Thin Solid Films 545 (2013) 8–12

Contents lists available at ScienceDirect

Thin Solid Films

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

Oxygen sensing properties of zinc oxide nanowires, nanorods, and nanoflowers: The effect of morphology and temperature

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ARTICLE INFO

Available online 14 June 2013

Keywords:
ZnO nanostructures
Oxygen gas sensor
Chemical vapour deposition
Gas sensitivity
Nanowires

ABSTRACT

In this paper, we report the synthesis of one-dimensional zinc oxide (ZnO) nanostructures and the impact of their morphology on oxygen gas sensing properties. The nanostructures were synthesised via chemical vapour deposition using direct oxidation in an electrical furnace.
Structural characterisation of the samples was performed with a field emission scanning electron microscope (SEM) and X-ray diffraction (XRD) methods. The SEM images revealed the formation of different sized nanowires, nanorods and nanoflower structures, and the XRD pattern showed hexagonal structures, without any impurities. The gas sensing properties of samples grown on silicon and alumina substrates were measured in different conditions. The samples grown on the alumina substrate showed better gas sensing properties than those grown on the silicon. To determine the optimal sensitivity, the oxygen gas sensing properties of the ZnO nanostructures were measured at different temperatures and gas flows. These nanostructural gas sensors showed high sensitivity at temperatures close to ambient. The effect of the morphology of ZnO nanostructures on their oxygen sensing properties was compared. Between the different synthesised nanostructures, ZnO nanowires exhibited the highest gas sensitivity.

1. Introduction

Zinc oxide (ZnO) is a II–VI semiconductor with a direct band gap (3.36 eV at room temperature) [1,2]. These include conductive oxide coatings with high permeability for solar cells, gas sensors, electric field-effect switching, single electron transistors, biological and chemical sensing, luminescence and solar energy conversion [3–6].

The high gas sensing ability of ZnO nanostructures has led to their use in gas sensors, which are widely used in different areas of science and industry. Numerous investigations have focused on the fabrication and synthesis of different ZnO nanostructures, such as thin films and one-dimensional (1-D) nanostructures, with laboratory and industrial methods [7–9].

ZnO with 1-D nanostructures exhibit more quantum effects compared to the two dimensional nanostructures. These effects are mostly regulated by two factors: increases in the surface-to-volume ratio and variations in the electronic structure of the material resulting from the quantum effects caused by the particle size reduction [10–14].

Different physical and chemical methods, such as sol–gel, spray pyrolysis and sputtering, have been used to synthesise 1-D ZnO nanostructures [15–24]. Despite difficulties with chemical methods in controlling the growth process, they have attracted significant attention due to their low cost and high capabilities in industrialization. In chemical vapour deposition (CVD), source materials and active gases are evaporated, and nanostructures are produced in a horizontal electric furnace through a reaction in the gas phase. The type of nanostructures produced can be determined by controlling synthesis parameters such as temperature, gas flows, substrates and the pressure of the system. The current study used CVD to produce a range of nanostructures and studied their gas sensing properties in terms of changes in their electrical conductivity in the presence of oxygen gas. The electrical parameters of ZnO changed when it absorbed the gases or reacted with the gases due to the high mobility of the conduction electrons in ZnO and its high chemical and thermal stability during the experimental conditions.

2. Experimental details

2.1. Materials

Zn shots (99.9999%, Alfa Aesar) with a diameter of 3–6 mm were used as the source material. Argon (99.9999%, Air Products) and oxygen (99.999%, Air Products) were used as the carrier and the active gas, respectively. For the synthesis of the ZnO nanostructures via CVD, alumina and silicon substrates were used. To clean the substrates, they

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http://dx.doi.org/10.1016/j.tsf.2013.05.155

were first washed with distilled water and ethanol and in diluted hydrochloric acid and sulphuric acid for 10 min at 50 °C. These substrates were then placed in a solution of hydrofluoric acid for 10 min at room temperature and dried with nitrogen gas.

2.2. Synthesis process and methods

A double-zone horizontal furnace with a quartz tube divided into two zones (hot and cold) was used to synthesise the ZnO nanostructures. One gram of the Zn shots was loaded in a quartz boat and placed in the hot zone of the furnace, and the silicon and alumina substrates were placed in the cold zone. The caps were closed and the rotary vacuum system was activated to ensure the exit of excess gas and ambient air. An oxygen:argon mixture was introduced to the reactor at a ratio of 1:8. The pressure in the reactor was maintained at 25 Pa before increasing the temperature.

The temperature of the hot zone was increased to 570 °C at the rate of 15 °C/min. The synthesis proceeded for 60 min. The ZnO nanostructures were synthesised by controlling the gas flow rates and the partial pressures of the oxygen, argon at 570 °C. The samples were removed from the furnace after cooling down normally to room temperature. A profilometer (ZEISS, Surfcom 1500) was used to measure the thickness of the samples collected at the same distance from the boat. The thickness of the layers was about 450–500 nm. The structures of the samples grown on the substrates were characterised with a field emission scanning electron microscope (FE-SEM, Hitachi, Model S-4160) operated at 15.0 kV. An X-ray diffractometer (Bruker, D8 Advance Model) with high-intensity Cu–Kα radiation ($\lambda = 1.5406$ Å) in the theta–2theta configuration was used for the X-ray diffraction (XRD) measurements.

