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Room temperature chemo-resistive sensor based on two dimensional ZnO nanoflakes for ammonia detection

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Abstract
Ammonia detection in the atmosphere is an extremely significant requirement with implications to the environment and living beings. In this current era of technology, there is a great demand for highly sensitive, compatible, low-cost portable sensors for the fabrication and improvement of sensing device performance. In this work, the ZnO nanoflakes were grown by a modified aqueous method on n-type silicon substrate, where zinc nitrate, hexamethylenetetramine (HMTA) and aluminum nitrate nonahydrate were taken as precursors. The structural and morphological properties with various concentration of aluminum were investigated using scanning electron microscopy (SEM) and X-Ray diffraction (XRD) techniques. Flakes-like nanostructures were observed by the SEM studies. The X-ray diffraction pattern has shown the evolution of (002) and (103) peaks for ZnO nanostructures. On the other hand, ZnO nanorods were grown on silicon substrates using Zinc nitrate and HMTA. The average length and width of the ZnO nanorods was found to be around 2-3 µm and 350-410 nm, respectively. A comparative study on the ammonia sensing behaviour of hydrothermally grown ZnO nanoflakes and nanorods were carried out by current-voltage measurement technique at room temperature. ZnO nanoflakes showed higher response rate for ammonia detection than as-grown ZnO nanorods.

Keywords: Nanoflakes, Zinc oxide, Aqueous method, Ammonia sensor

1. Introduction

Sensitivity of a material is mainly dependent on the surface area of the sensing material, which enhances the interaction between the materials and its surrounding environment. Among numerous chemicals, detection of ammonia is vital due to its toxic and extensive use in many areas, such as environmental monitoring, fertilizer and chemical industries [1]. Different types of semiconducting metal oxide materials, conducting polymers are used for ammonia detection [2]. However, polymers are thermally unstable and moisture sensitive, which limits their high temperature application [3]. On other hand, metal oxide semiconductor such as ZnO based NH_3 sensors require high operating temperatures (typically > 250 °C) to trigger the adsorption and desorption processes of NH_3, which results in consumption of high power and limits their use in low temperature applications [4-6]. Thus, sensitive detection of ammonia at room temperature is still highly required. Hence, an attempt has been made in this research work to study the sensing behavior of CuO thin films for OP detection. Zinc oxide (ZnO) possesses a rich family of nanostructures (nanowires, nanorods, nanoflakes, nanotubes etc.) and has their realistic applications for future next generation of electronic devices. The inspiration behind the development of low dimensional nanostructures (NS) with superior sensing behavior is its enhanced surface area. Therefore, extensive research on the growth of low dimension ZnO with various surface morphology is very essential. Since the performance of the sensors strongly depends on the morphology of ZnO NS, it is very essential to specifically control their orientation and surface morphology to exploit its properties in different realistic fields. In order to obtain ZnO NS with high aspect ratio and well-aligned orientation, many vacuum related techniques have been devoted such as vapor–liquid–solid (VLS) and metal organic chemical vapor deposition (MOCVD) method [7-8]. However, these methods have some drawbacks such as expensive apparatus, complicated procedure and high temperature operation. Thus, there is a need of simple robust technique for the growth of various types of ZnO NS. Hydrothermal and electrochemical processes are two important low temperature approaches for the growth of ZnO NS [9-10]. Hydrothermal method was introduced by Vaysseries et al. for the growth of ZnO nano wires [11]. The main advantages of low-temperature solution routes over other methods are their simplicity, low cost and large-area production [12]. In this work, ZnO nanoflakes and nanorod were grown on silicon substrates by hydrothermal method. Further, to develop the next generation of reliable and high-performance sensors, the ammonia sensing behavior of hydrothermally grown nanoflakes and nanorods, is discussed.

Materials and methods

Silicon substrates were used to grow ZnO NS by modified aqueous method. Before the growth process, pieces of silicon with a surface 1.5×1.5 cm^2 were ultrasonically cleaned by successive treatment of acetone, isopropanol and deionized water (Milli-Q system ~18.3 $M\Omega^-$ cm) for 10 min each followed by acid treatment. A seed layer of ZnO (200 nm) was deposited onto n-type silicon [(100), 1-10 Ω.cm] substrates using reactive radio frequency (RF) magnetron sputtering technique at 200 °C [13]. In order to grow ZnO nanorods, hydrothermal solution was prepared by mixing equimolar aqueous solutions of the zinc nitrate $Zn(NO_3)_2$ (purity > 99%) and HMTA (purity 99%). All chemicals were purchased from Sigma Aldrich and used without further purification. However, for the fabrication of nanoflakes an appropriate amount of $Al(NO_3)_3.9H_2O$ (99.997% Sigma Aldrich) powders were added according to 1-5 wt.% of aluminium in equimolar solution of $Zn(NO_3)_2$ and HMTA.

