ZnO nanorods decorated with Au nanoparticles applied as gas sensors

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ABSTRACT

Zinc oxide (ZnO) is an n-type semiconductor that have been considered as potential candidate for solar cells, gas sensors, photocatalysts, UV laser, field emitter, light emitting diodes (LED) application. ZnO nanostructures can be easily obtained with different morphologies by chemical and physical methods. Recently, researchers have demonstrated that the incorporation of Au nanoparticles into ZnO nanorods exhibited interesting characteristics, including bandgap emission enhancement, plasmonic effects, electric reliability reinforcement and biosensing improvement. In this paper, vertically aligned ZnO NRs were grown on Al_2O_3 substrate by using a simple wet chemistry method. Au NPs of 5 nm to 20 nm were deposited on ZnO NRs surface by sputtering. Sensors measures using H_2 as analyte gas show a n-type semiconductor behaviour for all the samples and the sensitivity depends of gas concentration and operation temperature.

Keywords: ZnO nanorods, Au nanoparticles, gas sensors

1 INTRODUCTION

ZnO is an n-type semiconductor that can be synthesized with different morphologies by different chemical and physical methods. Among them, it is possible to obtain nanotubes [1], nanoflowers [2], nanowires [3], nanospheres [4], nanosheets [5], nanorods [6] and others. 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 where the mechanism of ZnO crystals formation involves the phenomenon of crystallization, dissolution and recrystallization [7].

ZnO nanostructures have come to prominence due to low toxicity, good heat stability and high electron mobility, that makes their use promising in sensor devices with better performance and friendly-enviroment.

In a gas sensor occurs the interaction between the gas and the sensor material by alteration of the physical-chemical properties of materials[8]. The ZnO gas sensing mechanism is based on changes of the eletrical conductivity with the reversible chemisorption process of reactive gases on oxide surface. The mechanism responsible by sensitivity of the semiconductor for the gas is driven by the electrical and chemistry activities of the oxigen vacancies on oxide surface [9].

Recent researches have been performaded aiming to obtain more efficient dettection by functionalizing the nanostructures surface with metals, such as Au, Ag, Pt or Pt. Results have been showed that there are two mecanisms to explain the improved of the performance in the presence of the metal[10]. The first is the eletronic mecanism where metal nanoparticles act as electron acceptor on oxide surface, that contributes to increase the depletion layer. Then, a change of the resistence of the material can occur when the oxide surface is decorated with a metal. The second mechanism is chemical, wherein the metal catalytically active the dissociation of molecular oxygen and atomic products diffuse on nanostructures. This process increase both the amount of oxygen vacancy filling and the rate that this filling occur. As a consequence, the removal of electron of metal-decorated ZnO nanostructures is higher than compared with the ZnO nanostructures without the presence of metal.

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.

2 MATERIALS AND METHODS

A solution of zinc citrate was prepared by Pechini method [11], which was deposited by spin-coating on the Al_2O_3 substrate. After that, the film was heated treatment at 400 ºC for 3 h. During the growing of the nanostructures, 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. Two samples were prepared: one with pure nanorods and the second with Au decorated ZnO nanorods. Aiming to decorate the ZnO nanorods surface with Au nanoparticles, the samples were sputtered with Au for 5 seconds. After that, the samples were heated treatment at 400 ºC

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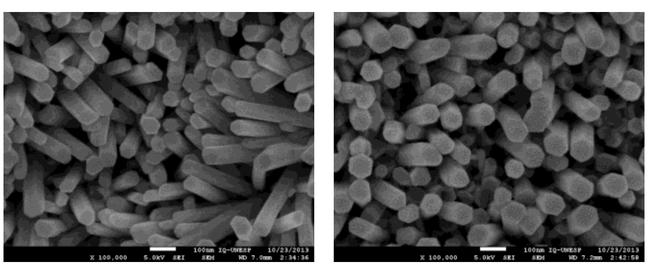
The morphology and crystal structure were investigated by high resolution scanning electron microscopy (FE-SEM) and X ray energy dispersive by using a JEOL – JSM 7500F. For gas-sensor measurements, the samples were put on a test chamber. High purity hydrogen gas was passed through the test chamber at different concentrations (0.2 to10 %), that was controlled by a mass flow controller. An air synthetic flux of 150 sccm was used as pattern line. The resistance of the pure or Au decorated ZnO nanorod sensors was measuring using a high voltage source (Keithley, modelo 237). The gas sensor measurements were realized at 200, 250 and 300 ºC.

