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Synthesis and low-temperature gas sensing properties of tungsten oxide nanowires/porous silicon composite

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ABSTRACT

A novel tungsten oxide nanowires/porous silicon composite has been successfully synthesized via a convenient thermal evaporation method with no catalyst. The morphology and crystal structure of products obtained were investigated by scanning electron microscopy, X-ray diffraction, and transmission electron microscopy. The diameters and lengths of nanowires were 40–60 nm and 20–30 μm, respectively, and the aspect ratio (length/diameter) of nanowires can be in range of 500–750. The factor influenced the morphology was substrate temperature. The diameter of nanowires decreased as the substrate temperature increased. The sensor made of tungsten oxide nanowires/porous silicon composite exhibited a high response (~3.32), fast response/recovery (~175/44 s) and excellent selectivity toward 2 ppm NO_2 at a low operating temperature of 100 °C. Modulations of the depletion width along the nanowires are likely to be the reasons for the low-temperature gas sensing properties. Furthermore, modulations of the potential barriers at both networked nanowires homojunctions and heterojunctions between porous silicon and tungsten oxide are also responsible for the good gas sensing properties at a low operating temperature.

1. Introduction

As the air pollution becoming more and more serious, requirements for gas sensitive devices increase. Out of the main key environmental pollutants, the nitrogen dioxide (NO_2) has been of the greatest concern as it leads to severe health hazards, including nerve system and asthma problem [1]. Moreover, NO_2 in the air could cause serious environmental problems such as acid rain, photochemical smog, and corrosion [2]. The air quality standard for NO_2, suggested by Italian legislation for ambient air, is 106 ppb [3], and the threshold concentration of NO_2 in air is 3 ppm as listed in the safety standards by the American Conference of Governmental Industrial Hygienists [4]. Thus, there is a strong demand for cheap, reliable and sensitive gas sensors targeting NO_2.

Semiconductor gas sensors have attracted considerable attention owing to their low cost, compatibility with microfabrication technologies and high-sensitivity [5]. Various metal oxide semiconductors, such as SnO_2, In_2O_3, TiO_2, WO_3 and ZnO, have been widely investigated as materials for gas sensors [6–10]. Among them, tungsten oxide (WO_3), is considered as one of the most interesting materials in the field of NO_2 sensors [11,12]. In particular, one-dimensional WO_3 nanostructures, including nanowires and nanorods, have been evaluated as ideal candidates for detecting NO_2 gases at low concentrations due to their high crystallinity and high surface-to-volume ratios [13,14]. Unfortunately, gas sensors based on WO_3 nanostructures usually work at a high temperature above 200 °C owing to high activation energy of reaction with gas molecules. The high operating temperature is unfavorable for power saving and device integration. Thus, many attempts have been made to reduce the operating temperature of WO_3 nanostructures sensors, such as morphology control, doping and composites. WO_3 nanowires were formed by Meng et al. [15] through the thermal evaporation method and showed the highest response to NO_2 at 100 °C. It was found the gas response was increased as the diameter of WO_3 nanowires decreased. Qin et al. [16] reported Ti-added $W_{18}O_{49}$ nanowires prepared by two basic additive introduction methods showed a high response to NO_2 at room temperature. The investigation of Espinosa et al. [17] indicated gas sensors made of multiwalled carbon nanotubes/WO_3 hybrid layers showed NO_2-sensing properties at room temperature. Sharma et al. [18] reported a novel sensor made of SnO_2 thin film with WO_3 microdiscs showed fast response and recovery times for detection NO_2 at 100 °C.

Porous silicon fabricated simply and at low cost by electrochemical etching of silicon in HF solution, shows a variety of interesting properties, including surface chemistry and high chemical reactivity [19]. With well-developed Si-based semiconductor technology, porous silicon has become an ideal candidate material for potential

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applications, such as optoelectronics, photovoltaics and gas sensors. Li et al. [20] reported a gas sensor based on porous silicon showed NO_2-sensing properties at room temperature. Therefore, a gas sensor based on low-dimensional nanomaterials/porous silicon composites may be beneficial in reducing operating temperature or enhancing gas response for their synergetic enhancement or heterojunction effects. To the best of our knowledge, studies in this area are not a lot although several nanomaterials/porous silicon composites have been reported. Cheah et al. [21] prepared ZnS nanoparticles/porous silicon composite structure, which demonstrated that luminescence color tuning was possible. Jin et al. [22] synthesized a structure of porous silicon-core/SnO_2-shell nanowires through a two-step process. Yu et al. [23] reported a better field emission uniformity of ZnO nanostructures/porous silicon. Additionally, Nikfarjam et al. [24] fabricated a gas ionization sensor of carbon nanotubes/porous silicon, which presented good sensitivity and selectivity. Unfortunately, little attention has been concentrated on WO_3 nanostructures/porous silicon composite except that Blackman et al. [25] reported to use of tungsten oxide hexaphenoxide to prepare micro- and nanostructured films on the porous silicon. A sensor of WO_3 nanorods onto porous silicon was fabricated by our group, and it showed room temperature operation [26].

