# Design an Electrical Nose with ZnO Nanowire Arrays

Amin Nekoubin, Abdolamir Nekoubin

*Abstract*—Vertical ZnO nanowire array films were synthesized based on aqueous method for sensing applications. ZnO nanowires were investigated structurally using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The gas-sensing properties of ZnO nanowires array films are studied. It is found that the ZnO nanowires array film sensor exhibits excellent sensing properties towards $O_2$ and $CO_2$ at 100 °C with the response time shorter than 5 s. High surface area / volume ratio of vertical ZnO nanowire and high mobility accounts for the fast response and recovery. The sensor response was measured in the range from 100 to 500 ppm $O_2$ and $CO_2$ in this study.

*Keywords*—Gas sensor, semiconductor, ZnO, Nanowire array

## I. INTRODUCTION

THE recognition of the gas-sensing capability of semiconducting oxides can date back to the 1960s when it was observed that the adsorption of reducing gas on metal oxides could result in a change in the electrical conductivity of the oxides and this phenomenon quickly led to extensive practical applications of gas sensors [1]. Detecting of gases is essential in many different fields such as household security, vehicle emission control and environmental monitoring. Most studies have concentrated on detecting of the three extensive classes of (i) for oxygen, because of its relation with the breathable atmospheres in addition to combustion process. (ii) For flammable gases in air in order to preventing the undesired fire or explosion. (iii) For poisonous gases in air intended for monitoring environmental pollutants [2-3].

The second and third categories are monitored in industry and in the home with solid state sensors. The majority of the well established types of gas sensor are solid state devices which combine rugged construction with sufficiently low purchase costs to allow widespread deployment [4-5]. There is a burgeoning interest in the use of arrays of solid state gas sensors in so-called 'electronic noses', [6]. There are three types of solid state gas sensor currently in large scale use based on solid electrolytes, on catalytic combustion and on resistance modulation of semiconducting oxides. The third widely used type of gas sensor is effectively a gas sensitive resistor [7-8]. Metal-oxide semiconductors such as $SnO_2$ [9, 10], ZnO [11], $In_2O_3$ [12] and $Fe_2O_3$ [13] are widely used for detecting small amount of target gas in air with which electrical resistance changes [14, 15]. Among the several metal-oxide sensing materials, ZnO is one of the earliest

investigated [16, 17] and the most widely applied gas-sensing materials due to its high mobility of conduction electrons (as reported in Ref. [18], the mobility of conduction electrons of ZnO is $200cm^2/Vs$, which is higher than $SnO_2$ and $In_2O_3$), good chemical and thermal stability [19] under the working conditions of sensors. Generally speaking, ZnO, especially with one-dimensional (1D) nanostructures, is a good gas-sensing material as per the previous reports [20-21].

Although, these sensors have better sensing performance, it is difficult to obtain single nanowire and fabricate this kind of device in large quantities. Thick film sensors based on ZnO nanowires were reported to have good gas-sensing properties by Wan et al. [22].

However, it is not easy to keep consistency and homogeneity in production on a large scale, and is difficult to integrate with other electronical components. Furthermore, low power consumption is the most important demand on the gas sensors since they work day and night [23–24]. Therefore, in comparison with conventional sintered bulk gas sensors, thin film sensors are especially more suitable for practical applications, which own higher effective surface and exhibit an increasing response and lower power consumption [25]. Hence, we report the fabrication and gas-sensing properties of ZnO nanowires array films through a sol–gel method for ZnO buffer layer on an $Al_2O_3$ substrate and subsequently a facile aqueous process for ZnO nanowires array films. Excellent $CO_2$ and $O_2$ sensing properties such as high response and quick response-recovery based on our sensor have been observed at 100 °C.

