Synthesis and Characterizations of ZnO Nanorods Arrays and Mesoporous Films for Device Applications

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ABSTRACT

We present a novel aqueous-solution synthesis technique to obtain uniform ZnO nanorod arrays with good crystalline and mesoporous films. This technique was preferred for reasons related to economical and ecological advantages, low-temperature and the flexibility to tailor the nanorod sizes and shapes, density and properties by doping and solution conditions. Most attention is paid to an aqueous-based solution route that involves the formation of a nanorods by hydrolysis, condensation and complexation reactions of metal salts without any templates and seeds.

Scanning electron microscope (SEM), transmission electron microscope, Rutherford backscattering (RBS), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD) were used for materials characterization.

The high sensitivity and stability of sensors made from ZnO nanorods and nano/mesoporous films demonstrate the potential for developing a new class of nanosensors and nanodevices for industrial applications.

Keywords: ZnO, nanorods, mesoporous, nanosensor.

1 INTRODUCTION

The synthesis and characterization of one-dimensional (1-D) nanoarchitectures (nanorods, nanowires and nanotubes) have received tremendous interest due to their unique physiochemical properties and their novel potential applications in novel nanodevices [1-4]. Significant efforts have been concentrated on semiconducting oxides such as SnO_2, TiO_2, WO_3, CeO_2, Cu_2O, ZrO_2, and ZnO. Among them zinc oxides – key functional materials – are especially interesting since they have important applications in a wide area of high-tech applications such as nanoscale electronics, optoelectronics, magnetoelectronics, transducers, sensing systems, and biomedical applications.

The small dimension of the ZnO nanostructures promises increase in device packing density, decrease in power consumption, and an increase in sensitivity in chemical sensing applications. Gas sensing with nanorods and nanowires are performed by monitoring of the electrical resistance change when exposed to a specific gas. 1D nanoarchitectures have very small radii with a larger surface-to-volume ratio that is very susceptible to altered electrophysical properties by chemisorption in the chemical environment. When the diameter becomes compatible to the Debye screening length, chemisorption induced surface states effectively alter the electronic structure of the system.

Synthesis and study of nanorod based solar cells and chemical sensors are quickly directed towards developing alternative, lightweight, flexible nanodevices for wide area of commercial applications [1-6]. Many research papers have been published in recent years, in the area of dye sensitized solid-state solar cells in particular, which is currently the most stable and efficient excitonic solar cell for large-scale solar energy conversion [6-7]. One-dimensional ZnO nanorods, with their high carrier mobility serve as the direct conduction pathways for the excitons. Also it is of importance to synthesize a porous structure with a high interfacial area to allow the creation of a 3-dimensional interpenetrating network between the semiconductor/dye and the solid-state electrolyte.

Much effort has been devoted for the preparation of 1D ZnO nanoarchitectures [1-8] using various methods, including vapor-liquid-solid (VLS), vapor-solid (VS) [9] processes, metal-organic chemical vapor deposition (MOCVD) [2], chemical vapor deposition [10], solution-liquid-solid growth in organic solvents [11], and a template-based method [12].

In this work we present a novel aqueous-solution synthesis technique to obtain size-controllable and uniform dimensional ZnO nanorod arrays with good crystalline and mesoporous films on glass and conducting substrates. The change of the morphology, structure orientation and composition of the ZnO is controlled through solution conditions.

2 EXPERIMENTAL

The conventional method to synthesize ZnO nanorods is undesirable, due to high-energy consumption, complicated and severe conditions. At the same time the use of catalysts or template brings impurities into the final nano-structures, which influence on the adherence and the purity of ZnO nanoarchitecture, on their electrical, light emission and sensitivity properties. Thus, the fabrication of ZnO nanorods with high purity and at low cost requires a simple

and low-temperature method. Our most attention is paid to an aqueous-based solution route that involves the formation of nanorods and nanowires by hydrolysis, condensation and complexation reactions of metal salts without any templates. Here, we report that the hydrolysis is effective to make ZnO nanorods from a zinc sulfate precursor at a low temperature (85-95°C).

Before the growth process, the glass substrates were cleaned in dilute HCl (20%) solution for 10 min and then rinsed in de-ionized (DI) water (~ 18.2 MΩ·cm). Then the substrates were rinsed in ethanol acetone (1:1) mixture, jet of DI water, and dried in a nitrogen flux. Solutions of $SnCl_2$/HCl were used for the sensitization, wets to the surface of the substrate and present the surface for deposition.

