The Sensing Characteristics of ZnO Tetrapods Synthesized by Microwave Evaporation

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***Abstract*—ZnO tetrapods have been grown by an environmental microwave evaporation approach in air atmosphere without any use of organic solvents or precursors. The synthesized powder was characterized using X-ray diffractometry (XRD) and Field emission Scanning Electron Microscopy (FE-SEM). The grown ZnO tetrapods exhibited a noteworthy microstructure and phase formation of crystalline and pure structure. ZnO tetrapods were deposited on Pt electrode to be employed as ZnO tetrapods structure-based sensors, then, they were investigated at room temperature in the relative humidity ranging from 0.0 to 96.0%. The sensors have shown a significant response towards relative humidity starting from 30%. Cross-sensitivity was investigated with respect to N2O (150 ppm in helium) and methane (1000 ppm in helium). The ZnO tetrapods-based sensors were insensitive towards the interfering gases, indicating a potential applicability for humidity sensing purposes.**

***Index Terms*—Chemical sensor, Electron microscopy, Humidity measurement, Zinc oxide.**

I. Introduction

This paper is an extension of the work originally presented in the 2nd International Multidisciplinary Conference on Computer and Energy Science (SpliTech 2017) [1]. Recently, many researchers have paid attention and focus on humidity sensors for industrial applications, the end-user market, medical equipment, agricultural, as well as for safety and environmental control systems [2-4]. Humidity is the presence of water in a gaseous form in the environment (water vapor) while relative humidity can be defined as the amount of water vapor present in the atmosphere to the maximum amount of water vapor that atmosphere can hold [5]. Inorganic materials are employed in many potential applications due to their durability and robustness [6]. A wide variety of materials have been studied as sensing elements for humidity sensors and used for commercial devices, one of them is ZnO. It is an n-type semiconductor with a wide band gap energy of 3.37 eV and a large binding energy (60 meV) which makes ZnO nanostructures very interesting for gas sensing applications. Zinc oxide-based sensors are characterized by their stability, low cost and high sensitivity [7–9]. The main drawback of ZnO as a sensing material is that it is usually sensitive to several gases simultaneously and thus, lacks selectivity. So far, various strategies have been reported to improve sensing properties of metal oxide semiconductor gas sensors. To this aim, noble metals and n- or p-type metal oxides, as well as hetero-structuring of sensing materials have been investigated [10–12]. Over the last 10 years, ZnO nanostructures with variety of morphologies including nanorods, nanowires, nanofibers, nanolines, nanobelts, nanoneedles, nanoprisms, nanotubes, nano/microflowers, quantum dots, nanoparticles, nanofilms, sheets, and plates, nano/microspheres, nanopyramids and nanotetrapods have been synthesized and extensively studied for gas sensing applications [13].

In this work, we aimed to produce humidity sensors by using zinc powder and a microwave oven. The produced powder was then characterized by X-ray diffractometry (XRD) and high resolution scanning electron microscopy (HR-SEM). Additionally, the determinations of sensors' sensitivity towards relative humidity as well as their response towards two other possible interfering gases (N2O & CH4) were studied.

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II. Materials and Methods

A. Preparation of the Interdigitated Platinum Electrodes

Platinum conductor paste (ESL 5545, from Electro-Science, King of Prussia, PA, USA) was manually deposited by screen-printing technique onto planar α-alumina substrates (ADS-96 R, 96% alumina, Coors Tek, USA, 0.85 cm × 5 cm) by using a rubber squeegee through a 270 mesh steel screen. After drying overnight, the devices were heated at 980 °C for 20 min with a 2 °C/min heating/cooling ramp to optimize the electrical conductivity of the electrodes, according to the ink's manufacturer recommendations. Electrodes are about 400 microns thick and are spaced about 450 microns each other.

B. Preparation of the Sensing Film

ZnO tetrapods were grown on the previously prepared substrates, where microwave evaporation of Zn powder (99.9% purity, Alfa Aesar) in atmospheric air was carried out, without any use of organic solvents or precursors, the method was described by Abidov et al. [14].

C. Powder Characterization

The tetrapods were characterized by X-ray diffractometry which carried out on (D/MAX-2500 Rigaku Corp.) in 2θ range from 20 to 70 degrees using Cu Kα (0.15418 nm) radiation. Samples were deposited on glass for characterization using Jade 9 software. Field Emssion Scanning Electron Microscope (Zeiss Merlin, Oberkochen, Germany) was used to obtain morphology of samples and crystal structure.

