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Full Length Article

Gas dependent sensing mechanism in ZnO nanobelt sensor

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ABSTRACT

Gas sensing properties of ZnO nanobelts synthesized using carbothermal reduction method has been investigated. At room temperature (28 °C), the sensor films exhibit an appreciable response towards H_2S and NO and response of these two gases were studied as a function of concentration. For NO the sensor films exhibit a complete reversible curve for the concentration range between 1 and 60 ppm. However, for H_2S a complete recovery was obtained for concentration <5 ppm and for higher concentration a partial recovery of the baseline resistance was observed. The reason for the incomplete recovery was investigated using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) studies of the sample before and after the H_2S exposure. After exposure, appearance of an additional peak at 26.6° corresponding to the formation of ZnS was observed in XRD. Formation of additional phase was further corroborated using the results of XPS. H_2S exposure causes decrease in the intensity of O 1s peak and appearance of sulphide peaks at binding energies of 162.8 and 161.8 eV corresponding to S-2p peaks – $2p_{3/2}$ and $2p_{1/2}$, confirms the formation of ZnS upon exposure.

1. Introduction

Semiconducting metal oxides are widely used as commercial sensors as they exhibit a wide range of electronic, chemical, and physical properties that are often highly sensitive to chemical environment [1]. These electronic, chemical, and physical properties of oxides are created and can be tuned due to their two unique structural features: mixed cation valencies and an adjustable oxygen deficiency. Among the various oxides, zinc oxide (ZnO) is one of the promising material for gas sensing due to its non-toxicity, high chemical and physical stability and low cost. The structure of ZnO mainly comprises of number of planes containing tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000$\bar{1}$)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis, as well as a divergence in surface energy [2]. It has three fastest growth directions namely ⟨0001⟩, ⟨0110⟩, and ⟨2110⟩. Importantly, ZnO exhibit a wealth of interesting nanostructures that have demonstrated the potential to realize highly sensitive gas sensors. The different nanoforms of ZnO include nanoparticles, nanowires, nanobelts, nanosheets, nanoflowers, hexagonal discs, cones and much more. The surface area to volume ratio exhibited by these nanoforms has been utilized effectively to realize sensors for various gases. These include CH_3CH_2OH, CH_3COCH_3, O_3, NO_2, CO, H_2S, H_2, HCHO, NH_3, LPG etc [3–11]. Sensor response is reported to increase with decrease in grain size [12–14]. Traditionally, ZnO gas sensors are implemented as chemiresistive sensors, which work on the principle of change in electrical resistance due to interaction between the semiconductor and the test gas [15,16].

Of the different nanoforms, nanobelts which have a rectangular cross section, in correspondence to a beltlike (or ribbonlike) morphology with width-to-thickness ratios of 5 to 10 are particularly promising for gas sensing applications due to their smaller thickness. Nanobelts are generally more defect rich in comparison to that of nanowire counterparts [17]. However there are only a few studies on investigation of gas sensing properties of ZnO nanobelts [18–22]. In the present work, H_2S and NO gas sensing properties of ZnO nanobelts sensor has been investigated.

Nitric oxide (NO) is readily converted in the air to nitrogen dioxide (NO_2) [23] with a formation rate constant of 1.2×10^{11} ppm^{-2} s^{-1} [24]. The time to reach 5 ppm NO_2 from 20 ppm nitric oxide in 100% oxygen is 12 min, while in air it is more than 1 h.

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Nitric oxide (NO) reacts with moisture and oxygen present in skin, eye and mucous membrane, and gets converted into nitric and nitrous acids, thus acting as an irritant. Inhalation of (NO) causes coughing and shortness of breath, along with a burning in the throat and chest [25]. Further NO makes the blood vessels expand, which would make people fainted [26].

At high concentration levels, nitrogen dioxide (NO_2) is potentially toxic to plants, it reduces growth and yield of leaves. In combination with either ozone (O_3) or sulphur dioxide (SO_2), nitrogen dioxide may cause injury at even lower concentration levels. As one of the components of smog, nitrogen dioxide (NO_2) is known to irritate the lungs and increase susceptibility to respiratory infections.

H_2S is one of the highly toxic and flammable gases being used in various industrial applications like oil and gas industries, pulp and paper industries, waste water treatment plants and nuclear reactors (heavy water plants). It has a characteristic rotten egg odor and can be detected at concentrations >0.13 ppm by human nose. However, repeated exposures or exposure to higher concentrations causes a drastic decline in the ability to smell. Importantly, it can interact with the enzymes in the blood stream inhibiting the cell respiration. This implies exposure to high concentrations can stop the functioning of lung and could be fatal. The long term (8 h) and short term (10 min) exposure limits of H_2S are 10 and 15 ppm, respectively [27]. Accordingly, it is crucial to detect H_2S at such concentration levels.

