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Fabrication of three-dimensional network of ZnO tetratpods and its response to ethanol

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Abstract

A three-dimensional network of ZnO tetrapods was fabricated on a quartz substrate. The interconnected tetrapods, having legs with length of several μm and diameter in the 0.1–1 μm range, were synthesized via a simple thermal oxidation reaction. Zn powder was heated in a furnace at a temperature of 900 °C and was made to react with air and water vapor. The content of water vapor in air was found to control the adherence onto the substrate and the morphology of the deposited layers. The layers developed a grain structure or a porous structure made of interconnected tetrapods, depending on the content of water vapor in air. The network of tetrapods which was obtained for a small content of water vapor formed a highly porous layer with a high surface to volume ratio. The tetrapod network was tested as a gas sensing element by measuring changes in its electrical resistance upon exposure to ethanol. The responses to ethanol were investigated as a function of the layer temperature and the ethanol concentration. The optimum temperature of the tetrapod network layer was found to be 400 °C, at which ethanol concentration as low as 0.5 ppm was easily detected. The tetrapod network exhibited a 10-fold increase in sensitivity when compared with a ZnO polycrystalline thick film.

Keywords: Metal oxide semiconductor; ZnO; Nanostructure; Tetrapod; Gas sensor

1. Introduction

ZnO, a II–VI compound semiconductor, has found a multitude of applications as a result of its wide and direct band gap, its high exciton binding energy at room temperature, its ease of fabrication and its good safety record (for a review see, for example [1,2]). Synthesis of ZnO nanostructures [3–6] has revealed more fields in which this material can be utilized. ZnO nanostructures have potential uses in catalysis [7,8], in field electron emission [9], in gas sensing [10,11] and in hydrogen storage [6]. Tetrapods were the first nanostructures of ZnO to be synthesized [3], but it is only recently that their photoluminescence [5] and gas sensing properties [11] have been investigated. Other ZnO nanostructures such as nanorods [4] and nanowires [6,10] have been produced in the form of powder. Investigations into the gas sensing properties of these nanostructures were conducted on thick layers prepared from powder of tetrapods and nanowires [10,11]. The method used in the fabrication of a gas sensing element from nanostructured powder typically consists of the following three steps: (1) ultrasonic dispersion of the ZnO nanostructured powder in a solution (may contain an adhesive), (2) layer deposition by spray or spin coating of the dispersed material, and (3) drying/curing of the resulting layer. In this paper, we report the direct deposition on quartz substrates of thick layers consisting of interconnected tetrapods of ZnO forming a three dimensional network. The crystal structure and morphology of the thick layers are characterized, and the layer electrical responses to ethanol vapor are investigated as a function of the layer temperature.

2. Experimental

Thick ZnO layers were prepared via a thermal oxidation reaction in air from Zn powder (Nilaco, 99.9998% purity) placed in a quartz tube heated in a furnace using the experimental setup depicted in Fig. 1. The furnace temperature was controlled at ±1 °C and had a temperature gradient of 3 °C cm^{-1} at 1000 °C in the heating zone. The furnace temperature was set at 900 °C as it was found in our previous study [12] that the thermal oxidation reaction which starts at a temperature of ≃ 900 °C produces a high yield of nanostructures. The fabrication process did not rely on metal catalysts. In this study, the effects of air flow and its humidity content on the layer morphology are investigated. Four layers were fabricated under the conditions summarized in Table 1. Gas circulation in the furnace quartz tube was obtained either by thermal convection (quartz tube apertures kept open) or by forced convection (quartz tube aperture connected to an

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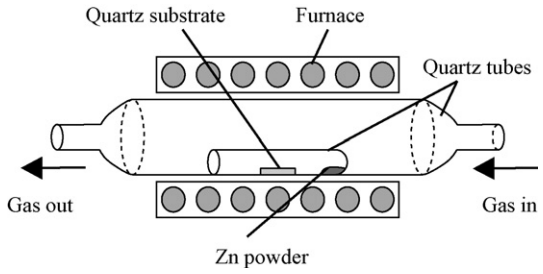

Fig. 1. Schematic of the experimental arrangement for the fabrication of the ZnO layers.

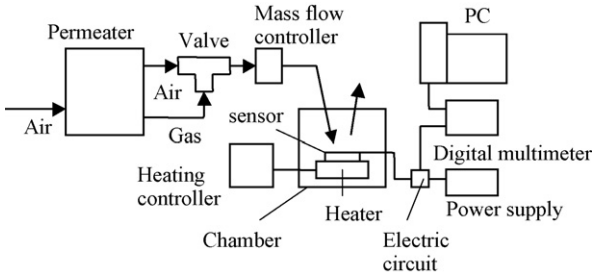

Fig. 2. Schematic of the measurement setup used to record gas responses.

air cylinder through a mass flow controller set at 100 standard cubic centimeters per minute). Humid air was obtained by three means (1) using ambient air, (2) using a humidifier, and (3) bubbling dry air through pure water. The amount of humidity in the circulated air was varied from nearly 0 to about 30 g m^{-3}. The reaction products consisted both of powder deposit and layer deposit. Powder samples obtained using thermal convection under low humidity conditions have been analyzed elsewhere [12]. The four fabricated layers, denoted A, B, C and D, with a texture resembling that of frosted glass diffuser were deposited on quartz substrates and used as sensing element in trace gas detection experiments.

