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Original Research Paper

Facile synthesis of Sn doped ZnO nanotetrapods for detection of relatively non-lethal volatiles

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ABSTRACT

While there's a perpetual buzz around zinc oxide superstructures for their unique optical features, the versatile material has been constantly utilized to manifest tailored electronic properties through rendition of distinct morphologies. And yet, the unorthodox approach of implementing the hierarchical structures of ZnO for volatile sensing applications has ample scope to accommodate new unconventional morphologies. Likewise, this article presents self-catalytic synthesis of Sn-doped ZnO nanotetrapods on Si (1 0 0) substrates through thermal evaporation–condensation method, and their subsequent deployment for volatile sensing. In particular, the sensors were utilized to detect molecules of acetone and ammonia below their permissible exposure limits which returned sensitivities of around 80% and 50% respectively. The influence of Sn concentration on the growth, microstructural and optical properties of the nanoprisms along with its role in augmenting the sensing parameters has been detailed. The features for the nanoprisms include a length of few micrometers along with a diameter ranging from 300 to 500 nm. High resolution microscopic images confirmed the hexagonal crystallography for the nanoprisms, while SAED pattern asserted the single crystalline nature. An estimate of the sensing parameters against dispensed target molecules highlighted the potential for the nanoprisms as an effective volatile sensing material.

1. Introduction

Volatile detection with solid state gas sensors refers to the manifestation of an electronic signal resulting from a physical imbalance in the sensing material upon exposure to target analytes. Though targeted engineering of the interfacing circuits [1], alteration of the operating temperature [2], and coupling of precise data analysis tools [3] are known to leverage the clarity and comprehension of the generated signal from the module, yet the sensor's integrity is normally encoded in the physicochemical properties of the sensing material. As a direct resolution to the inference, these properties are often tweaked to improve the sensing capability. Electronic attributes of the material are influenced through surface modification or doping for improving the sensing parameters. Of particular interest to nanotechnologists is the rendition of unique morphologies to the nanocrystals of the base material, a ground on which zinc oxide (ZnO) has enjoyed a steady ascension in the ensemble of functional materials. In addition to their unique physicochemical properties which include high electron mobility [4] and a direct wide band gap of 3.6 eV, the growth of ZnO crystals can be easily orchestrated to produce distinct forms in 1-D, 2-D or 3-D dimensions. Tuning the synthesis parameters have resulted in production of ZnO nanosheets, nanorods, nanoflakes, and other unconventional morphologies which have been duly utilized for chemical sensing with an improved margin for sensitivity [5]. The scope of producing such distinct superstructures with ZnO crystals have helped sustain the interest of researchers in face of stifling competition from other potent sensing materials like WO_3 [6], TiO_2 [7] and SnO_2 [8]. The effect of morphology and the anisotropy in different facets of form-controlled crystals of ZnO was highlighted by Gurlo [9]. More recently, an important work from Drobek and his colleagues has investigated zinc oxide nanowires coated with zeolite (ZIF-8) membrane acting as molecular sieve for highly selective detection of hydrogen [10].

Among various superstructures investigated for ZnO, the nanorods and nanosheets are perhaps the most extensively studied. In addition, exotic morphologies formed through hierarchical growth and conjoining of these basic structures have shown potential as gas sensors. Owing to their intrinsic twinning along the (1 1 2)

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plane during their growth along the *c*-axis the ZnO crystals often form morphologies resembling nanotetrapods or nanoprism [11]. In contrast to the 1-D nanorods, the tetrapods offer multiple facets for the target analytes to be adsorbed. Differing surface energy for each facet and the consequent variation in the magnitude of analyte binding results in selective detection of the target molecules. The investigations performed by Shi et al. elucidated the crystal growth of ZnO ranging from nanorods to prisms as a function of zinc ion depletion in presence of excess H_2O_2 and the sensitivity of individual shape towards nitrogen dioxide [12]. Zinc oxide nanotetrapods were once again in focus for the study made by Faiz et al. where they incorporated indium into the crystals for detection of hydrogen [13]. Enhanced response from the morphology controlled crystals in presence of a dopant indicated towards possible of a synergy between the unique morphology control and doping. In fact, the association between nanotetrapod structure and doping was earlier explored by the Wang et al. in their pursuits of ammonia and humidity sensors, where they used palladium as the dopant [14].

However, though the contributions of zinc oxide nanotetrapod sensors have been appreciated in detection of lethal toxic volatiles and flammable gases [15], their role in detecting relatively non-lethal gases have been subtle. While the world health regulatory bodies for monitoring occupational safety, Occupational Safety and Health Administration (OSHA) have laid out strict mandates for the permissible exposure limit (PEL) towards lethal gases, they simultaneously observe an exposure threshold towards relatively less toxic gases like ethanol and acetone. Despite their low degree of immediate physiological impact, prolonged exposure to these volatiles in workplaces shall result in adverse effects on the human health. In fact a time weighted threshold limit (TLV) of 500 ppm is maintained for acetone [16]. Moreover acetone has been recognized as a potential biomarker for diabetes, thus increasing the relevance of its detection down to ppm level [17]. In contrast, ammonia is far more toxic and poses a higher threat to human health which is reflected in their relatively low TLV value of 25 ppm [18]. In this article, we report on the synthesis of zinc oxide nanotetrapods by thermal evaporation method and their subsequent doping with tin. Extrinsic doping of zinc oxide crystals with tin ions have been reported to decrease the band gap [19] and increase the specific surface area apart from tuning the electronic properties and aiding the sensing process significantly. Detection of acetone with Sn-doped ZnO crystals have been investigated recently where the zinc oxide crystals were rendered 1-D nanorods [20], 2-D nanosheets [21] and 3-D nanoflower morphologies [22] thus corroborating the scientific interest in this domain. For the present investigation, ZnO nanotetrapods were prepared over Si substrates by a vapor-solid technique. The structural and photoluminescence properties of the as grown rod-like Sn doped ZnO nanotetrapods were investigated by using various analytic techniques before they were employed in fabrication of sensor modules. The growth mechanism of the nanostructures along with their modality of detecting the volatile molecules has been simultaneously delineated.

