Fabrication of Zinc Oxidenanorods Based Gas Sensor

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Abstract: Zinc oxide (ZnO) nanorods are considered as most suitable materials for the fabrication of gas sensors due to their high sensing properties. In this research a simple gas sensor has been fabricated based upon the principle of change in resistivity due to oxygen vacancies which make its surface chemically and electrically active. When charge accepting molecules adsorb at the vacancies significant variation appears in conductivity. A comb like structure was made on a substrate through photolithography. Gold was sputtered on the substrate for making contacts as well as catalyst for ZnO nanorods. Chromium was used as adhesive layer prior to gold sputtering. For ZnO nanorods growth hydrothermal method was adopted. The as prepared ZnO nanostructures, distribution and morphologies were characterized by scanning electron microscope (SEM) and x-ray diffraction. The SEM reveals the wurtzite hexagonal crystalline nanostructure grown along the [0001] direction. The ZnO nanosensor was tested for different concentrations of ethanol gas and different operating temperatures. The resistance between the two contacts has been evaluated as a function of temperature and gas concentration. The best sensor response was recorded at operating temperature of 300°C.

Key words: ZnO sensor • Nanorods • Nanostructures • Synthesis • Resistivity

INTRODUCTION

ZnO is an attractive nanoscale material which is used in many devices due to its regular structure and high surface to volume ratio. Synthesis of ZnO nanostructures require easy growth conditions and provide great potential for device applications. It has extra ordinary sensing applications such as in chemical, humidity, gas and pH sensors [1-4]. Due to its bio-compatibility it is also used for biomedical applications [5]. ZnO has been used for PN junction [6-7], field effect transistor [8], electron field emission [9], laser [10], photo detectors [11], gas sensors [12-13] and many other applications.

ZnO nanorods are synthesized by various methods and environments. The most common and easy methods to synthesize ZnO are hydrothermal [14], vapor transport process [15], patterned growth [16]. In vapor transport process high temperature is used to form ZnO nanostructures by transporting Zn and oxygen vapors in such a high temperature environment(1400°C) where they react with each other[15]. In the same process another relatively low temperature (500-700°C) may also be adopted where Zn powder is heat up providing oxygen flow [17]. This method requires more care to maintain the proper ratio between Zn vapor pressure and oxygen pressure in order to get the desired nanostructures. A small change in the Zn and oxygen flow ratio cause a huge variation in the morphology of the structures.

The application of zinc oxide nanostructures mainly depends upon the packing density, alignments and the ability to control the growth locations on a substrate. To overcome the above limitations ZnO nanorods and nanowires lithographic and non-lithographic patterning techniques have been utilized [16]. Different shapes of catalytic gold dot array are made on a substrate by photolithographic technique to grow ZnO wires. Shadow mask is also used for catalyst based deposition, where square gold matrix pattern are made by transmission electron microscope [18]. Anodic aluminum oxide membrane as a mask has also been used.
successfully to fabricate a well-ordered hexagonal ZnO nanorods array on a GaN substrate [19]. Beside the above mentioned some other methods have been used such as sol-gel, electro-deposition and polymer assisted growth [20-22]. In these methods relatively low temperature is used for ZnO nanorods growth.

The extra ordinary physical properties make ZnO nanorods more valuable and applicable in various fields. The developments at smaller size of ZnO nanorods change some of the physical properties called quantum size effect, such as quantum confinement which increases the band energy of the ZnO [23]. Photoluminescence, scanning photoelectron microscopy and X-ray absorption spectroscopy show the enhancement of surface states with the downscaling of ZnO nanorods [24-25]. To characterize the mechanical properties on ZnO nanorods bending modulus was calculated by Bai et al., using spatial TEM [26]. ZnO nanobelt is a favorable nanomaterial to use for the nanoresonator and nanocantilever, which improves the sensitivity than the conventional one made on micro-fabrication based [27]. Piezoelectricity is another important property of ZnO nanorods. Exploiting this property ZnO nanorods and wires demonstrated the operation of field effect transistor [8]. They dispersed the ZnO nanowires in the alcohol and then deposited this suspension on a Silicon and SiO₂ substrate. Prior to the deposition, photolithographic based electrodes array were made on the substrate. The optical property of ZnO nanorods is another important property which has been studied and implemented in photonic devices and optoelectronics [35-36]. Park et al. reported the excitonic emission from photoluminescence spectra of zinc oxide nanorods [37]. Visible emission such as red, green-yellow and blue are due to the oxygen vacancies and thinner nanowires having high surface to volume ratio [38-39]. Ultraviolet emission from ZnO nanowires has potential applications in the optical wave guide due to its high refractive index and near cylindrical geometry [40]. ZnO is a favorable material for ferromagnetic doping. Manganese (Mn), cobalt (Co) and Iron (Fe) have been used as dopants in the ZnO [41-43]. Wide band gap of ferromagnetic ZnO makes it more promising for short wavelength magneto-optical devices.

