Gas sensor properties of ZnO nanorods grown by chemical bath deposition

Gisane Gasparotto[1, 2, a*], Talita Mazon[1, b], Gisele Gasparotto[2, c], Maria Aparecida Zaghete[2, d], Leinig Antonio Perazolli[2, e], José Arana Varela[2, f]
1- Centro de Tecnologia da Informação Renato Archer – CTI, Campinas, SP, Brazil
2- Instituto de Química, UNESP- Araraquara, SP, Brazil.
[a]gigasparotto@hotmail.com, [b]talita.mazon@cti.gov.br, [c]gisegasp@gmail.com, [d]zaghete@iq.unesp.br, [e]leinigp@iq.unesp.br, [f]varela@iq.unesp.br

Keywords: ZnO, nanorods, chemical bath deposition, gas sensor

Abstract. The present work shows a study about the growing of ZnO nanorods by chemical bath deposition (CBD) and its application as gas sensor. It was prepared ZnO nanorods and Au decorated ZnO nanorods and the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and gas sensing response measurements. The results obtained by XRD show the growth of ZnO phase. It was possible to observe the formation of uniform dense well-aligned ZnO nanorods. The results obtained also revealed that Ag nanoparticles have decorated the surface of ZnO nanorods successfully. Au nanoparticles with diameter of a few nanometers were distributed over the ZnO surface nanorods. The gas sensing response measurements showed a behavior of n type semiconductor. Furthermore, the Au-functionalized ZnO nanorods gas sensors showed a considerably enhanced response at 250 and 300 ^{o}C.

Introduction

Zinc oxide (ZnO) is a n type semiconductor with wide direct bandgap (3,37eV) and large excitation binding energy (60 meV), besides of its excellent chemical, thermal and mechanical stability. Due to its excellent properties, higher piezoelectric constant and possibility to modify the electrical conductivity, ZnO nanostructures have been considered potential candidates for solar cell[1-2], gas sensor[3-6], photocatalyses[3, 6], UV laser[7], field emission displays[8], light emission diodes (LED)[9] applications between others.

ZnO nanostructures have attracted considerable attention for using as sensor gas. Sensing mechanism of ZnO generally involves the chemisorptions of oxygen on the oxide surface with variation of conductivity of the ZnO. Thus, when a ZnO gas sensor is exposed to reactive gases ambient, gas molecules are adsorbed on the surface of ZnO and then extract electrons from the surface, resulting in the increase of the depletion layer[10].

Recently, one-dimensional (1D) ZnO nanostructures such as nanorods, nanowires, nanotubes and nanobelts have attracted considerable attention due to their unique physical properties that strongly depend on their size andmorphologies. In addition, 1D ZnO nanostructures are excellent candidates for chemical sensing applications because of their ultrahigh surface-to-volume ratio, high sensitivity and short response time to the chemical surroundings.

Extensive efforts are currently devoted to the controlled synthesis and characterization of ZnO nanostructures. Several different methods for the fabrication of ZnO nanorods and arrays have been used, including hydrothermal synthesis, vapour–liquid–solid, vapour–solid processes, chemical vapour deposition, metal–organic chemical vapour deposition, solution-liquid–solid growth in organic solvents, and template-based process. Most of these synthesis techniques are complicated, time and energy consuming, and not environmentally friendly. For commercial use of ZnO nanorod arrays for unique nano/microdevice applications, a simple, inexpensive and bio-safe synthesis process is required.

Chemical bath deposition (CBD) is a simple and cheaper technique used to synthesize ZnO nanostructures at lower temperatures. The chemical bath may occur in aqueous solution and the mechanism of ZnO crystals formation involves crystallization, dissolution and recrystallization[11]. In this technique, the crystal morphology is influenced by experimental conditions, which include the chemical species in solution (ligand, pH, ionic force), the supersaturation level, the temperature and type of the substrate[12].

In this paper, pure and Au decorate well-aligned ZnO nanorods arrays were synthesized on Al_2O_3 substrates for detection of hydrogen gas. The proposed approach is promising for fabricating chemical sensors based on the ZnO nanorods arrays.

Experimental

Firstly, it was deposited a zinc nucleation layer on Al_2O_3 substrates prior to CBD by using zinc citrate solution and sin coating. The zinc citrate solution was obtained by using the polymeric precursors method, that consisted on mixing citric acid $C_6H_8O_7.H_2O$, 99.5 %), ethylene glycol ($C_2H_6O_2$, 99 %) and zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, 98 %) in the ratio 1:4:16, respectively under heat and stirring.After deposition, the samples were heated treatment at 550 ^oC for 4 hours.

Secondly, it was occurred the growth of ZnO nanorods by chemical bath deposition (CBD). During the CDB, potassium hydroxide solution and zinc acetate were mixed in a teflon cup and the synthesis was performed under stirring and heat at 90 ºC for 1 hour.

