidity because the water molecules could physically adsorb onto the Pd layer, blocking the adsorption of H_2 gas and inducing a lower sensing response.

Selectivity test of the am-Pd/ZnO NRs sensor was investigated at room temperature with a relatively high concentration (5 %) of methanol, ethanol, acetone, and CO_2 (Fig. S11). When above gases were injected, the am-Pd/ZnO NRs sensor exhibited negligible responses

(1.9, 2.0, 2.1, and 5.3 % to methanol, ethanol, acetone, and CO₂, respectively), which were much lower than the sensing response (680 %) to 0.1 % H₂. These results indicate a superior selectivity of the am-Pd/ZnO NRs sensor to H₂ gas at room temperature.

3.5. The effect of operating temperature on the sensing response

The effect of operating temperature on the am-Pd/ZnO NRs sensing performance was investigated by maintaining the substrate stage at a certain temperature below 100 °C (Fig. S12) to avoid undesirable morphology changes of the am-Pd layer. The increment in operating temperature slightly lowered the initial resistance of ZnO NRs owing to increased carrier mobility; meanwhile, the sensing response was significantly improved. The sensing response at 80 °C (28,000 %) was 3.5 times that (7,950 %) measured at 20 °C because high operating temperature was boosting the catalytic activity of Pd for H₂ cleavage and adsorption [36].

3.6. Long-term stability of the sensors

The fabricated sensors were tested after five months storage in ambient conditions without any sealing or treatment favorable for stability (Fig. 6a). The am-Pd/ZnO NRs sensor showed no noticeable changes in their base current after five months; the on-current was negligibly reduced from 8.6×10^{-5} to 8.2×10^{-5} A along with the same recovery behavior. In contrast, the base current of the c-Pd/ZnO NRs sensor was reduced remarkably from 1.8×10^{-6} to 4.0×10^{-7} A, and the on-current was altered from 1.9×10^{-5} to 2.4×10^{-6} A (Fig. 6b). The sensing response of the c-Pd/ZnO NRs sensor at 1 % concentration became 500 %, which was almost half of the initial response (960 %). This significant change was probably caused by the ZnO

surface contamination with the existing carbon or sulfur in air [42,43]. The adsorbed contaminants affect the depletion region of ZnO surface, inducing changes in base current and thus sensing response. In the case of am-Pd/ZnO NRs, the amorphous Pd layer fully covered the ZnO NRs and prevented the adsorption of contaminants on the ZnO surface, suggesting a promising approach for achieving highly stable H₂ gas sensor at room temperature.

4. Conclusion

In this report, ZnO NRs were synthesized and applied as a channel material for resistive hydrogen gas sensors. The amorphous Pd layer was produced via spin-coating a precursor solution and facile reduction reaction with a strong reducing agent (NaBH₄). The amorphous Pd layer covered the ZnO NRs completely with a thickness of 2 ~ 5 nm, and therefore the ZnO NRs were rarely exposed to the air. The uniformly coated Pd layer created a much larger interface between the Pd and ZnO, inducing much more sensitive sensing behavior compared to the crystalline Pd particles-decorated ZnO NRs with a similar Pd loading. The sensing response of am-Pd/ZnO NRs sensor (12,400 %) was 5 times that of the c-Pd/ZnO NRs sensor (2,400 %) at 2 % H₂ concentration. Despite of the low density of chemisorbed oxygen on the ZnO NR surface, the high sensing response could be explained by the reduced work function of amorphous Pd layer, inducing facile electron transfer at the Pd/ZnO interface. In addition, the fully covered amorphous Pd layer prevented the contamination of ZnO NRs, indicating that the intrinsic properties of ZnO could be maintained. Thus, the am-Pd/ZnO NRs sensor demonstrated superior stability even after 5 months of storage in air. The sensing performance of am-Pd/ZnO NRs sensor provides a promising strategy for developing highly

sensitive and stable H₂ gas sensors, operating at room temperature.

