

ZnO Nanobelt Based Conductometric H₂ and NO₂ Gas Sensors

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Abstract— Conductometric H₂ and NO₂ gas sensors based on single-crystalline ZnO nanobelt sensitive layers have been developed. These layers were deposited using a rf magnetron sputterer. TEM and SEM characterization methods were employed to study the morphology of the nanobelts. These sensors were exposed to H₂ and NO₂ gases at operating temperatures between 225°C and 420°C. Study showed that sensors responded with highest magnitude at above 300°C. The fastest response and recovery times, with greater repeatability occurred at 385°C and 350°C for H₂ and NO₂ gases, respectively. Sensor with ZnO nanobelts has a much lower optimum operational temperature than that of conductometric sensors with other forms of ZnO crystal layers.

I. INTRODUCTION

Recent advances in the synthesis, structural characterization and physical properties investigation of nano materials provide the opportunity to dramatically improve the response of these materials for gas sensing, as their performance is directly related to granularity, porosity and ratio of exposed surface area to volume. Due to their nanoscale size, these materials often show novel physical properties, which differ from those of the same material in bulk form. Those one-dimensional nanostructured materials are of great interest for fundamental physics, functional devices, molecular sensors and potential nano-device applications [1]. Superior performance devices have already been fabricated from nanostructured semiconductor oxides, metals, polymers and carbon.

Devices based on conductometric semiconductor metal oxide (SMO) thin films are the most promising among solid state gas sensors, due to their small dimensions, low cost, low power consumption, on-line operation, and high compatibility with microelectronic processing. They have been used extensively for gas sensing based on film conductivity changes caused by interaction with gas molecules [2-7]. Intense research and development have been conducted to design highly sensitive, selective and

stable gas sensors since Seiyama first observed gas sensing effects in metal oxides [8].

Gas sensing is concerned with surface and interface interactions between the surface molecules and the gas molecules to be detected. Many reactions on the surface of sensors are possible, which can be acceptable as the gas sensing mechanism. However, the most dominant reaction is a reversible gas adsorption mechanism that occurs on the sensor's surface. The adsorbed gas atoms inject electrons into or extract electrons from the semiconducting material, depending on whether they are reducing or oxidizing respectively [9]. This change in conductivity is directly related to the amount of analyte present in the environment, resulting in a quantitative determination of gas concentration.

Semiconducting oxides in the form of nanobelts, nanofibers, nanorods, nanoribbons, and nanowires are of growing importance for the development of highly sensitive gas sensors. The sensitivity of solid state gas sensors increases with decreasing grain size [10], as the entire thickness of the sensitive layer can be affected by the redox reaction of the gas species. ZnO nanobelts, with a distinct structural morphology (wurtzite family), characterized by a rectangular cross section and a uniform structure, are very promising for the development of gas sensors [11]. Their large exposed surface area and nanoscale dimensions allow quick diffusion of gases into and out of the belt which increases the intensity of reactions resulting in faster sensor response and recovery time. Numerous nanostructured materials have been reported to be usable as gas sensors in literature, such as SnO₂ nanobelts for CO and NO₂ sensing, In₂O₃ nanowires for NO₂ detection, WO₃ nanowires for NO₂ sensing, TiO₂ nanotubes for H₂ sensing, Mo and Pd nanowires for H₂ sensing and carbon nanotubes for H₂ detection [12-17].

Zinc Oxide (ZnO) is a wide band gap metal oxide that exhibits semiconducting, photoconducting, piezoelectric and pyroelectric properties with wide-ranging applications in varistors, gas sensors, SAW devices, transparent electrodes,

catalysts etc [18]. It has a hexagonal close-packed structure (wurtzite type) with the band gap of 3.37 eV, and a large exciton binding energy of 60 meV. The micro structural and physical properties of ZnO can be modified by introducing changes into the procedures of its chemical synthesis [19]. A common concern about the ZnO thin film based gas sensor is the lack of selectivity and higher operating temperature. In general, its optimum operating temperature is 400°C-450°C [10].

Various ZnO nanostructures growth techniques have been reported in literature, such as wet chemical process, chemical vapor deposition, pulsed laser deposition, metal-organic vapor phase epitaxy, molecular beam epitaxy, electrochemical deposition, thermal evaporation and sputtering [20].

