Low temperature detection of ammonia vapor based on Al-doped SnO$_2$ nanowires prepared by thermal evaporation technique

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ABSTRACT

With the growth of nanotechnology during the last few decades, development of novel materials, devices, or other structures possessing at least one dimension in nanoscale has found immense attractions for functional applications. The present work reports the in situ synthesis and ammonia-sensing behavior of pure and Al-doped SnO$_2$ nanowires (NWs) to study the effect of Al$^{3+}$ incorporation on host SnO$_2$ lattice. The Al-doped SnO$_2$ NWs are deposited by a catalyst-free simple evaporation–condensation method. The average diameter of the NWs ranges within 160–250 nm. We investigated sensitivity, repeatability, and response/recovery time of the as-deposited doped sensor. Responses at five different concentrations (10, 25, 50, 100, and 200 ppm) were investigated by varying the temperature (150–300°C range). The minimum and maximum sensitivity for Al-SnO$_2$ NWs was found to be 35% (10 ppm and 150°C) and the maximum as 73% (200 ppm and 300°C), which is considerably higher than the pristine SnO$_2$ nanostructures. The resistance transients were very sharp and prominent, taking less than 6 s for 90% response. The sensitivity of Al-SnO$_2$ NWs to NH$_3$ vapor witnessed a substantial increase due to the creation of additional oxygen vacancies at the surface of SnO$_2$.

1. Introduction

Since the time of industrialization, gas sensors have played a crucial role in detecting the possible risk of gas emission [1,2]. Sensors for these types of applications are usually classified into two groups: resistance type and non-resistance type. When the response mechanism of the gas sensor is associated with the resistance of sensing materials [3,4], resistance-type sensors rule. Conversely, once reacting with oxidizing (e.g. NO$_2$) or reducing gas (e.g. CO, NH$_3$), the resistance of the sensing materials may be increased or decreased by adding or releasing electrons when they are reacting with the test gas on the surface [5]. Thus, gas sensors have abilities to detect what are happening in environment quickly in real-time on the external monitor of their resistance.

Detection of ammonia with high level of accuracy is of great significance in various industrial processes, ranging from fertilizer production to food processing industry. In addition, NH$_3$ detection is also used in monitoring of greenhouse gases owing to the high toxicity of this gas [6,7]. Furthermore, breath analysis is considered as noninvasive and safe technique for hostile medical conditions and, therefore, is imperative in medical analysis [8]. For instance, ammonia is a disease indicator for liver matters. It is found that ammonia in humans is transformed to urea in the liver and then secretes in urines through the kidney, whereas unreacted ammonia is send out through breath of 10 ppb for a healthy person [9]. Inevitably, ammonia concentration enhances when the liver starts malfunctioning and the kidney reaches more than 1 ppm in occurrence of renal failure [10].

Tin oxide (SnO$_2$) is a very important n-type semiconductor ($E_g \sim 3.6$ eV) material for detecting reducing gases owing to its fast and efficient chemical reactivity to various gases (CH$_4$, CO, NH$_3$, etc.) in air, superior chemical stability, non-toxicity, and affordable cost.

Nevertheless, the conventional SnO$_2$-based gas sensors experience the obvious limitations of poor gas reaction and high working temperature (300–450°C). As the response of SnO$_2$-based chemical sensors largely depends on the interaction between toxic gas and SnO$_2$ host lattice surfaces, the concern of researchers is mostly triggered on altering the microstructure and morphology of SnO$_2$-based nanostructures. It is obvious that the metal-oxide semiconductor sensor must possess a higher surface area, so as to absorb the test gas as much as possible on its surface, yielding manifold increase in sensitivity and subsequently a more measurable response (in particular when tested at low concentrations).

Another way to enhance the sensing efficiency of SnO$_2$ is by varying the electronic band structure by inserting foreign elements, such as Ce-doped SnO$_2$ [11], Pd-doped SnO$_2$ [12], and Ni-doped SnO$_2$ [13] in the semiconductor lattice. In the present work, we...
report the facile synthesis of Aluminum-doped SnO\textsubscript{2} nanostructures via simple thermal evaporation method and its subsequent sensitivity on NH\textsubscript{3} vapors. The as-deposited Al-doped nanostructures have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS) in SEM, photoluminescence (PL) spectra, and transmission electron microscopy (TEM). To understand the inherent reason for enhanced sensing performance, the role of O\textsuperscript{2−} vacancy-related defects generating from Al\textsuperscript{3+} doping on the NH\textsubscript{3} sensing of SnO\textsubscript{2} nanoscale morphology were explored in detail.

