2-13-2017

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Digital Object Identifier (DOI)
https://doi.org/10.1088/1757-899X/167/1/012041

Notes/Citation Information

Published in *IOP Conference Series: Materials Science and Engineering*, v. 167, conference 1, 012041, p. 1-7.

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A novel composite hydrogen sensor based on Pd nanoclusters/TiO_2 nanotube arrays

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Abstract. A novel composite hydrogen sensor, consisting of Pd nanoclusters/TiO_2 nanotube arrays, was fabricated and evaluated at room temperature. The Pd nanoclusters layer was deposited on top surface of the nanotube arrays by using a direct current (DC) magnetron sputtering method. Resistive response of the composite sensors to 0.5% hydrogen was measured. Experimental results indicated that the Pd nanoclusters can quickly and continually form or break multiple passages by absorbing or desorbing hydrogen, so that the composite hydrogen sensors have promising hydrogen sensitivity at room temperature.

1. Introduction

As an important reductive gas and clean energy, hydrogen is being widely used in chemical, aviation, medical, petrochemical, transportation and energy [1-4]. However, several security issues should be taken into account because of the low spark ignition energy and explosive with wide flammable range (4%−75%) of H_2 in air. Hence, a sensor with high sensitivity, fast response and recovery times, long time stability and low cost is needed to detect the leakage of hydrogen at room temperature. In recent years, various structures and mechanisms of hydrogen sensor have been reported[5-7]. Nanostructured metal oxide films, such as SnO_2, ZnO and WO_3, have been found to be the active materials of hydrogen sensors, duo to their high surface-to-volume ratio, simple working principle and portability[8-10].

Recently, one-dimensional titanium dioxide nanotubes have attracted significant interest as an attractive sensor material, because of its unique structure and special physical/chemical properties. Varghese and co-workers studied hydrogen sensing properties of titania nanotubes made through

anodization. The results showed the nanotubes with smaller pore diameter (46 nm) have promising sensitivity to hydrogen at 290℃[11]. Erdem Sxennik et al. reported that sensors based on TiO_2 nanotubes synthesized through anodic oxidation of a titanium foil in an aqueous solution showed a good sensitivity, but relatively poor response/recover behaviours at room temperature[12]. Moreover, the high operating temperature (200℃ to 500℃) limited their applications.

In this work, we present a simple method to fabricate a novel "network" of Pd nanoclusters on the surface of TiO_2 nanotube arrays by using DC magnetron sputtering, with the amount of the Pd to be controllable by controlling the sputtering parameters. We will demonstrate that the Pd nanoclusters/TiO_2 nanotubes composite has promising hydrogen sensitivity at room temperature.

2. Proposition and design of the composite structure

Compared with TiO_2 powder, TiO_2 nanotubes have larger specific surface area and stronger adsorption capacity, and thus showed higher hydrogen sensitivity. Resistance of the TiO_2 nanotube arrays will be significantly decreased after they absorb hydrogen gas, which will recover to original state when the hydrogen gas is absent. TiO_2 nanotube surface has a strong chemical adsorption to the dissociated H atom, so as to make partial charge transfer from H to the TiO_2 conduction band, which produces an electron accumulation layer on surface of the TiO_2 nanotubes, resulting in an increase in the nanotube conductance. When the hydrogen gas is absent, the electron is transferred back to the H atom, so that the TiO_2 nanotubes return to their original resistance. Therefore, TiO_2 nanotubes have a sensitive resistance response to hydrogen. Although the TiO_2 nanotube arrays have good sensitivity and selectivity, high operating temperature limit their applications as hydrogen sensors.

Under normal circumstances, resistance of metallic Pd membrane will become larger after hydrogen adsorption. However, when the metal Pd membrane made of nanoclusters structure, in the non-absorbed hydrogen state, the binding between nanoclusters is not sufficient, so it has a higher resistance. As each nanoparticle absorbs hydrogen gas and the expansion of the phase shift from the alpha phase to the beta phase, the bonding between the neighboring particles will reduce the resistance. Therefore, this Pd nanoclusters based hydrogen sensor have a good response at room temperature. Before the hydrogen absorption, the mesoscopic Pd nanoclusters are in the off state, resistance value is very large, in the uptake of hydrogen, Pd nanoclusters expanded and connected to each other, resulting in resistance decreases, which is named "break-junction" mechanism. The resistance change of this structure showed the opposite trend with the metallic palladium (Pd) membrane

The results of previous studies showed that the response time of the hydrogen sensor prepared by Pd thin film deposited on anodic aluminium oxide (AAO) and other porous substrates is much faster than that of the sensor prepared by the corresponding flat substrate[13-16]. In order to prepare the sensor with faster response, it is needed to prepare a kind of good near discontinuity network structure to isolate the Pd nanometer point, and to prepare the highly sensitive hydrogen sensor using the "break-junction" principle of Pd nanoclusters. Based on Chen's former work on " break-junction " principle of Pd nanoclusters, TiO_2 nanotube arrays was determined as substrate to deposited Pd nanoclusters. Using the network of TiO_2 nanotube arrays structure, good process controllability and large hole and thin wall can make the Pd films become quasi isolated nano-islands, and also can make full use of the hydrogen sensing properties of TiO_2 nanotubes. At the same time, it also make use of the self-cleaning function of TiO_2 nanotubes.