The structural investigations were carried out by X-ray diffraction (Rigaku/Ultima IV) with a CuKα (λ=0.154nm) radiation. The morphological investigation were carried out using Field Emission Scanning Electron Microscopy (FESEM, Nova/NanoSEM 450). The electrical contacts between metal (aluminum) and semiconductor (CuO) samples were made by using thermal evaporation of aluminum. Ammonia sensing study of the grown nanostructures (nanorods and nanoflakes) were examined by current-voltage (I-V) measurements using a Keithley picoammeter (model 6487) at room temperature.

Results and discussion

Spectroscopic analysis

Fig. 1(a) depicts the crystalline nature of hydrothermally grown ZnO NS with the appearance of (002) peak. Besides, additional peaks along the plane (100), (101) and (103) planes are also observed [14]. Fig. 1(b) shows the XRD patterns of the nanostructures with the addition of aluminum nitrate. Two peaks along the (002) plane and (103) has been observed, which confirms the formation of ZnO phase. No characteristic peaks of other impurities were detected in the pattern [15].

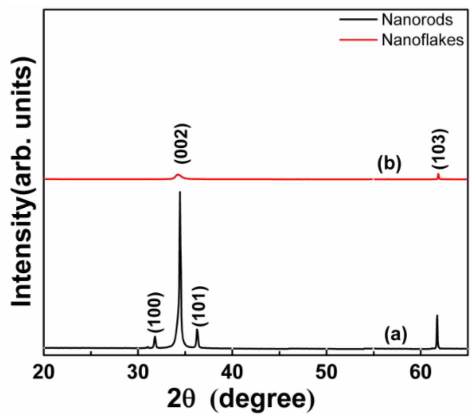

Fig. 1: X-ray diffraction pattern of ZnO nanostructures (a) Nanoflakes, addition of 5 at% aluminium, (b) Nanorods 0.01 M at 85 °C

Figure 2(a) shows the FESEM images of ZnO nanorods grown by hydrothermal method. Short ZnO nanorods (length: 1-2 μm, diameter: 150-250 nm) were obtained, when growth process was conducted at 85 °C. Although low temperature favors the formation of nucleation sites, it does not have enough energy for the subsequent growth of nanostructures. The FESEM micrograph shown in Fig. 2(b) depicts ultrathin flake-like nanostructures have grown on seed layer. FESEM images depicts the formation of non-uniform flakes like structures having width around 400-600 nm. In this study, the change in morphology of nanostructures has been observed due to the presence of Al species [16]. These Al-complexes bind to the polar surfaces and the growth of ZnO NS along c-axis is restricted. As a result, growth of ZnO NS along lateral direction takes place, which in fact gives rise to the formation of ZnO nanoflakes.

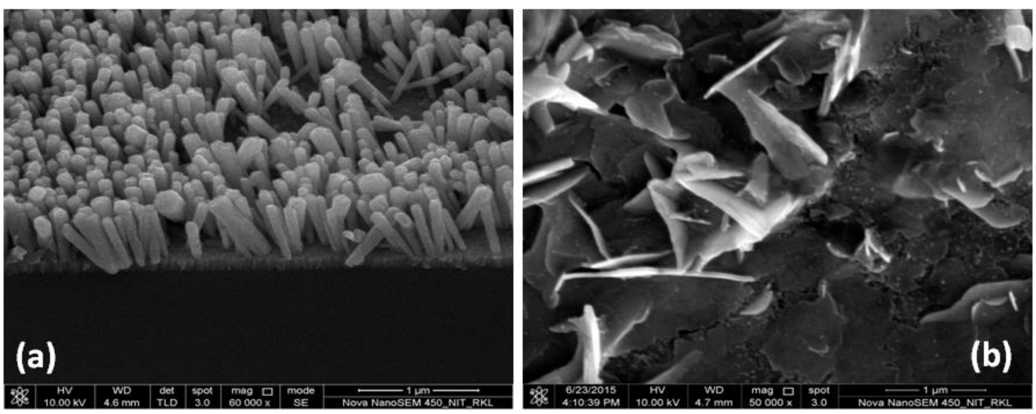

Fig. 2: FESEM images of (a) ZnO nanorods grown at 0.01 M at 85 C, (b) ZnO Nanoflakes with addition of 5 at.% aluminium. The scale bar represents 5 μm.