3 RESULTS

Typical FE-SEM images of the vertically well-aligned ZnO nanorod arrays pure and decorated with Au nanoparticles are shown in Fig. 1. It is possible to observe that the grain size and boundaries of the Al_2O_3 substrate influenced on the growing of ZnO nanorods arrays. However, the image showed reveals that each individual ZnO nanorod shows a 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. [12], 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. For Au decorated ZnO nanorods the results obtained reveals that Au nanoparticles have been decorated the ZnO nanorods surface successfully and show diameter between 5 and 20 nm.

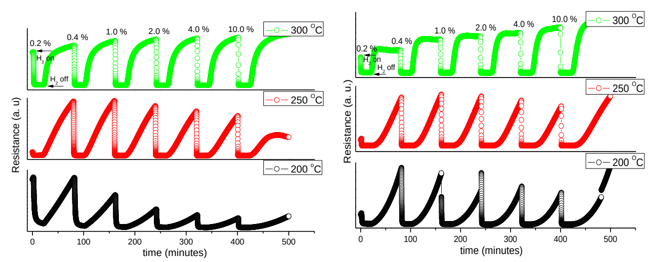


(a) (b)

Figure 1: Micrographs obtained by FE-SEM of the surface of the samples after chemical bath deposition. ZnO nanostructures: (a) pure and (b) decorated with Au

In order to test the ZnO nanorod arrays as gas sensor, its sensing properties were investigated for different hydrogen concentrations at 200, 250 and 300 °C. Figure 2 shows the change in resistance as a function of time with different hydrogen concentrations ranging from 0.2 to 10 % (0.2, 0.4. 1.0, 2.0, 4.0, 10.0 %). These temperatures were choosen because the surface reactions occur very slowly at low temperatures. Higher temperatures favor the promotion of electron to the conduction band [13].

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 2 is that the Au-decorated ZnO nanorods showed a significant improvement in the response of the nanorods, specially at 300 ºC. 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].



(a) (b)

Figure 2: Electrical resistance vs time during exposure to different flows of H_2 gas. ZnO nanostructures: (a) pure and (b) decorated with Au.

Sensor signal (S) is the ratio of the sensor response in the presence and absence of analyte gas. It can be observed in the Figure 3 that the sample with Au NPs showed better response in almost all variations of gas flux. It is also interesting to note that for both the largest and the smallest gas flow, the values were similar for the two samples.

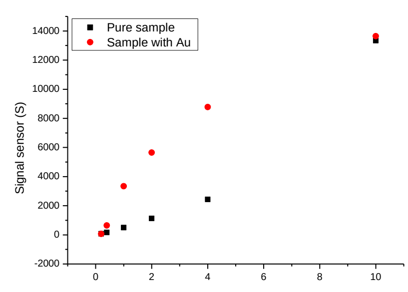


Figure 3: Sensor signal for different flows of H_2 reducing gas at 300 ºC.

4 CONCLUSION

It is possible to synthesize ZnO nanorods aligned perpendicular to the substrate using simple and cheaper method as chemical bath deposition. The decoration of nanorods with Au nanoparticles was sucessful with the formation of Au NPs of 5-20 nm. For sensors measures using the H_2 analyte gases, it was observed that pure ZnO nanorod and Au decorated ZnO nanorod present behave as an n-type semiconductor and the sensitivity was dependente of the concentration of gases and operation temperature.

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