2. Materials and methods

2.1. Synthesis and characterization of pure and Al-doped SNO\textsubscript{2} nanowires (NWS)

In the present work, pure and Al-doped SnO\textsubscript{2} NW powders were deposited on Si wafer substrate ((100) n-type, 20 mm x 20 mm) using a simple catalyst-free thermal evaporation (VS) technique. Prior to each deposition, the substrate wafers were made free from any organic or inorganic contaminations through ultrasonication in isopropyl alcohol (ACS, ISO, Reag. PhEur, Merck-Millipore, Massachusetts, USA) for a span of 20 min. The starting materials chosen for deposition of undoped SnO\textsubscript{2} NWs was metallic Sn powder (Sigma-Aldrich, St. Louis, Missouri, USA, 99.9 % pure), whereas a combination of Sn and Al metal powders (Alcoa, Pt. Comfort, TX, USA, 99.9% pure), with a stoichiometric ratio of 3:1, was used for deposition of Al-doped SnO\textsubscript{2} NWs. All of the elemental powders and other chemicals used in this work are of analytical purity and therefore, no further chemical treatment was necessary. For fast and efficient deposition through this thermal evaporation–condensation route, the single and combined powder mixtures were placed midway of the thermal zone of the hollow quartz tube (40 mm inner diameter) of a resistance heating furnace. Heating temperatures of 950°C and 1050°C was chosen for pure and Al-doped SnO\textsubscript{2} NWs, respectively, to transfer the elemental powders into their vapor phase. Pure Ar-gas with flow rates of 100 or 400 SCCM (standard cubic centimeter per minute) for pure and doped SnO\textsubscript{2}, respectively, was purged inside the compartment for carrying the gaseous mixtures onto the cooler zone of the tube. A growth and deposition time of 1 h in the oxidizing environment confirmed absolute phase change of metallic Sn to SnO\textsubscript{2} with the anticipated inclusion of Al\textsuperscript{3+} into the host SnO\textsubscript{2} lattice. The as-deposited white fluffy samples were collected by stripping off from the substrate. The structural features which include the microstructure, morphology, and surface topography of the as-deposited samples were explored using a XRD (Philips X-pert Pro MRD, Almelo, the Netherlands) with Cu – Kα radiation (0.15418 nm) in grazing incidence mode, field emission scanning electron microscopy (FESEM attached with EDS facility, SUPRA 40, Carl Zeiss, GmbH, Oberkochen, Germany) and high resolution transmission electron microscopy performed on a HRTEM, Tecnai G\textsuperscript{2} 30ST (Hilsboro, OR, USA). The PL spectra at room temperature were detected in the wavelength range 350–750 nm with a PL spectrometer using 325 nm of excitation wavelength obtained from a He–Cd laser.

2.2. Gas sensor fabrication and gas sensing test

Liquid ammonia vapor with predetermined concentrations was collected in desiccators of known volume (V) by pouring exact amount of droplets to vaporize and thereafter homogenize within the container. The vapor volume (V\textsubscript{i}) to be inserted in the cavity for a concentration (c in ppm) of test vapor was measured from the following relation:

\[
V_i (\mu\text{l}) = \frac{c (\text{ppm}) \cdot V \cdot (\text{desiccator}) (\text{l}) \cdot MW \left( \frac{m}{\text{mol}} \right) \cdot 10^{-3}}{22.45 \left( \frac{L}{\text{mol}} \right) \cdot D_i \left( \frac{g}{\text{ml} \cdot \text{s}} \right)}
\]

(1)

Here, MW denotes the molecular weight of the analyte gas and D\textsubscript{i} is its density. Five different concentrations (10, 25, 50, 100, and 200 ppm) of NH\textsubscript{3} vapor were arranged for testing the sensing ability of the developed sensors.