Sensing is one of the promising applications of ZnO nanorods due to the oxygen vacancies which make its surface chemically and electrically active. When charge accepting molecules adsorb at the vacancies these either increase or decrease the conductivity significantly. The working principle all metal oxide gas sensors based upon the change in conductivity. Nitrogen (N₂) and Oxygen (O₂), reduces the conductivity and carbon mono oxide (CO) and hydrogen (H₂) increase the conductivity of the ZnO nanorods when these adsorb on it [12]. Such types of sensors normally work at high temperatures (300-500°C). The performance and sensitivity of nanowires/nanorods based sensors is better than the thin film based sensors [44]. Here is this research we fabricated a simple gas sensor based upon the reactions between the ZnO nanorods spread over the surface and the gases in the atmosphere, which cause a variation in the electrical resistance between the two contact points. The electrical properties of the sensor were found on the overlying nanorods and making multiple bridges from two electrodes.

**Experimental**

**Microfabrication:** Prior to the growth of ZnO nanowires, comb pair like microstructure was made on a substrate applying microfabrication standard steps. First a positive photo resist PF341 was deposited on the substrate by spin coating at 3000 rpm for 30s. Then for soft backing, the substrate was placed on heater providing 90°C for 3min. The desired pattern as shown in the Fig. 1 was made on the substrate using photo mask (2x2cm) and ultraviolet source exposure. In the next step chromium and gold sputtering were done as adhesive and catalytic layers for ZnO growth. Later the photosensitive material along with the Au layer is wiped out and desired pattern remained on the substrate. In the last postbacking was carried out at 120°C by placing sample on heater for 3 min.
Electrical Characterization: The sensing properties of a gas sensor depend upon the reaction between the ZnO nanorods spread over the surface and the gases in the atmosphere, which causes a variation in the electrical resistance between the two contact points. We have studied the electrical properties of sensors focusing on the distribution of nanorods structures overlying and making multiple bridges from two electrodes. We placed the sample in a sealed quartz tube and measure the resistivity of the sample between two electrodes of comb like patterned sensor surface. The quartz tube having inlet and outlet valves for incoming and cleaning gases were placed in the furnace. Initially we closed the outlet valve, enter ethanol gas into the tube and measured the resistivity of the sensor. After the stabilization we removed the gas through vacuum pump and allow air to enter in the chamber. For next reading again closed the outlet valve and allowed ethanol gas to enter in the chamber. Similarly for different concentration of the allowed gases as well as atmospheric temperature we measured the resistivity. Figure 3 illustrates the path for conductivity of the charges and the effect of the gases reaction at the surface.

Gas Response of ZnO Nanorods: To analyze the gas response, quantities were varied such as concentration (ppm), temperature etc. We also observed the transient response of ZnO nanorods sensor. The ethanol gas responses for varying temperatures were recorded while keeping concentration constant at 100 ppm. Figure 4 shows the response of sensor as a function of temperature. The main variation was observed between temperatures 150°C to 400°C. The maximum response of the sensor was observed at 300°C which then start decreasing with the further rise in temperature.
Fig. 2: (a), (b) SEM images of ZnO nanostructures (c) TEM image of ZnO nano structure (d) EDS of the ZnO grown surface.

Fig. 3: Schematic diagram illustrate the sensors ZnO nanorods bridge between two electrodes, the arrow signs show the contact points of the rods.

Fig. 4: Response of the sensor at different working temperatures (100ppm concentration)

Fig. 5: Response of the sensor to different ethanol concentrations at 300°C

To examine the response of the ZnO nanorod sensor different concentrations of the ethanol gas were provided keeping the temperature constant at 300°C. Figure 5 shows that the response of sensor is directly proportional to the provided ethanol concentration. The sensor offer better response from few ppm to 200 ppm.

The transient response of ZnO nanorods sensor was demonstrated. As the response of the sensor at 300°C temperature is the best therefore transient response was seen at 300°C. The response recovery
The resistance between the two contacts has been evaluated as a function of temperature and gas concentration. The best sensor response was demonstrated at operating temperature of 300°C for different concentration. Our sensor can also be used for other gases, the only change occur in the response is the different energies of adsorption, desorption and therefore change in temperature of the sensing gas.

**REFERENCES**