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Reference

- [1] W. Lubitz, W. Tumas, Hydrogen: an overview, *Chem. Rev.* 107 (2007) 3900-3903.
- [2] A. Haryanto, S. Fernanodo, N. Murali, S. Adhikari, Current status of hydrogen production techniques by steam reforming of ethanol: a review, *Energy Fuels* 19 (2005) 2098-2106.
- [3] G. Korotcenkov, S.D. Han, J.R. Stetter. Review of electrochemical hydrogen sensors, *Chem. Rev.* 109 (2009) 1402-1433.
- [4] Y. Chao, S. Yao, W.J. Buttner, J.R. Stetter, Amperometric sensor for selective and stable hydrogen measurement, *Sens. Actuators, B* 106 (2005) 784-790.
- [5] M.E. Nasir, W. Dickson, G.A. Wurtz, W.P. Wardley, A.V. Zayats, Hydrogen detected by the naked eye: optical hydrogen gas sensors based on core/shell plasmonic nanorod metamaterials, *Adv. Mater.* 26 (2014) 3532-3537.
- [6] G. Lu, O.K. Farha, W. Zhang, F. Huo, J.T. Hupp, Engineering ZIF-8 Thin films for hybrid MOF-based devices, *Adv. Mater.* 24 (2012) 3970-3974.

- [7] G. Jiménez-Cadena, J. Riu, F.X. Rius, Gas sensors based on nanostructured materials, *Analyst* 132 (2007) 1083-1099.
- [8] Z. Zhang, Q. Zue, Y. Du, C. Ling, W. Xing, Highly enhanced sensitivity of hydrogen sensors using novel palladium-decorated graphene nanoribbon film/SiO₂/Si structures, *J. Mater. Chem. A* 2 (2014) 15931-15937.
- [9] Y. Pak, N. Lim, Y. Kumaresan, R. Kee, K. Kim, T.H. Kim, S.-M. Kim, H. Lee, M.-H. Ham, G.-Y. Jung, Palladium nanoribbon array for fast hydrogen gas sensing with ultrahigh sensitivity, *Adv. Mater.* 27 (2015) 6945-6952.
- [10] G. Korotcenkov, B.K. Cho, Bulk doping influence on the response of conductometric SnO₂ gas sensors: understanding through cathodoluminescence study, *Sens. Actuators, B* 196 (2014) 80-98.
- [11] V.R. Shinde, T.P. Gujar, C. D. Lokhande, R.S. Mane, S.H. Han, Use of chemically synthesized ZnO thin film as a liquefied petroleum gas sensor, *Mater. Sci. Eng. B* 137 (2007) 119-125.
- [12] J. Kukkola, J. Mäklin, N. Halonen, T. Kyllönen, G. Tóth, M. Szabó, A. Shchukarev, J.-P. Mikkola, H. Jantunen, K. Kordás, Gas sensors based on anodic tungsten oxide, *Sens. Actuators, B* 153 (2011) 293-300.
- [13] M.M. Arafat, B. Dinan, S.A. Akbar, A.S.M.A. Haseeb, Gas sensors based on one dimensional nanostructured metal-oxides: a review, *Sensors* 12 (2012) 7207-7258.
- [14] J. Zhang, X. Liu, G. Neri, N. Pinna, Nanostructured materials for room-temperature gas sensors, *Adv. Mater.* 28 (2016) 795-831.
- [15] J.X. Wang, X.W. Sun, Y. Yang, H. Huang, Y.C. Lee, O.K. Tan, L. Vayssieres, Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications, *Nanotechnology* 17 (2006) 4995-4998.
- [16] R. Ahmad, N. Tripathy, M.Y. Khan, K.S. Bhat, M.-S. Ahn, Y.-B. Hahn, Ammonium ion detection in solution using vertically grown ZnO nanorod based field-effect transistor, *RSC Adv.* 6 (2016) 54836-54840.
- [17] R. Zou, G. He, K. Xu, Q. Liu, Z. Zhang, J. Hu, ZnO nanorods on reduced graphene sheets with excellent field emission, gas sensor and photocatalytic properties, *J. Mater. Chem. A* 1 (2013) 8445-8452.
- [18] D. Yan, M. Hu, S. Li, J. Liang, Y. Wu, S. Ma, Electrochemical deposition of ZnO nanostructures onto porous silicon and their enhanced gas sensing to NO₂ at room temperature, *Electrochimica Acta* 115 (2014) 297-305.