2. Experimental

The vapor-solid technique adopted for developing nanotetrapods involve use of a conventional horizontal tube furnace. A 40 mm inner-diameter quartz tube mounted inside housed an alumina boat on which separate sources of Sn and Zn powders (purity 99.99%, 2:1 ratio) were adjacently placed with a distance of 60 mm in between. An array of *p*-Si (1 0 0) wafers (20 mm x 15 mm) was strategically positioned at the downstream end of the alumina boat for acquisition and subsequent growth of the tetrapods. The temperature within the furnace was ramped to 850 °C where it was maintained for 60 min. Argon containing 2% O_2 was flown at atmospheric pressure and a constant flow rate (50 SCCM; SCCM = standard cubic centimeters per minute at STP) as the carrier gas during the entire soaking period. The synthesis procedure resulted in acquisition of a white wool-like material on the wafers. The samples were scraped off the wafers and profiled for their morphological and optical attributes. Particularly, the samples were investigated by field-emission scanning electron microscopy (FE-SEM, ZEISS), glancing angle X-ray diffraction (XRD) (Philips X-Pert MRD) using Cu Kα radiation (0.15418 nm) in grazing incidence mode and transmission electron microscopy (TEM, JEOL). Pertinent to the optical properties, room temperature photoluminescence (PL) was measured using a He–Cd laser as an excitation source, operating at 325 nm with an output power of 45 mW and TRIAX 320 monochromator fitted with a cooled Hamamatsu R928 photomultiplier detector.

The gas sensors were constructed following a homemade customized set up. Acetone and ammonia measurements were done using a static testing apparatus. It is made up of polycarbonate desiccators of known volume (5.2 L and 15.5 L). The apparatus is attached with a built-in fan and an in-built heating system. The concentrations of the target gases (5, 10, 50, 100 and 200 ppm) were measured by inserting a calculated amount of organic analyte liquid through micropipette into the containers. The injected liquid volume was measured by the following equation.

$$\boldsymbol{V_i}(\mu\boldsymbol{l}) = \frac{\boldsymbol{C}(\boldsymbol{ppm}) \cdot \boldsymbol{V}(\boldsymbol{lt}) \cdot \boldsymbol{MW}\left(\frac{\boldsymbol{g}}{\boldsymbol{mol}}\right) \cdot 10^3}{22.45\left(\frac{\boldsymbol{lt}}{\boldsymbol{mol}}\right) \cdot \boldsymbol{Di}\left(\frac{\boldsymbol{g}}{\boldsymbol{cc}}\right)} \tag{1}$$

where $\boldsymbol{V_i}$ is the injected volume of liquid test compound. $\boldsymbol{D_i}$ is the density of the organic compound to be tested. Other symbols have their usual meaning.

The functioning temperature of the sensors was selected as 225 °C, 350 °C, 400 °C and 460 °C. The response (% S) of a sensor to a specific vapor is calculated as follows:

$$\%S = \frac{(R_a - R_g)}{R_a} \times 100 \tag{2}$$

where R_a and R_g are the resistances of the sensor in dry air and in the test environment, respectively. The sensor response was measured using agilent multimeter (U1252A) and the sensor temperature was maintained by a constant voltage/current source (Keithley 228A).

3. Results and discussion

The phase composition determined through XRD analysis is often a viable approach to discern the utility of the adopted synthesis protocol. The XRD pattern of the as-synthesized products shown in Fig. 1 reveals the presence of wurtzite ZnO crystal planes as the dominant moiety. In addition, pertinent peaks for tetragonal along with orthogonal SnO_2 phases are also visible within the pattern. Moreover, a weak but discernible peak of elemental Sn indicates the presence of unreacted phase from the precursor which were carried and deposited on the wafers by the carrier. The sample however is devoid of unwanted phases of either tin or zinc deeming it suitable for further investigation. Interestingly, in accordance to the convention followed by most XRD plots in instances of doping [23], the lattice parameters of ZnO tetrapods also deviate from bulk (JCPDS #36-1451; a = 0.32468 nm, c = 0.52036 nm). The Sn doping ensues a lattice distortion with revised parameters (a = 0.32242 ± 0.001 and c = 0.51604 ± 0.003), which might be ascribed to the slight mismatch (Sn^{4+}: 0.069 nm; Zn^{2+}: 0.074 nm) in ionic radii of the host zinc and the substituent. The slight lattice distortion is a clear indication of the Sn substitu-