D. Testing of the Humidity Sensors

Laboratory apparatus made of a thermostated chamber at 25°C in which RH could be varied from 0 to 96%. The experimental details have been previously reported [15]. RH values were measured by means of a commercial humidity and temperature probe (Delta Ohm DO9406, Padova, Italy). As water is a polarizable molecule and to avoid electrolysis due to the applied voltage, each tested sensor was alimented by an external alternating voltage (V = 3.6 V at the rate of 1 kHz) and then constituted a variable resistance of this electrical circuit. A 2000 Keithley digital multimeter (Beaverton, OR, USA) was used to measure the tension VDC at the output of the circuit. The sensor resistance was determined by substituting them, in the circuit, by known resistances and then plotting a calibrating curve R = f(VDC). The sensor response (SR), expressed in %, was defined as the relative variation of the starting resistance, compared with the resistance measured under gas exposure (eq. 1):

$$SR(\%) = 100\frac{|R_0 - Rg|}{R_0} \qquad (1)$$

Where R_0 and R_g are the starting resistance (in the absence of the test gas) and the gas exposed measured resistance of the sensors, respectively. Additionally, cross-sensitivity was investigated with respect to N_2O (150 ppm in helium) and methane (1000 ppm in helium) in 500 mL glass flasks in static tests during 10 minutes.

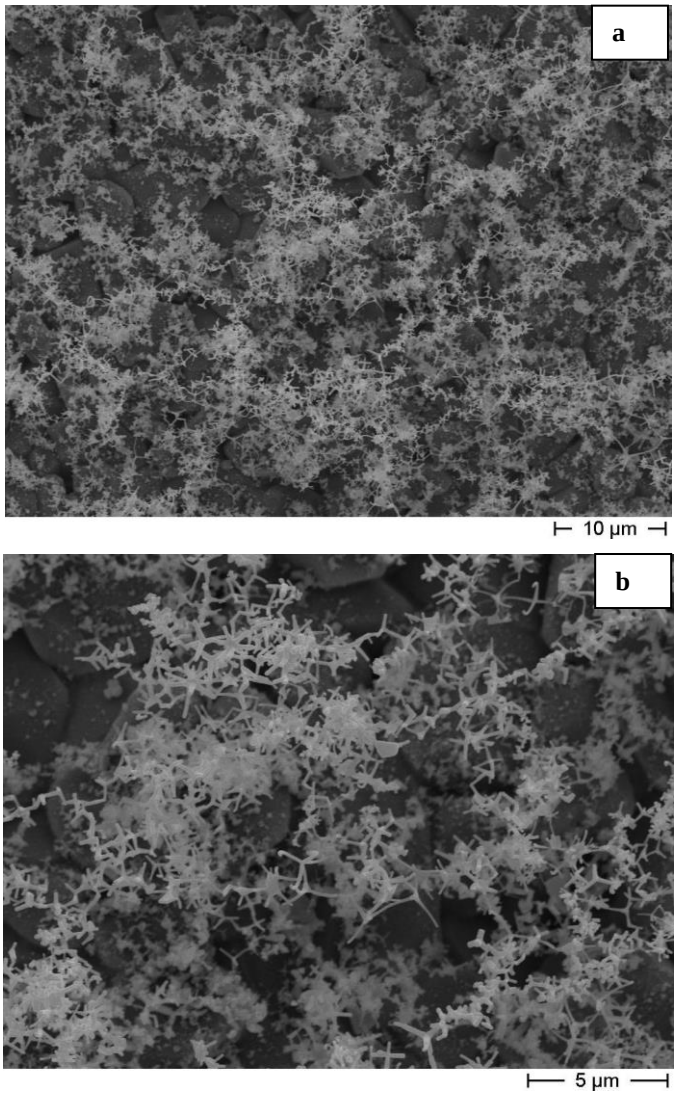
III. Result and Discussion

A. XRD Measurements

The test is performed to determine the crystallinity and purity of the investigated samples. The XRD pattern of ZnO nanostructures prepared by thermal evaporation in microwave oven contains sharp peaks which suggest that the product is highly crystallized. Strong XRD reflections at 36.2, 31.7 and 56.6 2θ degrees revealed hexagonal wurtzite structure with lattice parameters of a = 3.255 Å, c = 5.213 Å that which is in good agreement with JPCD no. 36-1451 which has lattice parameters of a = 3.249 Å and c = 5.206 Å. There are no reflection peaks observed in the pattern that can be assigned to metallic zinc, zinc compounds or other impurities which is a good indication of high quality ZnO crystals.