- [19] H. Tian, H. Fan, J. Ma, Z. Liu, L. Ma, S. Lei, J. Fang, C. Long, Pt-decorated zinc oxide nanorod arrays with graphitic carbon nitride nanosheets for highly efficient dual-functional gas sensing, *J. Hazard. Mater.* 341 (2018) 102-111.
- [20] H. Tian, H. Fan, J. Ma, L. Ma, G. Dong, Noble metal-free modified electrode of exfoliated graphitic carbon nitride/ZnO nanosheets for highly efficient hydrogen peroxide sensing, *Electrochimica Acta* 247 (2017) 787-794.
- [21] H. Tian, H. Fan, M. Li, L. Ma, Zeolitic Imidazolate Framework Coated ZnO Nanorods as Molecular Sieving to Improve Selectivity of Formaldehyde Gas Sensor, *ACS Sensors* 1 (2016) 243-250.
- [22] M. Drobek, J.-H. Kim, M. Bechelany, C. Vallicari, A. Julbe, S.S. Kim, MOF-based membrane encapsulated ZnO nanowires for enhanced gas sensor selectivity, *ACS Appl. Mater. Interfaces* 8 (2016) 8323-8328.
- [23] S. Park, T. Hong, J. Jung, C. Lee, Room temperature hydrogen sensing of multiple networked ZnO/WO₃ core-shell nanowire sensors under UV illumination, *Curr. Appl. Phys.* 14 (2014) 1171-1175.
- [24] T.-R. Rashid, D.-T. Phan, G.-S. Chung, A flexible hydrogen sensor based on Pd nanoparticles decorated ZnO nanorods grown on polyimide tape, *Sens. Actuators, B* 185 (2013) 777-784.
- [25] A. Kolmakov, D.O. Klenov, Y. Lilach, S. Stemmer, M. Moskovits, Enhanced gas sensing by individual SnO₂ nanowires and nanobelts functionalized with Pd catalyst particles, *Nano Lett.* 5 (2005) 667-673.
- [26] R. Jaisutti, J. Kim, S.K. Park, Y.-H. Kim, Low temperature photochemically activated amorphous indium-gallium-zinc oxide for highly stable room-temperature gas sensors, *ACS Appl. Mater. Interfaces* 8 (2016) 20192-20199.
- [27] P. Rai, S.M. Majhi, Y.-T. Yu, J.-H. Lee, Noble metal @ metal oxide semiconductor core @ shell nano-architectures as a new platform for gas sensor applications, *RSC Adv.* 5 (2015) 76229-76248.
- [28] N.M. Vuong, D. Kim, H. Kim, Porous Au-embedded WO₃ nanowire structure for efficient detection of CH₄ and H₂S, *Sci. Rep.* 5 (2015) 11040.
- [29] J.-S. Jang, S.-J. Choi, S.-J. Kim, M. Hakim, I.-D. Kim, Rational design of highly porous SnO₂ nanotubes functionalized with biomimetic nanocatalysts for direct observation of simulated diabetes, *Adv. Funct. Mater.* 26 (2016) 4740-4748.

- [30] P.A. Russo, N. Donanot, S.G. Leonardi, S. Baek, D.E. Conte, G. Neri, N. Pinna, Room- temperature hydrogen sensing with heteronanostructures based on reduced graphene oxide and tin oxide, *Angew. Chem. Int. Ed.* 51 (2012) 11053-11057.
- [31] J. Hong, S. Lee, J. Seo, S. Pyo, J. Kim, T. Lee, A highly sensitive hydrogen sensor with gas selectivity using a PMMA membrane-coated Pd nanoparticle/ single-layer graphene hybrid, *ACS Appl. Mater. Interfaces* 7 (2015) 3554-3561.
- [32] N. Ma, K. Suematsu, M. Yuasa, K. Shimanoe, Pd size effect on the gas sensing properties of Pd-loaded SnO₂ in humid atmosphere, *ACS Appl. Mater. Interfaces* 7 (2015) 15618-15625.
- [33] B. Alfano, T. Polichetti, M.L. Miglietta, E. Massera, C. Schiattarella, F. Ricciardella, G.D. Francia, Fully eco friendly H₂ sensing device based on Pd decorated graphene, *Sens. Actuators, B* 239 (2017) 1144-1152.
- [34] J.L. Johnson, A. Behnam, S.J. Pearton, A. Ural, Hydrogen sensing using Pd-functionalized multi- layer graphene nanoribbon networks, *Adv. Mater.* 22 (2010) 4877-4880.
- [35] Y. Pak, S.-M. Kim, H. Jeong, C.G. Kang, J.S. Park, H. Song, R. Lee, N. Myoung, B.H. Lee, S. Seo, J.T. Kim, G.-Y. Jung, Palladium decorated hydrogen gas sensors using periodically aligned graphene nanoribbons, *ACS Appl. Mater. Interfaces* 6 (2014) 13293-13298.
- [36] K. Hassan, G.-S. Chung, Catalytically activated quantum-size Pt/Pd bimetallic core-shell nanoparticles decorated on ZnO nanorod clusters for accelerated hydrogen gas detection, *Sens. Actuators, B* 239 (2017) 824-833.
- [37] D.H. Shin, J.S. Lee, J. Jun, J.H. An, S.G. Kim, K.H. Cho, J. Jang, Flower like palladium nanoclusters decorated graphene electrodes for ultrasensitive and flexible hydrogen gas sensing, *Sci. Rep.* 5 (2015) 12294.
- [38] M.A. Lim, D.H. Kim, C.-O. Park, Y.W. Lee, S.W. Han, Z. Li, R. S. Williams, I. Park, A new route toward ultrasensitive, flexible chemical sensors: metal nanotubes by wet-chemical synthesis along sacrificial nanowire templates, *ACS Nano* 6 (2012) 598-608.
- [39] J.S. Lee, S.G. Kim, S. Cho, J. Jang, Porous palladium coated conducting polymer nanoparticles for ultrasensitive hydrogen sensors, *Nanoscale* 7 (2015) 20665-20673.
- [40] X. Li, Y. Liu, J.C. Hemminger, R.M. Penner, Catalytically activated palladium@platinum nanowires for accelerated hydrogen gas detection, *ACS Nano* 9 (2015) 3215-3225.