Ammonia sensing study

For all the ZnO samples, the nanostructures obtained (nanorods, nanoflakes) has shown an enhancement in the sensitivity with an increase in ammonia concentration from 50-1000 ppm. This is attributed to the reduction in the adsorbed surface oxygen. Thus, decrease in adsorbed oxygen concentration gives rise to increase of free electron. Fig. 3 (a) shows the variation of sensitivity with various concentration of ammonia for ZnO nanorods. The sensitivity of ZnO nanorods varies between 1% and 16.9 % for 50–1000 ppm of ammonia concentration at room temperature [17]. Fig. 3 (b) reveals the sensitivity (%) of ZnO nanoflakes with the variation in concentration of ammonia at room temperature. For various ammonia concentrations 50-1000 ppm, nanoflakes (S6) sensitivity lies in the range 0.6–8.5% respectively. Addition of aluminum nonahydrate leads to restriction of growth of ZnO nanostructures along c-axis and results in nanoflakes with lower aspect ratio than nanorods. Thus, higher aspect ratio of nanorods as compared to nanoflakes leads to better sensitivity [18].

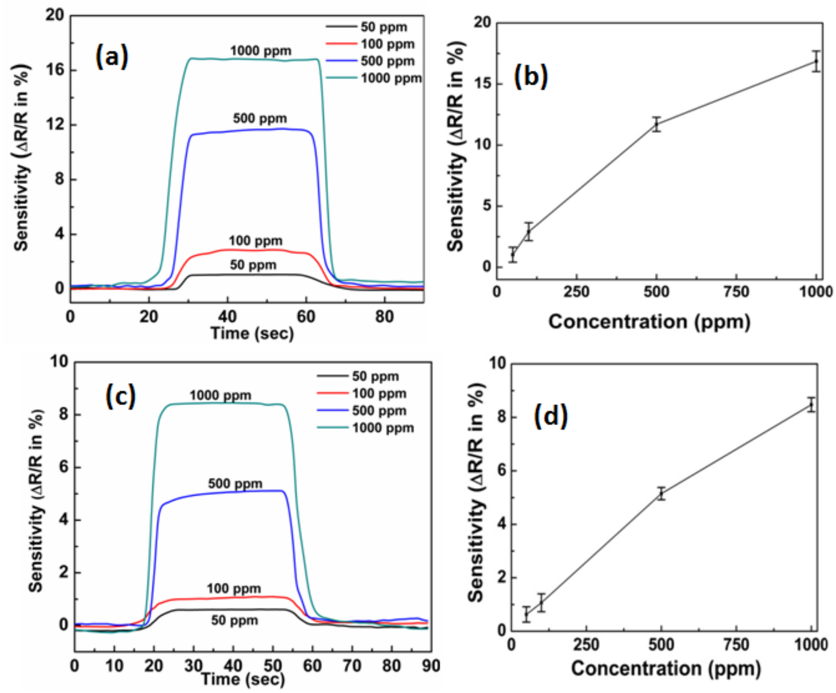

Fig. 3: Sensitivity plot of ammonia for various ZnO nanostructures (a&b) Nanoflakes, (c&d) Nanorods.

For all the ZnO samples, the nanostructures obtained (nanorods, nanoflakes) has shown an enhancement in the sensitivity with an increase in ammonia concentration from 50ppm-1000 ppm. This is attributed to the reduction in the adsorbed surface oxygen. Thus, decrease in adsorbed oxygen concentration gives rise to increase of free electron [19]. Fig. 3 (a) shows the variation of sensitivity with various concentration of ammonia for ZnO nanorods. The sensitivity of ZnO nanorods varies between 1% and 16.9 % for 50 ppm – 1000 ppm of ammonia concentration at room temperature. Fig. 3 (b) reveals the sensitivity (%) of ZnO nanoflakes with the variation in concentration of ammonia at room temperature. For various ammonia concentrations 50-1000 ppm, nanoflakes (S6) sensitivity lies in the range 0.6%–8.5% respectively. Addition of aluminum nonahydrate leads to restriction of growth of ZnO nanostructures along c-axis and results in nanoflakes with lower aspect ratio than nanorods. Thus, higher aspect ratio of nanorods as compared to nanoflakes leads to better sensitivity [20].

Conclusions

In this work, ammonia sensing behavior of nanorods and nanoflakes were obtained at different ammonia concentration by adopting current-time (I-t) measurement. The X-ray diffraction pattern has shown the evolution of (002) and (103) peaks for ZnO nanostructures. The average length and width of the ZnO nanorods was found to be around 2-3 µm and 350-410 nm, respectively. By calculating the change in sample resistance (ΔR/R), the sensitivity was estimated. Sensitivity of ZnO nanorods 8.2% was higher than that of nanoflakes for 1000 ppm of ammonia at room temperature which is due to high aspect ratio as well as higher surface area of the nanorods than nanoflakes. The above experimental results can provide a scope to achieve room temperature operated next generation metal oxide ammonia sensors.

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