For decorating the ZnO nanorods wit Au nanoparticles, the samples obtained by CDB were sputtered with Au for 5 seconds. After that, it was made a heating treatment at 400 ºC for 1h.

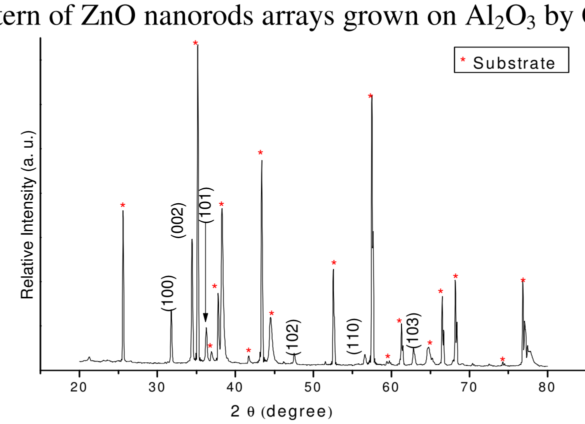
The X-Ray diffraction patterns of the samples were obtained by using a diffractometer Rigaku2000 provided with monochromic graphite irradiation. The morphology and crystal structure were investigated by high resolution scanning electron microscopy (FEG-SEM) and X ray energy dispersive by using a JEOL – JSM 7500F.

For gas-sensor measurements, the samples were put on a test chamber. High purity hydrogen gas was passed through the test chamber at different concentrations (0.2 to10 %) controlled by a mass flow controller. An air synthetic flux of 150 sccm was used as pattern line. The sample resistance of the pure or Au decorated ZnO nanorod sensor was measuring using a high voltage source (Keithley, modelo 237). The gas sensor measurements were realized at 250 ^{o} and 300 ^oC.

Results and discussion

The Fig.1 shows the XRD patterns of ZnO nanorods arrays grown on Al_2O_3 substrate. The diffraction peaks if Fig.1 can be indexed to a hexagonal wurtzite structure according to the standard JCPDS (36-1451). The sharp diffraction peaks demonstrate that the as-synthesized ZnO nanords have high crystallinity. The significantly higher intensity of the (002) diffraction peak indicates that the CBD-assisted grown ZnO rods are preferentially oriented in the (001) direction. Trace amounts of other diffraction peaks such as (100), (101), (102) and (110) do not mean that some ZnO nanorods were grown in those directions, but c-axis ZnO nanorods were so randomly orientated that these diffraction planes happen to meet Bragg's law.

Figure 1: XRD pattern of ZnO nanorods arrays grown on Al_2O_3 by CBD at 90 ºC for 1 h.



Typical FE-SEM images of the vertically well-aligned ZnO nanorod arrays pure and decorated with Au nanoparticles are shown in Fig.2 and Fig.3. It is possible to observe, Fig.2 that the grain size and boundaries of the Al_2O_3 substrate influenced on the growing of ZnO nanorods arrays. However, a high magnification image as showed on Fig.2.b reveals that each individual ZnO nanorod has well-developed hexagon facet and is well-perpendicular aligned to the substrate and that the ZnO nanorods arrays are uniforms. The presence of Zn nucleation layer on the substrate is necessary for obtaining well-perpendicular aligned nanorods. According to Wang et al.[13], the ZnO nucleation layer attract the Zn^{2+} and OH^- ions on the surface of the substrate and acts as a active site for growing vertically aligned nanorods.

Figure 2: FE-SEM images of ZnO nanorods surface obtained by CDB at 90 ºC for 1 h.