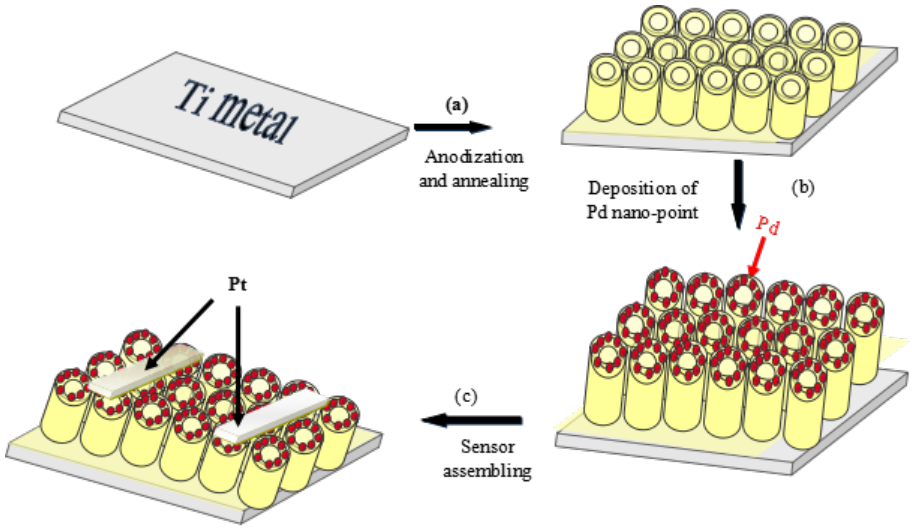

Figure 1. The Pd/TiO_2/Ti multilayer structure preparation process.

Thus the Pd/TiO_2/Ti multilayer and it preparation process are illustrated in Figure 1. Conductive copper wires were connected to the Pt electrode with silver conductive paint. The morphology of TiO_2 nanotubes and the surface composition of Pd were characterized using scanning electron microscope (SEM; FEI-Inspect F50, Holland). X-ray diffractometer (XRD; Bede D1 with Cu Kα radiation) was used to investigate the crystalline phase of the prepared TiO_2 nanotubes. The hydrogen sensitivity detection was conducted in a home-made chamber with a volume of 60 ml. Before each test, ambient air was circulated inside the chamber. All of the sensor testing was carried out at room-temperature. A Keithley 2700 multimeter (Tektronix (China) Co., Ltd, Chengdu, China) was used as a data collector to record the variation of the sensors in the atmospheres of H_2 in/out.

3. Preparation and hydrogen sensitivities of the Pd nanoclusters/ TiO_2 nanotube arrays composite structure

3.1. Preparation of TiO_2 nanotube arrays

For the growth of titania nanotubes, a 0.1-mm-thick Ti foil (99.8% purity, HeFei Ke Jing Materials Technology Co., LTD, Hefei, China) was cut into 20×25 mm^2 pieces. The titanium foil was then sonicated in acetone, ethanol, deionized water for 20 min and dried at 65℃ in drying cabinet. TiO_2 nanotubes were fabricated on the Ti substrate by electrochemical anodization[17,18]. TiO_2 nanotube arrays were first prepared by anodic oxidation of NH_4F/ glycol organic electrolyte aqueous solution in 0.25wt% for 3 hours, and then were annealed at 450 ℃ in atmosphere for 3 hours. After annealing treatment, the amorphous TiO_2 nanotubes were transformed into anatase (A) crystal phases with A (101), A (004), A (105), (200), A (211) strong characteristic peaks. Figure 2 (a)(b) showed the XRD diagrams of TiO_2 nanotubes before and after annealing. Figure 3 demonstrated the surface morphologies of TiO_2 nanotube arrays. The TiO_2 nanotube arrays prepared were very regular. The triangle area between the pipe and the pipe is very obvious.