Nanoarchitectured zinc oxides were synthesized using zinc sulfate and ammonia hydroxide as precursors for fabrication of single crystal ZnO nanorods. Adding Al_2SO_4 in solution greatly accelerates the hydrolysis process. First, 0.1-0.5 M of $Zn(SO_4)7H_2O$ and 0.001-0.005 M of Al_2SO_4 are dissolved in 100 ml de-ionized water. Then 100ml ammonia solution (25%) was added. The solution is placed on the heater for determined time. The substrates were immersed horizontally in the solutions.

Increasing the temperature of the zinc complex solution promote dissociations, leading to the controlled supersaturation of the free Zn ion. Experimental results confirm the possibility to tailor morphologies of ZnO nanoarchitectures by limiting the concentration of zinc ions or hydroxide in the presence of large excess of the other. Size of ZnO nanorod could be controlled by the solution conditions – precursor concentration, reaction time and temperature.

Complex solution (40 ml) and DI water of 20 ml were introduced into an autoclave and was maintained in an oven at 85-95 °C for 15-40 min. After the hydrothermal reaction, the autoclave was cooled to room temperature. The substrates with grown products was washed and dried at 200 °C for 5 min.

With this multi-step growth procedures ZnO nanowires of more than 10 µm length can be synthesized.

The phase structure of these deposited materials were studied using a Rigaku 'D/B max' X-ray diffractometer (XRD) equipped with graphite monochromatized CuK_α radiation (λ=1.54178 Å) and operating conditions of 30 mA and 40 kV at a scanning rate of 0.02°/s in the 2*q* range of 10-90°. The composition and morphologies of ZnO films were characterized by Rutherford Back Scattering (RBS) General IONEX 1.7 MV Tandetron, energy dispersion X-ray spectroscopy (EDX) and scanning electron microscope (SEM) VEGA TS5130MM. These investigations confirmed that these nanorods arrays are highly crystallinity with regular rods distributed throughout the substrate surface. This morphology is considered to play a vital role in the nanodevices applications.

The electrical characterizations were performed using two-point probe method. The sensor characterization was performed in a closed quartz chamber connected to a gas flow system. The concentration of test gases ethanol or hydrogen was measured using pre-calibrated gas flow meters. The temperature of the sensor element was controlled between 25 ºC and 250 ºC. A computer with suitable interface handled all controls and acquisition of data.

3 RESULTS AND DISCUTIONS

3.1 XRD, SEM and EDX analyses

Fig . 1 shows the X-ray power diffraction pattern (XRD) of the ZnO nanorods. All the strong diffraction peaks of investigated samples are quite similar to those of bulk zinc oxide. The diffraction peaks in the pattern can be readily assigned to pure hexagonal phase ZnO (wurtzite-type, space group: $P6_3mc$(186); with calculated cell constants of a=0.3249 nm, c=0.5206nm) which are in agreement with the JCPDS card for ZnO (JCPDS 036-1451).

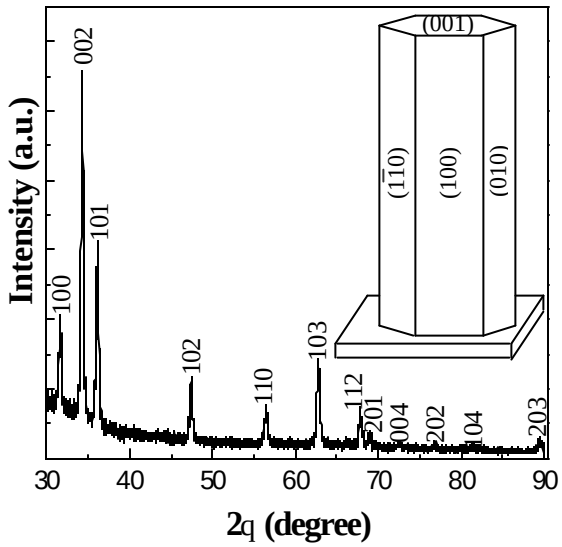

Figure 1: XRD pattern of the ZnO nanowires and nanorods synthesized by aqueous-solution method.

