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Selective H_2S sensing characteristics of hydrothermally grown ZnO-nanowires network tailored by ultrathin CuO layers

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ABSTRACT

Random networks of ZnO nanowires (ZnO-NWs) have been fabricated on the Si/SiO_2 substrates by hydrothermal process using ZnO-nanoparticles as seed. The ZnO-NWs networks have been modified by depositing ultrathin CuO layers (nominal thickness: 10 nm) using thermal evaporation of Cu followed by oxygen annealing at 600 °C. The results of photoluminescence measurements on ZnO-NWs and CuO:ZnO-NWs networks suggest formation of a p–n junction between p-CuO and n-type ZnO. The gas sensing characteristics of both ZnO-NWs and CuO:ZnO-NWs networks have been investigated. It has been demonstrated that CuO:ZnO-NWs network has selective response toward H_2S with a sensitivity of ~40 (for 10 ppm) at an operating temperature of 200 °C. A sensing mechanism based on the destruction of p–n junctions due to the formation of metallic CuS (product of chemical reaction between CuO and H_2S) has been proposed.

1. Introduction

One dimensional nanostructures of metal oxides namely nanowires (NWs) have emerged as a general platform for ultrasensitive direct electrical detection of biological and chemical species [1,2]. NWs, in particular offer various advantages like 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 and possibility of high integration densities [3–5]. Among the various metal oxide NWs, zinc oxide (ZnO) NWs have been widely investigated due to their excellent electrical, thermal and chemical properties [6,7]. These include wide band gap (3.37 eV), high exciton binding energy (60 meV), high thermal stability, flexibility of synthesis using physical and/or chemical processes, precise control over morphology and ease of incorporation into microelectronic devices [8,9]. 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 [10]. In this case, 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 deposited connecting NW and electrode using focused ion beam techniques [11,12]. The complexity and the randomness of the approach respectively raise the concern over the reproducibility and repeatability of the sensors.

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 [13]. This method is advantageous over the one involving the 'pick and place' approach as it removes the complexity and the randomness. Besides, it is easy and assures reproducible measurements. Accordingly, ZnO NWs have been investigated for their response toward various gases like H_2S [14], C_2H_5OH [15] and CO [16]. It is well established that the sensitivity and selectivity of metal-oxide sensors can be improved by using different strategies, such as, incorporation of noble metals (Pt, Pd, Au, etc.) [17,18] and making composites of metal-oxides [19–21]. In particular, for ppm level H_2S detection it has been demonstrated that the selectivity can be greatly enhanced if the sensing element consists of random p–n junctions, e.g. SnO_2/CuO, where SnO_2 is n-type and CuO is p-type [19,20]. Accordingly, in the present work, we demonstrate an easy method for the fabrication of random p–n junction networks consisting of ZnO-NWs and CuO that work as an excellent sensor toward H_2S. CuO:ZnO-NWs random networks were prepared in two steps: (i) ZnO-NWs random networks were grown on Si/SiO_2 substrates by hydrothermal method and (ii) ZnO-NWs networks were modified with ultrathin CuO layer by thermal evaporation. Our results indicate that the operating temperature of maximum

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sensitivity of ZnO NWs network can be brought down from 300 to 200 °C by modifying the surface of ZnO-NWs network with 10 nm of CuO layer. Besides, the sensor responded toward H_2S with high sensitivity ($S \sim 40$ for 10 ppm) and selectivity.

2. Experimental

The random networks of ZnO-NWs were grown on the Si/SiO_2 (100 nm) (size 10 mm × 10 mm) substrates by hydrothermal method using ZnO nanoparticles as seed. Fig. 1 schematically represents the different steps involved in the fabrication process. ZnO-nanoparticles employed as seed were synthesized using a chemical route as reported elsewhere [14,22]. In brief, a 3 mM NaOH solution (in methanol) was added drop wise to a 10 mM solution of zinc acetate (in methanol) at 60 °C under continuous stirring. The volume ratio of the two solutions was maintained at 2:1. The stirring was continued for over 100 min. The resulting nanoparticles in solution were having diameter between 5 and 10 nm and were stable for a period of upto two weeks [14]. Coating of seed particles onto the substrates was achieved by spin casting (3 times) as-synthesized nanoparticles solution. ZnO-NWs growth was carried out by suspending the coated wafer upside-down in an open beaker filled with an aqueous equimolar (0.025 M) solution of zinc nitrate hexahydrate, $Zn(NO_3)_2{\cdot}6H_2O$, and hexamethylenetetramine (HMTA), $(CH_2)_6N_4$, at 90 °C for 6 h. After growth, the substrates were rinsed thoroughly using de-ionized water and dried under Ar flow. In order to fabricate the p–n junctions using random ZnO-NWs networks, CuO layers with varying nominal thickness between 5 and 100 nm were deposited by thermal evaporation of Cu films (under a base vacuum of 10^{-6} Torr) followed by oxygen annealing at 600 °C for 1 h. Hereafter, these samples will be referred to as CuO (*d* nm):ZnO-NWs networks (*d* is the nominal thickness of the CuO layer). Using hydrothermal method ZnO NWs can be grown uniformly over a bigger size wafers (4 in.). The growth of NWs onto the substrate is highly reproducible and repeatable under identical conditions of temperature and solution concentrations. Besides, modification of NWs network by CuO layer or electrode deposition using a mask can easily be repeated/reproduced thereby making the complete fabrication process highly repeatable.

