Sensors and Actuators B 202 (2014) 708–713

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Vertically aligned tungsten oxide nanorod film with enhanced performance in photoluminescence humidity sensing

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ARTICLE INFO

Article history:
Received 19 March 2014
Received in revised form 30 May 2014
Accepted 4 June 2014
Available online 11 June 2014

Keywords:
Tungsten oxide
CVD
Photoluminescence
Humidity sensing
Oxygen vacancy

ABSTRACT

Vertically aligned uniform WO_3 nanorod film has been successfully synthesized by using chemical vapor deposition (CVD) technique without any catalyst. X-ray diffraction (XRD), Raman spectrum, field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images indicate that the as-prepared WO_3 nanorod film is monoclinic phase and consists of densely-aligned single crystalline nanorods with diameters approximately 30–110 nm and lengths around 1 μm. A room temperature photoluminescence-type humidity sensing device based on this WO_3 nanorod film integrated with Si supported substrate has been directly established to investigate their humidity sensing properties, which presents its high response, excellent linearity, quick response/recovery performance and reliable repeatability toward a very wide humidity range. Further comparison with the WO_3 control sample without oxygen vacancy or defect which has poor response demonstrates that oxygen vacancies in the structure play a pivotal role in the high response humidity sensing application.

1. Introduction

One-dimensional (1D) semiconductor nanostructures (nanowires, nanorods, nanobelts, nanofibers, and nanotubes etc.) have attracted extraordinary attention due to their high surface area to volume ratio from the reduced sizes, which allows for their distinct structural and physical behaviors as well as chemical reactivities [1]. Compared with randomly dispersed 1D nanostructure, it is an important prerequisite to assemble nanoscale building blocks into ordered nanostructured arrays or high-level nanoarchitectures as they can introduce and realize functionalities for practical device applications [2]. Therefore, synthesis of uniform 1D array on a supported substrate is expected to not only enhance their collective response to external analytes but also build synergetic multifunctionalities into an integral device [3].

Until now, 1D semiconductor arrays have been successfully applied in the fabrication of nanoscale electronic, optoelectronic, electrochemical and sensor devices [1–5]. Among these applications, the sensor devices for monitoring humidity is of great importance for maintaining human health and comfort as well as ensuring appropriate atmospheric conditions in various detection processes [6,7]. Generally, a good sensing device must possess a number of criteria such as high sensitivity, long-term repeatability, good stability, short response and recovery time to meet practical demand [8]. In recent years, various types of 1D semiconductor nanostructures, which are generally used as sensor devices, such as SnO_2, WO_3, ZnO, and V_2O_5, have shown good sensing properties [9–12]. As an important n-type semiconductor with a wide bandgap (E_g = 2.7 eV), WO_3 has aroused a great deal of interest due to its intriguing physiochemical properties and a wide variety of potential applications. To date, many nanodevices based on WO_3 nanostructures have been fabricated including gas sensors, solar energy devices, photocatalyst, smart windows, electrochromic and optochromic devices [13–18].

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http://dx.doi.org/10.1016/j.snb.2014.06.009
0925-4005/

In our previous work, several semiconductor oxides and sulfides based optical humidity or gas sensors have been fabricated [19,20]. In this work, we successfully synthesized vertically aligned uniform WO_3 nanorod film on Si substrate by using chemical vapor deposition method. Furthermore, a room temperature photoluminescence-type humidity sensing device based on this WO_3 nanorod film has been first established here to investigate their photoluminescence humidity sensing properties instead of normal resistance-type gas sensor. This 1D WO_3 nanorod film-based sensor has fast and sensitive response to relative humidity (RH) in a very wide range at room temperature compared with previous humidity sensors. In addition, it has relatively good repeatability and linear response to RH, which is easy to be calibrated. Further comparison with the annealed WO_3 control sample without oxygen vacancy or defect, which has poor response to RH, demonstrates that oxygen vacancies in the structure play an important role in humidity sensing application with high response. Moreover, compared with powder based humidity sensor, this 1D nanorod arrays integrated on Si substrate can offer direct electronic transport pathways and can also provide much more active surface toward sensed gas. More importantly, it can be directly used as a prototype sensor device to avoid inconvenient fabricating process.