The strong and sharp intensity of the peaks relative to the background signal demonstrates high purity of the ZnO hexagonal phase of the products and highly crystallinity of the samples. The characteristic peaks of $Zn(OH)_2$ was not observed, and no diffraction peaks except ZnO was found, which indicated a single phase hexagonal ZnO without other phases. The nanocrystallites are oriented along the *c* axis, [002] direction. The modification of ZnO crystal structure was not observed.

For surface morphology and estimation of the film thickness, SEM technique has been used. The overall morphology of the ZnO samples is shown in Fig. 2 (a),

which indicates the obtained product consisted of nanorods array with an average diameter of 200 nm.

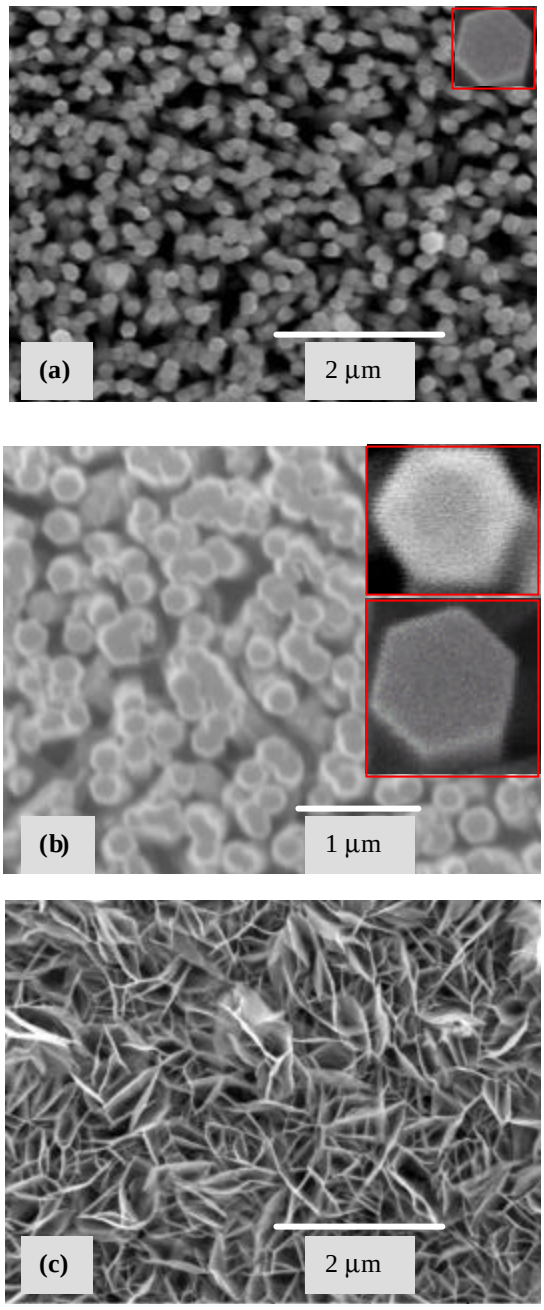

Figure 2: The SEM images of the zinc oxide nanorods chemically grown from: (a) (0.25 M) $ZnSO_4$ and ammonia aqueous bath on the glass substrate; (b) magnified image of (a) and inset 0.25 µm image; (c) $ZnSO_4$:Al_2SO_4:[NH_4OH] (0.10 M:0.002 M:0.5 M) aqueous bath.

The magnified SEM secondary electron image shown in Fig. 2 (b) clearly displays hexagonal nanorods on glass substrate. A close observation reveals that the individual ZnO nanorod has a hexagonal shape with a diameter of about 200nm and length up to 2 µm for sample grown during of 20 min.

Using EDX and RBS, the formation of the ZnO was confirmed. The Zn:O ratios in nanostructures were analyzed by EDX measurement and were found to be 1:1 atomic ratio in all the samples.

The impact of the rapid thermal processing on the surface morphology of the deposited nanoarchitectures has also been investigated. In the 100 – 700ºC temperature range the films surface morphology does not differ from that of the as-grown ZnO (see Fig. 2). For the annealing temperature higher than 800ºC the edges of ZnO nanorods start to melt. In Fig. 2 (c) are presented SEM image of the nano/mesoporous film obtained by aqueous solution.