The crystal structure of the fabricated layers was analyzed using X-ray diffraction on a MacScience instrument operating with the Cu Kα radiation and recording θ–2θ scans with a 0.02° resolution on 2θ. The sample morphology was investigated using a Scanning Electron Microscope (SEM Hitachi S2400 operated at an acceleration voltage of 20 kV). The samples were investigated for the presence of impurity with X-ray fluorescence analysis (Horiba, XGT5000). The structural analysis results of our ZnO layers were compared with those of a reference ZnO powder (Koch Chemicals, 99.999% purity).

The gas sensing characteristics of the fabricated ZnO layers deposited on quartz substrates (20 mm × 10 mm) were investigated using the experimental setup of Fig. 2. The variation in resistance of the thick ZnO layers upon exposure to ethanol vapor was recorded as a function of the layer temperature. The resistance of the sensing element was determined using a standard voltage divider circuit in which the sensing element was connected in series to a resistance of 1 MΩ and to a constant voltage source of 10 V. The material of the sensing element was found ohmic in the voltage range used in this study (1–10 V). The

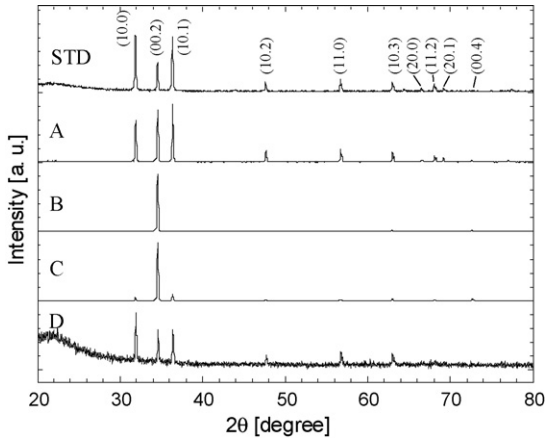

Fig. 3. X-ray diffraction data of fabricated ZnO layers (denoted A, B, C and D in the figure), together with that of the ZnO reference powder (denoted STD).

gas flow was generated by circulating pure air from a cylinder (air purity better than 100 ppb for the total hydrogenated carbon content) into a permeater (Gastec PD-1B-2, double line) containing a diffusion tube with liquid ethanol at a fixed temperature. All experiments used the same constant gas flow of 0.5 L min^{-1}. The gas concentration relative to pure air was controlled by varying the temperature and the size of the diffusion tube which contained the ethanol. The concentration of ethanol in air can be computed using the temperature, the partial pressure of the ethanol vapor, and the diffusion tube dimensions. Ethanol concentration varied in the range of 0.5–50 ppm. The second separate chamber of our double line permeater was used to generate a flow of pure air at the same temperature as that of the flow of ethanol vapor in air. The flow in the flask can be switched from pure air to ethanol vapor in air by using a valve. The flask where the sensing element was tested had a volume of 1 L. The temperature of the sensing element was controlled by a heater for use in vacuum systems, so that degassing from the heater itself was kept to a minimum. The temperature of the heater was calibrated against the temperature of the sensor element. Stainless steel and Teflon, both materials inert to the investigated gas mixtures, were used exclusively in connecting the different elements of the gas sensing setup (air cylinder, pressure regulator, permeater, mass flow controller and flask). Finally, the flask and the heater were baked for half a day prior to gas experiments so as to ensure minimum contamination.

3. Results

X-ray diffraction data for the four samples and the reference powder are shown in Fig. 3. The observed peaks of the reference ZnO powder sample could be indexed to the hexagonal wurtzite structure of the ZnO, with cell parameters of $a = 3.249$ Å and $c = 5.207$ Å [13]. Samples A and D exhibited very similar diffraction data to that of the reference powder sample, strongly

Table 1
Fabrication conditions of the ZnO samples

	Sample			
	A	B	C	D
Furnace temperature	900 °C			
Gas flow	Natural convection		100 sccm	
Water content	∼5 g m^{-3} (ambient air)	∼30 g m^{-3} (humidifier)	∼10 g m^{-3} (bubbling in water)	0 g m^{-3} (pure air)
Reaction time	30 min			
Process repetition	3	3	1	3

The masses of water vapor per unit volume of air computed from the measurements of air temperature and air relative humidity are given as estimates. For layers A and B, the deposition process was repeated so as to obtain a sheet resistance at room temperature less than 100 MΩ. For sample D, poor adherence on the quartz substrate was observed.