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Thermal-oxidative growth of aligned $W_{18}O_{49}$ nanowire arrays for high performance gas sensor

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ABSTRACT

Gas sensors based on aligned arrays of $W_{18}O_{49}$ nanowires were formed directly via a novel route of in situ thermal oxidation of sputtered W film on the substrate attached patterned Pt electrodes. The well-developed nanowires have diameter of 10–20 nm and show roughly aligned morphology. It is found that the duration of oxygen exposure during thermal annealing plays a crucial role to harvest a pure phase of $W_{18}O_{49}$ nanowire with desired length. The roughly aligned $W_{18}O_{49}$ nanowires show favourable microstructure for gas adsorption and rapid gas diffusion. The NO_2-sensing properties of aligned $W_{18}O_{49}$ nanowires sensor were evaluated at 50 °C up to 200 °C over NO_2 concentration ranging from 250 ppb to 2.5 ppm. The results indicate that the $W_{18}O_{49}$ nanowire arrays sensor exhibits good NO_2-sensing performances at its optimal operating temperature of 150 °C, especially perfect stability and fast response–recovery characteristics. The reliable interface performance and fast gas adsorption–desorption properties of the directly assembled vertically aligned nanowire array attribute to the superior stability and quick response/recovery. The growth mechanism of aligned $W_{18}O_{49}$ nanowires is proposed based on the direct SEM observations on the intermediate products, and meanwhile the sensing mechanism of the corresponding sensor is analyzed.

1. Introduction

Nowadays, air pollution is becoming more and more serious. Especially, nitrogen dioxide (NO_2), which results from fuel combustion and automobile exhaust emission, is a main source of acid rain and photochemical smog [1]. Detection of toxic NO_2 gas is, therefore, very important for the environmental protection and human health. At present, oxide semiconductors have been widely used for sensing various toxic and hazardous gases. In particular, tungsten oxide, which is a wide band-gap n-type semiconductor, has been found showing very promising sensing properties to NO_2 gas [2,3].

It is known that the sensing mechanism of metal oxides belongs to the surface-controlled type in which surface-to-volume ratio, surface and interface states play key roles in the response of the sensor [4]. Thus, the sensing response of an oxide sensor dependents heavily on the surface structure and morphology of the sensing oxide used [5,6]. Towards this end, various one-dimensional (1D) oxide nanostructures, including nanowires, nanorods and nanotubes, have been examined as candidates for high performance gas sensors application. They can exhibit enhanced capability to detect gases at low concentrations when the dimensions of 1D oxides become comparable with or smaller than Debye length [7–9]. Likely, 1D tungsten oxides, especially nanowires, have been proved experimentally to show good sensing properties while detecting toxic NO_2 gas.

Up to now, nanowire gas sensors have been fabricated using a variety of metal oxide semiconductors (e.g. ZnO, SnO_2, TiO_2, WO_3, etc.) as sensing materials. Nevertheless, the application of gas sensor based on single nanowire is limited because of weak sensing response and expensive and time-consuming fabrication techniques such as electron-beam lithography [10]. Comparatively, the nanowires film sensors are much promising to achieve high gas response. From the viewpoint of device structure, oxide nanowires-based sensors are usually fabricated by a series of processes involving synthesis, dispersal and transfer of oxide materials to the sensor substrate, followed by a required thermal treatment at a certain temperature. The complicated secondary preparation procedures for the sensing thick films degrade the intrinsic sensing properties of the 1D oxides undesirably, as well as the stability and reliability of the corresponding device [11]. To achieve fast response-recovery, sensing materials should have loose microstructure and then to exhibit high accessibility of gas molecules to the whole surface by diffusion [12]. It is reported that the sensor based on porous WO_3 hierarchical structure responses to

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NO_2 gas as low as 15 ppb with an ultrashort response time of short than 5 s at room temperature [13]. The sensor constructed with loose double-sided nanorod arrays of Co-doped WO_3 was found to achieve rapid response and recovery within several seconds towards 1-butanol vapor [14]. However, in the densely thick film of disordering nanowires formed by secondary transferring technique, desorption of gas molecules from the nanowires inside the film may not be very easy, which leads to a slow recovery [15]. In this respect, the sensor based on ordering arrays of 1D nanowires is much preferred due to its loose structure for gas diffusion. Meanwhile, the aligned array is expected to harvest much higher gas response since its whole surface could be "seen" by gas molecules. Up to now, limited works concerning gas sensors with aligned 1D WO_x nano-arrays as sensing elements have been reported. Cheng et al. assembled an aligned $W_{18}O_{49}$ nanowires sensor by Langmuir–Blodgett technique. They found that the formed sensor had outstanding sensitivity to H_2 at room temperature [16]. W. Zhou et al. have ever developed a WO_3 nanowire arrays sensor through preparing solid electrode film on top of nanowire arrays. It is reported that this nanowire arrays sensor exhibited a fast response speed with response time less than 30 s to 0.05–500 ppm NO_2 at 180 °C, while its recovery was relatively slow due to the top coating of the solid electrode film (the recovery time was more than 800 s) [17]. To achieve high performances especially fast recovery, gas sensors based on the direct assembly of well-developed, vertically aligned nanowire arrays will be desirable.