3.2 Electrical properties

Irreversible changes in the electrical characteristics have been observed when the ZnO were post-growth rapid thermal processed at temperatures higher than 300 ºC for 2 min duration. In the temperature range of 650 - 750 ºC, improvement of the quality and stability of the ZnO sensor samples has been observed. The stability measurement has been carried out for one month period and it was determined that the ZnO-based sensor elements have higher conductance stability, which ensures a stable zero level for gas sensor applications.

3.3 Gas sensing properties

For gas sensing characterizations, the sensor elements were placed in a 1000 cc gas chamber. The zinc oxide nano/mesoporous films and nanorods were used to detect ethanol or hydrogen at room temperature and up to 250°C in the concentrations of 100 ppm and 500 ppm, respectively. The gas was introduced in the test chamber 30 min after the sample. It was found that resistance change $\Delta R = \left| R_{gas} - R_{air} \right|$ increased with gas concentration. The sensitivity of the sensor element to gases was calculated according to the formula:

$$S = \frac{100 \cdot (\left| R_{gas} - R_{air} \right|)}{C \cdot R_{air}}, \qquad (1)$$

where C is the gas concentration, R_{gas} and R_{air} are the electrical resistance of the sensor element in the presence of gas and in air, respectively.

The sensitivity to 100 ppm ethanol and 500 ppm hydrogen of the ZnO nano/mesoporous films and ZnO nanorods sensor elements are shown in Fig. 3.

The sensitivity is increased for ZnO nano/mesoporous and attained a maximum of 130 %/ppm for ethanol (see Fig. 3(a,c)). The resistivity on the other hand, was restored to the 10 % original level within 3 min for sensors annealed 2 min at 700°C. Therefore, a annealing temperature in the

range 650-700°C and a duration of 2 min was desirable for these elements from the viewpoints of sensitivity. For instance, it has been observed that high annealing temperature leads to better sensor response. The large surface-to-volume ratio seems to play a key role on the detection sensitivity.

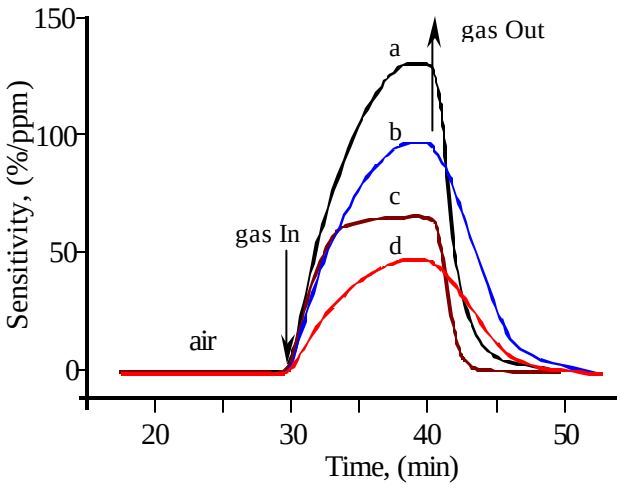

Figure 3: The response of the: (a) ZnO nano/mesoporous films to ethanol; (b) ZnO nano/mesoporous films to hydrogen; (c) ZnO nanorods array-based sensor to ethanol and (d) to hydrogen at a working temperature of 20 °C.

Fig. 3 (b,d) shows the sensing characteristics at 20 °C measured in 500 ppm hydrogen ambient. This is a clear demonstration of the higher sensitivity of nanomesoporous films to the presence of hydrogen in the ambient. The use of Al in ZnO mesoporous films increase sensitivity.

4 CONCLUSIONS

In this study, the aqueous-solution deposited size-controllable ZnO nanorods, nano/mesoporous film for device applications were synthesized and investigated. The merit of this new technology is in the simplicity of the process, economy in energy, short duration, accessible auxiliary materials and nonsophisticated equipment. Size of ZnO nanorod could be freely modified by controlling the aqueous solution regimes – precursor concentration, reaction time and temperature.

We demonstrated that the morphological, electrophysical and sensing properties of zinc oxide could be controlled through growth regimes, doping and post-growth treatment conditions.

We have demonstrated the ZnO nanorod sensor toward ethanol and hydrogen gas. The sensitivity is higher for the mesoporous sensor elements rapid thermal processed at 700°C, 2 min. Further investigations with different dopants and second components in ZnO nanorods and mesoporous films obtained by aqueous solution techniques and nano-devices are underway.

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