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Preparation of porous silicon/Pd-loaded WO_3 nanowires for enhancement of ammonia sensing properties at room temperature

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ABSTRACT

A sensitive resistive-type gas sensor based on porous silicon (PS)/Pd-loaded WO_3 nanowires (NWs) was successfully synthesized via facile methods for detection of ammonia at room temperature. PS/WO_3 NWs was synthesized by thermal evaporating W powder on the PS substrate, and Pd nanoparticles were decorated on the surface of WO_3 NWs by in-situ reduction method. Compared with PS/WO_3 NWs and Pd-loaded WO_3 NWs, the PS/Pd-loaded WO_3 NWs showed an enhanced response to ammonia at a low concentration down to 1 ppm and exhibited good selectivity, short response-recovery time at room temperature. The improved sensing characteristics indicated that the decoration of Pd NPs is effective for enhancing gas sensing performance.

1. Introduction

The current trend for development of gas sensor has focused on increasing sensitivity, reducing response time, and lowering the detection limit for application in different fields. Solid-state resistive-type nanoscale metal oxide gas sensors (MOGS) have been widely used ranging from health, safety, to energy efficiency and emission control in combustion process because of their high sensitivity, low cost, simplicity, and compatibility with modern electronic devices [1]. Among the materials used for MOGS, metal oxide semiconductors (MOS) such as WO_3, ZnO, Co_3O_4, CuO, In_2O_3, and V_2O_5 have attracted great attention because of their distinct properties [2–8]. Among the MOS, WO_3, an important n-type semiconductor with small band gap and stable physicochemical property, is regarded as a promising material to detect ammonia [9,10]. However, MOS-based gas sensors generally can not sufficiently identify an unknown gas or mixture of gases because of their poor selectivity and usually work at a high operating temperature above 100 °C [11–13]. High detection limit restricts the number of potential applications of the MOS-based gas sensors.

One of the key techniques to enhance the sensitivity and selectivity of MOS is decorating or doping noble metal nanoparticles (NPs) on the MOS surface. Different metal NPs such as Ag, Au, Pt, and Pd have been used to enhance sensor performance, and each metal nanoparticle (NP) exhibits a significant enhancement to response to a specific gas or certain gases [14–17]. For instance, Decoration of Ag NPs on the surface of ZnO nanosheets shows a preferable detection of C_2H_2 with high sensor response and fast response time [14]. With the decoration of Au NPs, Au-loaded PS/WO_3 NWs gas sensor performs enhanced NO_2-sensing characteristics [15]. Loading of Pt NPs on WO_3 films improves selectivity and response to H_2 [16]. In_2O_3 nanowire-like networks decorated with Pd NPs exhibits superior sensitivity with short response and recovery time [17].

Porous silicon, which was first observed by Arthur and Ingeborg Uhlir in 1956 [18]. Due to its high surface reactivity as well as the extremely large surface area of the porous structure at room temperature (RT) [14–16], PS has been one of the promising sensing applications to lower working temperature and enhance sensitivity. For instance, Chandra et al. deposited Pd/Mg thin films on the porous silicon substrate and showed fast response and low-temperature H_2 sensing characteristics [19]. Dhanekar et al. deposited TiO_2 film on PS substrate for selective alcohol sensing at room temperature [20]. Agarwal el al. deposited ZnO over macro-porous silicon substrate and obtained enhanced CO_2 sensitivity [21]. PS and noble metal NPs each has their own advantages, but there are few works about combining PS and noble metal NPs with MOS. MOGS based on PS and decorated with noble metal NPs could be essentially operated at low temperature with high sensitivity, resulting in be compatible with the existing micro-fabrication techniques.

In this work, we synthesized a novel PS/Pd-loaded WO_3 NWs and explored its enhanced NH_3-sensing performance. PS was prepared by

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electrochemical etching method, WO_3 NWs was fabricated by using thermal evaporating W powder method, and Pd decoration was achieved by in-situ reduction of Pd salt on the surface of WO_3 NWs with reduction agent Pluronic P123. The PS/Pd-loaded WO_3 NWs exhibited enhanced response at low concentration (1–100 ppm) and quick response-recovery characteristics at RT. The room working temperature make it promising in compatible with the integrated circuit technologies.

2. Experimental

PS substrate (24 mm × mm) was prepared by electrochemical etching p-type silicon ((1 0 0), 10–15 Ωcm) in the electrolyte (1:2 vol ratio of hydrofluoric and N, N-dimethyl formamide) with current density of 100 mA cm^{-2} for 10 min at RT. WO_3 NWs was synthesized directly on the PS substrate by thermal evaporating W powder in tube furnace which was equipped with a gas control system. 50 mg W powder (purity 99.99%) as source material and PS substrate were placed in two individual alumina boats. Both the two alumina boats were placed in the quarts tube and distance between them was 18 cm. The temperature of the tube furnace increased from RT to 1100 ℃ at a rate of 10 ℃/min, the 1100 ℃ was maintained for 1.5 h. During the thermal evaporation process, a mixture of Ar and O_2 was introduced at rate of 10 and 1 sccm, respectively. After the tube furnace was cooled to RT, the PS/WO_3 NWs composite was achieved and immersed in a Pd complex which was prepared by dissolving 2 mg $PdCl_2$ in 2 mL H_2O and ultrasonic stirring for minutes, then a solution of 1 g Pluronic P123 dissolving in 40 mL H_2O was added to the Pd complex solution to reduce Pd^{2+} to Pd nanocrystals. The reduction process was conducted for 9 h in air atmosphere at RT. Fig. 1 illustrates the synthesis process of PS/Pd-loaded WO_3 NWs resistive-type gas sensor. The obtained PS/Pd-loaded WO_3 NWs was characterized by scanning electronic microscope (SEM, ZEISS MERLIN compact) with energy dispersive spectrometer (EDS), transmission electron microcopy (TEM, Tecnai G2 F20) and X-ray diffraction with Cu Kα radiation (XRD, RIGAKU D/MAX-2500 V/PC).