- [41] C. Wadell, F.A.A. Nugroho, E. Lidström, B. Iandolo, J.B. Wagner, C. Langhammer, Hysteresis-free nanoplasmonic Pd–Au alloy hydrogen sensors, *Nano lett.* 15 (2015) 3563-3570.
- [42] G. Korotcenkov, B.K. Cho, Instability of metal oxide based conductometric gas sensors and approaches to stability improvement (short survey), *Sens. Actuators, B* 156 (2011) 527-538.
- [43] S.J. Gentry, T.A. Jones, The role of catalysis in solid-state gas sensors, *Sens. Actuators* 10 (1986) 141-163.
- [44] Y. Zhao, Z. Ning, J. Tian, H. Wang, X. Liang, S. Nie, Y. Yu, X. Li, Hydrogen generation by hydrolysis of alkaline NaBH₄ solution on Co–Mo–Pd–B amorphous catalyst with efficient catalytic properties, *J. Power Sources* 207 (2012) 120-126.
- [45] K.C. Poon, D.C.L. Tan, T.D.T. Vo, B. Khezri, H. Su, R.D. Webster, H. Sato, Newly developed stepwise electroless deposition enables a remarkably facile synthesis of highly active and stable amorphous Pd nanoparticle electrocatalysts for oxygen reduction reaction, *J. Am. Chem. Soc.* 136 (2014) 5217-5220.
- [46] A. Indra, P.W. Menezes, N.R. Sahraie, A. Bergmann, C. Das, M. Tallarida, D. Schmeißer, P. Strasser, M. Driess, Unification of catalytic water oxidation and oxygen reduction reactions: amorphous beat crystalline cobalt iron oxides, *J. Am. Chem. Soc.* 136 (2014) 17530-17536.
- [47] K.S. Kim, H. Jeong, M.S. Jeong, G.Y. Jung, Polymer- templated hydrothermal growth of vertically aligned single- crystal ZnO nanorods and morphological transformations using structural polarity, *Adv. Funct. Mater.* 20 (2010) 3055-3063.
- [48] X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, Reversible superhydrophobicity to superhydrophilicity transition of aligned ZnO nanorod films, *J. Am. Chem. Soc.* 126 (2004) 62-63.
- [49] W. Lu, B. Wang, K. Wang, X. Wang, J.G. Hou, Synthesis and characterization of crystalline and amorphous palladium nanoparticles, *Langmuir* 19 (2003) 5887-5891.
- [50] L. Gröschel, R. Haidar, A. Beyer, K.-H. Reichert, R. Schomäcker, Characterization of palladium nanoparticles adsorpt on polyacrylic acid particles as hydrogenation catalyst, *Catal. Lett.* 95 (2004) 67-75.
- [51] D. Polsongkram, P. Chamninok, S. Pukird, L. Chow, O. Lupan, G. Chai, H. Khallaf, S. Park, A. Schulte, Effect of synthesis conditions on the growth of ZnO nanorods via hydrothermal method, *Phys. B: Condens. Matter* 403 (2008) 3713-3717.