For gas sensing measurements, two gold electrodes (120 nm thick at a spacing of 1 mm) were thermally deposited onto ZnO-NW and CuO:ZnO networks. A Pt wire heater was attached at the backside of the substrate to maintain and control the operating temperature of the sensor. The response of the sensor to various test gases (CO, NO, NH_3, H_2S, CO_2, Cl_2) was recorded using a static gas sensing set-up as shown in Fig. 2. Briefly, the sensor was mounted in a stainless steel chamber having volume of 250 cm^3. Required concentration of a test gas in the chamber was attained by introducing a measured quantity of desired gas using a syringe. The response curves were measured by applying a fixed bias of 2 V across the electrodes and the time dependence of current was recorded using Labview based data acquisition system. After attainment of a steady state, recovery of the sensors was recorded by exposing them to the fresh air. The sensitivity of the sensors was calculated from the response curves using the relation:

$$S = \frac{I_g}{I_a} \quad \text{or} \quad \frac{I_a}{I_g} \tag{1}$$

where I_g and I_a are current values of the sensor in test gas and fresh air, respectively. Response and recovery times were defined as the times needed for 90% of total change in current on exposure to test gas and ambient air, respectively.

Surface morphology of the samples was investigated using scanning electron microscope (SEM), (TESCAN, model: TS 5130MM) equipped with energy dispersive X-ray analysis (EDX), (Oxford INCA). The structure of nanowires was identified by X-ray diffraction (XRD) using Cu-Kα radiation. Photoluminescence (PL) studies were carried out using Edinburgh Fluorescence Spectrometer FLP

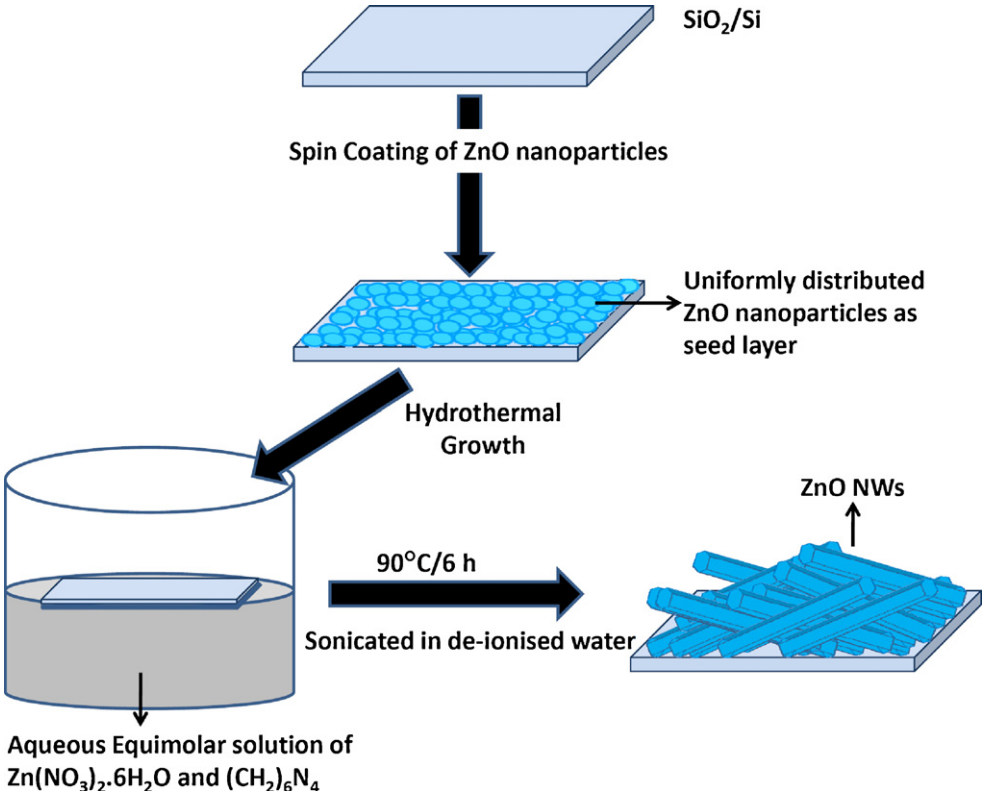

Fig. 1. Schematic showing the steps involved in the growth of ZnO-NWs random networks on Si substrate by hydrothermal process.