B. Field Emission Scanning Electron Microscopy (FE-SEM) Observation

Fig.1 shows a typical SEM of microwave oven grown ZnO tetrapod. The powder under investigation is considered to be colorless, transparent, contamination-free and crystalline which is in a good agreement with the abovementioned XRD measurements. The FE-SEM images show that the tetrapod exhibits a needle-like structure with a hexagonal tip where ZnO has well developed tetrapod form with conical tips. The average tip length is 0.7 micrometers which suggests a single-crystal structure with preferred growth direction. The average tertapods dimension can be strongly dependent on synthesis atmosphere and temperature which was analyzed in our previous study [14]. In general, the thickness of tetrapods increases according to some factors such as: the lower flow of the carrier gas, the higher source temperature and the higher oxidation temperature [16]. There is no anisotropy in the arm's length of the ZnO tetrapods was observed.



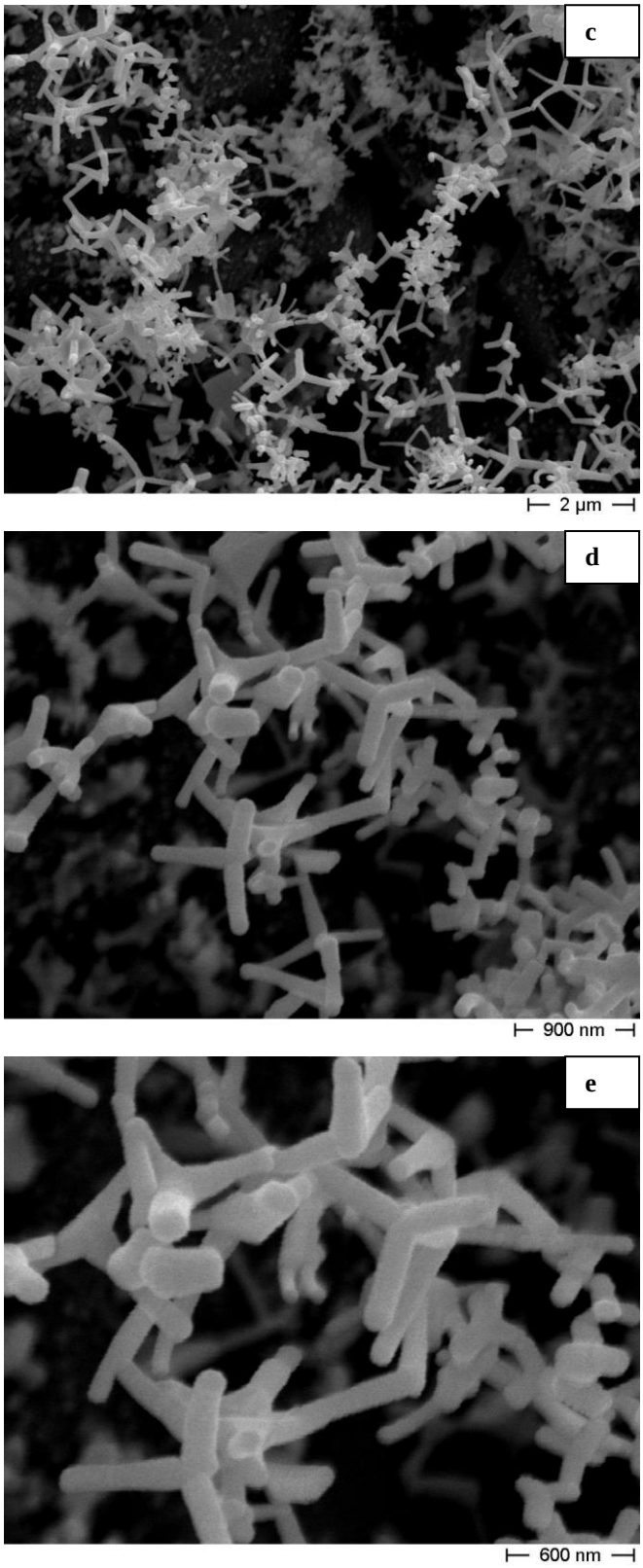


Fig. 1. (a, b, c, d, and e) FESEM micrograph of prepared ZnO tetrapods at different magnefications

