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Zinc oxide hierarchical nanostructures as potential NO_2 sensors

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ABSTRACT

A superficial thermal evaporation method has been employed for the fabrication of hierarchical zinc oxide (ZnO) nanostructured films, composed of nanorods (NR's) and bunch of nanowires (BNW's), on glass substrate and the diverse atmospheric annealing effect on their structural, morphological, compositional, and gas sensing properties has been systematically studied and reported. Structural investigation corroborates the formation of crystalline hexagonal wurtzite ZnO. The arrays of vertically aligned nanorods and bunch of nanowires of ZnO were observed on the substrate surface. As-prepared ZnO NR's and BNW's are utilized as a sensing material for detection of toxic nitrogen dioxide (NO_2). The ZnO sensors exhibit high response to NO_2 along with rapid response and recovery time values @200 °C. In addition, ZnO sensors respond to a very small exposure of NO_2 gas i.e. 1 ppm. Furthermore, the developed sensors attain excellent stability and reproducibility in response. Finally, the interaction of NO_2 gas molecules with hierarchical nanostructured ZnO sensors has successfully been studied and discussed by employing an electrochemical impedance spectroscopy measurement.

1. Introduction

Metal oxide semiconductor-based gas sensors have been extensively investigated for the purpose of monitoring environmental biodiversity and detection of explosive and toxic gases at their lower concentrations [1–3]. Also, the detection of harmful gases is extremely essential for personal safety protection. In recent years, new morphologies like single-walled carbon nanotubes [4–6], nanoparticles [7–9], and semiconducting nanowires [10–13] etc., hold exhilarating prospects in sensors application, due to of their minuscule sizes; miniature molecules are enough active to vary the electrical properties of the sensor elements when used in electronic devices. One-dimensional (1D) nanostructured sensors have received considerable attraction as compared to thin film gas sensors due to their rapid response, superior spatial resolution, and higher sensitivity that arises from the elevated surface-to-volume ratio [14]. Recently, 1D semiconductor metal oxide nanostructures such as tin oxide (SnO_2), zinc oxide (ZnO), vanadium oxide (V_2O_5), and tungsten oxide (WO_3) have demonstrated excellent sensing properties with rapid response and recovery time values [15–22]. A wurzite crystal structure and wide band gap energy (3.37 eV) of ZnO made it a potential gas sensing material, which can be synthesized by chemical vapor deposition [23–26], thermal evaporation [25], plasma reaction [26], laser ablation [27], and arc/solution methods [28,29]. Among the abovementioned methods, growth of ZnO by thermal evaporation has several advantages as the growth is free from the catalyst. Due to intrinsic properties, ZnO (II–VI type semiconductor) has widely been used in several applications such as photocatalysts [30], solar cells [31], field effect transistors [32], luminescent materials [33], and gas sensor [34] etc. Moreover, it's less toxicity, low cost, availability of diverse morphologies, optimal conductivity, and amazing stability has additional benefits while scaling up the devices, used commercially.

Different types of ZnO nanostructures have been synthesized in literature and used in gas sensing application for the detection of methane, ethanol, nitric oxide, acetone, chlorobenzene, hydrogen, ammonia, nitrogen dioxide, and chlorine etc. [35–37]. A common air pollutant nitrogen dioxide (NO_2) gas is produced throughout combustion in industrial factories, automotive engines, and power plants. According to environmental protection agency (EPA), the toxicity limit of the NO_2 gas for the environmental issue is 53 ppb [38]. Therefore, there is a need to develop highly sensitive NO_2 gas sensors that can detect low concentrations of NO_2 with excellent