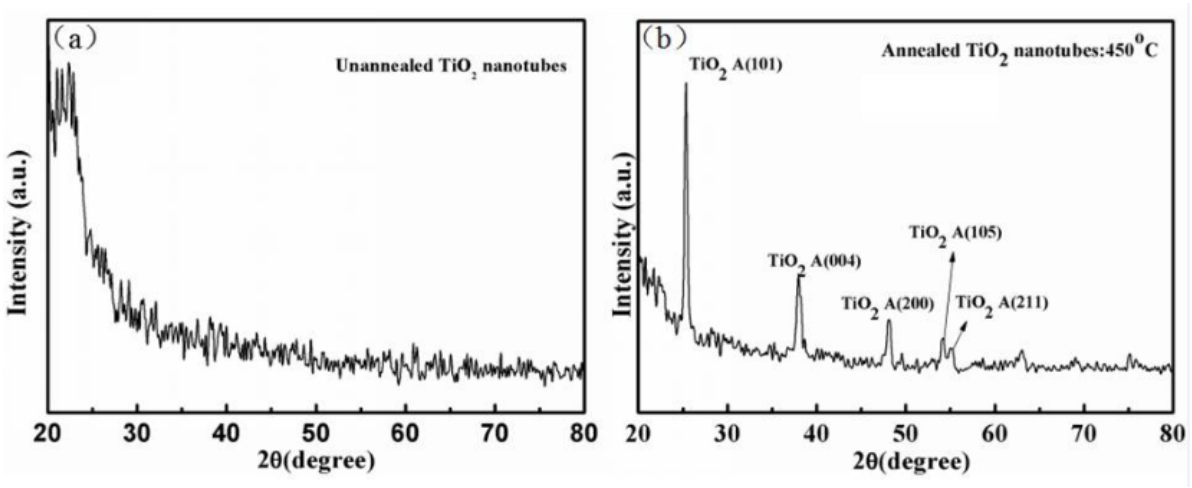

Figure 2. XRD diagrams of TiO2 nanotubes before and after annealing.

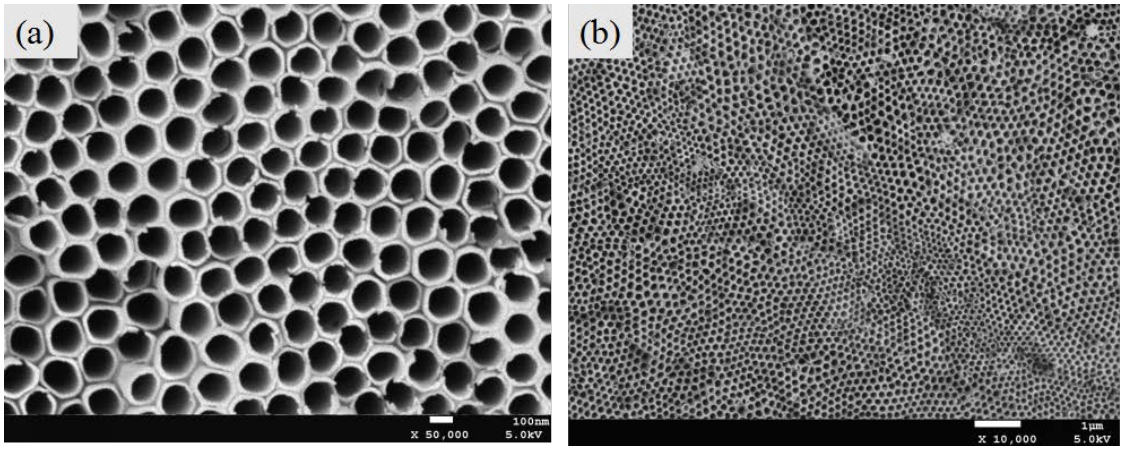

Figure 3. Surface images of TiO2 nanotube arrays with magnification of (a)50000, and (b)10000.

3.2. Preparation of the Pd nanoclusters and measurements of the Pd nanoclusters/TiO_2 nanotube arrays composite structure

The Pd nanoclusters were isolated from the surface of TiO_2 nanotubes by magnetron sputtering, and the parameters such as vacuum degree, sputtering power and sputtering time were controlled. Figure 4 was a typical hydrogen response-recovery curves of Pd nanoclusters/ TiO_2 nanotube arrays composite structure. In this structure, the Pd nanoclusters was 30 nm-thickness and the TiO_2 nanotube arrays pore diameter was about 90 nm. The response and recovery time of the sensor were 21 s and 23 s at room temperature and 0.5% hydrogen concentration.

Figure 4 is a typical 30 nm-thickness Pd nanocluster/90 nm pore diameter TiO_2 nanotubes composite structure surface SEM diagram. As can be seen from the figure, Pd nanoclusters show an obvious quasi-isolated state. The resistance change of the composite before and after the injection of hydrogen proved this point, as shown in Figure 5.