In order to fabricate the sensor device, the as-deposited pure and Al-doped SnO\textsubscript{2} nanostructured powders were converted into a thick homogeneous paste. Next, the paste was brush-coated on a hollow cylindrical ceramic tube. A pair of Au electrodes was inserted in the tube to create electrical contacts (see Figure 1(a–b)). Ni–Cr coil was inserted into the ceramic tube which functions as a micro-heater. The operating temperature was controlled by using a proportional–integral–derivative controller (PDI) controller attached with a Chromel-Alumel K-type thermocouple placed nearby the sensing material surface. The sensing element was pre-heated at 100°C for 2 h in air prior to each test in order to avoid fluctuations and noise in resistance transient’s measurements during actual test conditions. The as-fabricated sensor modules were heated at operating temperatures of 150°C, 200°C, 250°C, and 300°C under a relative air humidity of 50–60%. Next, 20 mL of test analyte gas (NH\textsubscript{3}) was purged onto the sensor surface by a microinjector and the variation in the electrical conductance was calculated through an Agilent B2901A source-meter and displayed using a LabView-based graphical user
The response/sensitivity ($S$) of the sensors for reducing gas (e.g. NH$_3$ and CO where $R_g < R_a$) is defined as:

$$S = \frac{(R_g - R_x)}{R_a} \times 100 \%,$$

(2)

where $R_a$ and $R_x$ are the resistances of the sensors in ambient air and in the presence of a mixture of NH$_3$ vapor and air, respectively. Response ($\tau_{res}$) and recovery ($\tau_{rec}$) times of semiconducting gas sensors are generally described as the time taken to reach 90% of the final equilibrium resistance (conductance) value in the onset of absorption and desorption, respectively.

3. Results and discussion

3.1 Structural and morphological analysis

The phase and crystal structure of the as-deposited (pure and Al-doped SnO$_2$) products were determined by XRD patterns, as evident in Figure 2(a). The samples are single crystalline in nature. The prominent peaks correspond to (110), (101), (111) crystal lattice planes for pure SnO$_2$, while only (110) lattice plane is observed in case of Al-doped SnO$_2$. All the XRD peaks correspond with the rutile structure of SnO$_2$ given in standard data file (JCPDS File no, 77–0452) [14]. To explore the scope of doping on the crystallinity of the SnO$_2$ NWs, the (110) diffraction peak is examined. Figure 2(a) exhibits that there is a 0.62° lower angle shift in (110) diffraction peak of Al-doped SnO$_2$ NW when compared with those of pure SnO$_2$ NW. This proves that the incorporation of Al leads to lattice deformation in the doped SnO$_2$. However, no characteristic diffraction peaks of SnO, Al$_2$O$_3$, or other impurities are found in these samples. Nevertheless, one unidentified XRD peak at ~ 34.72° for Al-doped SnO$_2$ samples has been detected and this might arise from intermediate tin oxide (Sn$_3$O$_4$) or other unreacted phase in the structure. It is interesting to note here that the overall peak intensities and the total number of XRD peaks got reduced in the Al-doped SnO$_2$ structure, as evident in Figure 2(a). This might attributed to the fact that the presence of Al as dopant changed the diffusion pattern of Sn and O on Si substrate throughout deposition. Therefore, it alters the energetic balance between (110) and (101) peak orientations which eventually leads to preferred (101) orientation occurrence [15]. It is now known that the covalent radius of Al is smaller than that of Sn.
[16], and therefore inclusion of Al$^{3+}$ into the tetragonal SnO$_2$ crystal leads to an increase in both lattice constants (d-value) and cell volume. The 0.62$^\circ$ (2θ) peak shift (as evident in Figure 2(a)) of Al-doped SnO$_2$ single crystalline NWs confirms the substitution of Al$^{3+}$ species partly into the SnO$_2$ host lattice. The overall effect is distortion of the SnO$_2$ host lattice. The lattice fringe of the NWs can be clearly seen, indicating its high degree of crystallinity. The overlapping of another nanoparticle beneath the base NW lattice. The lattice fringe of the NWs can be clearly seen, indicating its high degree of crystallinity. The measured lattice spacing of 0.35 nm, as-obtained from HRTEM image Figure 4(c)) of single crystalline SnO$_2$ is in good agreement with that of (110) d-spacing of rutile SnO$_2$ phase. The corresponding selected area electron diffraction (SAED) pattern with (1–11) zone axis shown in Figure 4(d) revealed the single crystalline nature of the SnO$_2$ NW.