- [52] X. Zhang, J. Qin, Y. Xue, P. Yu, B. Zhang, L. Wang, R. Liu, Effect of aspect ratio and surface defects on the photocatalytic activity of ZnO nanorods, *Sci. Rep.* 4 (2014) 4596.
- [53] C.-M. Chang, M.-H. Hon, I.-C. Leu, Improvement in CO sensing characteristics by decorating ZnO nanorod arrays with Pd nanoparticles and the related mechanisms, *RSC Adv.* 2 (2012) 2469-2475.
- [54] J. Radnik, C. Mohr, P. Claus, On the origin of binding energy shifts of core levels of supported gold nanoparticles and dependence of pretreatment and material synthesis, *Phys. Chem. Chem. Phys.* 5 (2003) 172-177.
- [55] H. Kobayashi, K. Kishimoto, Y. Nakato, Reactions of hydrogen at the interface of palladium-titanium dioxide Schottky diodes as hydrogen sensors, studied by work function and electrical characteristic measurements, *Surf. Sci.* 306 (1994) 393-405.
- [56] L.L. Jewell, B.H. Davis, Review of absorption and adsorption in the hydrogen–palladium system, *Appl. Catal. A: Gen.* 310 (2006) 1-15.
- [57] D.S. Dossantos, P. E. V. Demiranda, Hydrogen solubility in amorphous and crystalline materials, *Int. J. Hydrogen Energy* 23 (1998) 1011-1017.
- [58] Y.-I. Wang, J.-Y. Suh, Y.-S. Lee, J.-H. Shim, E. Fleury, Y. W. Cho, S.-U. Koh, Direct measurement of hydrogen diffusivity through Pd-coated Ni-based amorphous metallic membranes, *J. Membr. Sci.* 436 (2013) 195-201.
- [59] J.-S. Noh, J.M. Lee, W. Lee, Low-dimensional palladium nanostructures for fast and reliable hydrogen gas detection, *Sensors* 11 (2011) 825-851.

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Figure captions

Scheme 1 A schematic diagram describing the fabrication of the am-Pd/ZnO NRs sensor.

Fig. 1 SEM images of the (a-b) ZnO NRs and (c-d) am-Pd/ZnO NRs.

Fig. 2 TEM images of the (a-b) ZnO NR, (c-d) am-Pd/ZnO NR, and (e-f) c-Pd/ZnO NR. Insets of (d and f) show the FFT patterns of am-Pd/ZnO NR and c-Pd/ZnO NR, respectively.

Fig. 3 (a) High-resolved O1s XPS spectra of the ZnO NRs, c-Pd/ZnO NRs and am-Pd/ZnO NRs. (b) High- resolved Pd3d XPS spectra of the c-Pd/ZnO NRs and am-Pd/ZnO NRs.

Fig. 4 (a) Steady-state resistance responses and (b) sensing responses of the am-Pd/ZnO NRs and c-Pd/ZnO NRs sensors at different H₂ concentrations (0.5, 1, 2, 4, and 6 %). (c) Sensing response curves of the am-Pd/ZnO NRs and c-Pd/ZnO NRs sensors at 2 % H₂ concentration. Inset shows the normalized sensing response curves at 2 % H₂ concentration.

Fig. 5 (a) Sensing responses of the am-Pd/ZnO NRs and c-Pd/ZnO NRs sensors at low H₂ concentrations (0.01, 0.05 and 0.1 %). Sensing responses as a function of [H₂ concentration]^{1/2} (b) below 0.5 % and (c) above 0.5 %. Lines are provided to guide the eye.

f. 6 Stability test; comparison of the sensing responses at 1 % H₂ concentration for the (a) am-Pd/ZnO NRs and (b) c-Pd/ZnO NRs sensors measured after 5 months of storage in air.

Scheme 1 Kim *et al.*

Fig. 1 Kim *et al.*

Fig. 2 Kim *et al.*

Fig. 3 Kim *et al.*

Fig. 4 Kim *et al.*

Fig. 5 Kim *et al.*

Fig. 6 Kim *et al.*