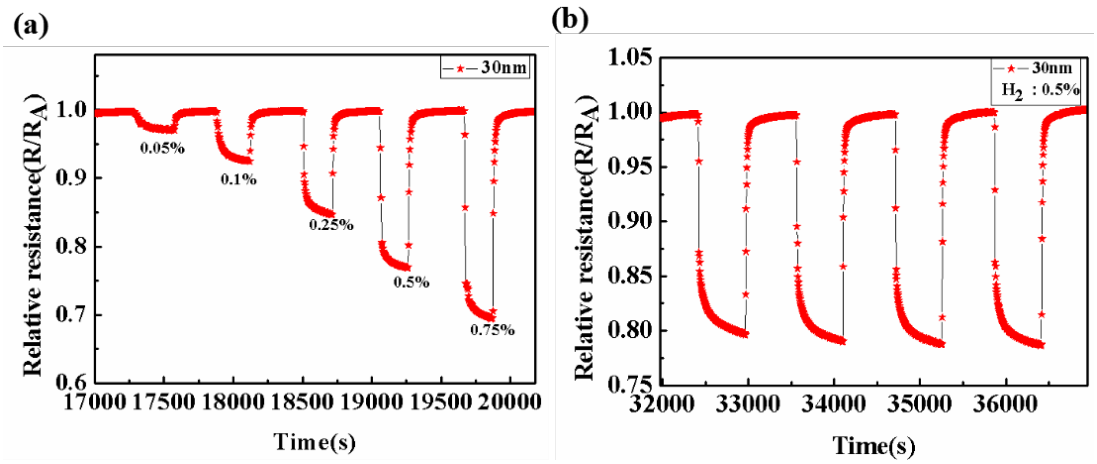

Figure 4. Hydrogen response-recovery curves of the Pd nanoclusters/TiO_2 nanotube arrays composite structure with Pd nanoclusters 30 nm-thickness and TiO_2 nanotube arrays pore diameter about 90 nm (a) response-recovery curves at different concentrations; (b) device performance repeatability test with hydrogen concentration of 0.5%.

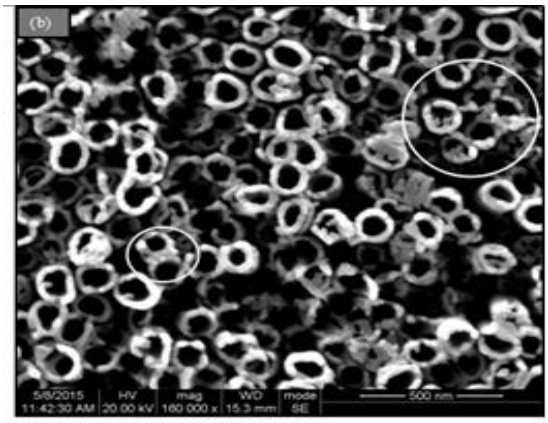

Figure 5. SEM image of a typical 30 nm-thickness Pd nanocluster/90 nm pore diameter TiO_2 nanotubes composite structure surface.

As we all know, the Pd nanoclusters can absorb a large amount of H_2 and lead to rapid volume expansion. In the case, the expansion of Pd nanoclusters will cause the separated nanoclusters connected with each other and then one or more conducting passage between the electrodes were created, which will result resistance decrease. When the Pd deposited get a certain thickness, the separated Pd nanoclusters could connect with each other and create more conducting passages between the electrodes, which will result rapid resistance decrease. In this case, the ideal isolated Pd nanoclusters can quickly and continually form or break multiple passages by absorbing or desorbing hydrogen, and the hydrogen sensors have the optimum response and recovery characteristics.

4. Conclusions

A novel composite structural hydrogen sensor of Pd nanoclusters/TiO_2 nanotube arrays was fabricated and tested. This novel composite structure is based on the "break-junction" principle of Pd

nanoclusters and make full use of the quasi-isolated areas on top of the TiO_2 nanotube arrays. Combined with the advantages of the structure, hydrogen sensing properties of the materials themselves, the potential room temperature hydrogen sensing sensor was obtained. Hydrogen sensor was fabricated by sputtering network Pd nanoclusters on TiO_2 nanotube arrays, which is capable of working at room temperature. Well-dispersed Pd nanoclusters was obtained on the TiO_2 nanotube arrays. The composite structure sensor has better hydrogen sensing performance when the diameter is about 90 nm for TiO_2 nanotube and the Pd nanoclusters is about 30 nm-thickness. A typical better hydrogen sensing performance was obtained that the response time and recovery time is 21 s and 23 s at 0.5% H_2, respectively.

Acknowledgements
This work was supported by National Natural Science Foundation of China under Grant Nos. 61474016 and 61405026, 61371046.

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