Zinc Oxide Nanowires for Gas Sensing Application

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Abstract

We present the growth of ZnO nanowires (NWs) using vapor phase and hydrothermal methods. In order to investigate the gas sensing characteristics, two types of sensors were prepared: (i) mat-type and (ii) as-grown random network of ZnO NWs. Mat-type sensors detected H$_2$S at room temperature with fast response and recovery times of 250 and 700 s, respectively. On the other hand, as-grown random network of ZnO NWs were less sensitive to H$_2$S. However, modification of random networks by CuO layer improved the sensing properties, which is explained on the basis of the formation and destruction of p-n junction among p-type CuO and n-type ZnO.

1. Introduction

One dimensional nanostructures of metal oxides namely nanowires (NWs) have emerged as a general platform for ultra-sensitive direct electrical detection of biological and chemical species$^{1,2}$. NWs in particular, offer various advantages that include high surface area to volume ratio, Debye length (the distance over which a local electric field affects the distribution of free charge carriers) comparable to the target molecule, low power consumption, possibility of high integration densities and ease of incorporation into microelectronic devices. Among various semiconducting oxide materials, ZnO has generated a great deal of interest due to its direct wide band gap of 3.37 eV, large exciton binding energy of 60 meV, and processing advantages for its nanostructures$^3$. There are two different approaches to the production of 1D structures: top-down and bottom up technologies. The first one is based on standard micro fabrication methods with deposition, etching and ion beam milling on planar substrates in order to reduce the lateral dimensions of the films to the nanometer size. Electron beam, focused ion beam, X-ray lithography, nano-imprinting and scanning probe microscopy techniques can be used for the selective removal processes. The advantages are the use of the well developed technology of semiconductor industry and the ability to work on planar surfaces, while disadvantages are their extremely elevated costs and preparation times. Furthermore the 1D nanostructures produced with these techniques are in general not single-crystalline. The second approach, bottom-up, consists of the assembly of molecular building blocks or chemical synthesis by vapor phase transport, electrochemical deposition, solution-based techniques or template growth. Its advantages are the high purity of the nano-crystalline materials produced, their small diameters, the low cost of the experimental set ups. The main disadvantage is their integration on planar substrates for the exploitation of their useful properties, for example transfer and making contacts can be troublesome.

Providing electrical contacts to NWs is often considered as a complex and tedious process. An electrical contact to sensors based on single NWs is often realized using a ‘pick and place’ approach. In this, NWs are first drop-casted or spin-coated onto the substrates containing predefined electrodes and then aligned using dielectrophoresis technique. To assure proper contact, additional electrode material
is often deposited connecting NW and electrode using Focused Ion Beam techniques. One of the promising approaches is to use ordered or random networks of NWs. Herein NWs can be selectively grown between the predefined electrodes or electrical contacts can be provided by depositing the electrodes with known dimensions on the NWs network itself. This method is advantageous over the one involving the ‘pick and place’ approach as it removes the complexity involved towards a longer extent. Besides, it is easy and can assure reproducible measurements. Accordingly, in the present work, ZnO NWs have been investigated in detail for possible gas sensing application.

2. Growth of ZnO nanowires

NWs have been synthesized using two approaches namely vapor phase deposition and hydrothermal method\textsuperscript{1,2}. For vapor phase deposition, Zn metal powder was heated in a quartz boat placed inside a quartz tube at 900°C under controlled Ar and \( \text{O}_2 \) atmosphere. Zn was found to evaporate and deposit in the quartz tube in the direction of the gas flow. For hydrothermal growth, ZnO nanoparticles (NPs) were first synthesized using chemical route and then spin coated onto the substrate which acts as a seed\textsuperscript{3}. NWs growth was accomplished by suspending NP coated substrates upside-down in an open beaker filled with an aqueous equimolar (0.025 M) solution of zinc nitrate hydrate and hexamine at 90°C. The aspect ratio of NWs was controlled using the duration of the reaction. Fig. 1 shows the corresponding SEM images of the ZnO NWs grown using both the methods. ZnO NWs grown at 700°C after heating Zn powder for 5 h have diameters \( \leq 100 \) nm. On the other hand, hydrothermally grown NWs exhibit diameter between 50 and 200 nm and length 1-2 \( \mu \text{m} \) forming a dense network over the substrate. The quasi-hexagonal ends of the ZnO-NWs indicate that their main axis is preferentially oriented along the [0001] direction, which is in accordance with the growth habit of wurtzite crystals.