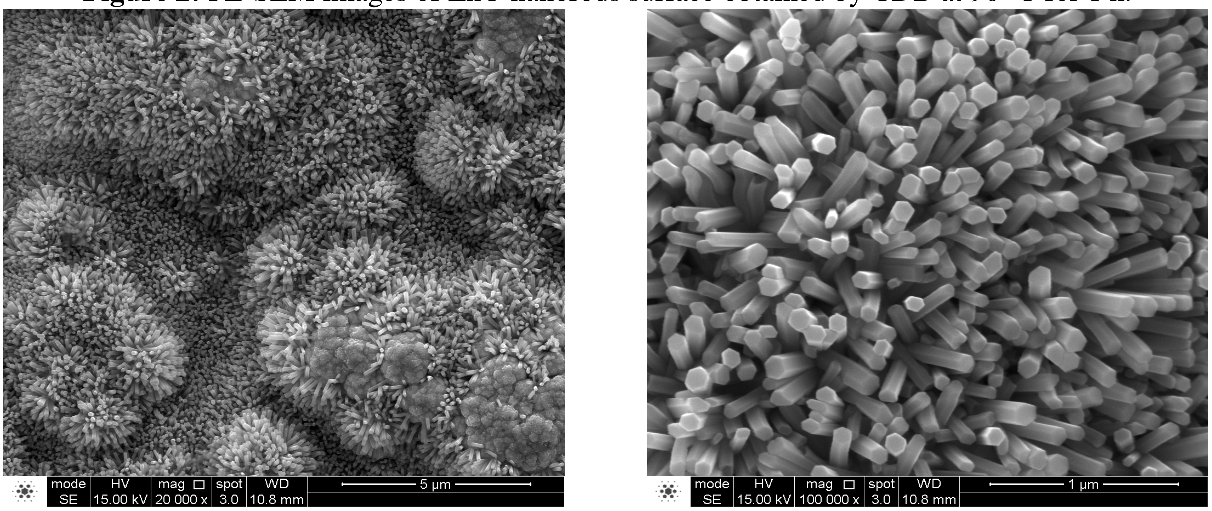
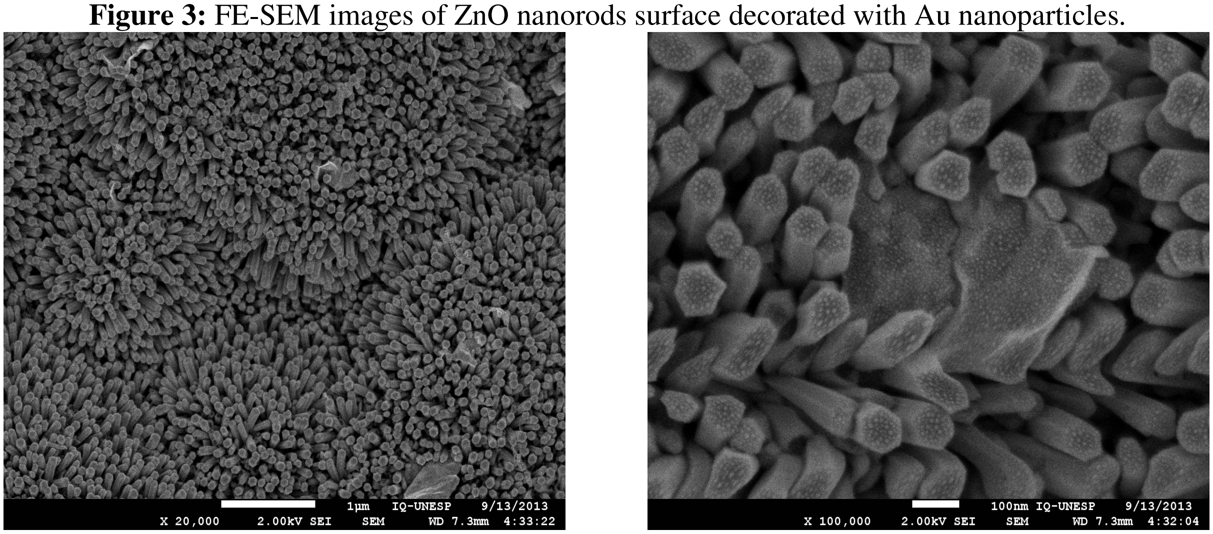


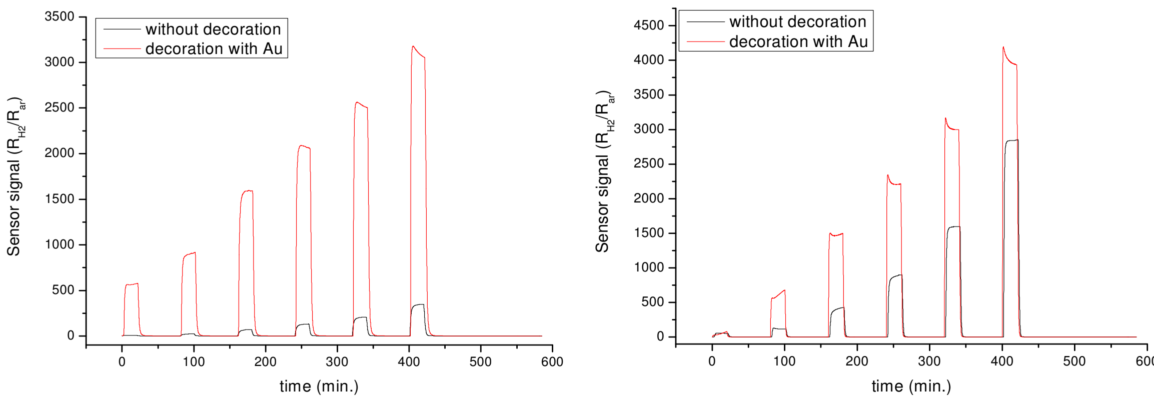
Fig.3 shows the images obtained for Au decorated ZnO nanorods arrays. The results obtained revealed that Ag nanoparticles have decorated the surface of ZnO nanorods successfully.