3.2. Gas sensing characteristics

It is well established that sensor response to any analyte gas/vapor depends on numerous external parameters, such as operating temperature, dopant concentration, metal-oxide stoichiometry, and exposed surface area of the nanostructured materials. To determine the optimum working temperature, fabricated sensors were tested at four distinct different temperatures 150°C, 200°C, 250°C, and 350°C exposed to 10, 25, 50, 100, and 250 of NH$_3$ vapor. The sensitivity of the as-prepared sensors was calculated from the dynamic resistance transient plots using Eq. (1) under changing vapor concentrations. Besides the usual linear calibration tests, a rapid response and recovery kinetics are also desirable for a chemo-resistive sensor. Representative dynamic response plots for the two fabricated nanostructured sensor materials tested in 25 ppm NH$_3$ vapor at 150°C have been depicted in Figure 5(a). The reversible response nature of the curves signifies a reasonably stable and repeatable response of NH$_3$ vapor sensing. The response and recovery times for ammonia sensing were estimated to be 19–41 s and 93–45 s for Al-doped SnO$_2$ NW sensors Figure 5(b)), respectively. Equivalent comparison shows a drastic increase in response and recovery times to 35–53 s and 120–56 s, respectively, for pure SnO$_2$ NW sensor. Therefore, it is evident that Al-doped SnO$_2$ NW sensors perform much faster. It is worth noting here that the response and recovery behavior of both the nanostructured sensors rises in a fairly linear manner with increasing working temperature. Figure 6(a) shows the sensitivity vs. temperature plots of Al-doped SnO$_2$ NW-based sensor toward ammonia vapor at four different operating temperatures, as
already mentioned. The pure materials SnO\textsubscript{2} NWs exhibit rather low response as compared with the doped NWs at all test temperatures. The plots clearly indicate that the sensor response of all the samples to NH\textsubscript{3} vapor increases with increasing test temperature, achieves maximum at around 250°C, and finally experiences a decrease with further increase in operating temperature (i.e. 300°C). Figure 6(a) shows the difference in sensitivity as a function of varying NH\textsubscript{3} concentration, for both undoped and doped ZnO nanostructures, maintaining an optimum working temperature. The response of undoped SnO\textsubscript{2} and Al-doped SnO\textsubscript{2} was 21%, 29%, 37%, 46%, 53% and 28%, 39%, 51%, 57%, 66%, respectively, for 10, 25, 50, 100, and 200 ppm ammonia at an operating temperature of 250°C. It is obvious as depicted from the plot that the dynamic response of the Al-doped SnO\textsubscript{2} nanostructures is higher as compared to its undoped
equivalent. The change follows almost a linear relationship in both the cases. In general, NWs possess high aspect ratio, i.e. enhanced surface-to-volume ratio leading to superior sensitivity as compared to its bulk or thin film structures. In the present study, morphology has some contribution for enhanced sensitivity of the Al-doped nanostructures when analyzed with respect to its pristine structure. Here, from the FESM and TEM images, it can be seen that the Al-doped SnO$_2$ nanostructures possess much more variation in terms of morphology and distribution. Particles attached to their original stem, curvy and sometimes porous-like features add more exposed surfaces in the Al-doped SnO$_2$ deposits. These, along with additional vacancy (V$^O$) concentrations due to Al$^{3+}$ incorporation in the host lattice contribute to the enhanced sensitivity of these materials.

3.3 PL spectra

Room temperature PL spectra offers information about impurity assisted structural defects in metal oxide semiconductor materials. Oxygen vacancies in semiconductor oxides present in various charge states, for example, neutral oxygen vacancy (V$^O$), singly and doubly charged oxygen vacancy (V$^{O-}$ and V$^{O-2}$). Figure (7) shows Gaussian curve-fitted PL spectra of undoped and Al-doped SnO$_2$ nanostructures obtained using an excitation wavelength of 325 nm. Al-doped SnO$_2$ NWs exhibit emission peaks centered at 510 and 568 nm. These peaks are associated with defect energy levels originating from the oxygen vacancies or tin interstitials in SnO$_2$. The peak at 510 nm is marked by a strong green emission defect state and the peak at 568 nm by a yellow emission state. The near band-edge emission is not detected in the doped SnO$_2$ morphology which may be due to its nonstoichiometric nature. Earlier, Lei et al. [16] observed a similar spectral distribution for Al-doped SnO$_2$ NWs. The yellow and orange deep-level emissions at higher wavelengths are probably created due to a range of defect-dominated electronic states in the band structure, frequently the oxygen vacancy (V$^O$) and tin interstitial (Sn$_i$) in SnO$_2$ [17]. The PL spectrum of undoped SnO$_2$ NWs reveals a broad emission band, splitting into two visible peaks at 521 and 618 nm. The observed broad emission peaks can be largely attributed to the diverse luminescence sources, which consist of surface defects and/or Sn interstitials. A large blue shift of PL emission in Al-doped SnO$_2$ NWs was simultaneously observed when analyzed with pure SnO$_2$. This might have produced from the lattice distortion due to the incorporation of Al 3p [16].

