

**SCIREA Journal of Materials** 

http://www.scirea.org/journal/Materials

**February** 12, 2017 Volume 2, Issue 1, February 2017

# Fabrication of gas sensor based on p-type ZnO nanorods at room temperature under UV-LED illumination

# P.M.Perillo<sup>\*</sup>, D.F.Rodr guez.

Comisión Nacional de Energ á Atómica, CAC, Micro y Nanotecnolog á, Av. Gral. Paz 1499 (1650) Bs As., Argentina. \* Corresponding author. Tel.: +541176627180 E-mail address: <u>perillo@cnea.gov.ar</u>

# Abstract

In the present study, the use of ZnO nanorods sensor under the irradiation of 400 nm UV-LED illumination at room temperature was tested. The non-intentionally C-doped flower-like zinc oxide (ZnO) nanorods were synthesized through a chemical method at low temperature (60–65  $^{\circ}$ C). The hexagonal wurtzite phase of ZnO was confirmed by X-ray diffraction (XRD). The samples were too characterized using SEM, EDX, TEM, XPS, BET and UV-Vis spectroscopy. The results show that the ZnO nanorods behave as a p-type sensor with a high response and reversibility towards ethanol and ammonia and it is an attractive chemical sensing material.

Keywords: ZnO nanorods; C-doped; sensor response; ethanol; ammonia.

# **1. Introduction**

Metal oxide semiconductor materials such as SnO<sub>2</sub>, ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> were widely used for gas sensor applications [1–3]. However, most of these metal oxides have to work at high temperatures (200–500 °C) to achieve any notable gas responses. Several methods have been employed to reduce the operating temperature of gas sensors e.g. noble metal doping [4], ultraviolet (UV) illumination [5], micro-electro-mechanical system fabrication [6] and development of nanostructures materials [7–12] etc. ZnO is almost always n-type semiconductor by the existence of intrinsic defects such as oxygen vacancies and/or zinc interstitials and is one of the materials most investigated as gas sensor [13–15].

To obtain p-type ZnO nanostructure has proved to be a very difficult task [16–18]. One reason is the fact that there are very few candidate shallow acceptors in ZnO. When doping with nonmetal such a C and N elements it is possible to obtain p-type [19]. Carbon could be considerate as a good dopant for a semiconductor due to its chemical stability, high mechanical strength, and extraordinary electronic properties.

The development of p-type ZnO nanostructures has been widely studied. These studies have mainly focused on ferromagnetism, magneto transport properties and visible-light photocatalysis [20–22]. However, few studies have been reported on gas sensing activity [23].

Some methodologies have been successfully established for the synthesis of C-doped nanostructures: pyrolysis of Zn containing inorganic–organic precursors, polymer or carbon templated syntheses, thermal decomposition of Zn precursor, metal organic chemical vapor deposition and hydrothermal process [24–26].

In this work, non-intentionally C-doped ZnO nanorods arrays have been successfully synthesized by the sonochemical method. Zinc acetate dehydrate was used as raw material, which is known to induce Zn vacancies in ZnO [27]. This method is a relative simple and hence involve lower costs and makes it attractive for develop gas sensor devices. We performed a p-type gas sensor which is used to investigate the signal response to ethanol and ammonia at room temperature under UV-LED illumination.

## 2. Experimental Procedure

#### 2.1 ZnO nanorods synthesis

The C-doped ZnO nanorods were synthesized as follows:  $2.195 \text{ g Zn}(CH_3COO)_2 \cdot 2H_2O$  zinc acetate dihydrate were dissolved in 100 mL deionized water forming the solution A. Under similar procedure 0.4 g NaOH were completely dissolved in 50 mL of deionized water, resulting in the solution B. The molar ratio of NaOH: Zn acetate was 2:1. The reagents were analytical grade, and were used without further purification. The solution A was added dropwise into the solution B during 1 hour with mechanical stirring at 60–65 °C. The resulting precipitate was continuously aged for 3 h. After that, the white precipitate was cooled at room temperature and then filtered and washed several times with deionized water, finally vacuum dried in an oven at 80 °C for 8 hours.

#### 2.2 Characterization

Scanning electron microscopy (SEM) (Zeiss Supra40 Gemini, 3 KV microscope) combined with an energy dispersive X-ray analyzer (EDX) attached to the SEM was employed for the morphological characterization of the ZnO nanorods samples. Transmission electron microscopy (TEM) observation was carried out on a Philips CM200 microscope operating at an accelerating voltage of 160 kV. X-ray diffraction (XRD) patterns were recorded in a diffractometer (PANalytical model Empyrean) with Cu K $\alpha$  radiation of 0.15418 nm having  $\theta$ - $\theta$  configuration and a graphite secondary-beam monochromator, using a generator voltage of 40 kV and current of 40 mA. The data were collected for scattering angles (2 $\theta$ ) ranging from 20 ° to 55 ° with a step of 0.026 ° for 2 s per point.

The surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on the adsorption data. The BET specific surface area and pore distribution of the samples which were degassed at 150  $^{\circ}$ C for 8 h were determined by N<sub>2</sub> adsorption/desorption method, which were carried out on a Micromeritics Accelerated Surface Area and Porosimetry System ASAP 2020 v 3.01 instrument.

The UV-Vis absorption spectrum was recorded using a Shimadzu 1800 UV-Vis spectrophotometer by ultrasonic dispersion of the sample in water with SDS 10 wt. % (sodium dodecyl sulphate).

The surface chemical composition of samples was analyzed by high resolution X-ray photoelectron spectroscopy (HR-XPS) in a hemispherical electrostatic energy analyzer (r = 10

cm) with Al K $\alpha$  radiation source (1486.6 eV). Binding energies in all XPS spectra were calibrated using C 1s peak (284.8 eV). All the experiments were conducted at room temperature.

#### 2.3 Fabrication of interdigitated gold electrodes

The interdigitated gold electrodes (IDE) were fabricated by photolithography in a lift-off process on p-type Si (100) wafer with 300 nm SiO<sub>2</sub> layer on substrate. A glass/Cr mask and a negative photoresist layer (AZ 5214E, 1.7  $\mu$ m) was used. The deposition of a Cr/Au (10 nm/200 nm) layer was performed via sputtering (QUORUMQ300TD). There are two IDE with two connection tracks and the number of fingers is 12.

Shown in Fig. 1 is a schematic diagram of the IDE structure fabricated in this work. Spacing between fingers was designed at about 30  $\mu$ m. The width and total length of the electrodes are 5.1 mm and 12.4 mm, respectively.



Fig.1. Schematic figure of the ZnO nanorods sensor.

#### 2.4 Sensor fabrication

ZnO gas sensor have been fabricated by deposition of a ZnO solution with ethyl alcohol using spin coating with 2000 rpm (rotation per minute) speed over IDE. Previously, ZnO powder with ethyl alcohol was sonicated for 15 min in order to assure good dispersion of the ZnO [28]. The IDE was placed on the rotor part of the spin coater. The solution was dropped over the IDE electrode through a micro syringe. As a result ZnO nanorods were uniformly deposited in a circular fashion over the IDE. The process was repeated for 15 times to get the uniform multilayer structure. LEDs have been used as light source ( $\lambda$ =400 nm) in all experiments. The irradiance emitted by the LEDs was measured using a wideband spectrometer (Ocean Optics USB4000).

The detection measurements were conducted in a chamber with a volume of  $250 \text{ cm}^3$ . The temperature inside the chamber was kept at room temperature. The relative humidity (R.H.)

was measured by an electronic hygrometer fixed inside the chamber. The electrical resistance of the nanotubes was measured by a Keithley sourcemeter 2612A with data acquisition capability under a constant voltage of 2 V.

The measurements were performed in static form. In first place, high purity synthetic air was passed into the chamber, the flow was 25 sccm and the sample under test was maintained at the desired humidity. The humidity was obtained by using a mass flow controller system which allowed mixture dry and moist air. Afterwards, the air flow was closed and the ethanol or ammonia was injecting into the camera by a micro syringe. Finally high purity air was passed into the chamber.

## 3. Results and Discussion

#### 3.1 Microstructure characterizations

The corresponding X-ray diffraction pattern of ZnO powder is shown in Fig.2. The diffraction peaks at  $2\theta = 31.7^{\circ}$ ,  $34.3^{\circ}$ ,  $36.2^{\circ}$ ,  $47.5^{\circ}$ ,  $56.5^{\circ}$ ,  $62.7^{\circ}$ ,  $66.2^{\circ}$  and  $67.8^{\circ}$  are identified to be the (100), (002), (101), (102), (110), (103), (200) and (112). All of the indexed peaks in the obtained spectrum are well matched with the planes of ZnO hexagonal wurtzite structure (01-079-0207). The lattice constants calculated from the XRD data for (101) and (002) planes are a=b=3.259Å, c=5.222Å [29]. The other peaks observed (\*) are probably related to the intermediates (e.g.C<sub>26</sub>H<sub>27</sub>O<sub>2</sub>) of the chemical synthesis. The average crystallite size calculated by Scherrer equation was 25 nm. The small grains sizes can lead to increase the sensor s responses.