## II. PREPARATION OF SENSING ELEMENT

ZnO nanowire arrays were grown by an aqueous method. The precursor solution was prepared by mixing zinc nitrate hexahydrate (Zn $(NO_3)_2$ .$6H_2O$; 0.05 M) with hexamine ($(CH_2)_6N_4$; 0.05 M) while keeping their molar ratio at 1:1. The aqueous growth was performed on the seeded substrate in a 95 °C temperature autoclave.10mm×10mm alumina plates coated with Au electrodes was used as substrates. substrate structure are shown in Figure 1 .They were cleaned by deionizer (DI) water, rinsed with ethanol and DI water, in an ultrasonic bath. To grow a buffer ZnO layer The ZnO films were prepared by the e-beam deposition technique at a residual-gas pressure of $3×10^{-5}$ mbar. The substrate was located parallel to the target surface at a distance of 120 mm. and the temperature of the substrate was fixed at room temperature. The ZnO target was prepared from a pressed pure ZnO powder (99.99%) from. The film growth rate was approximately 0.15 $nms^{-1}$. Thicknesses of the films were about 100 nm. This served as seed layer for nanowire growth without any post treatment.

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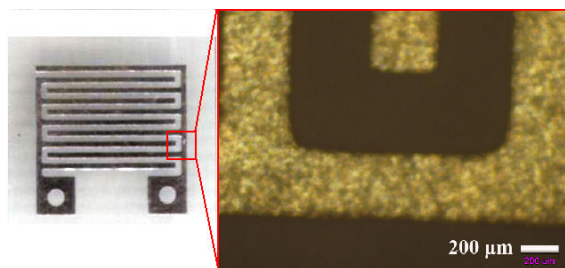
Fig. 1  Structure of the alumina plates coated with Au electrodes was used as substrates

### III. SEM, XRD CHARACTERIZATIONS

Please The morphology, size distribution and crystalline of the ZnO samples were characterized by scanning electron microscopy (SEM, Leo 435vp) and by means of X-ray diffractometry (PANalytical X'pert, Philips) with *Cu-kα₁* radiation. The optical configuration included a four-bounce hybrid monochromator and parallel plate collimator.

Figure 2 are shown XRD spectra indicating the wurtzite phase of ZnO with lattice constant of a=0.325 and c=0.521 nm (JCPDS card No. 36-1451) without any peaks from impurities. The overpower (002) peak designate that the preferred direction of the ZnO crystals is along the *c*-axis [4-6].The morphologies of the deposited ZnO nanowire arrays are shown in figure 3. Figure 3(a) shows the top view of the nanowires which indicate the formation of ZnO nanowire arrays over large area. Diameters of these nanowires are under the 100 nm also; the density of the nanowires is estimated about $1.5 \times 10^{10}$/cm$^2$. Figure 3(b) shows the cross-sectional view of the nanowire arrays which indicate the harmonized structure and perpendicular morphologies. The length of these nanowires is ~6μm. Such characteristics are necessary meant for producing nanowire based devices (e.g. chemical and biological sensors, solar cells, light emitting diodes) [6,7].
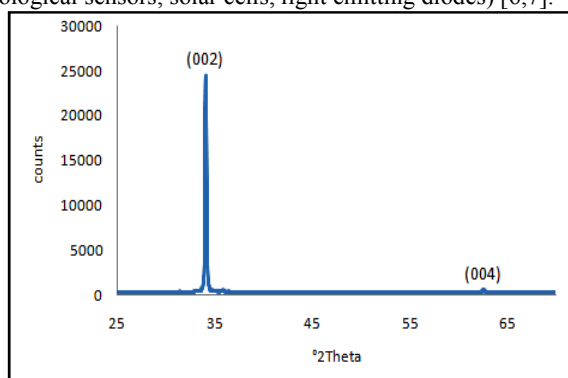