3.4 Ammonia sensing mechanism

It is well understood now that sensing mechanism of metal-oxides-based semiconductors can be best attributed to the change in its electric conductivity when it comes in contact with analyte gas. The
primary mechanism largely involves in three steps, i.e. adsorption, charge transfer, and desorption. In view of the electron depletion region theory, electrons in SnO$_2$ surface are transferred from conduction band by adsorbing air oxygen molecules, consequently generates various ionic species (O$^2-$, O$^-$, O$_2^-$) [18], decreasing the electrical conductivity of the fabricated sensor. The increase in the width and height of the potential barrier at the contacts among the single crystalline nanostructures leads to increase in sensor resistance. Once the sensors are exposed to reducing gases such as C$_2$H$_5$OH, CO, or NH$_3$, the adsorbed O$^-$ on the surface of the sensors respond to the analyte gas. The trapped electrons are released back to the conduction band. At the contacts of SnO$_2$ NWs, the width and height of the barrier potential decreased, thus leading to a sudden drop in sensor resistance. In the present case, pure and Al-doped SnO$_2$ slurry (mixture of as-deposited NW powder and water) has been coated on ceramic hollow cylinder and dried at 150°C to form a highly porous layer with numerous defect centers (O-vacancy and tin interstitials), which assists in the adding of active reaction sites. The whole event consequently leads to superior gas/vapor sensing performance. The feasible reaction with NH$_3$ and atmospheric oxygen is provided as follows [19]:

\[
O_2(g) \leftrightarrow O_{\text{abs}},
\]

\[
O_2(\text{abs.}) + e^- \leftrightarrow O_2^-,
\]

\[
O^{2-} + e^- \leftrightarrow 2O^-,
\]

\[
\text{NH}_3 + O^{2-}/O^- = \text{NO}_2 + \text{H}_2\text{O} + e^-.
\]

In order to perform the long-term stability and efficiency of a sensor in a particular environment, time-dependent test of gas responses are necessary to conduct for practical applications. Figure 8 shows the long-time stability of the sensor based on pure and Al-doped SnO$_2$ NWs toward 100 ppm of NH$_3$ at 250°C was recorded for duration of 60 days.

At the end, the selectivity of the as-prepared Al-doped SnO$_2$ NW sensors were studied after comparing the same with various available volatile organic vapors with respect to pure SnO$_2$ NW sensors. The test conditions were maintained at 250°C working temperature with 100-ppm vapor concentrations with five typical volatile organic compound species, namely formaldehyde (HCHO), ammonia (NH$_3$), n-Hexane [CH$_3$(CH$_2$)$_4$CH$_3$], N,N-dimethylformamide [(HCON(CH$_3$)$_2$)$_2$] or DMF, and anhydrous or glacial acetic acid (CH$_3$CO$_2$H). Figure 9 depicts a complete selectivity chart and it comprises the entire test data.

Owing to the higher specific surface area and defect density (especially in the form of (O-vacancy and tin interstitials), the sensitivity of Al-doped SnO$_2$ NW sensors exhibits significantly higher value of gas response than that of pure SnO$_2$-based NW sensors. Moreover, it is known that NH$_3$ is generally very unstable and displays higher reaction kinetics. Consequently, it can easily adsorb on the surface of the as-developed sensor and aggravate surface reactions inside.

**Conclusions**

In summary, we have deposited undoped and Al-doped SnO$_2$ NWs by a simple catalyst-free thermal evaporation method. The inclusion of Al$^{3+}$ atoms in the SnO$_2$ backbone is confirmed by the lower angle shift in the XRD pattern in the SnO$_2$ lattice, in addition to the usual FESEM-EDS and TEM investigations. It is found that
compared to the undoped SnO₂ NWs, Al-doped SnO₂ NWs are highly sensitive to NH₃ vapor and the extent of response differs by varying either the operating temperature or the vapor concentration. PL investigations revealed large number of oxygen vacancies in Al-doped SnO₂ NWs. The increase in sensitivity not only attributed to the superior topographical features of the Al-doped SnO₂ NW sensors but also modified defect structures, such as oxygen vacancy and Sn interstitials due to the incorporation of Al³⁺ in the host SnO₂ lattice. Finally, it might be concluded that these Al-substituted SnO₂ nanostructured sensors might find promising applications in detecting lethal gases and vapor concerning human health.

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Disclosure statement
No potential conflict of interest was reported by the author.

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