2. Experimental

2.1. Synthesis of WO_3 nanorod film

The CVD synthesis of WO_3 nanorod film was carried out in a self-established vacuum tube furnace using $WO_{2.9}$ powder (0.4 g, Alfa, 99.99% in purity) as vapor source and n-type (100) Si wafers (4″ diameter × 0.525 mm thickness, As doped, resistivity: <0.005 ohm cm, MTI corporation) as substrates. Before the CVD growth, the Si substrate was cleaned by acetone and isopropanol to remove organic contaminations, followed by HF solution etching to remove the native oxide of the Si substrates. $WO_{2.9}$ powder was put in a tungsten boat and placed in the left uniform temperature zone of the tube furnace, which acted as the vapor source material. The Si wafer was placed in the right low temperature zone, 14 cm downstream from the source, and acted as the substrate for products collection. The set temperatures of the source and Si substrates were 980 and 400 °C, respectively. After the system evacuated down to 1.1 Torr, 300 standard cubic centimeters per minute (sccm) argon gas was flowed as carrier gas. The pressure of the furnace was maintained at ∼2.6 Torr. After 200 min growth, the temperature decreased gradually to room temperature and WO_3 nanorod film was produced on the Si substrate.

2.2. Characterization

Field emission scanning electron microscopy (FESEM) images were taken using a JEOL JSM-6340F field emission scanning electron microscope. The X-ray diffraction (XRD) was taken on a Bruker AXS D8 Discover XRD diffractometer system equipped with a Cu Kα radiation source (λ = 1.5418 Å) and a GADDS area detector. Transmission electron microscopy (TEM) and selective area electron diffraction (SAED) was taken on JEOL JEM-2100F operating at 200 kV, and the WO_3 nanorods were dispersed in ethanol solution via sonication process in order to prepare the TEM samples. Raman spectrum was measured on a Thermo Scientific DXR Raman Microscope with 523 nm laser and 5 mW power. The photoluminescence (PL) measurements of the samples were performed on a Hitachi F-4500 FL spectrophotometer at room temperature (25 °C). The excitation was set at 275 nm throughout the work, with the excitation and emission slit width both of 5 nm. For humidity measurement, the program of time scan was employed, with excitation also at 275 nm and emission at the PL peak of the sensing sample. X-ray photoelectron spectroscopy (XPS) was recorded with a Thermo Scientific ESCALAB 250 Xi XPS system by using a monochromatized Al Kα ($h\nu$ = 1486.6 eV) X-ray source. All of the spectra were referenced to the C1s binding energy of 284.9 eV and analyzed using CasaXPS software (version 2.3.16).

2.3. Photoluminescence humidity sensing measurements

The humidity sensing measurements could be referred to our previous reports [21,22]. The RH response was tested by using an adapted photoluminescence-type setup operated at room temperature (25 °C), which consisted of a gas flow control system, a colorimetric cuvette and a Hitachi F-4500 FL spectrophotometer. The WO_3 nanorod film on Si wafer can be easily used as sensor device, by directly putting the sample in the colorimetric cuvette, operating with high purity nitrogen as a carrier gas for PL measurements. Measurements of the sensor's response to different RH were performed by introducing nitrogen gas through water vapor with different concentrations. The total flow rate was maintained at 1000 mL min^{-1}. After PL intensity was stable, the water vapor was subsequently blown off by purging the system with pure nitrogen gas. The relative humidity was calibrated by a commercial hygrometer.

3. Results and discussion

XRD and Raman measurements are used to investigate the crystal structure of the prepared products. From the XRD pattern in Fig. 1a, all the diffraction peaks could be well indexed to the standard monoclinic phase WO_3 structure (JCPDS card no. 72-1465). Fig. 1b shows the typical Raman spectrum of WO_3 nanorods where the well-resolved peaks can be observed (133, 272, 325, 716 and 806 cm^{-1}), except the peak observed at 519 cm^{-1}, which is the signal from the Si crystalline substrate. The comparison of Raman spectrum data with those reported in the literature, suggests that

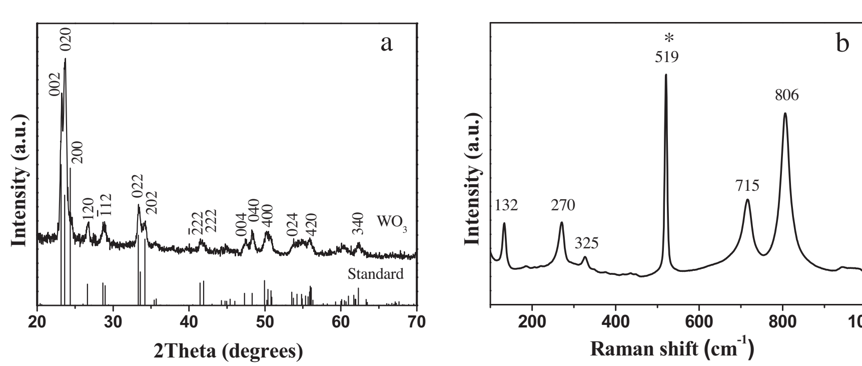

Fig. 1. XRD pattern (a) and Raman spectrum (b) of WO_3 nanorod film.