Hydrogen gas is a reducing agent for an n-type ZnO layer, increasing its conductivity on interaction. As the hydrogen dissociates on the surface of the sensor it injects electrons in the ZnO selective layer. As a result, the conductivity between the electrodes increases i.e. resistance decreases when hydrogen is exposed to the device.

In this paper, ZnO nanobelts were synthesized using radio frequency (rf) magnetron sputtering technique for gas sensing applications. The sensor design, fabrication and synthesis of the deposited ZnO nanobelts are investigated. Finally, the response of the sensors to different H₂ gas concentration between 225°C and 420°C is illustrated.

II. EXPERIMENTAL

The conductometric transducer was designed and fabricated to operate as a resistive element. It was made up of two important physical components: the sensitive ZnO nanobelts layer, which interacts with the gas media and the transducer, which converts the chemical reaction to an electrical signal. Sapphire 3X3 mm² transducer with platinum (Pt) – sputtered electrodes and heater was fabricated for the experiment.

Zinc oxide was deposited on the conductometric sapphire substrate using rf sputtering without the presence of a metal catalyst [20]. Initially, the sputtering chamber was evacuated to a pressure lower than 10⁻⁵ torr. Deposition of ZnO products was then carried out at a pressure of 40 mtorr and an rf power of 300 W for 60 minutes duration. The ZnO target was prepared by conventional solid-state method from 99.9% pure ZnO powder. During deposition of ZnO, there was no external heating provided to the substrate. Normally, deposition of ZnO by sputtering technique would result in the formation of thin films, which are transparent. However, ZnO products deposited on sapphire substrate appear white, indicating randomly oriented nanostructures.

The scanning electron microscopy (SEM) (Fig. 1 and 2) and transmission electron microscopy (TEM) (Fig. 3) results indicate that the ZnO layer deposited on the substrate consist of nanobelts with a single crystal hexagonal structures having thickness, width and length of about 10nm, 50nm and

several micrometers, respectively. The TEM analysis also indicated that the ZnO nanobelts grew along $[1\bar{1}20]$ and $[2\bar{1}10]$ direction on (0001) plane. The TEM image (Fig. 3) reveals that the geometrical shape of the ZnO nanostructures are nanobelts. Additionally, the cross streaking of the spot in the inset of Fig. 3 indicates that ZnO nanostructure has belt-like structure. The ZnO nanobelts have a distinct structural morphology characterized by a rectangular cross section and a uniform structure.

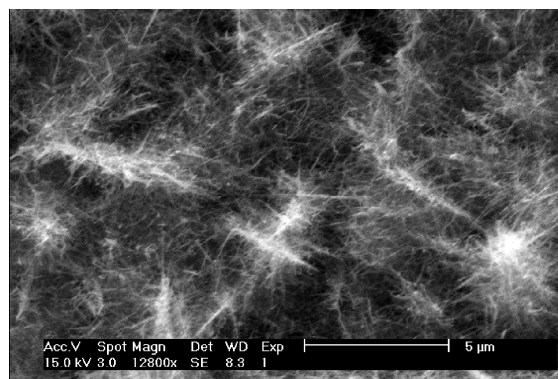


Figure 1. SEM image of ZnO nanobelts on alumina substrate in 5 μm scale.

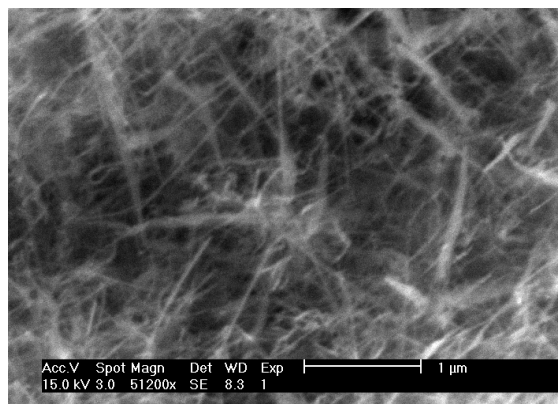


Figure 2. SEM image of ZnO nanobelts on alumina substrate in 1 μm scale.