Figure 3: FE-SEM images of ZnO nanorods surface decorated with Au nanoparticles.



In order to practically test the ZnO nanorod arrays gas sensor, its sensing properties were investigated for different hidrogen concentrations at 250 ° and 300 °C. Fig.4 shows the change in resistance as a function of time with different hidrogen concentrations ranging from 0.2 to 10 %. It is observed that as the hydrogen concentration increases the sensor signal is higher. This means that the sensitivity of the nanorods arrays depends on H_2 concentration. In this case, the H_2 acts as electron donor. In this way, some molecules are adsorbed on nanorods surface and donate electrons when the ZnO nanords are exposed on H_2. As the H_2 concentration increase, the number of electrons transferred from the gas molecules to nanostructures surface increase and the electrical resistance of the sensor is lower. This behavior (the decrease of the electrical resistance on the presence of reducer gas) is typical of n-type semiconductor material. Then, higher sensor response is obtained when the ZnO nanorods are exposed at higher H_2 concentration. Another observation that can be obtained from Figure 4 is that the Au-decorated ZnO nanorods showed a significant improvement in the response of the nanorods, specially at 250 ^{o}C. This can be explained by the fact that the metal increases the sensitivity of the material due to chemical and/or electronic interactions and reduces the temperature required for optimal response of the gas[10].

Figure 4: Responses of ZnO nanorods arrays and Au-decorated ZnO nanorods arrays as function of time to H_2 gas at different concentration (a) 250 º and (b) 300 °C.



(a) (b)

Conclusion

Uniform well- perpendicularly aligned ZnO nanorods was grown by CBD. Au nanoparticles with diameter of a few nanometers were distributed over the ZnO surface nanorods after a sputtering deposition. The sensor gas measurement showed that ZnO nanorods have a behaviour of n-type semiconductor and the sensibility of the sensor depending on H_2 concentratio and temperature of operate. For obtaining a better response of the sensor, it was necessary to decorate the ZnO nanorods surface with Au nanoparticles.

References

[1] N. Shojaee, T. Ebadzadeh, A. Aghaei, Effect of concentration and heating conditions on microwave-assisted hydrothermal synthesis of ZnO nanorods, Mater. Charact., 61 (2010), 1418-1423.

[2] S. He, M. Zheng, L. Yao, X. Yuan, M. Li, L. Ma, W. Shen, Preparation and properties of ZnO nanostructures by electrochemical anodization method, Appl. Surf. Sci., 256 (2010), 2557-2563.

[3] S. Ma, R. Li, C. Lv, W. Xu, X. Gou, Facile synthesis of ZnO nanorods arrays and hierarchical nanostructures for photocatalysis and gas sensor applications, J. Hazard. Mater., 192 (2011), 730-740.

[4] Y. Cao, X. Hu, D. Wang, Y. Sun, P. Sun, J. Zheng, J. Ma, G. Lu, Flower-like hierarchical zinc oxide architecture: Synthesis and gás sensing properties, Mater. Lett., 69 (2012), 45-47.

[5] P. Rai, H. M. Song, Y. S. Kim, M. K. Song, P. R. Oh, J. M. Yoon, Y. T. Yu, Microwave assisted hydrothermal synthesis of single crystalline ZnO nanorods for gas sensor application, Mater. Lett., 68 (2012), 90-93.

[6] A. Wei, L. Pan, W. Huang, Recent progress in the ZnO nanostructure-based sensors, Mater. Sci. Eng. B, 176 (2011), 1409-1421.

[7] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Room-temperature ultraviolet nanowire nanolasers, Sci., 292 (2001), 1897-1899.

[8] N. S. Ramgir, D. J. Late, A. B. Bhise, M. A. More, I. S. Mulla, D. S. Joag, K. Vijayamohanan, ZnO multipods, submicron wires, and spherical structures and their unique field emission behavior, J. Phys. Chem. B, 110 (2006), 18236-18242.
[9] J. J. Berry, D. S. Ginley, P. E. Burrows, Organic light emitting diodes using a Ga:ZnO anode, Appl. Phys. Lett., 92 (2008), 1933041-1933043.
[10] M. Tiemann, Porous Metal Oxides as Gas Sensors, Chem. Eur. J., 13 (2007), 8376-8388.
[11] S. I. Issler, C. C. Torardi, state chemistry and luminescence of X-ray phosphor, J. of Alloy. Compd., 229 (1995), 54-65.
[12] K. Govender, D. S. Boyle, P. B. Kenway, P. O'Brien, Understanding the factors that govern the deposition and morphology of thin fims of ZnO from aqueous solution, J. Mater. Chem., 12 (2004), 2575-2591.
[13] N. Wang, Y. Cai, R. Q. Zhang, Growth of nanowires, Mater. Sci. Eng. R, 60 (2008), 1-51.