The gas sensing measurements were performed in a quartz chamber consisting of a controllable heater, a gas flowmeter and a PC-based

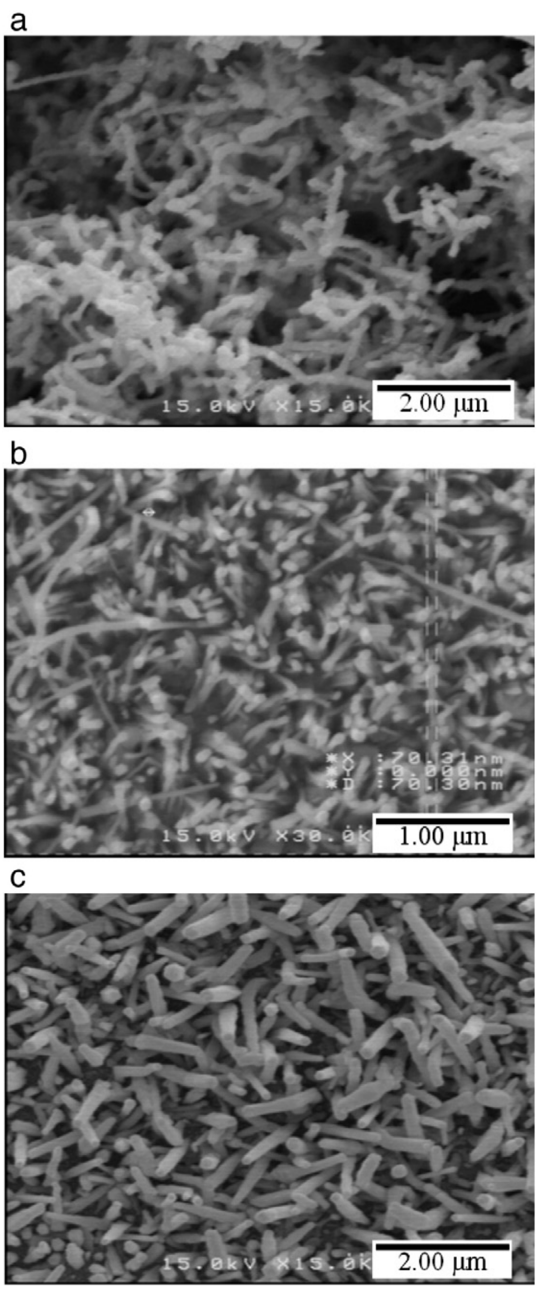

Fig. 1. SEM images of ZnO nanostructures synthesised on Si (100) with CVD method (a), (b) 1-D nanowires with 70–80 nm width and (c) 1-D nanorods with hexagonal wurtzite structure.

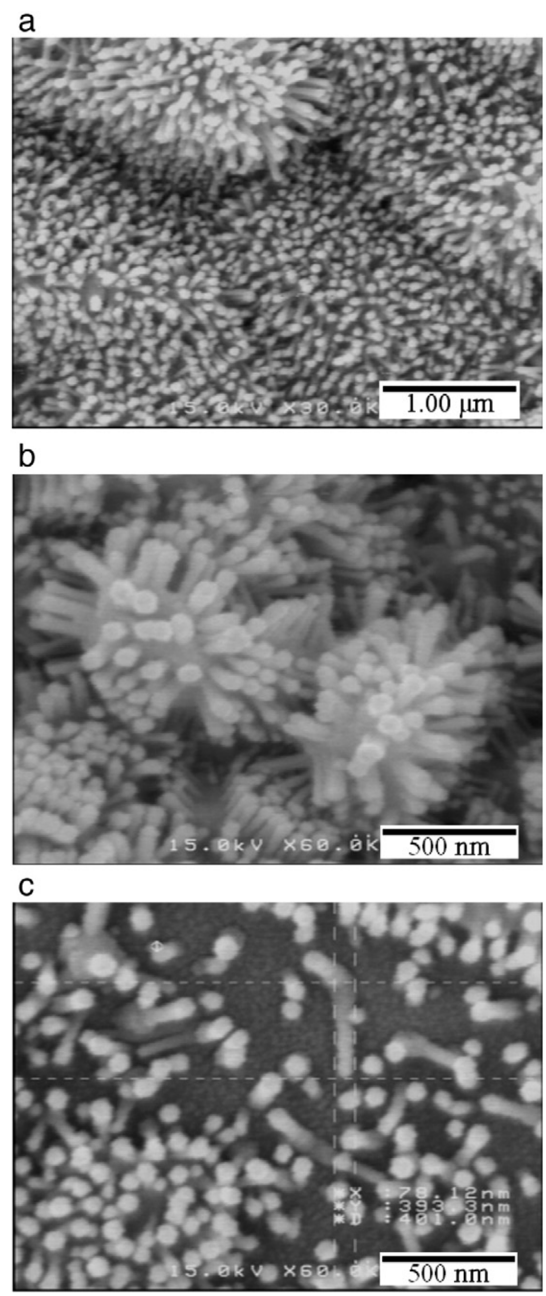

Fig. 2. SEM images of ZnO nanoflowers synthesised on alumina substrate with CVD method.