Fig.2. X-ray diffractogram of the ZnO.

From SEM images, we observed that the products are flowerlike structures composed of nanorods with diameters of 30–40 nm and their length up to 400 nm. In this flower architecture, the rods fused together at one end and extended outside at the other end. The surfaces of ZnO nanorods were very smooth (Fig.3).



Fig.3. SEM micrographs of the flower like ZnO nanorods (a) low and (b) high magnification.

The carbon content of ZnO nanorods was determined by EDX (Fig. 4). Numerous dots were selected for determining the doping element content. The C atoms could be distributed homogeneously in the sample, forming amorphous C (free carbon) and/or incorporating in the crystal structure (C dopants). In the latter case, C atoms may allocate at the interstitial sites in the wurtzite or they can substitute Zn cites or O cites to form O-C and Zn-C bonds [30].



Fig. 4. EDX analysis of ZnO nanorods

TEM images further confirm the formation of flowerlike ZnO nanorods structure (Fig.5).



Fig.5. (a) low and (b) high magnification TEM images of ZnO nanorods.

The surface area and pore volume of the ZnO were investigated using nitrogen gas adsorption–desorption method. To characterize the specific surface area and porosity, nitrogen sorption measurements of the samples were carried out at 77 K. Nitrogen adsorption–desorption isothermal and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution desorption are presented in Fig.6. The pore volume distribution curve of ZnO is given as an inset image in the figure. The profile can be categorized to type III isotherm with a type I hysteresis loop in the Fig. 6 [31, 32].



Fig.6. N2 adsorption-desorption isotherms and pore size distribution curves of ZnO.

The BET specific surface area is estimated about 21.36 m<sup>2</sup>/g and the total pore volume (single point) (cm<sup>3</sup>/g): 0.170. The pore size distributed from 2 to 63 nm as seen in the inset figure indicating the mesoporous nanostructure. These porous microstructure and specific surface area are desirable for a chemical gas sensor.

The room temperature UV–Vis absorbance spectrum of the ZnO nanorods is given in Fig. 7. The shown spectrum is corrected for the solvent contribution. The optical band gap ( $E_g$ ) of the as-prepared ZnO samples was calculated using the Tauc s relationship [33]. The extrapolation of the straight line in the Fig. 7 to  $(\alpha hv)^2 = 0$  gives the value of band gap energy  $E_g = 3.15$  eV.



Fig.7. Absorbance spectrum of ZnO powder. In the inset: (αhv)2 vs hv and extrapolating for optical Energy gap Eg.

This value is smaller than the bulk (3.37 eV). The  $E_g$  is found to be size dependent and there is an increase in the band gap of the semiconductor with a decrease in particle size. And with doping, shallow level acceptor impurities create energy levels in the band gap near the valence band edge. The density of states of these dopants forms a continuum of states and the bandgap decreases. Thus, mechanisms for band gap narrowing in materials are very complex processes dependent crystallite size and the type of elements involved in the doping process.

Fig.8. shows the narrow XPS spectra for ZnO [34]. The binding energies (BE) at 286.3 and 290.9 eV appear at the initial; after first minute of  $Ar^+$  ion bombardment the 286.3 eV component decreases drastically, so that it is attributed to surface contamination. The component 290.9 eV, however, is narrowed but remains relatively intense. This very different behavior with the  $Ar^+$  ion bombardment indicates that carbon atoms are forming part of the material.

The minor binding energy of  $O_{1s}$  and  $Zn_{3p}$  always has the same intensity ratio and are allocated on both O and Zn in the crystal lattice. The higher binding energy in the  $O_{1s}$  and  $Zn_{3p}$  initial spectra quickly disappear with bombardment, leading to assume that they are associated with Zn and O in the area disturbed by surface contamination.

Carbon is incorporated into the material replacing Zn, in which case each carbon would be linked to 4 oxygen atoms. This assumption is consistent with the  $C_{1s}$  component remaining after bombardment is the higher binding energy, because the binding energy of  $C_{1s}$  level CO links is always greater than in C-C bonds (and more than links C-Zn).

The lower bonding energy  $O_{1s}$  spectrum corresponds to the O atoms linked to Zn atoms, and the higher binding energy is then allocated to the O atoms neighbors to a site where Zn was replaced by C. This assignment is consistent with the  $O_{1s}$  level is expected to be made more closely linked when one of the four neighbors Zn is replaced by a C (O-Zn<sub>4</sub>  $\rightarrow$  C-O-Zn<sub>3</sub>), but nevertheless appears difficult to explain that having C so little this second component is so intense. The results are summarizing in Table 1:

	High BE	Low BE
O <sub>1s</sub>	O neighbors to a site in which a Zn has been replaced by a C	O atoms with 4 Zn neighbors
C <sub>1s</sub>	C atoms incorporated in the crystal lattice replaces an atom of Zn	Surface contamination
Zn <sub>3p</sub>	The only component of the Zn atoms is assigned to the ZnO crystal lattice, each surrounded by four O atoms.	