The sensor device was mounted inside an enclosed environmental cell. The four mass flow controllers (MFC) were connected to form a single output that supplied gas to the cell. Teflon tubing ensured the minimization of atmospheric changes. A constant flow rate of 0.2 litres per minute was delivered via the MFCs. A computerized gas calibration system is used to vary the concentration of H₂ and NO₂ in synthetic air. Custom LabVIEW-based software was used to autonomously control the experimental setup and take measurement of the sensors. The sensor responses were displayed in real-time and saved for off-line processing and analysis.

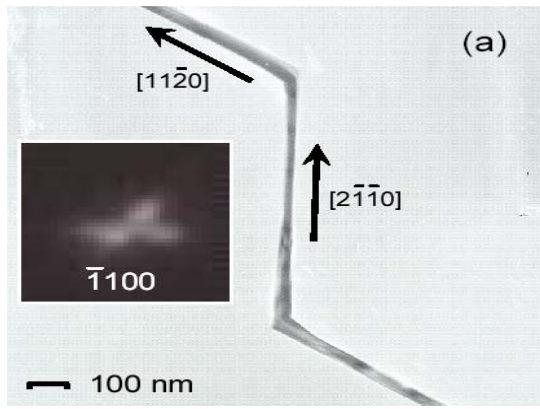


Figure 3. TEM bright field image of a ZnO nanobelt, the inset is a zoom of $\bar{1}100$ spot.

Gas exposure time was fixed at one minute for each pulse of H_2 and two minutes for NO_2 gas. The cell was purged with synthetic air for four minutes between each pulse to allow the surface of the sensor to recover to the atmospheric conditions.

Heating for the transducer is provided by a micro heater fabricated on its back face with a patterned platinum resistive element. The operating temperature of the sensor was controlled by a regulated DC power supply. The sensor was tested between the range of $225^\circ C$ and $420^\circ C$ in increments of approximately $30^\circ C$. From the experiment conducted, operational temperature was found to be an important parameter. The adsorption and desorption are temperature activated processes, thus dynamic properties of the sensor (sensitivity, stability and response and recovery time) depend on the temperature [21].

The sensor was exposed to H_2 gas pulse sequence of 0.06%, 0.125%, 0.25%, 0.50%, 1%, and 0.125% (repeat) concentration in synthetic air and NO_2 gas pulse sequence of 0.6, 1.25, 2.5, 5, 10 and 1.25 (repeat) ppm concentrations in synthetic air at different operating temperatures between $225^\circ C$ and $420^\circ C$. The sensor was connected in series with a Keithley 2001 multimeter and a computer was used to log data from the multimeter, related to resistance variation in real-time.

III. RESULTS

ZnO nanobelts based sensors require an elevated operating temperature to enhance redox reactions so as to achieve the optimum sensitivity. The normalized sensor response magnitude to different concentrations of H_2 and NO_2 gases with temperature variation are shown in Fig. 4 and 5. It was found that the sensor responded with highest magnitude at above $300^\circ C$ operational temperatures for both H_2 and NO_2 . However, at operational temperatures of $350^\circ C$ and $385^\circ C$, the sensor was found to have fastest response and recovery time with greater repeatability and baseline stability. Fig. 6 and 7 shows the dynamic responses of the

sensor to different concentrations of H_2 at $385^\circ C$ and NO_2 at $350^\circ C$, respectively.

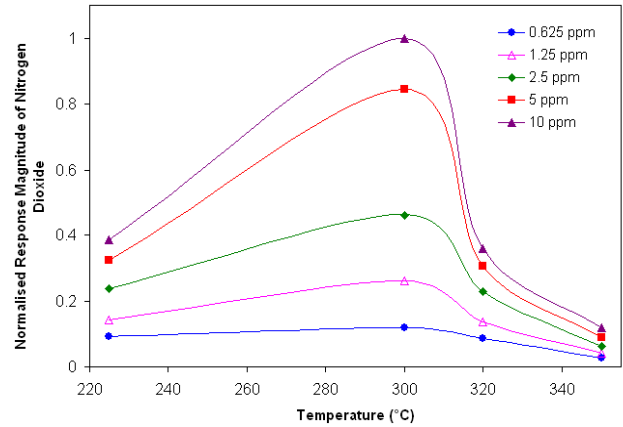


Figure 4. Comparison of normalized response magnitude for different NO_2 concentrations vs operational temperature.