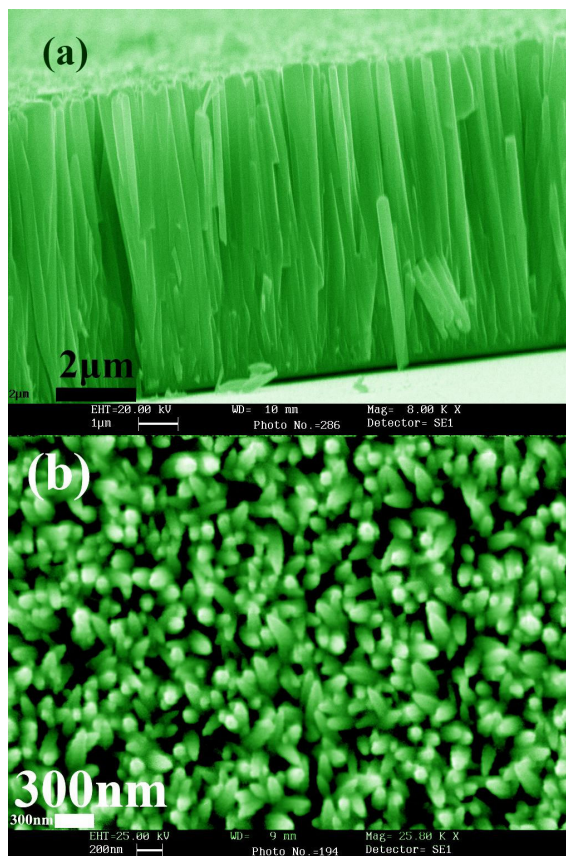Fig. 2 XRD patterns of ZnO nanowires array films



Fig. 3 SEM images of ZnO nanowire array film (a) cross-section view (b) top-view

TABLE I
SENSOR RESPONSE UNDER 300 PPM OF $CO_2$ AND $O_2$ GASES

| Kind of gases | Sensor response $(S=R_A/R_G)$ | $T_{90}/S$ |
|---|---|---|
| $O_2$ | 1.07 | 4.5 |
| $CO_2$ | 1.06 | 6.5 |

### IV. SENSING MECHANISM

As we know the metal oxide layer in contact with atmosphere adsorb oxygen from air and the oxygen that chemisorbed to the surface produce ion with negative charge($O_2^-$, $O^{2-}$ and $O^-$ ) and this procedure extract electron from conduction; and resulting an increase in sensor resistance. Equations of producing oxygen ions are shown below: that equation (1) and (2) are used in high temperature and equation number (3) is used for room temperature. Because of our testing in 100 °C we choose the second equation.

$$\tfrac{1}{2}O_2 + e^- \leftrightarrow O^- \tag{1}$$

$$\tfrac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-} \tag{2}$$

$$O_2\,(gas) + e^- \leftrightarrow O_2^- \tag{3}$$

In next step after infusing gasses ($CO_2$, $O_2$) some change occur in resistance of sensor. The oxygen ions on the surface of ZnO are active with the CO and $O_2$ molecule and give up the electrons from surface back to the conduction band of ZnO semiconductor ; causing the resistance of semiconductor decreases and relatively sensitivity of sensor ($R_a/R_g$) increase.

## V. EXPERIMENTAL RESULTS

The produced sensors were placed in a quartz chamber that served as a gas sensitivity test. The total volume of the chamber is 1 l. Gas response (S) is calculated as: S = $R_{gas}/R_{air,}$ Gas sensing examinations were carried out with an indigenous-made gas sensing setup shown in figure 4,and figure 5attached with mass flow controllers (MFC) for precise measurements of the gas flow at ppm level. As mentioned in the section II the sensing element is a 10mm×10mm ZnO nanowires array film which a same actual area of the film was exposed to the gas. To study the response of the ZnO nanowire array films to $O_2$ and $CO_2$ gases at room temperature the gases was infused into the chamber.
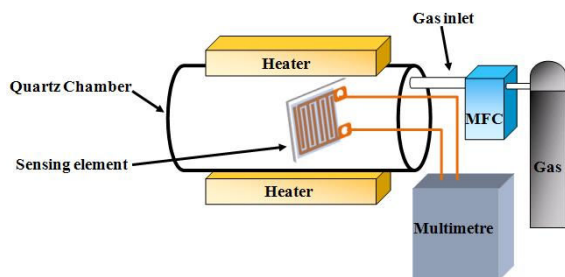