In this work, we demonstrated the synthesis of WO_3 nanowires/porous silicon composite through the thermal evaporation without catalysts. Large-scale WO_3 nanowires, with the length of 20–30 μm, grown onto porous silicon, and the aspect ratio (length/diameter) can be a range of 500–750, which was rarely reported before. The WO_3 nanowires became shorter and larger in the length and diameter, and even converted into nanorods or particles as the substrate temperature increased. Furthermore, the WO_3 nanowires/porous silicon composite was found to be capable of NO_2 detection at sub-ppm level with a fast response-recovery characteristic and good selectivity at a low operating temperature of 100 °C.

2. Experimental

2.1. Synthesis and characterization of WO_3 nanowires/porous silicon composite

The porous silicon substrates were prepared by electrochemical etching of p-type silicon (1 0 0) samples in the electrolyte, which was composed of a 1:2 volume mixture of 40 wt.% hydrofluoric acid and 99.5 wt.% N,N-dimethyl formamide (DMF). The etching current density and etching time were 100 mA cm^{-2} and 10 min, respectively, which was reported in our previous work [27]. The synthesis of WO_3 nanowires was carried out in a thermal evaporation setup using a horizontal tube furnace equipped with a gas control system. The schematic diagram for synthesis of WO_3 nanowires/porous silicon composite is shown in Fig. 1. Tungsten powder (50 mg, 99.99% purity) as source material was deposited on an alumina boat and placed in the hot zone of the quartz tube (60 mm in diameter and 1000 mm in length). Porous silicon substrates were loaded on another alumina boat away from the W powder. The distance (D) between the substrates and source were 14, 15, 16, 17, 18 and 19 cm, respectively. After the quartz tube was pumped to the vacuum of 4–5 × 10^{-4} Torr, a mixture of argon and oxygen was introduced at rates of 10 and 1 sccm, respectively. The temperature of the furnace was increased from room temperature to 1150 °C at a rate of 10 °C/min and was maintained at this temperature for 1.5 h. After the furnace was cooled to room temperature, a layer of product was obtained on the substrate.

The morphology and crystalline structure of as-obtained products are characterized by field emission scanning electron microscope (FESEM, FEI Nanosem 430, and Hitachhi S-4800), X-ray powder diffraction with Cu Kα radiation (XRD, RIGAKUD/MAX 2500 V/PC), transmission electron microscope (FETEM, TECNAIG^{2}F-20), selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) attached on the FETEM.

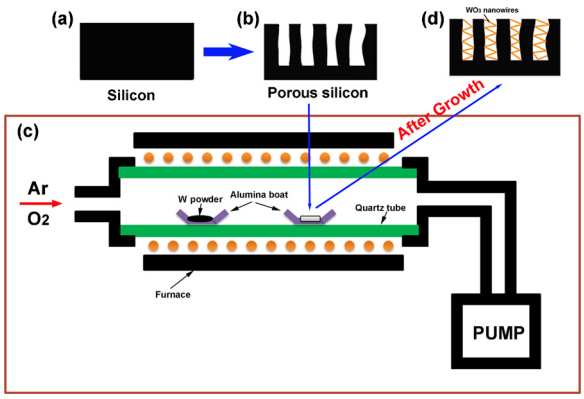

Fig. 1. The schematic diagram for synthesis of WO_3 nanowires/porous silicon composite.

2.2. Gas sensor preparation and measurement

In order to fabricate gas sensors, two Pt electrodes of dimensions 3 mm × 6 mm were deposited on top of the porous silicon and WO_3 nanowires/porous silicon composite by RF magnetron sputtering using a shadow making process, respectively. A DPS-III high vacuum facing-target magnetron sputtering system with a Pt target (2-in. diameter with 99.95% purity) was used. The vacuum chamber was first evacuated to a base pressure of 4 × 10^{-4} Pa and then kept at 2 Pa during Pt film deposition. The pure argon was used as the sputtering gas in the RF power of 90 W and the deposition process was performed for 8 min. Then, the obtained Pt electrodes were about 100 nm in thickness.

The gas sensing characteristics were measured in a static gas sensing testing system, which had been reported in our previous works [16,20,26–29]. The pure target gas was injected into the system directly to get the desired concentration. During the whole measurement process, the change in the electrical resistance of the sensor was continuously monitored and recorded by a personal computer when gas was introduced and exhausted at an operating temperature from room temperature 25 °C to 250 °C. The sampling interval was set to 1 s, and the acquired resistance data were stored in the computer for future analysis. The gas response was defined to be Rg/Ra for oxidizing gas and Ra/Rg for reducing gas, where Rg and Ra are the electrical resistances of the sensor in detected gas and in air, respectively. The response time is defined as the time for 90% of the total resistance change. Conversely, the recovery time is the time for 90% recovery of the resistance change.

3. Results and discussion

3.1. Structure characterizations

Typical FESEM images of the porous silicon and as-synthesized WO_3 nanowires/porous silicon composite are shown in Fig. 2. Fig. 2a and b shows the top and cross-sectional view of porous silicon samples, respectively. For the samples, an orderly and uniform distribution of pores, with the thickness around 8 μm, average pore sizes about 1.5 μm and porosity 39.8%, has been observed. The morphology of WO_3 nanowires onto the porous silicon is shown in Fig. 2c when the distance between the substrates and source was 18 cm. The synthesized nanowires exhibited one-dimensional