3. Gas sensing measurements

Gas sensing properties of NWs were investigated in a static gas sensing set-up as shown in Fig. 2. In brief, sensor films were mounted in a stainless steel test-chamber (volume: 250 cm\(^3\)) equipped with a temperature control unit. The desired temperature was achieved using a Pt-wire based heater attached to the backside of the sensor film. The desired concentration of the test gas was achieved by injecting the measured quantity of commercial gas inside the chamber. The resistance of the film was

![Fig. 1: SEM images of ZnO NWs (a) vapor phase grown at 700°C after heating Zn powder for 5 h and (b) hydrothermally grown for 6 h growth time.](image1.png)

![Fig. 2: Static environment gas sensing set-up](image2.png)
monitored and acquired as a function of time using a personal computer equipped with Labview software. Recovery of the sensors was achieved by opening the housing to the atmosphere.

3.1. *Drop-casted mat-type ZnO NW films*

NWs films were prepared by first making a paste in methanol and painting them on substrate containing predefined electrodes followed by annealing at 500°C. NWs were aligned dielectrophoretically between the microelectrode gaps under the application of electric field of 20 Vpp at 100 KHz. Consequently, NWs were trapped and aligned along the electric field lines bridging the electrode gap where the electric field becomes higher. As shown in Fig. 3, sensor films exhibited good sensitivity ($S = R_a/R_g$) towards H$_2$S and NO gases at room temperature with very little or no response towards other gases. Typical response and recovery times for 10 ppm concentration are 250 and 700 s for H$_2$S and 250 and 150 s for NO, respectively. The response and recovery times were found to increase with concentration.

3.2. *ZnO NPs and hydrothermally grown NWs*

Fig. 4 shows the response curves of NW-films towards different concentrations of H$_2$S at 350°C with corresponding concentration dependence of response. NW-films can reliably detect H$_2$S at 1 ppm concentration. Sensor response [$S = (I_g - I_a)/I_a$] is also observed to increase with concentration saturating at around 15 ppm. It exhibits a power law dependence on concentration given as:

$$S = AC^{\alpha}$$

where, $A$ is constant. From the fit of Fig. 5 (b) the value of $\alpha$ was found to be 0.7. The power law dependence arises from receptor and transducer functions i.e., the adsorption or interaction of H$_2$S with the sensor surface and the change of surface potential, respectively.

Response of NP-films (size: 10 nm) was also studied on exposure to H$_2$S and Cl$_2$ gases at 350°C as shown in Fig. 5. NPs are found to have lower response to the gases and interestingly the change in resistance is in opposite direction to that of NWs indicating p-type conduction.

The formation of n-type NWs and p-type NPs were independently confirmed by hot probe and Kelvin probe Contact Potential Difference (CPD) measurements, respectively. For hot probe measurements, thin films of required nanomaterial (with two Au electrode contacts) were
heated from one end and the developed thermo-
e.m.f was measured. With the hot and cold probes
connected to positive and negative terminal of the
voltmeter respectively, a negative voltage for NP-
films and positive voltage for NW-films were
obtained, confirming the p-type and n-type nature
of NPs and NWs, respectively. Fermi level of a
semiconductor is close to conduction band for n-
type and to valence band for p-type materials.
Therefore, it is expected that the work function of a
material should increase when the nature of
conductivity changes from n to p-type. To confirm
difference in nature of conduction for NPs and NWs,
work function was scanned across the samples by
Kelvin probe. The average work functions of 4.8
and 5.3 eV for NW- and NP-films respectively is
obtained, which is in accordance with the change
in nature of conductivity from n to p-type.

**Cu** is known to be an excellent promoter for **H₂S**
causing an enhancement of both the sensitivity and
the selectivity of the sensor towards **H₂S**. Accordingly, we have investigated the effect of **Cu**
on **H₂S** sensing properties of ZnO NWs'. The sensor
modified with 10 nm of **Cu** responded with
maximum sensitivity at an operating temperature
of 250°C. Fig. 6 shows the response curves recorded
towards increasing concentration of **H₂S**. The sensor
exhibited a fast response and recovery times for
example, towards 5 ppm of **H₂S** response and
recovery times were 62 and 150 s, respectively. This
fast response kinetics could be attributed to the
effective electron conduction pathway provided by
NWs.