In this work, we prepared vertically aligned $W_{18}O_{49}$ nanowires on the alumina substrate with patterned Pt electrodes via a new developed route of in situ thermal oxidation of sputtered W film. Liu, et al. ever prepared disordering tungsten oxide nanowires (bundles) through heating tungsten tip (or tungsten plate) at 700 °C under Ar flow [18]. Comparatively, the growth process presented here has many advantages, such as low growth temperature, few limitations to substrate materials, and especially, the capability for aligned nanowire array growth in a large scale. These features are all favourable for applications of one-dimensional nanowires in nanoelectronic and nanophotonic devices. For instance, the directly bottom-up growth of aligned nanowires can build favourable sensing microstructures as well as good interface adhesion and electric contact. In this work, we evaluate the gas sensing performance of the as-grown $W_{18}O_{49}$ nanowire arrays. It is found that the sensor based on the aligned nanowires is efficient for the detection of NO_2 gas at ppb level with high stability, good selectivity and fast response-recovery characteristic. The growth mechanism of aligned nanowires was suggested based on the direct observations on nanowire growth process. And the responsible sensing mechanism was also analyzed.

2. Experimental

2.1. Preparation and characterization of $W_{18}O_{49}$ nanowire arrays

$W_{18}O_{49}$ nanowire array was prepared on the alumina substrate via a novel route of in situ thermal oxidation of sputtering-deposited metallic W film. Prior to the W film deposition, a pair of interdigitated Pt electrodes in 100 nm thickness was preformed on the cleaned alumina substrate by RF magnetron sputtering technique [19]. To deposit W film, the electrodes-attached substrate was placed in the same sputter chamber, and the sputtering was processed in a pure argon ambience using a metallic W target (99.95%). The working pressure and the sputtering power were respectively kept at 2.0 Pa and 90 W during sputtering. The deposition was performed for 15 min and the obtained W film was about 150 nm in thickness. A physical mask was used during sputtering to avoid the coating of W film at the end of the electrodes. Next, the aligned $W_{18}O_{49}$ nanowire arrays were grew on the substrate by in situ thermal oxidation of the metallic W film in a horizontal tube furnace. For this purpose, the W film-deposited alumina substrate was placed at the hot zone of the tubal furnace. After pumped to 1 Pa, the furnace was heated up to 650 °C in ramp of 5 °C/min and held for 60 min under argon and oxygen flow with Ar/O_2 flow ratio of 350. In order to grow well-developed nanowires arrays of tungsten oxide, the flow of oxygen should be controlled strictly (0.1 sccm in this work). Besides, the furnace pressure also is found to be a key parameter for nanowire formation. At present experiment, to create a proper ambience for $W_{18}O_{49}$ nanowires growth, the pressure of the furnace was maintained at 150 Pa through adjustment of Ar flow and the flapper valve. After the furnace was cooled to room temperature naturally in Ar/O_2 gases, the alumina substrate coated with $W_{18}O_{49}$ nanowires was taken out, and was directly used as sensor to carry out the sensing evaluation. Fig. 1 shows the schematic diagram of the used annealing setup and a brief procedure for in situ synthesis of aligned $W_{18}O_{49}$ nanowires.

To further clarify the crucial effect of oxygen ambience on tungsten oxide nanowires formation and then to explore the possible growth mechanism, in the present work, other samples with different duration of oxygen exposure were also prepared by shutting off oxygen flow at different moments (never turned on, turned off after 10/20/40/60 min of holding time at 650 °C, respectively)

The morphology and crystalline structures of the tungsten oxides were characterized by using a field emission scanning electron microscopy (FESEM, FEI Nanosem 430), an X-ray diffractometer (XRD, RIGAKU D/MAX 2500 V/PC, Cu Kα radiation) and a field emission transmission electron microscope (FETEM, TECNAI G^2F-20) with selected area electron diffraction (SAED).

2.2. Measurement of gas-sensing properties

The gas-sensing properties of the as-grown $W_{18}O_{49}$ nanowire arrays were evaluated in a home-built static gas-sensing testing system consisting of a test chamber, a controllable flat heating plate, a professional digital multimeter and a data acquisition computer [19]. The sensors were placed on the heating plate fixed in test chamber. The measured gas was introduced into test chamber by static volumetric method, That is, appropriate volume of pure NO_2 gas, which was first calculated according to the volume of the test chamber, was injected into the chamber directly to get the desired concentration. The resistance change of the sensor during the whole measurement was continuously monitored by an UNI-T UT61E professional digital multimeter with the function of automatic measuring range adjustment. As shown in Fig. 1, the tungsten oxide nanowires are found only growing on the area deposited W film after thermal process. So during sensing test, the bare ends of Pt electrodes can be used to realize the electrically connection between the sensor and the digital multimeter. The sampling interval was set to 1 s, and the test temperature was changed from 50 °C to 200 °C by adjusting the temperature controller of the heating plate. The test equipment is set in a humidity-controlled testing room, and during the measurement, the ambient relative humidity is about 30–35%. The sensor response is defined as R_{gas}/R_{air}, where R_{gas} and R_{air} are the electrical resistances of $W_{18}O_{49}$ nanowires sensor in a tested gas of NO_2 and in clean air, respectively.

3. Results and discussion

3.1. Structure characterization

The typical morphologies of the $W_{18}O_{49}$ nanowires grown on the alumina substrate at 650 °C are shown in Fig. 2(a)–(c). In present work, the growth of tungsten oxide nanowires is first based on