The gas-sensing properties were evaluated by measuring the changes of resistance under target gas. In order to fabricate gas sensor, two Pt electrodes (3 mm × 3 mm) were deposited on the top of the PS/Pd-loaded WO_3 NWs by RF magnetron sputtering with the aid of shadow mask. The as-fabricated gas sensors (18 mm × mm) were measured in a homemade static gas sensing testing system [19]. During sensing measurement, the resistance of the sensors was continuously measured using a programmable digital multimeter (UNI-UT70D) interfaced with a computer, the target gases were switched on/off in cycles. Gas sensing characteristics were measured at different temperature with various gas concentration. The ambient relative humidity was kept at about 30% during the measuring process by using a dehumidifier. To explore the effect of PS substrate, a Si/Pd-loaded WO_3 NWs gas sensor was also fabricated. The fabrication process of Si/Pd-loaded WO_3 NWs gas sensor was similar to that of the PS/Pd-loaded WO_3 NWs gas sensor, the only difference was that replacing the PS substrate with Si substrate in the same size.

The gas response is defined to be R_a/R_g, where R_a and R_g are the resistances of the gas sensor in the air and in the target gas, respectively. The response time and recovery time are defined as the elapsed time to reach 90% of the final equilibrium value [22].

3. Results and discussion

3.1. Materials characterization

Fig. 2a shows the SEM image of PS, as can be seen from the top view and cross-section view, PS with an approximate thickness of 5.3 μm and mean pore size of 1.1 μm uniformly and orderly distributed. Fig. 2b shows the quantity proportion of PS pore size. The statistical result shows that the PS pore size mainly ranged from 0.6 μm to 1.6 μm. Such pore size is helpful for much more growing of WO_3 NWs on the PS pore walls and beneficial to gas adsorption/desorption during sensing performance.

The morphology of Si/Pd-loaded WO_3 NWs is shown in Fig. 3a, tilted WO_3 NWs with a diameter of 20–60 nm were randomly formed on the surface of Si substrate, Pd NPs were successfully decorated on the surface of WO_3 NWs. Fig. 3b shows the synthesized WO_3 NWs on the PS substrate. WO_3 NWs orderly distributed on the PS pore walls and exhibited one-dimensional structure with diameter of 30–50 nm and length of 1–3 μm. Furthermore, the surface of the WO_3 NWs was very smooth and clean. Fig. 3c shows the morphology of the PS/Pd-loaded WO_3 NWs, many small Pd NPs were homogenously and orderly decorated on the surface of WO_3 NWs. The density of the Pd NPs was estimated to be approximately 35 particles or less per WO_3 NW. Fig. 3d shows the XRD patterns of PS/WO_3 NWs and PS/Pd-loaded WO_3 NWs. The pattern of PS/WO_3 exhibits that main diffraction peaks were well indexed to the monoclinic WO_3 (JCPDS card No. 43–1035). The diffraction peaks of the standard cubic Pd (JCPDS card No. 46–1043) are observed in the pattern of PS/ Pd-loaded WO_3. The intensity of the (1 1 1) diffraction peak was higher than that of the (2 0 0) diffraction peak, suggesting that the Pd NPs were highly crystalline and mainly bound by [1 1 1] face [21]. Fig. 3e-f shows the EDS analysis of PS/WO_3 NWs and PS/Pd-loaded WO_3 NWs, peaks of W, O, and Pd testify the existence of

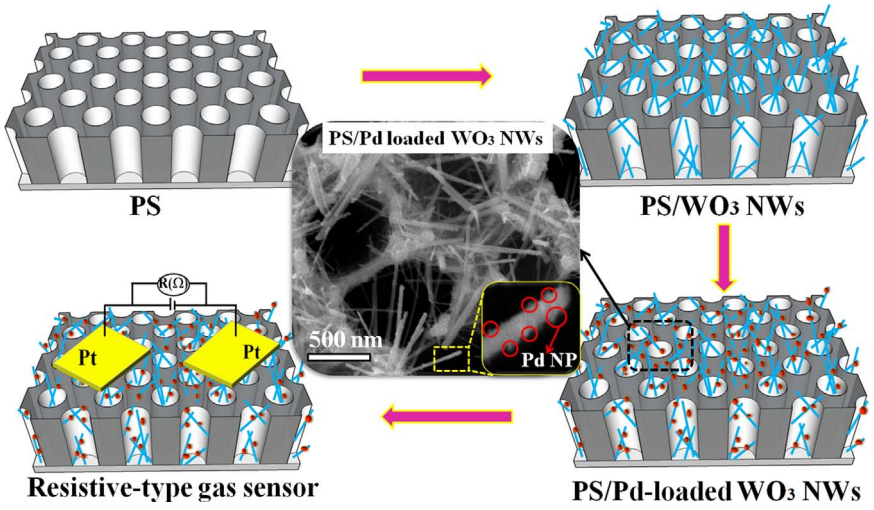

Fig. 1. Schematic diagram of synthesis process of PS/Pd-loaded WO_3 NWs resistive-type gas sensor.