In order to investigate the nature of interaction
between ZnO-NWs and **CuO**, we have carried out
photoluminescence (PL) studies (Fig. 7 (a)). Both the ZnO-NW and **CuO**(10nm):ZnO-NW
random networks exhibit a peak at 384 nm
corresponding to a Near Band edge Emission (NBE).
ZnO-NWs network exhibited a broad band peak at
595 nm attributed to oxygen vacancies. For
**CuO**(10nm):ZnO-NWs network, this peak
broadens, intensifies and
shifts to higher wave
length (i.e. 627 nm). The
origin of such a peak
has been attributed to the
plasma resonances of oxidized copper
aggregates. Interestingly
on **CuO** deposition NBE
peak quenches by ~42%.
This can be explained based
upon the formation of p-n
junction between p-type
CuO and n-type ZnO, as schematically shown in Fig. 7 (b). When a photon is incident on the sample, electron gets excited into the conduction band leading to the formation of an exciton. The p-n junction enhances the dissociation of excitons as ZnO transports electrons away and CuO transports the holes. Dissociation of excitons greatly suppresses the electron-hole recombination necessary for PL emissions.

In order to further investigate the effect of p-n junction, we have measured the room temperature electrical resistance as a function of CuO layer thickness. The results unambiguously show that the resistance increases sharply up to a nominal thickness of 10 nm and then decreases monotonically. The electrical resistance ($R_1$) of bare ZnO-NWs network can be represented as the series resistance of the ZnO-NWs ($R_{ZnO}$) and the junction resistance ($R_{JN}$) (Fig. 8). The resistance ($R_2$) of ZnO-NWs network modified with a CuO layer up to a nominal thickness of 10 nm can be represented as a series equivalent to that of $R_1$, p-n junction and CuO aggregates. Due to the presence of p-n junction, the value of $R_2$ is expected to be very high. However, at very high nominal thickness, CuO fully covers the ZnO-NWs network. Thus a continuous CuO layer acts as a parallel resistance, which reduces the total resistance ($R_3$) of the sample. Herein the CuO layer contributes two resistances one corresponding to CuO layer ($R_{CuO}$) and the other corresponding to the grain boundary ($R_{GB}$) resistance between CuO grains. Thus $R_1 < R_2 > R_3$ is in accordance with experimental results.

Modification of ZnO NWs network with CuO (10 nm) results in the formation of random n-p-n type junctions. The potential barrier formed at the ZnO/CuO/ZnO heterojunction results in a very high resistance of the film. Exposure to $H_2S$ causes the potential barrier to disappear. CuO reacts with $H_2S$ forming CuS as per the following reaction:

$$CuO + H_2S \rightarrow CuS + H_2O$$
CuO + H₂S → CuS + H₂O  \[ (2) \]
CuS being metallic will destroy the n/p/n junction as well as the potential barrier, and a new type of n-ZnO/metallic-CuS/n-ZnO heterojunction will be formed. The destruction of potential barrier results in a sharp decrease in the electrical resistance. During recovery, CuS reacts with oxygen forming once again CuO. The potential barrier reappears due to the formation of n-ZnO/p-CuO/n-ZnO heterojunctions, and original high resistance is regained.

4. Summary

ZnO NWs grown using both the physical as well as the chemical methods have been investigated for gas sensing applications. In particular, techniques like vapor phase deposition and hydrothermal growth were used effectively to realize these nanostructures. Proper electrode contacts were realized using dielectrophoresis technique and by directly depositing the electrode over NW network film. ZnO NPs exhibited a p-type response towards gases while NW film detected H₂S with faster response and recovery time of 13 and 78 s, respectively towards 20 ppm at 350°C. Cu incorporation over NW surface has been demonstrated to improve both the sensitivity and the selectivity towards H₂S. Our results clearly illustrate that ZnO NWs are the potential candidates for the realization of next generation of sensors. Hopes are high that significant practical devices will soon evolve from the integration of these structures with conventional microelectronics.

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References