C. Sensitivity towards Relative Humidity (RH)

It is well known in the literature that water molecules chemisorb on the available sites of the oxide surface by a dissociative mechanism to form two hydroxyl ions for each water molecule [17, 18]. These hydroxyl groups adsorb on the metal cations and the protons react with an adjacent surface O^{2-} group to form a second OH^- group. Once the group is formed, this chemisorbed layer is no more affected by surrounding humidity. Chemisorption is likely to be completed at a water pressure of the order of 0.1 Pa. At temperatures lower than 100 °C, subsequent layers of water molecules are physically adsorbed on the first hydroxyl layer when relative humidity increases. Water molecules in the succeeding physisorbed layers are singly bonded, dissociate to H_3O^+ and form a liquid-like network. The conduction mechanism depends on the surface coverage of adsorbed water. When only hydroxyl ions are present on the oxide surface, the charge carriers are protons, from hydroxyl dissociation, which hop between adjacent hydroxyl groups. When water is present, but surface coverage is incomplete, H_3O^+ diffusion on hydroxyl groups dominates, but proton transfer between adjacent water molecules in clusters also takes place. When the first physisorbed water layer is continuous, charge transport is governed by proton hopping between neighboring water molecules in the continuous film (Grotthuss chain reaction). This mechanism means that higher resistivity of the oxides is observed at low RH values [17, 18]. When the pores are cylindrical with one end closed, condensation occurs in pores with radii up to the Kelvin radius given by the Kelvin equation (eq. 2) [19], at given temperature and water vapor pressures:

$$\ln\left(\frac{P_s}{P}\right) = -\frac{\gamma M}{\rho R T r} \qquad (2)$$

Where, P and P_s are water vapor pressures in the surrounding environment and at saturation, respectively. γM, r, and ρ are the molecular weight, surface tension, pore's radius and density of water, respectively. Pores has a great influence on the process of sensitivity towards humidity as there is no effect for the pores above 100 nm on the contrary, water vapor starts to condense at room temperature in mesopores with a size of 2 nm around 15% RH and continues to around 100 nm under saturated atmosphere at this time, the electrical conduction is likely to occur through the continuous water layers within the porous sample [19, 20]. The results obtained of the sensor sensitivity towards relative humidity is illustrated in Fig. 2 where a noticeable response was observed at room temperature starting from 30% RH, even if impedance changes were already observed from 20% RH. The sensors resistance started from about 4-4.2 MOhm at 0% RH and decreased to 2.6-3.0 MOhm at 95% RH. The maximum sensor response was close to 35% under 95% RH, which may be attributed to the amount of tetrapods deposited onto the electrodes. It is worth mentioning that response of all the eight sensors was quite similar.

D. Cross-Sensitivity towards N_2O and Methane

Cross-sensitivity measurements, done by exposing the sensors to N_2O and methane, showed no significant change of their impedance values which is a good property of the sensing film in term of selectivity towards relative humidity.

The sensing mechanism of ZnO was investigated by impedance spectroscopy in [21] and results indicate that at lower humidity values, the adsorption process is chemically dominant due to limited number of adsorbed water molecules.

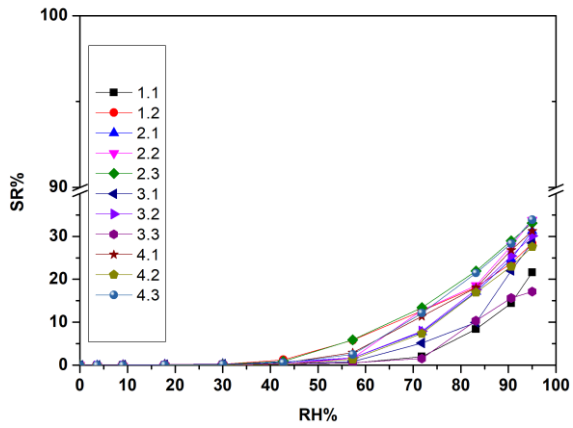


Fig. 2. Sensors' response to humidity at room temperature. Inset evidences the response below 30% RH.

Moreover, the chemisorbed molecules are not able to produce a continuous water layer on the surface of the sample. After that, at higher relative humidity values, the physical adsorption proportionally increases. This can be attributed to the idea that the number of ions contributing to the conductance also increases. Increasing humidity level keeps the surface wet. With the increasing number and then higher number of ions H_3O^+ contributing to the conductance (due to the Grotthuss mechanism), the impedance progressively decreases, as experimentally observed in this work. These adsorption phenomena are well known and fully described in literature [17].

IV. Conclusion

An environmental microwave evaporation approach was undertaken to grow ZnO tetrapods in air atmosphere without any use of organic solvents or precursors. FESEM observation show that the ZnO tetrapods were crystalline, pure and uniform in size and shape which is in a good agreement with XRD measurements. The humidity sensing properties of the ZnO tetrapods based sensors were investigated at room temperature in the relative humidity range from 0.0 to 96.0%. ZnO tetrapods exhibited a significant sensitivity response towards relative humidity starting from 30% relative humidity. Cross-sensitivity measurements on the prepared sensors showed no interference with N_2O and methane at room temperature. Further research shall be carried out on different interfering gases, recovery and response test for the prepared ZnO tertapods.

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