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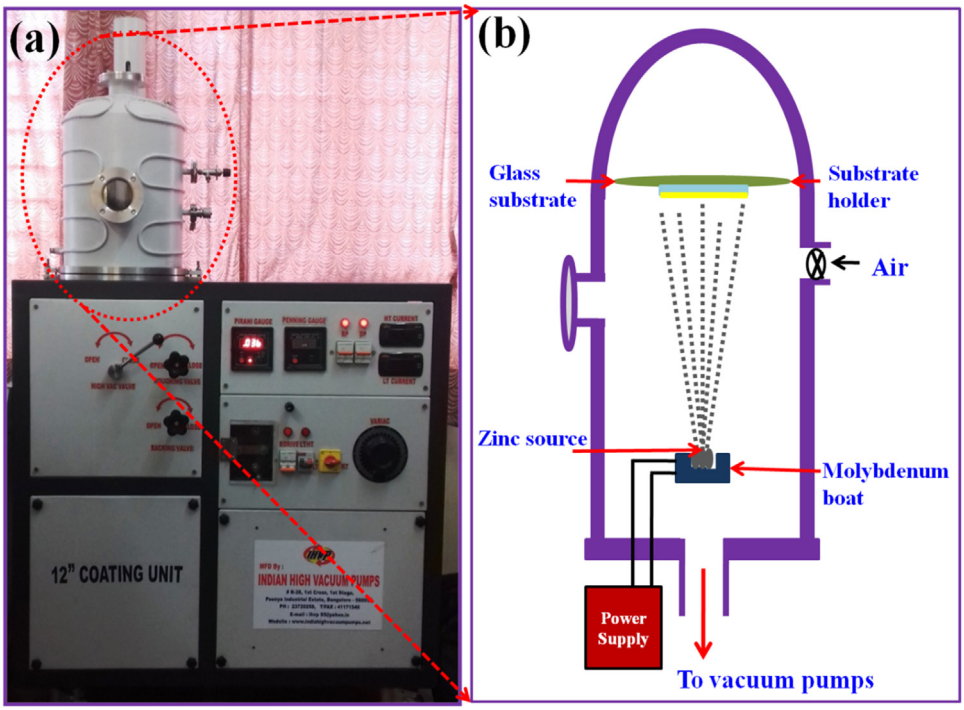

Fig. 1. Thermal evaporation set up (a) Photograph and (b) Schematic view.

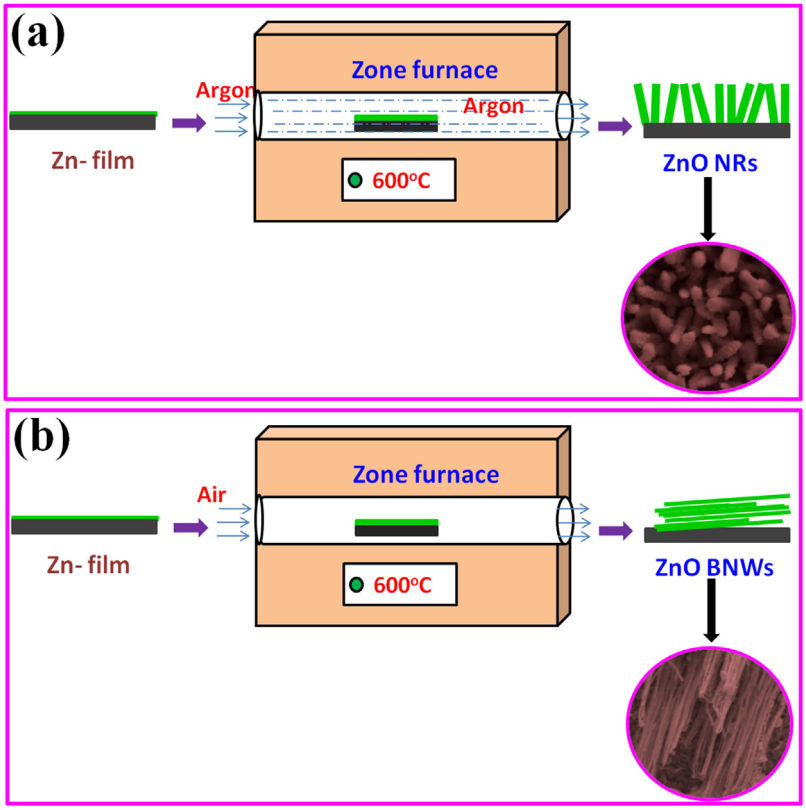

Fig. 2. Scheme of formation of ZnO (a) NR's (b) BNW's.

stability. Such type of sensors can be used for effective environmental monitoring.

The main thrust of the present work is to synthesize the hierarchical ZnO nanorods (NR's)/bunch of nanowires (BNW's) by simple thermal evaporation method, followed by annealed in argon gas & air, respectively, and examine their sensing properties to diverse toxic gases at different temperatures. Gas sensing results revealed the ability of ZnO NR's/BNW's to detect NO_2 gas with fast response time and recovery time at operating temperature 200 °C. The physical (structural and surface morphological) and gas sens-