Fig. 4 The schematic of gas sensor component utilized for gas detection



Fig. 5 Labratorty setup for gas detection

ZnO layer on the substrate is an n-type semiconductor. N-types semiconductors in contact with oxidizing gasses like $CO_2$, $O_2$ and $NO_2$ show the increasing in resistance; because of adding some new oxygen ion in surface. Figure 6 shows the sensor responses (S=$R_a/R_g$) as a function of $CO_2$ and $O_2$ concentration at room temperature. Once the gas induced into the chamber the resistance of the films increased. The increase in concentration of gas reasonably increases the change in resistance of the films indicating an enhancement in sensitivity. It is observed that the ZnO film shows larger

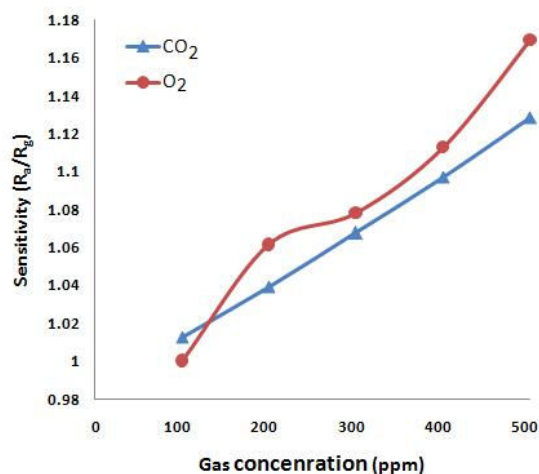response to $O_2$ gas than $CO_2$ for concentrations greater than 150 ppm.



Fig. 6 Response (S) of the ZnO nanowire array films toward $CO_2$ and $O_2$ gases (100–500 ppm) measured at 100 °C

The transient responses of the ZnO nanowire array films towards various gases in the room temperature are shown in Figure.7. The response increases with the operating time, particularly for the sensor towards $O_2$. The sensor response and response time of the ZnO nanowire sensor to $O_2$ and $CO_2$ are revealed in the table 1.
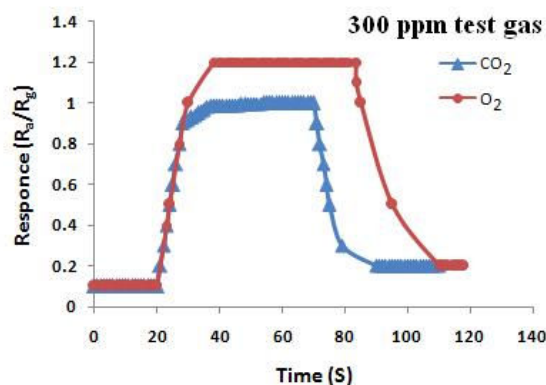


Fig. 7 Response transients of the ZnO nanowires array films to 300ppm various gases at 100 °C

## VI. CONCLUSION

ZnO nanowire array films were grown on seeded substrates and its effect on the gas sensing characteristics working at 100 °C to $CO_2$ and $O_2$ were investigated. The SEM and XRD studies demonstrate the ZnO nanowires grown on a ZnO seeded layer are perpendicularly aligned. The aspect ratios of wires are about 60. The high density ZnO nanowires are single crystalline wurtzite ZnO structure. The $CO_2$ and $O_2$ sensing properties of ZnO nanowires were studied. Under 300 ppm $CO_2$ and $O_2$, ZnO nanowires showed a rapid response time of

4.5 and 6.5 S respectively. The sensor response to $CO_2$ and $O_2$ (S, the ratio of the resistance in gas to resistance in air, S = $R_{gas}/R_{air}$) is 1.06 and 1.07 respectively.

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