In the present work, gas sensing properties of ZnO nanobelts synthesized using carbothermal reduction method have been investigated in detail. At room temperature (~28 °C) nanobelts were found to be sensitive towards H_2S and NO. In case of NO, a complete recovery was observed for concentration <60 ppm whereas for H_2S, complete recovery was observed for concentration <5 ppm. For higher concentrations, a complete recovery is achieved upon heating the sensor film at higher temperature of 250 °C. The slow or partial recovery at H_2S concentrations >5 ppm has been attributed to formation of ZnS. The results of x-ray photo electron and x-ray diffraction further confirmed the formation of ZnS.

2. Experimental

2.1. ZnO nanobelts synthesis

ZnO nanobelts were grown using a carbothermal reduction method. For this a homogeneous mixture of ZnO and graphite in 3:1 ratio (by weight) was used as the source material. The reaction mixture was kept at the middle of the high temperature furnace and heated at 1050 °C with a controlled rate of 6 °C/min under Ar environment (500 sccm). Oxygen at a flow rate of 50 sccm was introduced in the furnace when the temperature reached 700 °C. The furnace was kept at the deposition temperature of 1050 °C for 5 h and was allowed to cool to room temperature. ZnO nanobelts in the form of spongy material like cotton were deposited at the downstream of the tubular furnace and collected for further measurements.

2.2. Characterization

The surface morphology of the ZnO nanobelts were investigated using scanning electron microscope (SEM) (VEGA MV2300T/40 TS 5130 MM, TESCAN) equipped with an energy dispersive X-ray analysis unit (Oxford make INCA X-ACT model). Transmission electron microscope (TEM) measurements were performed on JEOL 2010 instrument equipped with a LaB_6 filament. For this ZnO nanobelts were first dispersed in ethanol and then drop casted onto carbon coated Cu grids. X-ray diffraction (XRD) measurements were performed to determine the structure and phase of nanobelts. X-ray photoelectron spectroscopy (XPS) measurements were performed with Mg-K_α (1253.6 eV) X-ray source and DESA-150 electron analyzer (M/s. Staib Instruments, Germany). The binding energy scale for XPS was calibrated using Au-4f $_{7/2}$ line at 84.0 eV.

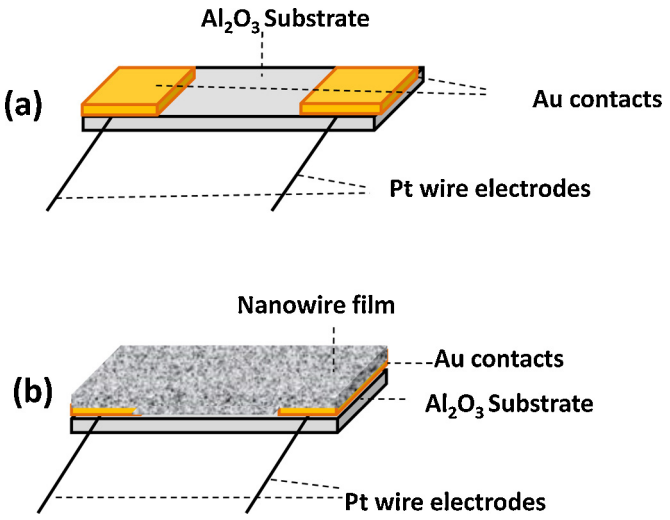

Fig. 1. Schematic of Alumina substrate with (a) predefined contacts and (b) sensor film.

2.3. Sensor fabrication and gas sensing measurements

Sensor films were realized by drop casting a solution of ZnO nanobelts in methanol on an alumina substrate containing prefabricated gold electrodes having thickness of ~120 nm separated by 1 mm spacing as shown in Fig. 1. Sensor films were then annealed in oxygen atmosphere at 500 °C/1 h. The operating temperatures of the sensor film were controlled using a Pt-100 based heater and a temperature control circuit. Sensing measurements were performed in a static setup which comprises of a stainless steel sensing chamber (volume 250 cm^3), a pico-ammeter/voltage source (Keithley 6487) interfaced with a PC facilitated with lab view software [27]. Response curves were measured as a function of temperature and gas concentration. The required concentration of the test gas was achieved by injecting the known amount of gas in the chamber. For recovery, the sensors were subjected to the ambient environment. From the response curves, sensor response (S) was calculated using the relation

$$S = R_a/R_g, \quad \text{for reducing gases } (H_2S) \tag{1}$$

$$S = R_g/R_a \quad \text{for oxidizing gases (NO)} \tag{2}$$

where, R_a and R_g, are resistances in air and test gas, respectively. Response and recovery times were defined as the time required by the sensor films to reach 90% of total change upon exposure to test gas and fresh air, respectively.

3. Results and discussion

3.1. Microstructural characterization of ZnO nanobelts

As shown in Fig. 2, ZnO nanobelts exhibit the characteristic lengths of several micrometers and diameter in the range 100–200 nm. XRD pattern of ZnO as shown in Fig. 2(b) can be indexed to the hexagonal phase of ZnO as per JCPDS Card number 80.0075, with no trace of other phases. Lattice parameters as calculated from the diffraction pattern were found to be $a = b = 0.324$ nm