Table 1: XPS results summarized.



Fig.8. XPS spectrum of the ZnO nanorods

#### 3.2. Gas sensor characteristics

The behavior of the nanorods samples in the presence of ethanol and ammonia was tested at room temperature in a wide range of operating concentrations from 8 to 8000 ppm with 40% R.H. The tests were chosen to perform at intermediate humidity compared with that in a dry atmosphere and at high humidity.

The resistance changes obtained is given with the sensor response curves shown in Figs. 9 and 10. The resistance of the sensor increase on exposure of reducing gases (ethanol and ammonia), as a typical p-type semiconductor gas sensor.

ZnO is almost always n-type semiconductor by the existence of intrinsic defects as oxygen vacancies but intentional or un-intentional doping can transform it into a p-type semiconductor. In the case of carbon doping, carbon immobilizes the oxygen in the interstitial site forming a carbon–oxygen cluster defect that acts as an acceptor [35], which increasing the concentration of holes. The n-type to p-type transition it occur when the hole concentration overcome electron concentration. When the sensor was exposed to the target gas, the resistance of the film increased within few minutes and recovered completely to the initial value when the gas supply was stopped and synthetic air was introduced into the chamber. This indicates good reversibility. Sensor responses reaching 90% of the maximum were 10 min, but recovery was slower, 25 min to achieve full recovery. The large recovery time may be due to the gas species which were generated by gas interaction, producing a decrease in the desorption rate. As it can be seen in Figs. 9 and 10, the responses increase with increasing concentration, which indicates a good sensitivity of the sensor.



Fig.9. Response of the ZnO nanorods sensors to ethanol.



Fig.10. Response of the ZnO nanorods sensors to ammonia.

When the sensor is exposed to air, the oxygen molecules are adsorbed on the semiconductor surface and form,  $O_2^-$ ,  $O^-$  and  $O^{2-}$ . The ionsorption specie of  $O_2^-$  is dominant at room temperature. The adsorption of the oxygen with a negative charge on a p-type oxide semiconductor leads to the formation of holes (h<sup>+</sup>) accumulation layer on the surface.

With UV light irradiation, photogenerated holes and electrons appeared (1), in p-type oxide semiconductor, the electrons migrate to the surface and reacts with  $O_2$  (g), producing the adsorption of  $O_2^-$  (2), thus increasing the hole accumulation layer decreasing the electrical resistance. This effect is more pronounced at low temperatures because if the sensor temperature is high the thermal activation is dominant and UV light has little effect.

$$h \nu \rightarrow h^+ + e^- \qquad (1)$$

$$O_{2(g)} + e^{-} \rightarrow O_{2(ads)}$$
 (2)

When reducing gases such as  $C_2H_5OH$ ,  $NH_3$  are present in the surrounding atmosphere, the reaction between reducing gas and the negative adsorbed surface oxygen; releasing electrons back to the conduction band. The reaction may be described as follows:

$$CH_{2}CH_{3}OH + 3 O_{2}^{-}_{(ads)} \rightarrow 2 CO_{2} + 3 H_{2}O + 3e^{-} (3)$$

$$4 NH_{3} + 3 O_{2}^{-}_{(ads)} \rightarrow 2 N_{2} + 6 H_{2}O + 3e^{-} (4)$$

The electrons released from this process are recombined with the holes  $(h^+)$ . Therefore the resistance of p-type semiconductor increases.

## 4. Conclusions

To summarize, we have developed a very simple and cheap chemical synthesis to fabricate non-intentionally C-doped ZnO nanorods. ZnO is almost always n-type semiconductor, but the transition of n-type to p-type was caused by the carbon doping. This gas sensor was measured by exposing to different concentrations of ethanol and ammonia, and experimental results showed that the sensor exhibited high response, reversibility, excellent stability and good repeatability at room temperature under UV-LED illumination.

The facile fabrication method and sensing properties of the obtained ZnO nanostructures is promising for the fabrication of sensor devices.

#### Acknowledgement

The authors would like to acknowledge Daniel Vega from Condensed Matter Division, GAYANN, CNEA for XRD analysis, Gonzalo Zbhilei from Materials Department, CNEA for TEM analysis and Guillermo Zampieri from CAB, CNEA for XPS analysis.

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