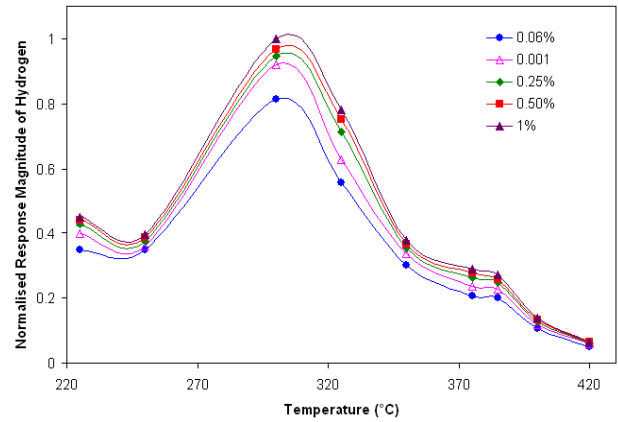


Figure 5. Comparison of normalized response magnitude for different H_2 concentrations vs operational temperature.

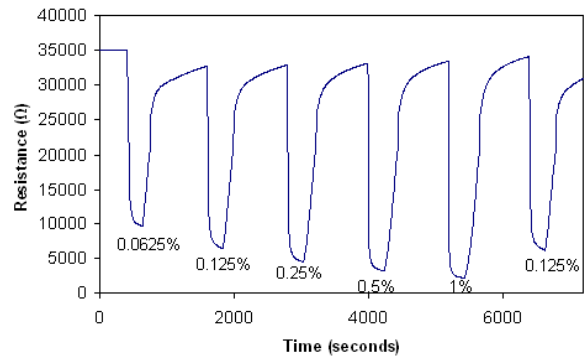


Figure 6. Dynamic response of the conductometric sensor to different H_2 gas concentrations in synthetic air at $385^\circ C$.

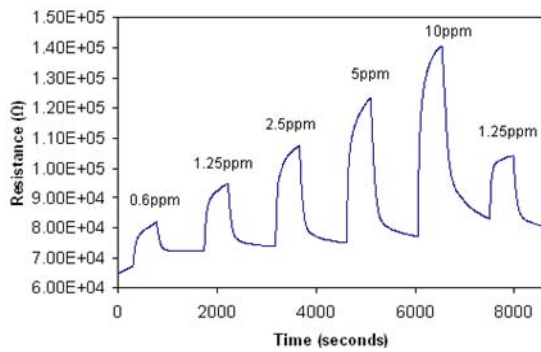


Figure 7. Dynamic response of the conductometric sensor to different NO_2 gas concentrations in synthetic air at 350°C .

The sensor response for reducing gas, defined as the ratio of the baseline resistance to the sensor resistance after exposure to gas ($R_{\text{air}}/R_{\text{gas}}$), is 15.32, towards 1% of H_2 at 385°C . For oxidizing gas, the sensor response defined as the ratio of the sensor resistance after exposure to gas to the baseline resistance ($R_{\text{gas}}/R_{\text{air}}$), is 1.81, towards 10 ppm of NO_2 at 350°C . A relatively fast response time of 40 seconds and a recovery time of 120 seconds were observed for 1% H_2 at 385°C . For 5 ppm NO_2 , a relatively fast response time of 120 seconds and a recovery time of 150 seconds were observed at 350°C . Repeatability was also observed when two pulses of 0.125% H_2 and 1.25 ppm NO_2 introduced to the sensor chamber. We have found that the ZnO nanobelt based sensor gives repeatable responses of same magnitude with good baseline stability towards H_2 gas at 385°C and NO_2 gas at 350°C .

IV. CONCLUSION

We have fabricated conductometric H_2 and NO_2 gas sensors based on ZnO nanobelts synthesized by rf sputtering of a zinc oxide target under controlled conditions. Novel conductometric gas sensors based on these ZnO nanobelts have been investigated towards H_2 and NO_2 gases at different operating temperatures between 225 and 420°C . Study shows that the sensors responded with highest magnitude at above 300°C for both gasses. The fastest response and recovery time with greater repeatability for H_2 and NO_2 gases occurred at 385°C and 350°C , respectively. Sensor with ZnO nanobelts has a much lower optimum operational temperature than that of conductometric sensors with other forms of pure ZnO crystal layers. The results demonstrate that the developed sensors are promising for industrial applications.

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